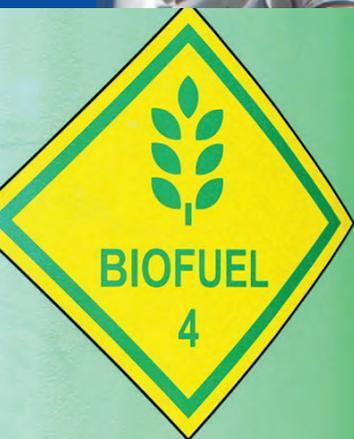


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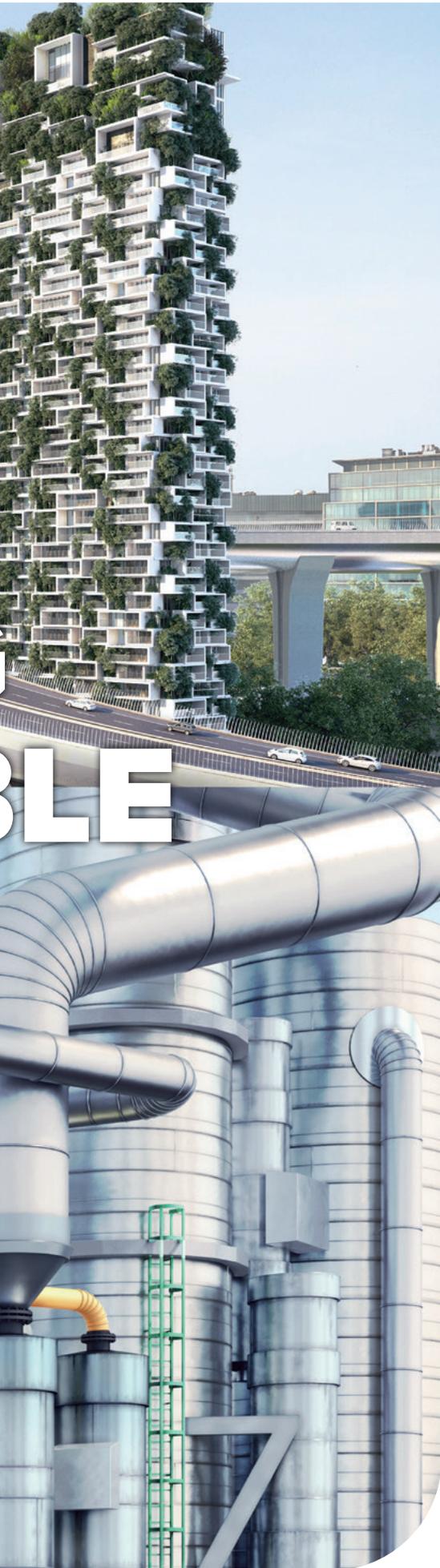
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Visbreaker at Galp Energia's Sines refinery, Portugal
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Spending your way out

Assuming that this pandemic has an end-point, businesses in general – and refiners more than most – would prefer a restoration of near-normal to some realignment of reality. Will max-oil arrive much sooner? Perhaps. Will we all drive electric by the end of the decade? Probably not. And what about young chemical engineers in search of a career path? What is their view of oil refining for a reliable future? So far, there are plenty of statements on the breeze, but few certainties.

At PTQ's press time, Europe's refiners through their trade body, the European Petroleum Refiners Association, set out their view on a 'climate neutral' industry by 2050. The association's task is to coordinate with the European Union executive; 2050 is a target set previously by the EU. The refiners were detailing some practical requirements for climate neutrality in the form of a 'potential pathway'. They base their case on the development of low carbon liquid fuels for road, marine, and air transport, meaning second and third generation biofuels and green hydrogen. Next comes the financial hit: "To deliver such a pathway an investment estimated between €400 to €650 billion will be needed."

Provided the cash is to hand, the pathway indicates that a cut of 100 million t/y in carbon dioxide output from the transport sector could be possible by 2035. At the end of the road to 2050, the refiners say, automobiles would have largely shifted to electric drives, so that the market for liquid fuels in transport would fall to as little as a third of current levels, or about 150 million t/y of liquid fuel products. The balance of demand from air, sea, and heavy road transport would be met by liquid fuels.

Finding the finance to at least kick-start this pathway to mid-century may prove troublesome for the foreseeable future. In mid-June oil prices were dipping significantly for the first time since April while margins were already running at low levels, especially in Europe where diesel is in heavy over-supply. The tipping point for some upstream operations, particularly shale oil production, continues to loom. BP, meanwhile, has earmarked up to \$17.5 billion of operating write-downs to counter continued low prices and declining demand.

The International Energy Agency has been tracking investment in energy projects all the more closely in response to the pandemic. At the start of 2020 the IEA projected a rise in investment spending of perhaps 2% on the year. Lower demand, reduced earnings, and restricted movement of people have hit the energy industry particularly hard and so wrecked a once-reasonable estimate. The current year is likely to experience the biggest decline in energy investment on record, by a fifth, or almost \$400 billion, set against spending in 2019.

By aggregating investment data and announcements the agency has revised its estimates. Petroleum based operations are taking the biggest hit, largely because of cuts to movement by land and air which together account for nearly 60% of the world's demand for oil. At the height of the crisis in April, year-on-year demand for oil was down by around 25 million b/d. At best, demand in 2020 could slip by an average 9 million b/d, which is where we were in 2012.

CHRIS CUNNINGHAM



Process Notes

Modular units can have modern technology

Modern Crude Distillation, Modularized

Global interest in modular refinery construction is surging. Small modular refineries are attractive to investors for several important reasons:

SPEED

Project time from contract execution to start-up can be as short as 18-24 months.

LOGISTICAL ADVANTAGES

Modular refineries can be built in remote locations to realize efficiencies in supply and transportation of raw crude and refined products.

LOW INITIAL COST

Small relative size makes initial capital cost more manageable. Modules can be constructed in the shop with nearly 100% productive time, and turnkey fabrication and construction services lower the likelihood of project delays or cost overruns.

For a project to realize the benefits listed above, it has to start up and run reliably. Saving initial capital by cutting corners is a doomed strategy. Cost savings should result from clever flow schemes that minimize equipment and module count without sacrificing product yields or unit reliability.

With the right expertise, it is possible to design industrially proven, reliable equipment to be easily modularized.

Process Consulting Services has engineered over 100 crude/vacuum unit revamps and over 4 MMBPD of grassroots crude unit capacity. We have drawn on all of this experience to develop a unique flow scheme for modular crude/vacuum units. Our modular crude distillation process is fully modern, incorporating time-tested technologies to eliminate common reliability issues. Some of these features, developed in much larger units, have been re-thought to be affordable on a modular scale.

No matter how low the initial cost of a crude unit is, the investment will not pay off if the unit is plagued by avoidable problems. Poor desalting (corrosion), pre-flash tower foaming (off-spec naphtha), tray plugging (poor fractionation and product quality), etc. can all be mitigated by thoughtful front-end design.

Through creative flowsheet and equipment design, PCS is able to significantly reduce the number of modules required to build a modern crude distillation unit that maximizes valuable product yield, energy efficiency, and reliability.

Photo Credit: Honeywell UOP



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Q Our cheaper crude intake has relatively high chloride levels at the cost of increased preheat exchanger fouling. What measures can we take to minimise the problem?

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A further problem caused by high levels of chloride in crude can be witnessed in the FCC unit. Chlorides are often found in heavy portions of crude, meaning they end up in the FCC unit, either in residue or VGO cuts. In the FCC, chlorides can affect product yields and are highly deleterious in both of the process outlets. When chlorides enter the FCC, it can be observed that hydrogen yield increases and coke selectivity deteriorates. Several documented cases point to the issue of chloride increasing the activity of contaminant nickel in the FCC unit when such effects are observed without a subsequent increase in metals loading. Routine analysis is advised in the event this phenomenon is seen, but as chlorides often enter the FCC in brief slugs, reactivating the nickel present, it is rare to be able to capture these effects within the normal sampling schedule.

Focusing on the hydrocarbon outlet, where chlorides leave with cracked products, serious problems can be found in the upper sections of the main fractionator and in the gas plant. In the main fractionator, chloride combines with ammonia, which is typically found in excess due to the cracking of amines in feed, to form ammonium chloride. Ammonium chloride salt deposition may occur under certain conditions as a function of partial pressure of NH_3 and HCl and the dewpoint of water. Where NH_4Cl deposits form on trays, increased pressure drop or tower flooding issues can occur. This situation is typically seen towards the top of the tower, especially when a side cut naphtha stream is taken, such as heavy cut naphtha (HCN), which results in a cooler tower top temperature of $<120^\circ\text{C}$. A water wash in the reflux can help alleviate this situation as NH_4Cl is highly soluble in water. However, if the material has already solidified, this is unlikely to help. Further, amine filmers, which are supplied by water treatment companies, can be used to add a protective layer on the trays, but this is more effective for clean trays as a preventative measure. Typically, mechanical removal of the deposits is required following a unit shutdown.

Additionally, and at higher tower top temperatures, corrosion problems can be seen further downstream, such as chloride stress corrosion cracking (SCC) in the wet gas compressor and interstage cooling system. A suitable water wash system is required to minimise corrosion in this vulnerable area.

On the regenerator side, chlorides also cause corrosion problems through SCC in flue gas ducting and other

downstream systems. In the regenerator itself there are cases where combustion problems manifest as a result of high chlorides, leading to rapid and severe CO excursions, with the associated environmental compliance and afterburn implications.

Good desalting is essential to remove as much chloride as possible from the eventual FCC feed components. If an exhaustive investigation of typical sources of chloride has not explained an increase, FCC catalyst should also be considered. It is known that FCC fresh catalyst can release chlorides when injected to the FCC¹ due to incomplete calcination of the FCC catalyst before leaving the supplier's factory. These effects are typically observed on the regenerator/flue gas side where catalyst is exposed to high temperatures. Retention of fresh catalyst samples for retrospective testing is advised when a history of chloride corrosion has been experienced.

¹ Salt deposition in FCC gas concentration units, Michel Melin, Colin Baillie and Gordon McElhiney, Grace Davison Refining Technologies Europe, *PTQ Q4 2009*.

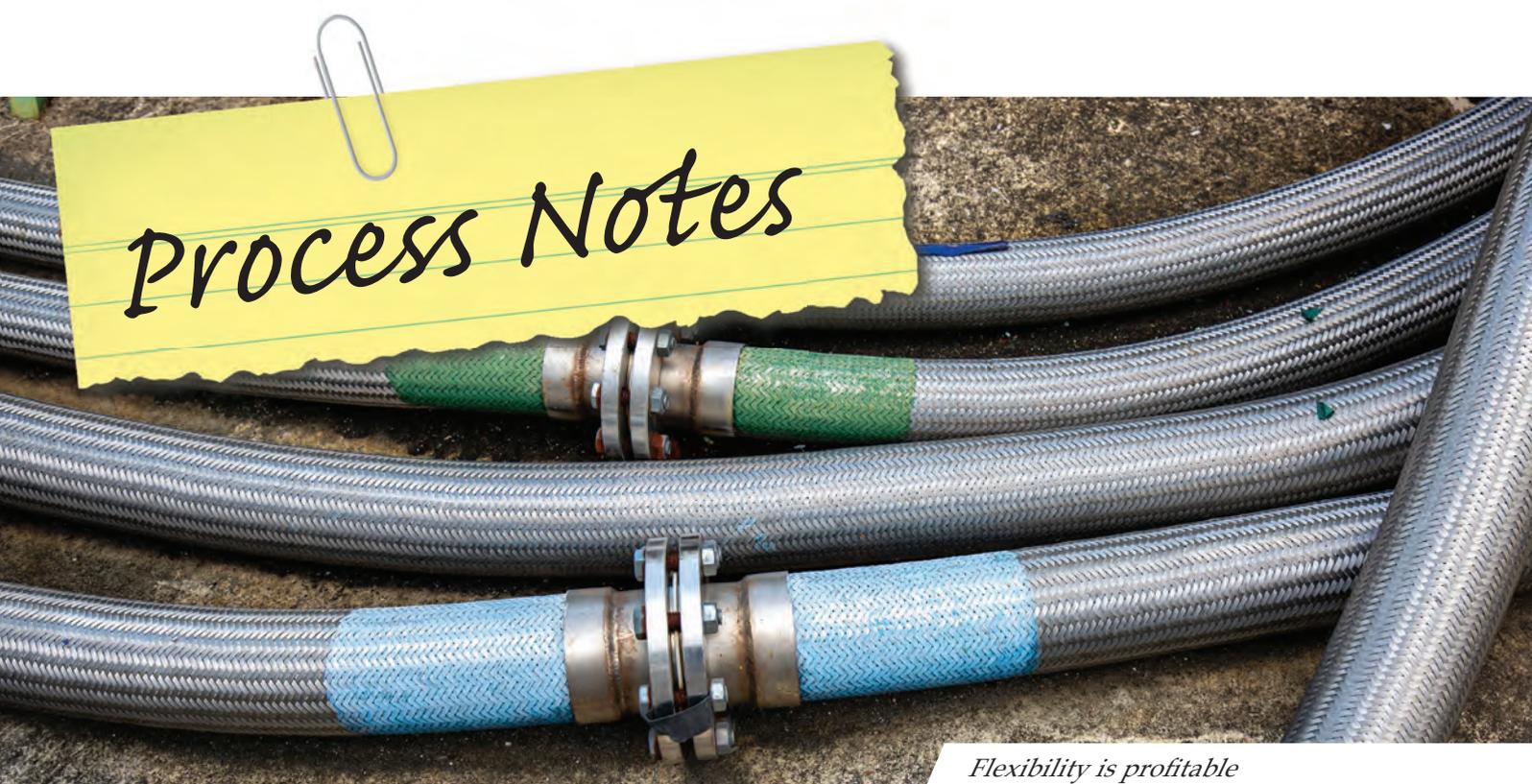
A Melissa Clough Mastry, Technology Manager EMEA, BASF, melissa.mastry@basf.com

Another point to consider is if the chlorides are making their way past crude processing, there is a chance for chlorides to also enter the FCC if your refinery is configured with one. Once chlorides enter an FCC, they may cause problems downstream, including fouling of the main column overhead system (NH_4Cl deposition) or even within the FCC by reactivating old contaminant nickel (leading to higher hydrogen and coke). The preferred option to minimise the problem is to avoid all sources of chlorides – so optimising the crude desalting processing or using an FCC catalyst that has zero chloride content. (It is known that if present in the fresh catalyst, not all the chlorides will leave from the regenerator stack, but some will entrain to the riser side.)

A Xiomara Price, Senior Product Analytics/Support Manager, SUEZ – Water Technologies & Solutions, xiomara.price@suez.com

Salt and solids fouling can occur either in the cold preheat exchangers before the desalter or the hot preheat exchangers after the desalter. This type of cold preheat fouling can be typically addressed by adding a portion of the desalter water wash to the front end of the preheat exchangers.

The desalter is the primary defence against salt and solids fouling in the hot preheat exchangers. Desalter performance optimisation is essential to mitigate the fouling. It can be achieved by adjusting any number of variables depending on your specific system design, operation, and limitations. Some of those variables include percent wash water, mix valve pressure drop,



Process Notes

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.



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water wash quality, desalter temperature, slop addition, chemical addition, and desalter level.

Your service provider should be able to provide you with specific guidance on what variables are negatively impacting your system, and how to best improve them. If for some reason the desalter operation cannot be further optimised due to design or operational restrictions, an effective dispersant can help reduce fouling until the design or operational problem can be resolved.

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

If you have not already done so, I suggest doing a root cause investigation. Find the exact location of the fouling: is it in the cold or hot preheat and which specific exchangers are fouling? Running a rigorous preheat monitor model such as Monitor can help with this. If possible, try to get a deposit sample and have it analysed, and the fouling mechanism determined or confirmed. Also perform the necessary analyses to determine if the increased chloride levels are due to inorganic chlorides (salt) or organic chlorides.

Check with the company that treats your desalters and overhead if they have processing experience with the specific crude and if they have seen any problems associated with it. Having access to a database with processing experience such as the Nalco CrudeFlex database that points out potential problems linked to a crude can certainly help with the investigation.

Look at the crude stability and blending stability; the crude may already be self-unstable or blending with other crudes can cause instability of asphaltenes which can lead to increased preheat fouling.

Check if the increased chloride content is linked with an increase in other contaminants such as increased water and solids content. If these have increased above your normal values, a crude tank settling programme using crude tank demulsifiers can help reduce them.

Verify how the desalter is responding to the increased chloride levels. Have the chloride levels (salt levels) of the desalted crude increased? Refiners often respond to increased desalted crude chloride levels by increasing the caustic dosage after the desalter and this may lead to increased fouling in the hot preheat exchangers. Caustic usage should be minimised by optimising desalter performance, for example by increasing washwater to the desalters and optimising washwater distribution over the cold preheat and upstream the mix valve, and optimising mix valve pressure drop.

If not controlled properly, the increased desalted crude chloride content may lead to higher levels of hydrochloric acid going to the overhead and an increased overhead salt formation potential; deposited salt decreases heat exchange in the overhead/cold crude heat exchangers. If this happens, it would normally also be noticed by an increased pressure drop over these exchangers on the overhead side and an increased tower top pressure.

If the preheat exchanger fouling cannot be controlled by changes in pretreatment, blending, or desalter operation, an antifoulant programme may help reduce the

fouling. To select a suited antifoulant, the fouling mechanism must have been confirmed, as suggested earlier.

A **Marco Roncato, Senior Product Manager Process Development & Marketing, Chimec, process@chimec.it**

Refinery crude feeds contain water and inorganic salts such as sodium, magnesium, and calcium chloride. In the case of cheap crudes, the water content – hence the salts content – can be higher.

The first measure in order to manage this higher content is obviously to maximise desalting efficiency. But after this first step, despite good desalting efficiency, some inorganic chlorides remain in the desalted crude and it is well known that they can hydrolyse, generating HCl. In order to minimise this phenomenon, a common practice is to inject NaOH into the desalted crude. Caustic injection downstream of the desalter is recognised as a cheap, effective method to reduce overhead corrosion. Unfortunately, at the same time, NaOH injection into the desalted crude can be detrimental for the following reasons:

- Concentrated caustic solutions can cause general corrosion of carbon steel equipment at these temperatures. Additionally, caustic can cause caustic stress corrosion cracking (CSCC or caustic embrittlement) of non-post weld heat treated carbon steel and of austenitic alloys including stainless steels and nickel alloys such as Alloy 825 (UNS N08825).
- If allowed to precipitate (usually in the hottest CDU heat exchangers, where water flash occurs), caustic/salt reaction products (calcium and magnesium hydroxide) and unreacted caustic can cause plugging of heat exchanger tubes (inorganic fouling). This leads to losses of heat exchanger efficiency (lower energy saving and higher maintenance costs) and increases the ΔP of the equipment.
- NaOH can contaminate the bottom streams affecting downstream units:
 - Catalyst poisoning in the downstream catalytic plants – the FCC unit, hydrocracking unit, residue desulphurisation and so on
 - Increased coking rate in the downstream unit furnaces; for instance, the vacuum and visbreaker units
 - Low quality produced fuel oil (fouling problems in the burners, for instance in a power station or in the fuel oil furnaces)

Caustic Replacer

In order to manage these issues, Chimec has developed Chimec 3034 – Caustic Replacer to substitute completely or partially the injection of NaOH downstream the desalter; the overall effect is the reduction of the sodium content in the atmospheric residue.

This implies:

- Lower catalyst poisoning (hence deactivation) in the downstream unit
- Lower coking rate catalysed by Na in the downstream furnaces
- Higher fuel oil quality
- Lower Cl level in the overhead systems, thus lower corrosion rate

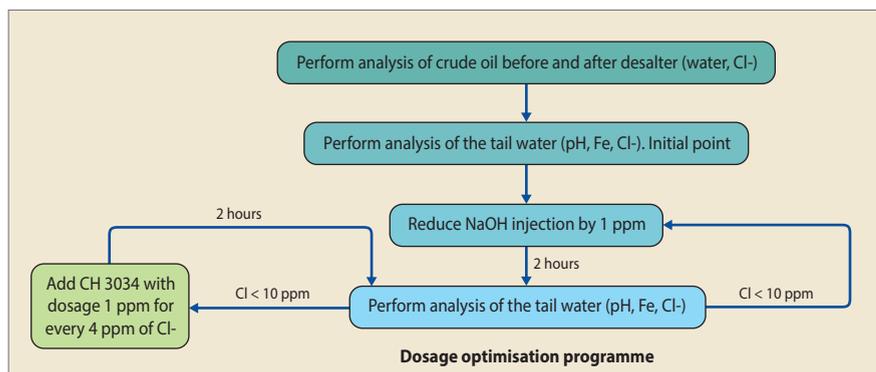


Figure 1 Dosage optimisation programme

- Lower risk of Na embrittlement
- No risk of NaOH induced fouling in the hot preheat train

Chimec 3034 is an oil soluble blend of high molecular weight polyamines able to neutralise free chlorides in the desalted crude oil, thus forming salts that show higher thermal stability compared with the inorganic chlorides, especially magnesium and calcium that hydrolyse at the hot train preheat exchangers and furnace outlet temperatures. This would increase the HCl that distils at the top of the pre-flash and main fractionator columns in CDUs.

Furthermore Chimec 3034, compared with most commercially available caustic replacers based on other lighter amines and diamines, ethylenediamine, diethylenetriamine, diethanolamine, triethanolamine, triethylenetetramine, offers the following advantages:

- Its oil based formulation conveys the active compounds in the crude oil matrix in a more efficient way
- The higher boiling point range of the active components decreases vaporisation, thus preventing salts formation on the columns' trays
- The higher thermal stability of the salts produced by the reaction with hydrolysed chlorides ensures a reduction of chlorides ending up in the overhead system of the CDU preflash column and main fractionator, in turn decreasing the corrosion rate
- It is completely organic and metal free, i.e. no impact on the coke promotion and on the catalyst deactivation)
- It has a fast reaction

Injection strategy

Chimec 3034 has to be injected downstream of the desalter. If NaOH will be only partially substituted, it must be injected in a separate line with respect to the NaOH, being in a different solvent.

Chimec 3034 dosage strongly depends on the quantity of salts in the desalted crude. Approximately 1 ppm of NaOH (considered as pure NaOH) can be replaced by 7 ppm of Chimec 3034.

To confirm the results of applying Caustic Replacer, the dosage of Chimec 3034 should be kept constant for 12-24 hours and analyses should be repeated on:

- The desalter inlet and outlet crude
- Overhead tail water

Optimisation of the dosage can be performed as outlined in **Figure 1**.

Q With IMO 2020 in place, we need more hydrogen. Can we uprate our existing hydrogen plant without a major revamp? How much extra production is possible?

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Several capital intensive options exist to increase hydrogen production from a hydrogen plant, including

adding a pre-reformer, a post-reformer (GHR or EHTR), or re-tubing the SMR with lower wall thickness tubes to give a moderate increase in catalyst volume or pressure drop allowance. All of these options are expensive and time consuming to implement, as well as being considered major projects for a refinery to undertake.

A 'drop-in' option would be preferred, where more hydrogen is produced from the steam methane reformer (SMR). Magma, a UK company with extensive manufacturing experience in the ceramic industry, has applied novel texturing techniques to hydrogen catalyst production, leading to a 10-15% increase in hydrogen production. Guided by experts in SMR, Magma has adapted this technology to commercialise a new type of SMR catalyst which utilises external surface texturing, new shapes, improved heat transfer, porosity to increase activity, and pressure drop characteristics of the catalyst with the aim of producing significantly higher hydrogen yields from the SMR.

This catalyst can also be applied in other ways if increased hydrogen production is not immediately required, such as significantly reducing fuel and energy requirements through more efficient production of hydrogen. These fuel and CO₂ savings have cost and environmental benefits in some global regions today.

As this is a catalyst pellet, it can be loaded, started, operated, shut down, and unloaded in the same way as a conventional SMR catalyst. Furthermore, increased pellet strength avoids breakage related pressure drop escalations. A unique approach to potash promotion eliminates the potassium elution problem seen with traditional doped catalysts. Improved heat transfer and lower drag coefficient mean greater feed flows are able to be processed, leading to higher hydrogen yield. Currently installed by two of the top three refining companies in the US, with orders for both Europe and Asia to be loaded in 2020, this SMR catalyst from Magma (supplied by Unicat in some regions) can provide more hydrogen in a way that is cost-effective, flexible, and user-friendly.

A Tom Ventham, Sales & Technical, Europe and Africa Unicat BV/G.W.Aru, LLC, tom.ventham@gwaru.com; and Xavi Llorente, Technical Sales Engineer - Asia, Europe, MEA, Unicat BV, Xavier.llorente@unicatcatalyst.com

Producing more hydrogen using advanced technology is only a partial solution to the challenge. It is also

UNMATCHED TECHNOLOGIES

TO HELP MEET IMO 2020 REGULATIONS



Chevron Lummus Global



Only Chevron Lummus Global combines leading technologies and catalysts with expertise and know-how to provide innovative solutions for the cost-effective production of low sulfur fuel oil. Our novel LC-LSFO technology combines our well established LC-FINING and RDS platforms to increase conversion while still producing low sulfur fuel oil, helping refiners meet IMO 2020 requirements globally. To get the performance and flexibility needed to keep pace with changing market dynamics, start by visiting www.chevronlummus.com.



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important to capture it. The pressure swing absorption (PSA) system sits at the end of the modern hydrogen plant and is the last opportunity to capture the valuable hydrogen produced. When uprating a hydrogen plant, a similar uprating of the PSA should be performed to handle additional throughput and maintain or improve the purity of the hydrogen processed. The first adjustment for this new operating mode is typically focused on the capacity of the PSA system. Is the current design of the PSA able to handle up to 20% more throughput? PSAs are often oversized by 120% of nominal capacity. Thus, most PSA units could potentially handle the feed increase expected. However, there are a significant number of critical points that must be considered. For instance, is the tail gas drum capacity sufficient to handle the increase in tail gas generation? Also close attention must be given if the throughput increase impacts any operational parameters such as the feed pressure. In that case, modification of the programmable logic control (PLC) can take place. Eventually, if there is a requirement to maintain high recovery and high purities, revamping must be considered. This implies an increase in the number of absorbing vessels, PLC replacement, as well as a redesign of the absorbents loading scheme.

PSA units operating in hydrogen flow schemes contain several layers of absorbent material, including alumina, activated carbon, and molecular sieves used to remove the contaminants found in the hydrogen rich stream. However, the most crucial layer in achieving high performance tends to be the carbon layer. The ability to load a higher density activated carbon layer increases the absorption capacity in a fixed volume which is an ideal solution for these uprate cases. Unicat can supply a wide range of PSA advanced absorbents and also offers the whole range of PSA solutions. As an independent supplier, Unicat can offer absorbents and solutions to all PSA designs and licences. A number of successful case studies and a long reference list of PSA applications Unicat have been involved in are available to discuss.

Q We are aiming to boost our FCC propylene output. What recent developments would you recommend?

A Nicolas Lambert, Technology Team Manager – RDS, FCC & Sweetening Segment, Axens, Nicolas.LAMBERT@axens.net and Thibault Reffet, Technology Team Manager – Clean Fuels, Axens, Thibault.REFFET@axens.net

Beyond the obvious adjustments to the catalytic systems to include ZSM-5 and follow closely the latest catalytic developments, some upgrades on the technology side are possible. The principal hurdle will be the hydraulic limitations of the unit which could require reducing the unit throughput to achieve better performance.

Not so recent, but efficient in generating some margin in an existing unit, which can in turn be used to increase unit severity, is the FCC Alliance Stripper Packing. This largely proven equipment aims at thorough stripping of spent catalyst under all circumstances in the unit. Through an important reduction of hydrogen content in

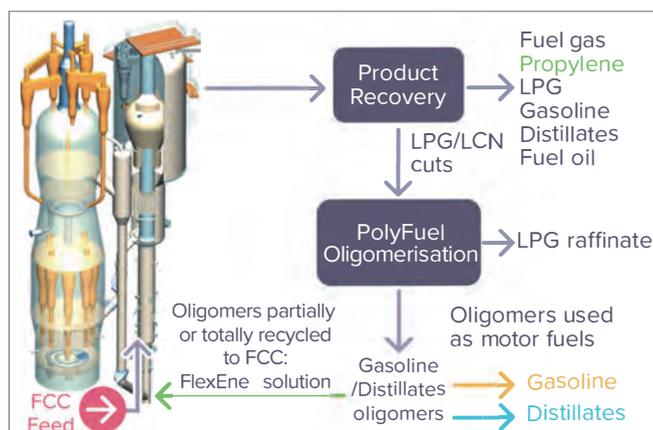


Figure 1 Oligomerisation within FCC block

coke (versus disc and donuts, baffles, or other technologies), the air demand and regenerator(s) temperature are drastically reduced. Temperature drops of 10-15°C are routinely achieved, and possibly more depending on the starting point. The 'room' thus freed in the regenerator enables increasing the ROT in order to reach higher propylene yields.

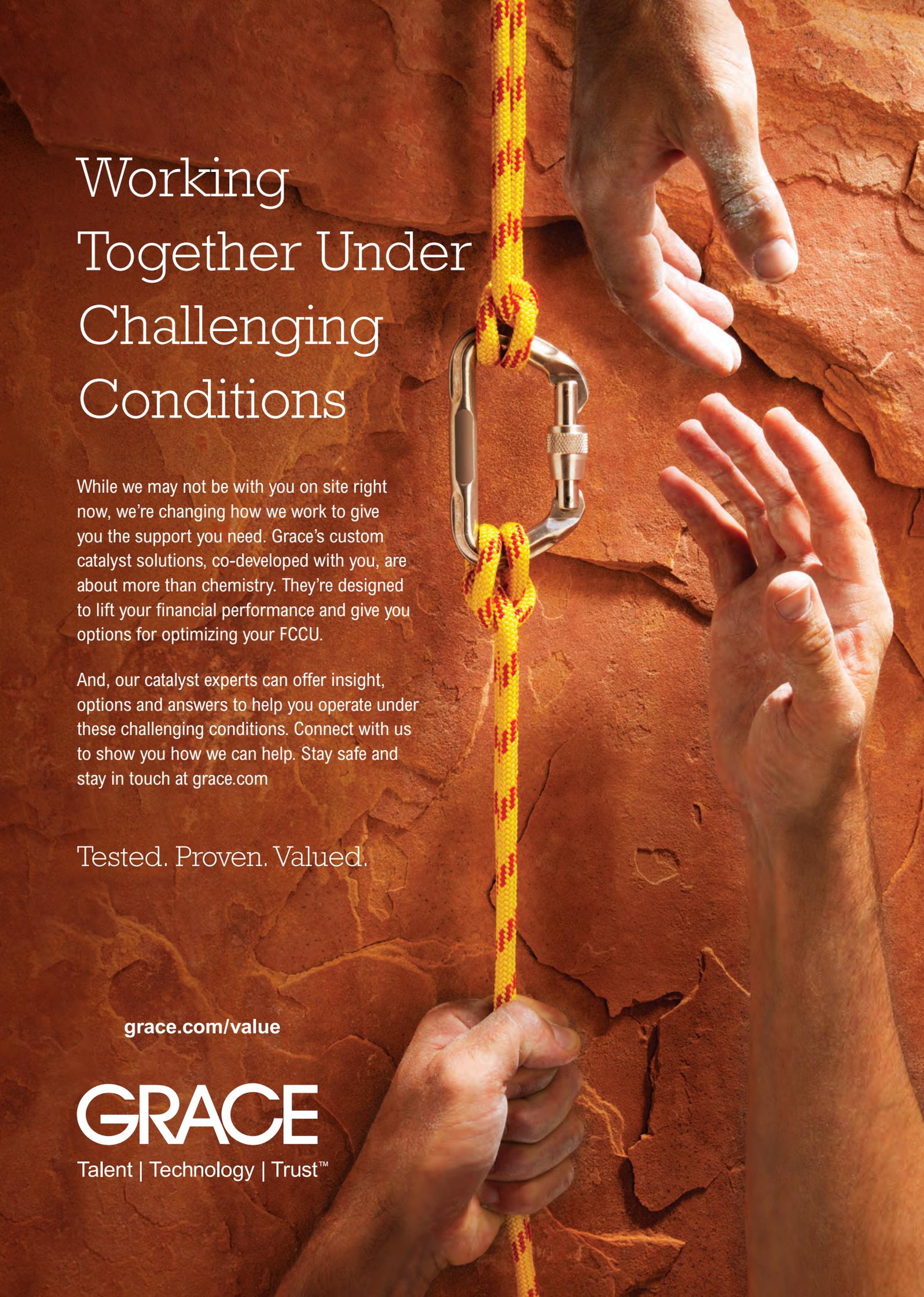
Some other technical elements offered by the FCC Alliance and Axens have similar effects, albeit to a lesser extent:

- Feed injectors: FIT G-Series or FIT R-Series (depending on the unit feed diet) will reduce coke production through better, more intimate contacting of the feed. The liquid hydrocarbons are more efficiently and quickly vaporised to promote vapour phase cracking in order to limit coke formation by deposition on the catalyst. Following the same principle as above, reduced demand on the regenerator side allows increased severity
- The RS2 riser termination device will ensure minimum thermal degradation. The same load on the wet gas compressor can thus be achieved at the same unit throughput but operating at higher severity to promote propylene production
- MTC Technology: a riser quench that will force an increase in the catalyst circulation rate, bringing more energy to the riser and thus improving feed vaporisation and performances

In addition, if the LCN or external olefin-rich cuts can be disposed of, coupling the FCC unit with an external oligomerisation unit will prove a very efficient substitute to a secondary riser.

Indeed, the principal pathway for propylene from LCN cracking is through the intermediate oligomerisation of olefins subsequently followed by cracking. Cracking of paraffins requires much more energy for limited results. Externalising the oligomerisation step through Polynaphtha or PolyFuel processes will ensure a much higher extent of this reaction step, leaving only the cracking part to be performed by the cat cracker. In such a case, only oligomers are recycled to the FCC unit, requiring far less space than the full LCN cut, for instance, for much better results.

Moreover in addition to the LCN, the oligomerisation unit can convert the C₄ olefins into oligomers that can be cracked to propylene. Hence, by using this type of



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technology, it is possible to tune the FCC product slate towards the desired products. This coupling of FCC with an oligomerisation process is called FlexEne (see Figure 1).

A **Hernando Salgado, Technical Service Manager ME, BASF,** hernando.salgado@basf.com; **Amid Shah, Technical Service Manager India, BASF,** amit.shah@basf.com; and **Stefano Celestino Riva, Technical Service Manager EMEA, BASF,** stefano.riva@basf.com

If all conventional and easy ways to increase propylene yield from the FCC unit have already been evaluated and implemented to the furthest extent possible – operating conditions, feed quality, naphtha recycle – then the market can be scouted for the latest technology in the development of ZSM-5 additives.

Recent R&D developments have enabled an increase in ZSM-5 additives' crystal content from a traditional 25-40% level to higher than 50% crystals. BASF's ZEAL is the latest ZSM-5 additive in that category. Using such a high crystal ZSM-5 additive, while maintaining the dosing rate the same as the incumbent additive, can significantly boost propylene yield by minimising the additive dilution effect, provided that sufficient olefin precursors are available in the light gasoline stream. The extent of incremental propylene production depends on the specific application. However, it is always a good idea to consult your FCC catalyst supplier to receive brainstorming support for new ideas or simply to evaluate the impact of conventional operational changes.

For instance, one of the operating variables that is often neglected but affects propylene yield a lot is the hydrocarbon partial pressure, impacting both the olefinicity of the C₃ fraction (C₃=/C₃ ratio) and the overall yield. A decrease of hydrocarbon partial pressure can be achieved by increasing injection steam or any other steam going to the riser, such as lift steam. Hydrogen transfer reactions are expected to be reduced under low hydrocarbon partial pressure conditions, hence preserving the olefins already made, and increasing cracking reactions (that are thermodynamically favoured by low pressure) towards products including light olefins such as propylene. Figure 1 shows the potential impact

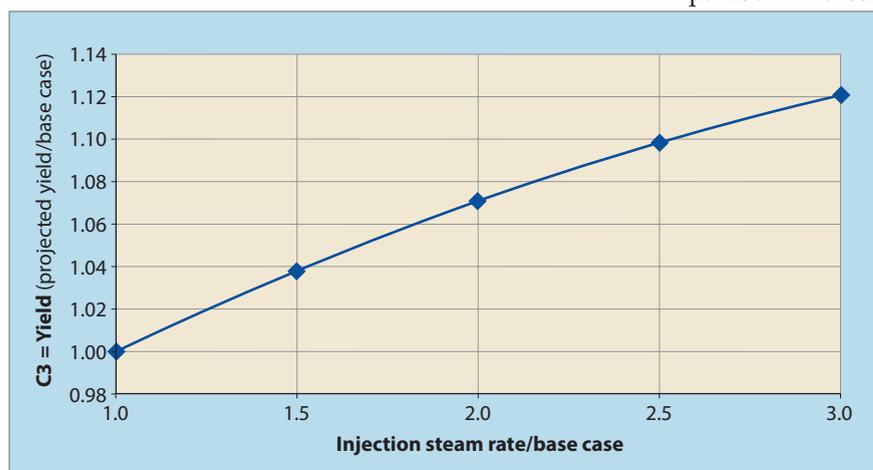


Figure 1 C₃ = yield vs injection steam ratio

of increasing injection/lift steam in a typical high propylene unit with high ZSM-5 addition:

It must be noted that graph is specific for each unit since the actual response to light olefins yield depends on other process variables as well as unit design aspects. In addition, a substantial increase in injection steam or lift steam might require plant modifications to accommodate the higher steam rates, and a careful review of the capacity of some downstream systems such as the lines and pumps of the sour water system, including the main fractionator overhead drum collection boot, and the sour water stripping unit. Other design aspects such as maximum feed injector pressure drop and cyclone inlet velocities should also be monitored as they will directionally increase. As a side benefit, higher injection steam will also improve feed atomisation and vaporisation, thus reducing coke yields and coke deposition tendency.

Finally, producing maximum propylene from the FCC riser is only the start; it should also be recovered by reducing/minimising losses in the dry gas/fuel gas. In one patented application, a refinery added a chiller to cool the naphtha used in the primary absorber to minimise the loss of propylene to the fuel gas. The value of propylene in a petro-refinery can be high enough to pay back additional investment in a short time.

A **Kevin Le, Senior Technologist – FCC, Shell Global Solutions (US) Inc.,** Kevin.Le@shell.com

On an existing unit, ZSM-5 additive has been used as the main handle for maximising propylene production. It provides the most flexibility for managing a unit's constraints, as well as a quick response to the need for incremental propylene barrels. Optimising fresh catalyst formulation is also important to target for maximum LPG production, along with ZSM-5, while minimising the bottoms or slurry production. Generally, a fresh catalyst that works best in this case is formulated with a 'lower' rare earth and a 'higher' matrix surface area than the 'typical' catalyst formulation.

In most cases, an existing unit is typically constrained by the volumetric flow on one or more gas fractionation pieces of equipment – namely, the wet gas compressor (WGC), the absorber, the debutaniser, or the depropaniser. The constraint in these columns can often be

relieved by upgrading the column internal designs to expand the capacities of these columns within existing vessels. To manage the constraints on an existing unit, optimal solutions are often found by balancing the riser outlet temperature (ROT), ZSM-5 concentration, fresh catalyst formulation, and in some cases feed rate and/or feed quality to the unit.

Maximising ROT could be a low cost option to maximise LPG production, by increasing conversion and over-cracking of gasoline into

LPG; however, it also comes with a higher dry gas yield and a poorer propylene selectivity when compared to the effect of ZSM-5. Feed nozzle performance has a significant impact on the dry gas yield. Choosing the right feed nozzle technology is also important in the mix of options for maximising propylene production while managing constraints on an existing unit. Shell's latest feed nozzle technology offers an excellent dry gas yield reduction that has been proven in many units.

Other operating variables that would impact propylene production include feed quality, conversion, and reactor pressure. In general, an 'easier to crack' feed, typically with higher hydrogen content and lower aromatics content, would result in higher propylene yield. The FCC feed is typically made up of several feed streams. It is important to accurately predict yield from each feed stream in order to optimise the FCC feed slate for maximising propylene production. Using a well-tuned kinetic model, such as Shell Advanced and Rigorous Catalytic Cracking (SHARC) proprietary software, is recommended for quantifying yield from each feed stream.

For a given feed quality, maximising the cat-to-oil (C/O) ratio also plays an important role in increasing unit conversion and propylene production. Shell designs FCC units with a unique feature that allows sour water to be recycled to the riser, besides the more typical naphtha recycle. The company has successfully utilised this feature to maximise C/O ratio and lower the partial pressure of the hydrocarbon feed in the riser, and at the same time to maximise the unit's conversion and thus propylene production. It is a great addition to the tool kit for maximising the C/O ratio which could include lowering the feed preheat temperature, increasing CO concentration in the flue gas on a partial burn regenerator unit, and raising the catalyst cooler duty. It is important to note that recycling sour water and/or naphtha to the riser will impact coke yield and riser residence time, as well as loading to the reactor cyclones and main fractionator (MF).

Lowering the reactor pressure to reduce hydrocarbon partial pressure is good for unit conversion and propylene production, yet it is typically not a practical solution for an existing unit because of various constraints, like pressure balance, loadings to the MF and WGC, and so on.

For an existing unit operating without constraints in the gas fractionation section, a propylene yield up to 7-8 wt% of fresh feed has been achieved by using a combination of the above mentioned variables. To further boost propylene yield, up to 15-20 wt% of fresh feed will typically require major revamps for an existing unit. Shell has developed MILOS (Middle Distillate and Lower Olefins Selective) technology for maximising light olefins while offering a flexible operating mode for distillate (LCO/LGO) production. The MILOS process features a dedicated riser for naphtha recycle that is operated with a high ROT and C/O ratio, utilising a high ZSM-5 concentration in the catalyst to maximise the overall olefin production.

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Propylene is a key product for many FCC operations. This area is receiving renewed focus as the current market sees reduced gasoline demand and over-supply. ZSM-5 based additives provide the means to increase valuable propylene production as well as to destroy low value gasoline blend components. The response given here by G. W. Aru, LLC and Unicat B.V. hopes to break a common myth in the FCC world – that producing propylene using ZSM-5 has a finite limit. Attempts to increase propylene with ZSM-5 above 10% fresh feed appear to reach an asymptote, but additional increases in propylene are possible.¹ A complex set of reactions takes place over ZSM-5 which provide additional feedstock for cracking reactions to produce LPG olefins, propylene, and butylene. ZSM-5 efficiency can be improved through optimisation: minimising FCC catalyst rare earth content, reducing FCC catalyst zeolite-to-matrix ratio, reducing hydrocarbon partial pressure in the FCC riser, increasing Ecat activity, and adjusting FCC feed quality, including the recycling of a naphtha or butylene stream. Further increases in propylene production can be achieved through incremental increases in ZSM-5 addition. The best ZSM-5 for this type of high propylene operation is one of high intrinsic activity, good hydrothermal stability, and excellent retention.

Numerous studies conclude, and we agree, that ZSM-5 is the most selective and cost-effective method to generate incremental propylene from the FCC unit, especially in units that have dry gas or wet gas compressor limitations. It is far more economical to use ZSM-5 rather than elevating riser temperature or adjusting other operating variables. There can be significant positive synergy from proper design of the base FCC catalyst formulation; this cannot be ignored in the unit optimisation effort. ZSM-5 use is a near-real time optimisation tool that allows the entire refinery a rapid response to changing market conditions. However, full value can only be realised if the ZSM-5 is separately added rather than pre-blended or incorporated with the FCC main catalyst.

With the extremes currently seen in how refinery operation needs to be continuously manipulated to maintain optimum profitability, reducing flexibility by not having independent control of ZSM-5 addition for precise control of LPG production greatly diminishes the value that can be achieved. Further to this, inefficient addition of either ZSM-5 or fresh catalyst by not decoupling this process means unnecessary added costs to the FCC budget at a time when all opex is under pressure and should be minimised.

¹ How ZSM-5 works in FCC, Bart De Graaf, Johnson Matthey Process Technologies Inc., AFPM 113th Annual Meeting day two Tuesday | March 24, 2015.

Q What is hydrogen embrittlement in metals, where in the plant is it most likely to occur, and how can we avoid it?

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

Hydrogen embrittlement is a kind of stress corrosion cracking, resulting in several forms of damage. Known effects are loss of ductility and fracture strength, and macroscopic damage due to entrapment at mechanical interfaces. The reduction of hydrogen is the corresponding cathodic reaction to the anodic reaction to initiate aqueous corrosion. Cathodic hydrogen adsorbs on the metal surface, while gaseous hydrogen adsorbs in the molecular form. Nascent hydrogen is a chemisorbed species on the metal surface, which can enter the metal. Gaseous hydrogen must first dissociate to form atomic hydrogen. The crystal structure of iron based alloys has small holes between the metal atoms. Between these holes there are wide channels. The hydrogen has a low solubility in such alloys, but a relatively high diffusion coefficient.

In aqueous systems, the entry of hydrogen is promoted by poisons that inhibit the recombination of nascent hydrogen on the metal surface. Hydrogen sulphide, other ionic species of sulphur, antimony, phosphorus, bismuth, and cyanides are such poisons. Hydrogen embrittlement is observed at plants where those impurities are present. Hydrogen embrittlement is strongly influenced by the strength level of the metal, where hydrogen sulphide is known to be most aggressive in promoting hydrogen entry. Common metals and alloys are qualified to heat treatment and to strength level in terms of the resistance to hydrogen induced failures. These qualifications are reported in NACE standards RP-04-75, MR-01-75, and MR-01-76. The selection of suitable alloys can help to reduce the risk of hydrogen embrittlement.

Please download the published *PTQ* article (Q2 2009, Hydrogen-induced cracking and blistering) where a very effective corrosion inhibition is described. Powerful filming amines can help to reduce the risk of hydrogen embrittlement by providing a reaction barrier for the nascent hydrogen.

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

Hydrogen embrittlement (HE) is a type of damage suffered in various high strength steels. It is caused by penetration of monoatomic hydrogen into the metal. It then recombines to form molecular hydrogen leading to internal pressures that weaken the intergranular structure. Various forms of specific damage occur from HE, but generally all are versions of cracking. The differences in types of cracking are due to the specifics surrounding impact on ductility, types of environments, and types of stresses leading to the damage. The alloys most affected by this mechanism are certain carbon alloy steels, certain stainless steels, and some high strength nickel alloys.

Units affected by HE in refineries are units that contain environments with high concentrations of hot

hydrogen, proper chemical conditions, the right type of steel, and are subjected to various types of mechanical stress. There are also several special reasons HE can occur, such as welding practices, cleaning practices, and metal manufacturing processes. While these are important mechanisms that can cause HE, for the discussion here we will focus on unit types that provide the correct hydrogen-rich chemical environments and which are often the most at risk.

For HE to occur, generally three factors are necessary, including high concentrations of hot (<300°F) gaseous hydrogen, alkaline conditions, and poisoning agents that slow the recombination of monoatomic hydrogen as molecular hydrogen. Examples of common poisoning agents are cyanide, arsenic, and sulphides. The name for the type of corrosion that favours these conditions is 'wet H₂S corrosion'; it most frequently occurs in cracking units such as the FCC unit, hydroprocessing units, and cokers. However, units that take feeds from cracking units such as amine units, sour water service units, and HF alkylation units can also experience wet H₂S corrosion.

To avoid HE, many strategies should be employed. Routine inspection and monitoring help the detection and mitigation of HE. Proper alloy, post weld heat treating (PWHT) of components, proper welding practices, and proper start-up/shutdown procedures of at-risk units are all important. Protective linings can also be used in the proper circumstances to prevent hydrogen reactions from occurring as favourably. Finally, chemical mitigation can also be used to control HE to a large extent.

Chemical treatment generally falls into two categories: scavenging and passivating. Traditionally, the use of a scavenger was called for, and many equipment OEMs still call for this method of mitigation. The most common scavengers used are either ammonium or sodium polysulphide. These chemicals are often called 'cyanide scavengers' because they work to destroy the poisoning agent and thereby lower the concentration of monoatomic hydrogen to prevent its penetration. While polysulphide scavengers work well and are still used today, they have several negative side effects that have caused a decline in usage in recent decades considering the development of newer and less problematic chemical methods. The problematical side effects of polysulphides include downstream equipment fouling, toxicity, pumpability, and handleability.

Newer chemical mitigation methods surround the use of specialised high pH passivating inhibitors, or filmers, somewhat like those commonly used in other fractionator overhead corrosion service. While filmers do not directly eliminate the cyanide (or other poisoning agents) as do polysulphides, they do help to prevent monoatomic hydrogen penetration and subsequent HE. HE is prevented in this case because the passivating film fosters rapid recombination from monoatomic hydrogen back to molecular hydrogen outside the metal, thus preventing the penetration necessary for embrittlement to occur. Many refineries today prefer the use of filmers to polysulphides due to their lack of negative side effects, favourable economics, and strong ability to prevent HE.



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Q What are the advantages of installing a pre-reformer upstream of our steam reformer?

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

Installation of a pre-reformer can add up to a 10% increased capacity advantage. However, the high cost in both time and money of the installation must be fully investigated prior to any decision being taken. The operating conditions for alternative feedstocks differ significantly as well as having an impact on the site steam and fuel balance with comprehensive vessel instrumentation being necessary.

Start-up and shutdown procedures need detailed review as both fresh and discharged catalyst is pyrophoric in nature and the operational lifetime is notoriously difficult to align with that of the SMR. Pre-reforming catalyst is far more expensive and delicate than SMR catalyst with high susceptibility to poisons. Ultra-purification is frequently implemented as any poisoning is irreversible, as well as requiring adjusted steaming procedures. Both pre- and post-convection section heating coils may be necessary to accommodate the inlet temperature and enthalpy requirements versus that of a standard SMR. Pre-reformers tend to be new technology for operational personnel to incorporate into procedures. Unfamiliarity with a new unit leads to plant mishaps and these tend to irreversibly destroy the catalyst. If more than 10% additional hydrogen is required, the installation of a pre-reformer will not be a viable option. Increases of hydrogen greater than 10% are possible when using Magma catalyst as a direct replacement for the current SMR catalyst, and without the capital expense and other complications that are seen when installing new equipment.

Q We would like to switch our hydrocracking from maximum distillate to maximum naphtha for higher LPG and aromatics output. Any thoughts on achieving this?

A Adrienne Van Kooperen, PhD, Senior Technical Services Engineer & Hydrocracking Specialist, Shell Catalysts & Technologies, Adrienne.Lukaski@shell.com

Many refiners are moving towards integrated crude-oil-to-chemicals plants with the projected decline in gasoline consumption by 2050 and the global growth in the demand for chemicals. This creates a substantial economic incentive to generate 'in-house' feedstocks for petrochemicals production either from revamping existing hardware or modifying the operation of current assets. The inherent flexibility of hydrocracking, with the ability to tune yield slates from distillate to naphtha production or anywhere in between by appropriate design of the catalytic system, provides the integrated refiner with an avenue to generate feeds for chemicals manufacturing without limitations on future return to transportation fuel production. As an active participant in the petrochemicals field since

1929, Shell possesses a long history of product and technology development in the chemicals value chain that we, as Shell Catalysts & Technologies, leverage to support our customers in repurposing molecules into the petrochemical pool.

Moderate adjustments to yield selectivity via catalyst changes alone or by swinging once-through operations into recycle mode provide refiners with handles to modify hydrocracker yield slates and product qualities for chemical applications without substantial capital investment. We have worked with a number of customers in Asia to convert conventional distillate hydrotreaters into naphtha hydrocrackers to redirect these molecules into aromatics plant feed in response to the increased demand for chemicals, while several of our domestic partners have leveraged our tailored hydrocracking systems for maximum hydrogenation and ring opening to generate high quality hydrocracked unconverted oil that swings between refinery FCC and chemical steam cracker feedstock. The latter effectively strives towards the best of both worlds by selectively cracking heavy molecules into more valuable refining products and saturating the remaining unconverted oil which improves the feed quality to the steam cracker. This saturated unconverted oil, or hydrowax, becomes an economically attractive steam cracker feedstock when the material possesses sufficient hydrogen content and the requisite end point to ensure adequate vaporisation in the steam cracker furnace.

The migration from a less active, flexible or distillate selective catalyst to a high activity and highly naphtha selective platform, or vice versa, however requires broader assessment of the end-to-end process to ensure smooth operations in all equipment sections. We have seen operations where sites changed from a naphtha selective catalyst to a more mid-distillate selective, flexible system for higher diesel production and then encountered operational issues in the work-up (fractionation) section due to the significant reduction in light ends make and the resultant shift in vapour/liquid traffic. Shell Catalysts & Technologies executed studies that identified several mitigation options ranging from adjusting operating conditions to equipment upgrades which optimised the overall hydrocracker performance and reliability.

The situation posed in this question – to switch hydrocracking from maximum distillate to maximum naphtha production – most likely requires some modifications in the work-up section to address higher vapour/liquid traffic in the fractionator and the need to debottleneck the naphtha run-down system. The degree of modification depends on the level of catalytic changes involved and the capabilities of the specific equipment on the existing unit.

Hydrocracking is an incredibly adaptable process that enables refiners to convert a wide range of feedstocks to higher quality products with excellent properties. The heart of the hydrocracking process is the catalyst system that can be designed to produce yield slates ranging from maximum distillate to maximum naphtha or to operate



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with the flexibility to 'swing' between low and high conversion modes. Depending on the product disposition, refiners can optimise the hydrocracking product slate to generate highly naphthenic/alkyl-naphthenic C₆ to C₉ feedstock for aromatics, LPG, and highly paraffinic light naphtha for steam cracking, or a combination of high quality transportation fuels products with highly hydrogenated hydrowax for steam cracker feedstock. Selection of the appropriate catalytic system however depends on the hydrocracker feed type, process operating window, conversion target, and product quality specifications. Similarly, the effective transition of an existing hydrocracking unit from maximum distillate operation to a maximum naphtha mode targeting chemical applications depends on the specific feedstock, operating severity and, most importantly, the need to utilise existing catalyst or the option to load a catalyst system tuned specifically to the target chemical objectives.

Feedstock to a large extent dictates the aromatics, naphthene, and paraffin content of the naphtha product. Aromatic feed sources generally yield naphtha qualities highly suited to supplying hydrocracker products for reforming operations or aromatics chemical complexes, while steam crackers benefit more from naphtha produced from highly paraffinic feeds, such as materials derived from light tight oil. When contemplating the conversion of an existing hydrocracker operating in maximum distillate service into chemical feedstock production, the refiner should work with their catalyst supplier to determine the impact of their specific feed diet and crude slate on the end naphtha product.

Operating severity also influences naphtha qualities in the aromaticity and iso- to normal paraffin ratio. Increasing conversion across a given catalyst directionally generates more naphtha with a greater degree of isomerisation and aromatics saturation. This means that there will be an optimal operating window for each catalyst system that generates the maximum amount of naphtha with the desired product qualities. The final product disposition, heavy naphtha for aromatics feedstock or lighter, more paraffinic naphtha, and LPG for steam cracking further defines where these optima lie.

Hydrocracking provides the flexibility to shift operations between production of heavy naphtha suitable as aromatics feedstock and lighter naphtha material for steam cracking with the appropriate catalyst system and operating strategy. Operating at higher conversion per pass directionally generates more light naphtha, while reduced severity produces greater yields of high quality heavy naphtha. Naphtha qualities however change more fundamentally as a function of catalyst type. Utilising a high zeolite content catalyst with low hydrogenation capacity at low to moderate severity (at lower conversion per pass) maximises the aromatic content of the naphtha product. Increasing conversion per pass by operating at higher severity drives the production of light naphtha and LPG which benefits from a lower zeolitic content catalyst with more hydrogenation capability to enhance paraffin production for steam

cracker feed. Properly tuning the overall catalyst system and rationally designing the operating strategy therefore allows the refiner to deliver the highest quality chemical feedstock.

Expert evaluation of the entire hydrocracker unit capabilities from the feed diet to the catalyst workhorse to the back-end process equipment is the key to ensuring the successful, safe, and profitable conversion of a maximum distillate hydrocracker to maximum naphtha production or vice versa.

Q Is it possible to remove all chloride species from reformer streams?

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

The purpose of catalytic reforming is to convert low octane feedstocks into higher octane iso-paraffins and aromatics. The catalyst commonly contains platinum supported on a silica or silica-alumina base, often in combination with rhenium to form a more stable catalyst. The active side of the catalyst is stimulated with tetrachloromethane (PERC) because the activity is reduced during operation by coke deposition and chloride loss.

After catalytic reaction, the condensed liquid is sent to a stabiliser (debutaniser) column, where light ends are recovered. The stabiliser column can experience severe corrosion and fouling due to ammonium chloride precipitation. Standard cleaning approaches such as solvent washing are often ineffective and do not provide the expected results. Ammonium salt fouling is sometimes also reported on the recycle gas compressor blades.

The installation of a chloride trap upstream of the stabiliser column can help to reduce the chloride concentration and salt fouling potential. But it is of course a very costly investment that needs to be well thought out and planned. Alternatively, the much cheaper Kurita ACF Technology can be used, which is a chemical programme. Here, liquid ACF salts are created from the ammonium salts through an immediate reaction. These liquid salts have a very low corrosion potential and can be easily separated and removed from the hydrocarbons.

Q Fouling in the feed/effluent exchangers to our naphtha hydrotreater is at unacceptable levels. The feed is straight-run naphtha. Solutions please.

A **Shone Abraham, Senior Naphtha Specialist, Honeywell UOP, Shone.Abraham@Honeywell.com**

Preheat exchanger fouling can be a persistent problem in some naphtha hydrotreaters (NHT). Listed below are the most common foulants that are observed in NHT feed/effluent (F/E) exchangers which include NHT units that only process straight-run naphtha:

- Gums (feed-side fouling)
- Corrosion products (feed-side fouling)
- Salts (effluent-side fouling)

Gums

The primary cause is polymers forming due to olefins in the naphtha that are exposed to oxygen during transport or storage. This leads to the formation of combined oxygen compounds, such as peroxides. When heated in process units these combined oxygen compounds form polymers which cause fouling of heat exchangers. The most effective means of preventing the problem is to prevent the exposure of the olefins to oxygen. This is done by feeding the hydrotreater directly from an upstream processing unit rather than route the naphtha through intermediate storage. If that is not feasible, the next best preventative measure would be to ensure that any intermediate storage tank is effectively blanketed with nitrogen. These methods work by preventing the exposure of olefins to oxygen. Where these approaches are not adequate or practical, it is possible to use additives such as antioxidants and dispersants to mitigate the rate of fouling. However, the use of dispersants while the unit is online has a risk of dislodging material from the exchangers, creating pressure drop issues in the downstream reactor.

The most severe fouling problems typically occur in units where the naphtha has been imported to the hydrotreating unit. There is an increased chance that the naphtha will be exposed to oxygen during transit and the time that elapses between exposure and processing increases the total amount of peroxides formed. In these cases, a reboiled oxygen stripper is the preferred means of preventing excessive exchanger fouling. The purpose of the oxygen stripper is to break down the polymer forming combined oxygen compounds and to provide sufficient vapour and liquid contact for stripping free oxygen from the naphtha. Typically, only hydrotreaters designed to directly process imported naphtha have such oxygen strippers. Those that attempt to process such naphtha without first oxygen stripping inevitably have exchanger fouling problems.

Corrosion products

Corrosion products like iron oxides (Fe_2O_3) or iron sulphides (FeS or FeS_2) can also contribute to fouling of F/E exchangers. Scale flakes off the metal surfaces and is entrained in feed flow. This could happen either from the seals of floating roof storage tanks scraping rust from the tank walls or corrosion products from the crude unit itself. Filtering the feed can be helpful in such cases. Nonetheless, the effectiveness of having a feed filter will depend on the relative size of particles to feed filter mesh size (microns). FeS particles can be as small as 5 microns, and not all may be captured by a typical feed filter.

Salts

Effluent side fouling in F/E exchangers is typically caused by ammonium sulphides. The more nitrogen in the feed, the greater the risk. Ammonium chloride could also be the cause of fouling if feed contains organic chlorides. This type of fouling is typically observed in the last two bundles where the temperature

falls below the desublimation point. The most effective way to reduce the effluent side fouling is by intermittent wash water injection to dissolve the salts. There should be a wash water injection point towards the last set of exchanger bundles. Wash water can temporarily be injected at this location to dissolve salts and a higher than normal rate of injection (typically 7-10 l/v% of feed rate) would be required to maintain at least 25% of the injected water in the liquid state (due to the higher process temperature).

Q What is sintering in relation to catalyst deactivation and how can it be avoided?

A Simerjeet Singh, Principal Hydroprocessing Specialist, Honeywell UOP, Simerjeet.Singh@Honeywell.com

Irrespective of the technology type, catalyst deactivation can be described as a physical or chemical process that reduces the activity of the given catalysts. One of the most common ways of measuring the deactivation rate is to estimate drop in conversion or reaction rate at a given temperature for the same feed rate and quality. Several mechanisms exist for catalysts deactivation, some of which are reversible while others cause irreversible loss of catalyst activity.

Coke deposition

Under normal operating conditions, catalysts deactivate continuously over the cycle due to coke formation and gradual loss of active sites. This type of deactivation begins with adsorption of high molecular weight molecules and proceeds with further loss of hydrogen due to formation of polynuclear aromatic domains and, eventually, coke. Coke deposition is a time-temperature phenomenon. Deactivation increases with time and the temperature of the catalyst. Coke deposition occurs at a relatively slow rate and the catalyst can operate effectively for a couple of years or more before regeneration becomes necessary. The coke can cover active sites and, in extreme cases, prevent access to these sites by physical blockage of the entrance to the pores leading to the active sites. Reactor temperatures must be increased to compensate for the decline in activity caused by the accumulation of coke (and metals) on the catalyst. Unplanned upsets can expose catalyst to operating conditions beyond the design limits of the unit, accelerating the coke formation and reducing the catalyst life drastically at times.

Feedstock type, catalyst composition, reaction temperature, time on stream, and other process variables affect the yield and nature of coke. In most cases, coke on the catalysts can be burnt readily for its reuse by performing either an in situ or ex situ regeneration. Regenerated catalyst performance depends on the quality and frequency of regeneration.

Poisoning

At the front end of a processing unit, metallo-organic compounds in the feed decompose at the reactor operating conditions and deposit on the catalysts, often

referred to as metal poisoning. Strong bonds formed as a result of chemisorption may at times make it difficult to remove these impurities, resulting in irreversible damage to catalyst performance. In most cases, these poisons block or hinder the access of reactants to active sites, resulting in a drop in catalyst activity. Other sources of metals are inorganic compounds entrained in the feed with particle sizes too small to be filtered out and which, for example, may be due to incomplete desalting operations. Efficient crude desalting, limiting the total metals in the feed and customising the guard bed in fixed bed units to selectively remove the catalyst poisons, can eliminate or reduce the poisoning of the main catalysts. The amount of poison required to kill the catalysts is usually very small (ppm or ppb levels in feed to the unit) in comparison to total catalyst quantity and varies from one impurity to other.

Impact of each impurity on catalyst performance varies with catalyst support (alumina/zeolite, supported/unsupported), type (bi- or uni-function), metal (base or noble), and reaction chemistry. For bifunctional catalysts having both metal and acidic functions, like hydrocracking or reforming catalysts, each impurity can selectively target one of the two functions. For example, organic nitrogen in hydrocracker feed is a temporary poison for acid sites/function only, but the resulting drop in activity would necessitate an increase in temperature, promoting coke make.

Sintering

Sintering is broadly termed as a physical and/or thermal phenomenon that leads to agglomeration, a reduction in the surface to volume ratio of catalyst. It normally results in the loss of active sites due to alteration of the catalyst's structure. Depending on the catalyst's type, it can either result in loss of active sites due to agglomeration of dispersed metal or crystallites to larger ones or partial to total collapse of the internal pore structure and a corresponding loss of surface area.

Catalyst support and active metal sites can be sintered upon exposure to high temperatures usually during the process of regeneration or a temperature excursion/runaway. High water partial pressures can also lead to sintering, especially in the case of noble metal and high activity catalysts with chelating agent. Too much water increases the mobility of active metals, increasing the probability of agglomeration under these conditions. For some zeolitic catalysts like FCC, feed contaminants like sodium also promote sintering by acting as a flux agent which lowers the catalyst support melting point. Sintering occurs when the catalyst melts just sufficiently close to pores, blocking the access of oxygen for coke burning. All of these scenarios can result in loss of active surface, reduction in catalyst activity, and degradation of catalyst performance. In most cases, alteration to catalyst structure is permanent and the resultant loss in activity is irreversible.

Catalyst sintering can be avoided by controlling the temperature of the burn front during the catalyst regeneration process. If the temperature gets too high, there can be localised sintering of the base, causing a loss of surface area. A high temperature also causes metal crystallites to cluster together (agglomerate) and significantly reduce the catalyst's metal function. If temperatures get even higher, the support can change and permanently deactivate the catalyst. Many technologies have built-in safety logics in place to shut off the regenerator or stop the reactions to avoid catalyst temperatures from exceeding the recommended limits.

For fixed bed reactors loaded with noble metal catalysts or high activity hydroprocessing catalysts, limiting free water in the feed to the reactor, especially prior to catalyst wetting and activation, is usually an effective way of reducing the risk of sintering. Similarly, proper crude desalting can help limit the sodium carryover to HVGO/FCC feedstocks and minimise the risk of sintering in FCC catalysts.

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Rapid and Accurate Analysis of Sulphur and Chlorine in Biofuels by XRF

All biofuels - blended or not - must meet certain sulphur regulatory limits. In addition, some biofuels contain fairly high levels of chlorine which can cause corrosion damage during and after the production stages. **X-ray Fluorescence (XRF) delivers rapid and accurate results for testing sulphur and chlorine in biofuels**, backed by international standard test methods (ASTM, ISO, etc.). Advantages of XRF technology include its non-destructive nature, easy sample preparation process, and quick results, in addition to accuracy that is on par with alternative technologies like UVF (ultraviolet fluorescence).

We conducted a study using Sindie +Cl, XRF benchtop analyser, to test sulphur and chlorine in eight real-world samples: B10, B20, Gasoil, Hydrotreated Vegetable Oil, Rapeseed Methyl Ester, Soybean Methyl Ester, Tallow Methyl Ester, and Used Cooking Oil Methyl Ester. Having the correct sulphur value for biofuels is critical as they are typically blended with fuels that have a maximum specification of 10 mg/kg for sulphur (15 mg/kg in the US). This is important to note because oxygen absorbs XRF signals and as a result, can cause analysers to report falsely low sulphur and chlorine concentrations.

Sindie +Cl is a viable solution, delivering total sulphur and chlorine in one measurement without the need for a matrix-matched calibration by simply applying a correction factor to the results. This allows professionals to certify their biofuel products more efficiently than with other methods.

Table 1: Tallow Methyl Ester (TME) (mg/kg)

Test	Sulphur (300s)	Sulphur Corrected	Chlorine (300s)	Chlorine Corrected
average of 10 repeats	8.18	9.74	0.48	0.57
st. dev.	0.45	0.53	0.07	0.09
RSD%	5.48	5.48	15.06	15.06

Table 2: Used Cooking Oil Methyl Ester (UCOME) (mg/kg)

Test	Sulphur (300s)	Sulphur Corrected	Chlorine (300s)	Chlorine Corrected
average of 10 repeats	7.74	9.22	425	509
st. dev.	0.40	0.48	2.88	3.45
RSD%	5.16	5.16	0.68	0.68

An example of the excellent repeatability obtained in this study by Sindie +Cl is demonstrated in Tables 1 and 2: TME and UCOME samples. The summarized data of the two samples show the average of 10 repeats with their respective standard deviation and relative standard deviation percent, as well as the corrected results for oxygen content. All data has been acquired under repeatability conditions and show very accurate results.

View the full study by visiting

[xos.com/
biofuelsXRF](https://xos.com/biofuelsXRF)



Sindie +Cl delivers exceptional reproducibility for both sulphur and chlorine analysis and can measure both elements concurrently. Samples are measured directly, which means it can analyze even the heaviest of hydrocarbons, like crude oil or coker residuals, without the hassle of boats, injectors, furnaces, or changing detectors. **Sindie +Cl complies with ASTM D2622, and therefore meets the regulatory limit of ASTM D6751 and ASTM D7467. It also meets the precision requirements for ISO 20884 and can be used for EN 14214.**



Sindie® Online is an industrial grade process sulphur analyzer with breakthrough detection capability to monitor ultra-low sulphur in biofuels. This process analyser can take a measurement every 30 seconds, enabling refiners to fine-tune their process control and maximize profits. Powered by MWDXRF®, Sindie Online uses ASTM D7039 technology, the same technology used in Sindie benchtop, and offers resilience to feedstock changes with the ability to measure a variety of challenging sample types without the need for significant changes to sample conditioning.



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Capturing carbon dioxide from refinery streams

Using hydrogen manufacturing units to demonstrate the relative benefits of technologies for capturing carbon from low and high pressure streams

LAURENT THOMAS and GARY BOWERBANK
Shell Catalysts & Technologies

Governments around the world are increasingly expected to penalise carbon dioxide (CO₂) emissions to help fulfil their responsibilities under the 2015 Paris Agreement on climate change. This leaves refiners and chemical plants with a mandate to reduce their CO₂ emissions substantially, and many companies are committing to reducing their carbon footprints.

For most businesses, this will involve a mosaic of solutions, including energy efficiency initiatives, fuel switching, and process optimisation. However, serious ambitions to reduce refineries' carbon intensity are likely to be spearheaded by carbon capture, utilisation and storage (CCUS). Indeed, the UN's Intergovernmental Panel on Climate Change special report on the impact of 1.5°C global warming concludes that "early scale-up of industry carbon capture and storage is essential to achieve the stringent temperature target". The International Energy Agency agrees, stating that CCUS is a key technology for reducing CO₂ emissions in carbon-intensive industrial processes and offers one of the lowest cost ways of doing so. In today's capital constrained environment, one of the principal challenges that refiners may face is finding ways to do this economically.

By 2050, 2.8 billion t/y of CO₂ needs to be captured and permanently stored to meet the International Energy Agency's sustainable development scenario, which meets the UN's sustainable development goals for energy access, emissions, and air quality,

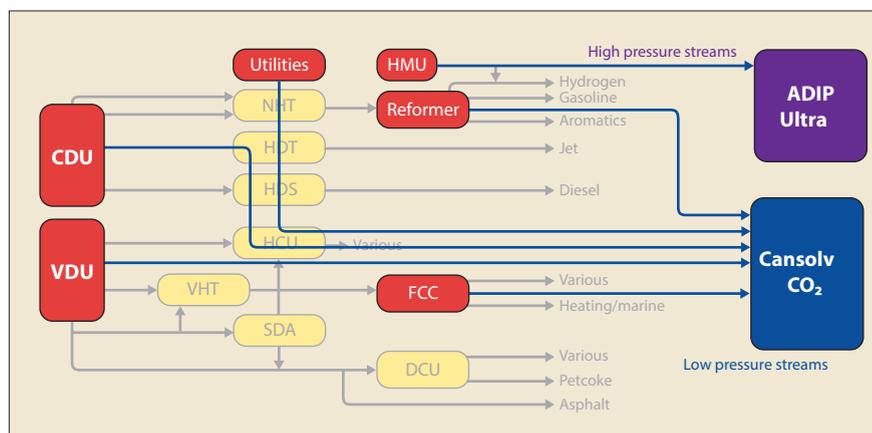


Figure 1 The main sources of CO₂ (red) and high and low pressure capture technologies

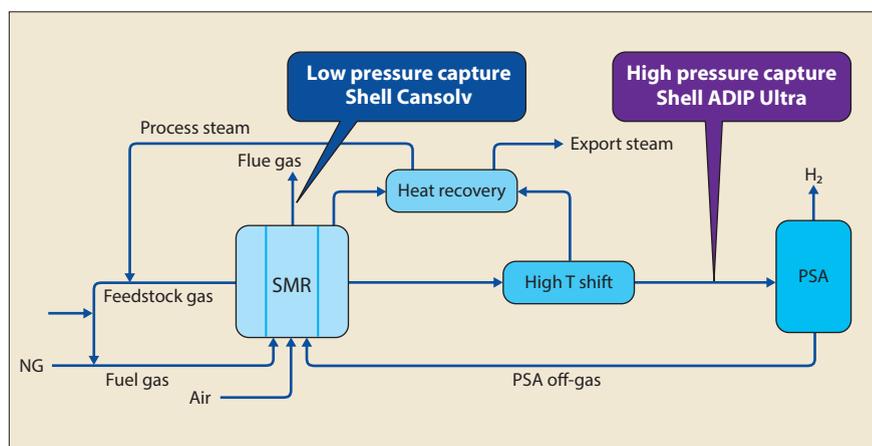


Figure 2 Options for CO₂ capture from an SMR unit using Shell's technologies

and has a 66% probability of limiting global temperatures to 1.8°C.¹ Currently, CCUS projects capture about 40 million t/y of CO₂, so many more projects are needed in the coming decades.²

Over the last decade, CCUS capacity has nearly doubled while the project pipeline shrank from 2010 to 2017 in response to the global financial crisis that focused governments on short term economic recovery and the private sector on survival.² However, dur-

ing the last three years, project momentum has recovered, driven by the Paris Agreement. There is growing interest from refineries and chemical plants because CCUS offers a cost-effective way to enable carbon-intensive industries to continue to operate through the energy transition.

Upgrading the bottom of the barrel to clean fuels requires hydrogen, so it is common for refineries to have a hydrogen manufacturing unit (HMU), most often based on

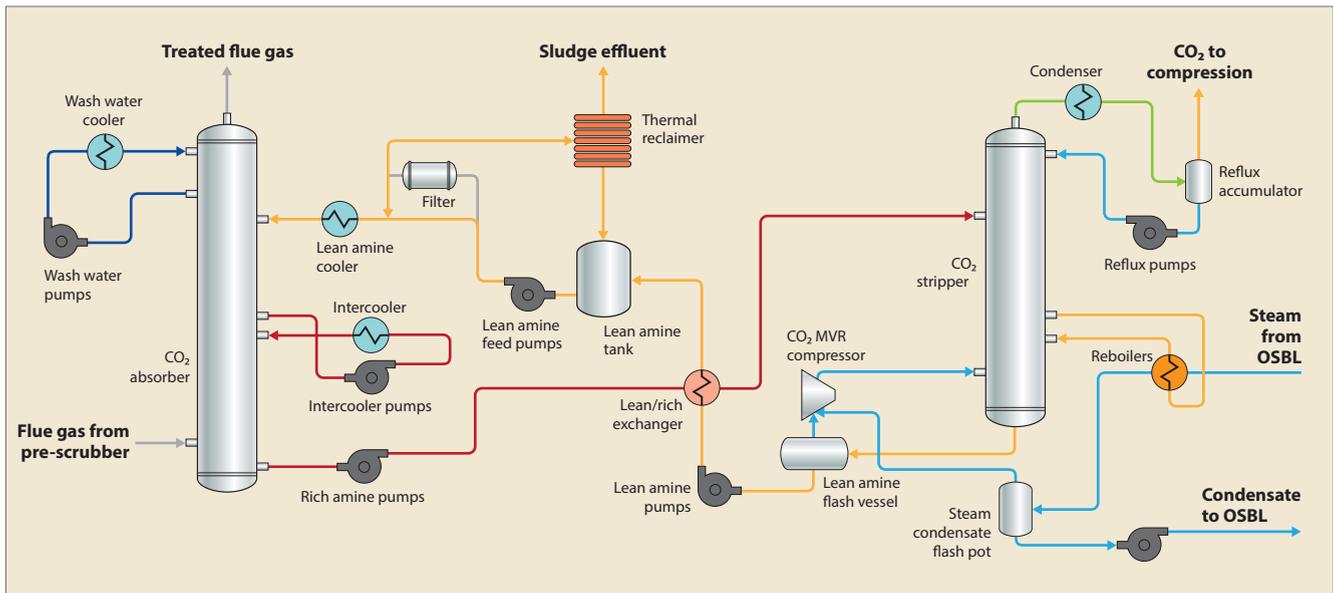


Figure 3 Cansolv CO₂ Capture System

steam methane reforming (SMR) technology, that creates CO₂ from both the chemical reactions and from burning fuel to power the process chemistry. Although many refinery units produce CO₂ (see Figure 1), this article focuses on carbon capture from the HMU because it generates a large, relatively pure stream of CO₂ and provides opportunities to capture CO₂ from high pressure, pre-combustion and low pressure, post-combustion streams, thereby enabling a cost-benefit comparison between two mature capture technologies developed by Shell (see Figure 2).

This article showcases two leading technologies with established records for cost-effective carbon capture in a wide range of industries:

- Shell's Cansolv CO₂ Capture System for capturing CO₂ from low pressure streams, including flue gas; and
- Shell's ADIP Ultra technology for capturing CO₂ from high pressure process streams.

Selection of a retrofitting option for a refinery (pre- or post-combustion) depends on, among other factors, the value assigned to the captured CO₂ (from avoided tax, tradable credits or income from its use in enhanced oil recovery [EOR] or other industrial applications).

Leveraging experience

CO₂ capture technology is not new;

it is established and proven. In the 1930s, carbon capture technologies began commercial operation in the processing of natural gas. In the 1970s, commercial-scale CO₂ injection into reservoirs started. To date, more than 260 million tonnes of anthropogenic CO₂ has been captured and stored, mostly through EOR projects, and the current CCUS capacity is about 40 million t/y.²

Other energy-intensive sectors, for example coal-fired power generation, oil sands extraction, and cement manufacture, have already been charged with dramatically reducing the carbon intensity of their operations. Refiners can leverage the operational experience, technologies, and expertise from these sectors to do the same.

For example, the coal-fired power generation sector, after a first generation of carbon capture projects with a capture cost of about \$100/t CO₂, is now targeting costs of half this, about \$50/t CO₂, for its future projects.¹

Low pressure streams

Shell's Cansolv CO₂ Capture System can capture up to 99% of the CO₂ from post-combustion low pressure off-gases. As a tail-end, low pressure CO₂ capture technology, it is well suited for retrofitting. It uses a regenerable solvent based on a proprietary amine to capture the CO₂, which is released as a pure stream

that can be sold, sequestered, or used in EOR.

In refiners' technical and economic evaluations for capturing CO₂ from flue gas, the Cansolv CO₂ Capture System may emerge as the preferred option because of key features such as:

- **CO₂ purity:** the pure CO₂ product enables EOR, CCS, or carbon capture and use downstream of the plant
- **Adaptability:** the system is highly adaptable to a wide variety of industrial applications, CO₂ concentrations (from 3.5% to 25% and higher), and gas flow rates (licensed units treating gas at flow rates of 11 000-685 000 Nm³/h are in operation or under construction)
- **Asset integrity:** the system has been designed for reliability through its flexible turndown capacity and improved resistance to oxidative and thermal degradation
- **Low waste:** the process uses a regenerable solvent, so there are no direct waste by-products, which can reduce project costs since the effluents are minimal
- **Retrofit suitability:** as a standalone system, it is ideal for retrofit scenarios and greenfield projects
- **Low operating costs:** the system offers cutting-edge performance. For example, its low parasitic energy consumption, fast kinetics, and extremely low volatility help to reduce the costs of operation and amine consumption
- **Track record:** the largest appli-

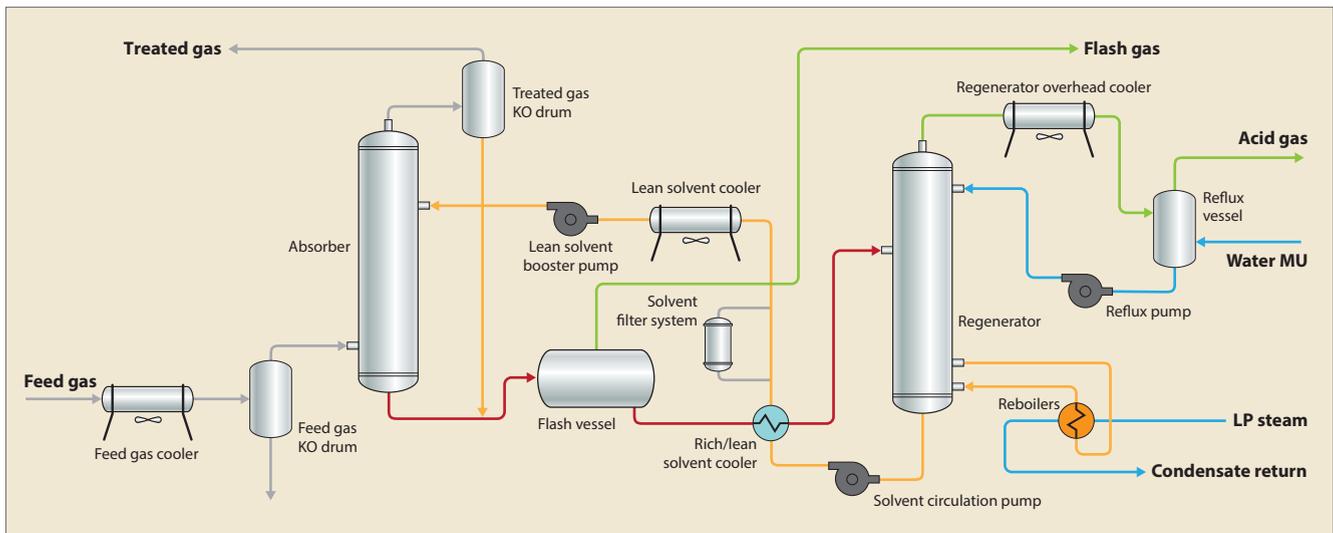


Figure 4 A typical ADIP Ultra line-up

cation is designed to capture 1 million t/y of CO₂ and has been operating successfully for four years (see case study below)

- **Potential for integrated sulphur dioxide (SO₂) removal:** it can be integrated with the Cansolv SO₂ Scrubbing System for near-complete SO₂ removal

Process description

The key steps of the Cansolv CO₂ Capture System (see Figure 3) are as follows:

1. The feed gas is quenched and saturated in a circulated water pre-scrubber
2. The gas contacts the lean amine solution in a counter-current packed absorption column
3. CO₂ is absorbed and the treated gas exits to atmosphere
4. Midway along the column, partially loaded amine is removed from the tower, cooled, and reintroduced over a layer of mass transfer packing
5. CO₂-rich amine from the absorption column is pumped through a lean-rich amine heat exchanger and then to the regeneration column
6. Rising, low pressure, saturated steam in the column regenerates the lean amine solution. CO₂ is recovered as a pure, water-saturated product
7. Lean amine is pumped from the stripper reboiler to the absorption column for reuse in capturing CO₂
8. The CO₂ is directed to by-product management systems

Case study: SaskPower

To extend the operating life of the 150 MW Unit 3 of its Boundary Dam power station in Saskatchewan, Canada, SaskPower needed to reduce CO₂ and SO₂ emissions. This six-unit, lignite-fired plant is SaskPower's largest coal-fired power station and a significant source of electricity for the region.

After carefully evaluating a range of technical options, SaskPower chose to add a Cansolv SO₂-CO₂ Integrated Capture System for combined carbon capture and flue gas desulphurisation. This involved adding a 55m tall CO₂ absorber, a 25m tall CO₂ stripper, a 31m tall SO₂ absorber, and a 17m tall SO₂ stripper.

The unit is designed to capture 1 million t/y of CO₂, which is compressed, transported through pipelines, and used for EOR in nearby oilfields. The CO₂ is thus permanently stored in deep geological formations where it cannot contribute to climate change.

SO₂ from the flue gas is converted to up to 60 t/d of sulphuric acid – a marketable by-product. Among its many other potential applications, the acid can be used as a feedstock for the local fertiliser industry.

The SO₂-CO₂ capture plant and its underlying chemistry enable SaskPower to continue to operate under strict Canadian CO₂ emissions regulations.

High pressure streams

In addition to capturing CO₂ from low pressure flue gas, it is increas-

ingly important for many refiners to capture CO₂ from high pressure process streams such as those from HMUs. This is possible using amine based ADIP technology. ADIP technology is deployed at more than 500 Shell and non-Shell sites worldwide and has a proven record in the natural gas sector for deep removal of CO₂. It is increasingly finding applications in refining.

The latest generation of this technology is ADIP Ultra, which uses an optimised solvent formulation and an improved design based on years of operational lessons learning. Used with the latest generation column internals (Shell Turbo Trays), this technology can easily achieve bulk removal, thereby maximising CO₂ capture and meeting deep specifications for the treated gas while optimising both the capacity of the solvent and the regeneration duty (see Figure 4).

Compared with using conventional accelerated methyl diethanolamine, ADIP Ultra can help to:

- Reduce capital costs by up to 30%, thereby increasing project net present value
- Lower regeneration energy requirements by up to 30%
- Capture up to 25% more CO₂, thereby enabling monetisation of difficult gas without capital investment
- Provide operating stability, which enables operators to push the limits

ADIP technology's applications include the removal of hydrogen sulphide and CO₂ from refinery and

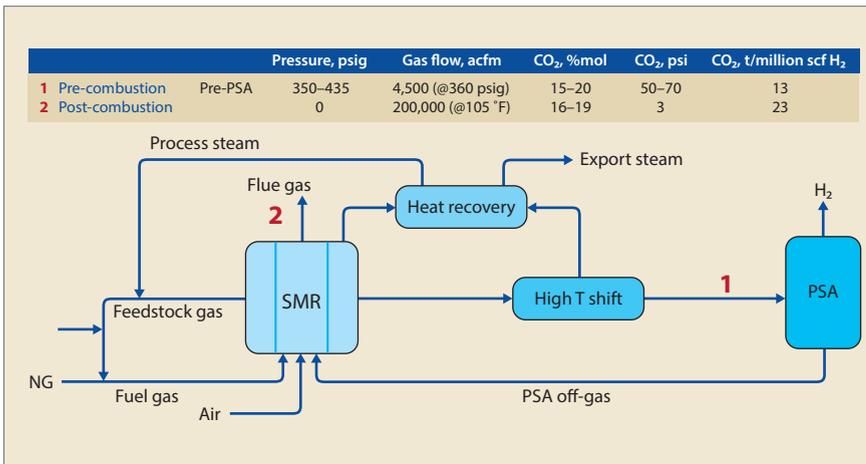


Figure 5 HMU carbon capture Options 1 and 2

natural gas streams, and the bulk removal of CO₂ from gas streams.

Targeting HMUs

HMUs generate large, relatively pure CO₂ streams and provide opportunities for CO₂ capture from high pressure, pre-combustion and low pressure, post-combustion streams. This gives refiners the flexibility to consider these two different routes to capturing significant quantities of CO₂ at their facilities. It also provides the opportunity for a cost-benefit comparison of the two technologies described to illustrate their relative benefits.

A typical 100 million scf/d HMU with an SMR, high temperature shift, and pressure swing adsorption (PSA) line-up (see Figure 5), and natural gas fuel and feedstock can generate 830 000 t/y of CO₂. This CO₂ can be captured from the high pressure, pre-combustion stream after the shift reactor before PSA using ADIP Ultra technology (see Figure 5, Option 1). High pres-

sure capture recovers less CO₂, as the CO₂ generated by the SMR process reactions amounts to about 45% of the total CO₂ emitted by the HMU. However, higher pressure means smaller gas volumes and a higher absorption driving force, which usually results in a lower capture cost per tonne of CO₂.

Alternatively, a Cansolv CO₂ Capture System can capture nearly all of the CO₂ (99.9%) from the low pressure, post-combustion flue gas (see Figure 5, Option 2). This option maximises the amount of CO₂ captured, as the treated gas contains CO₂ generated both by the process reactions and combustion in the furnace. However, the low pressure stream means larger gas volumes and lower CO₂ partial pressure, and thus a larger, more expensive unit requiring more space.

The choice between Options 1 and 2 depends on, among other factors, including available space, the value of the captured CO₂

(avoided tax, credits gained or income from commercial use for EOR, and so on) minus the cost of capture (unit construction and operating costs) multiplied by the amount of CO₂ captured. This is illustrated in Table 1.

In this example, hypothetical yet credible values have been used to illustrate the relationship between captured amount and unit capture cost which operators often face. The unit cost of post-combustion capture is greater than for pre-combustion capture, and if a low or moderate value is assigned to the captured CO₂, this usually results in lower profit.

However, if the value assigned to the captured CO₂ is high, then the larger amount of CO₂ captured significantly increases project revenues and offsets the higher capture cost to the point where the post-combustion capture option becomes more attractive.

HMU case study: Quest

The Scotford upgrader at the Athabasca oil sands project in Alberta, Canada, produces synthetic crude oil by processing mined bitumen with hydrogen at high temperature and pressure to break up the large hydrocarbon molecules of the bitumen. The hydrogen is generated by three on-site HMUs which create significant CO₂ emissions.

Quest, the world's first commercial scale CCS project for an oil sands operation, uses amine absorbers and ADIP-X technology to capture about 80% of the CO₂ from the HMUs' process gas streams. The captured CO₂ is then dehydrated, compressed, and transported for about 75 km by pipeline for injection into a layer of rock more than 2 km underground.

During its first four years of operation, the Quest project has successfully captured and sequestered more than 4 million tonnes of CO₂ from the Scotford upgrader. The facility has proven to be capable of capturing in excess of its nameplate capacity of 1 million t/y of CO₂. Reducing CO₂ emissions by 1 million t/y is equivalent to taking 175 000 North American cars off the road.

An example of the benefits of high vs low pressure capture

Benefits = CO₂ captured x (CO₂ value - cost of capture)
Example for a 100 million scfd plant (hypothetical capture cost and CO₂ value)

	Pre-combustion		Post-combustion	
CO ₂ captured*, million t/y	0.41		0.74	
CO ₂ avoided, million t/y	0.35		0.60	
Cost of capture, \$/t average	50		80	
CO ₂ value, \$/t	60	200	60	200
Revenues, million \$/y	3.5	53	-12	72

* Assumes emissions of 25 USt/million scf CO₂ in syngas 55% of total emissions and 90% capture in each case

Table 1

Conclusions

SMR based HMUs offer the choice of capturing CO₂ from the high pressure, pre-combustion, pre-PSA process stream or from the low pressure, post-combustion furnace off-gas. The decision to opt for pre- or post-combustion capture depends on the operator's long-term view of the value/cost of CO₂ over the life of the plant and whether its capture project is driven by minimising unit capture cost or maximising captured tonnage.

For low pressure applications, Shell's Cansolv CO₂ Capture System provides robust, adaptable, reliable, and proven technology for capturing up to 99% of the CO₂ in exhaust gases, thereby producing a CO₂ product suitable for sequestration, EOR, or other industrial uses. It has been in use commercially for several years, with reference sites capturing up to 1 million t/y of CO₂.

For high pressure process streams, including those from HMUs and gasification units, Shell's latest generation ADIP Ultra technology offers robust CO₂ capture

with high levels of performance and reliability. ADIP technology is used at more than 500 sites to capture CO₂ from high pressure process streams. It is cost-effective and can help to reduce capital expenditure by up to 30% and lower regeneration energy requirements by up to 30% compared with conventional accelerated methyl diethanolamine technology.

New units

This article discusses retrofitting CO₂ capture technologies to high and low pressure streams from existing HMUs. However, blue hydrogen (hydrogen produced from natural gas with CCUS) is likely to be an important part of the future energy mix requiring many greenfield CO₂ capture units.

For such greenfield developments, there are more efficient alternatives to SMR technology that incorporate CO₂ capture. An article on the technologies Shell can offer for greenfield blue hydrogen plants will be available in a future edition of *PTQ*.

CANSOLV is a mark of Shell.

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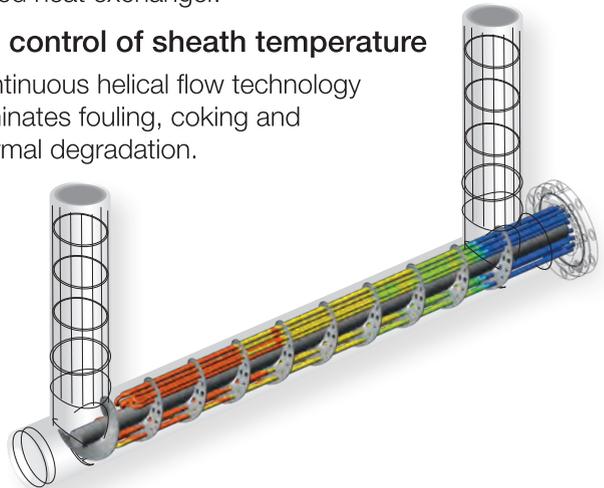
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MOHAMMAD UMAR and HIREN SHETHNA
Anukoolan Solutions

In the case of a heat exchanger, fouling causes substantial energy losses, leading to less efficient heat exchange between the streams. It also increases resistance to fluid flow, resulting in higher pressure drops across the exchanger. As a result of the combination of these effects, the resultant temperature of the process stream is lower than the anticipated value. Furthermore, in a network of exchangers, the downstream exchangers' behaviour could become counterintuitive. Usually as an upstream exchanger fouls, the driving forces on the downstream exchangers increase, so they could appear to perform better. However, the net effect usually is additional load on downstream furnaces and steam heaters.

In a traditional petroleum refinery, a number of these heat exchangers are connected in series,

followed by a fired heater before the crude stream is allowed to enter the atmospheric and vacuum distillation columns. If any of the heat exchangers are fouled, the result will be a lower furnace inlet temperature which would require additional duty in the furnace to achieve the desired column inlet temperature.

The impact of fouling is not limited to furnace duty and energy consumption increase alone. At the end of the preheat train and beyond the furnace is a set of distillation columns which separates the useful products present in crude oil. Considering that everything is interconnected as a network, the column throughput, the condenser duty, and the product flows and compositions are affected by fouled exchangers. The column may no longer produce the desired quantity of useful prod-

ucts, leading to a bigger economic loss as well as a loss of energy. The aim of this article is to highlight the effects of fouling on the performance of heat exchangers, condensers, furnaces, and distillation.

Moreover, if the exchangers are not cleaned, not only is their performance reduced, but it can also lead to a failure of the equipment, resulting in a safety issue in some cases.

Methodology

A fouling analysis was conducted to evaluate the effect of fouling on the performance of a typical preheat train and distillation columns, as well as to determine the detrimental effect of fouling on the economic value of the products.

Aspen Hysys was used for the simulation of a model required to perform the analysis in conjunction with Aspen Simulation

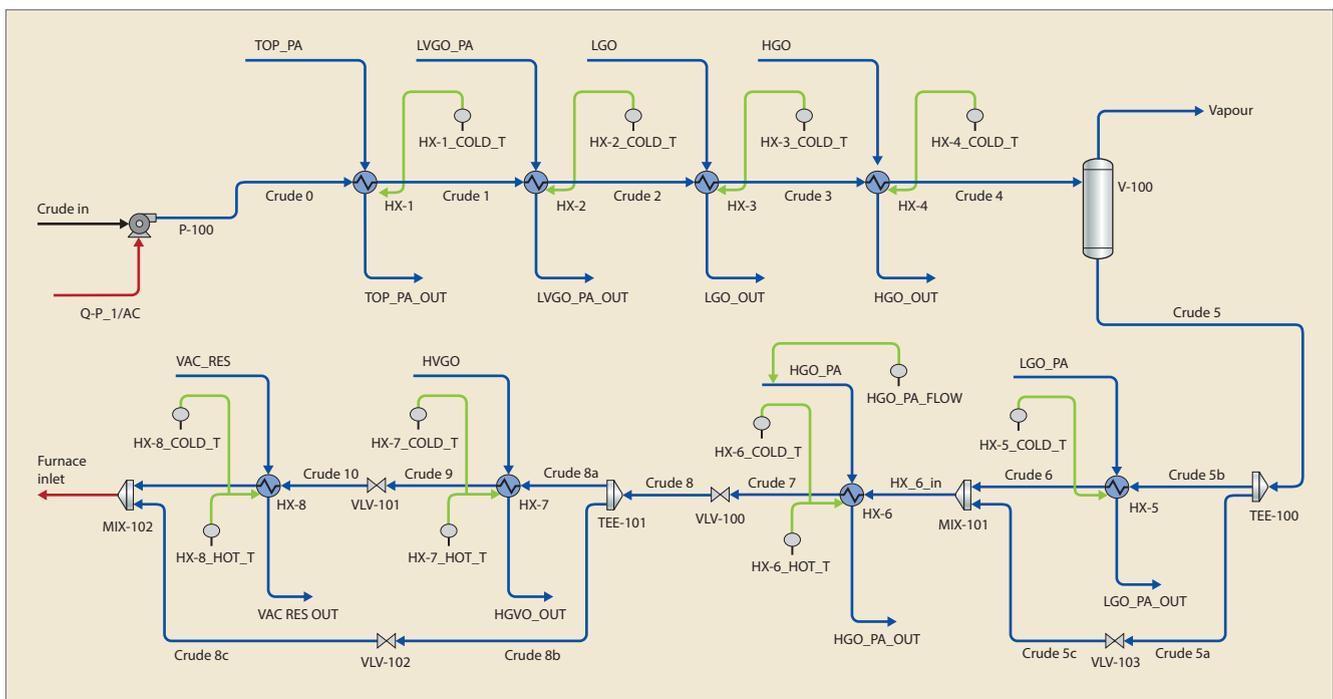


Figure 1 EO model of the preheat train developed in Aspen Hysys

Workbook (ASW) and Virtual Basic for Applications (VBA) in Microsoft Excel.

An equation oriented (EO) model was developed for data reconciliation with the help of an objective function to minimise the offset between plant and model values. **Figure 1** shows the schematic of a preheat train with some measurements in their respective places for temperatures and flows.

As the schematic shows, a temperature measurement was added on the crude side (cold outlet) of each exchanger as well as on the product stream side (hot side) for some of the exchangers to control the outlet temperature of the crude stream. A flow measurement was installed on the HGO pumparound stream to monitor and control the effect of the hot side stream in this scenario.

An objective function was created, aiming to minimise the offset between the measured and calculated values for the measurement variables. **Equation 1** shows the calculation for the objective function:

$$Objective = \text{Minimise} \left(\sum_{i=1}^n \text{offset}_i^2 \right) \quad (1)$$

where 'n' stands for the number of offset value inputs in the objective function.

$$\text{offset} = T_p - T_m \quad (2)$$

where T_p and T_m stand for plant and model temperature values respectively.

$$\text{offset} = F_p - F_m \quad (3)$$

where F_p and F_m stand for plant and model flow values respectively.

The duties of the exchangers in this model are reconciled to achieve the goal for this EO model – minimum offset between the plant measurements and model values. In addition to this, we use rigorous heat exchanger capabilities to obtain the fouling factor for each of the exchangers post data reconciliation.

Several cases were run on the existing model to simulate the highest and least fouled conditions for the heat exchangers, and the output values were recorded to further investigate the extreme situations.

A simulation case consisting of the preheat train was attached to atmospheric and vacuum distillation columns to obtain the products. The products and the pumparounds from the column are used in turn back in the preheat train as hot fluids to preheat the crude oil. This model helps in analysing different fouling scenarios and their effect on the performance and economics of the process.

An ideal case with a very low fouling factor for each exchanger was run as well as a case with a high fouling for each exchanger to highlight the contrast between two extreme cases. These cases were run again, side by side, under different conditions and parameters for the furnace duty, condenser duty, and reflux ratio. A price index was appointed to each product and crude oil to calculate the overall profit under different circumstances.

Subsequently, a price amount was also associated with the energy requirements to compare the loss of energy to product flow, thereby establishing the dominant parameter.

Results and discussion

Multiple cases were run based on different fouling conditions, furnace duties, condenser duties, and reflux ratios to compare the profit generated based on the output product flows. The results are shown in **Table 1**.

The first case (Case 1) in **Table 1** is an ideal case which can be taken as a reference case. The second case (Case 2) is the worst-case scenario where all the exchangers are highly fouled to their maximum limit. However, as exchangers foul, some equipment, such as the fired heater and crude column condenser, starts to hit its limits. From a modelling perspective, those are calculated values in Case 2, and therefore we need to adjust those constraints in the model. This is done in Case 3.

Case 3 represents a realistic scenario where furnace duty and condenser duty have been restricted, representing capacity constraints. The naphtha and kerosene flow have been maintained close to the original clean case to obtain unbiased results. The flow of crude has to be reduced to maintain the crude unit fired heater duty. Further, due to limitations in condenser duty, we

Flow comparison for fouling cases under different constraints

Flow, t/h	Case 1: min fouling	Case 2: max fouling	Case 3: adjusted conditions
Crude	729.0	722.0	702.5
Condensate vapour	0.1	0	7.2
Naphtha	116.8	135.5	109.8
Kerosene	92.3	68.8	87.1
LGO	122.7	125.4	116.8
GO	98.7	95.4	94.9
Vacuum overhead	1.1	1.1	1.1
LVGO	17.8	17.8	17.9
HVGO	92.4	92.9	88.4
Vacuum residue	188.1	186.0	181.0

Table 1

Prices of raw material and products

Price, \$/ton											Price, \$/MMBtu
Crude	Condensate vapour	Naphtha	Kero	LGO	HGO	Vacuum overhead	LVGO	HVGO	Vacuum residue	Duty	
425	200	475	510	520	510	200	425	375	300	4	

Table 2



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Price comparison for fouling cases under different constraints

Price, \$/t	Case 1: min fouling	Case 2: max fouling	Case 3: adjusted conditions
Crude	-309 825	-306 850	-298 563
Condensate vapour	19	0.00	1441
Naphtha	55 480	64 363	52 167
Kerosene	47 078	35 078	44 407
LGO	63 804	65 208	60 728
HGO	50 317	48 674	48 423
Vacuum overhead	224	226	221
LVGO	7582	7578	7590
HVGO	34 643	34 823	33 164
Vacuum residue	56 430	55 800	54 310
Furnace duty	-1270	-1370	-1333
Profit	4481	3529	2555
Profit per unit crude flow	6.2	4.9	3.6

Table 3

Mass flow rate of various components after cleaning individual exchangers

Flow, t/h	HX-1	HX-2	HX-3	HX-4	HX-5	HX-6	HX-7	HX-8
Crude (-)	702.5	702.5	702.5	702.5	702.5	702.5	702.5	702.5
Condensate vapour	4.5	5.3	5.3	5.3	4.0	4.8	6.8	7.1
Naphtha	109.3	109.4	109.4	109.4	109.2	109.3	109.5	109.5
Kerosene	91.3	89.9	89.9	89.9	90.5	90.0	89.0	88.8
LGO	115.9	116.1	116.1	116.1	118.7	116.0	116.7	116.8
HGO	96.6	95.2	95.2	95.2	99.7	98.0	98.8	99.4
Vacuum overhead	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
LVGO	17.9	17.9	17.9	17.9	17.9	17.9	17.9	17.9
HVGO	86.1	88.2	88.2	88.3	80.5	85.5	82.7	81.7
Vacuum residue	181.4	181.1	181.1	181.0	182.1	181.4	181.8	182.0

Table 4

are unable to condense all the overhead gas and it stays in the gaseous state. The economic value of overhead gas is generally lower than that of liquid product naphtha.

Table 3 compares these three cases on the basis of notional profits from this process using typical representative prices (\$/t) for components (see Table 2). Since in refineries these are only intermediate prod-

ucts, it is a challenge to obtain such prices, though we could get them based on shadow prices from a refinery linear programming model. An energy cost value of \$4/MMBtu is assumed. Such a profit comparison is for indicative purposes to assess quantitative impact.

According to the calculations provided in Table 3, the most profitable scenario is the one with the least

fouling, as expected. The maximum fouling case has no restrictions on duty for the furnace and condenser which does not represent a realistic case. Therefore, Case 3 has been discussed with given limitations to replicate real life scenarios.

The data show that the realistic case (Case 3) has even lower profits than the maximum fouling case. The maximum fouling case is a hypothetical case where the exchangers are fouled to the maximum level and no restrictions on duties have been applied. Such a case would never exist in real life.

Heat exchanger with maximum impact

An analysis was performed comparing the different exchangers after cleaning them one by one to understand which exchanger has the biggest impact on profits. Similar conditions were applied for each scenario as discussed for Case 3; that is, we obey the constraints on furnace duty and condenser duty

Table 4 shows the mass flow data of various components for all eight heat exchangers next to each other.

Table 5 shows the data for all eight heat exchangers next to each other, along with the individual revenue generated after cleaning them one at a time.

After comparing the profits across all exchangers, it is evident that cleaning of HX-5 will have the largest impact economically. The profit value per unit flow of crude is almost the same as Case 1 with no fouling. It is also clear that by

Price comparison to identify the heat exchanger with largest impact after cleaning

Price, \$	HX-1	HX-2	HX-3	HX-4	HX-5	HX-6	HX-7	HX-8
Crude (-)	298 563	298 563	298 563	298 563	298 563	298 563	298 548	298 548
Condensate vapour	899	1062	1061	1056	801	954	1354	1428
Naphtha	51 918	51 965	51 965	51 965	51 870	51 918	52 009	52 027
Kerosene	46 568	45 834	45 844	45 854	46 170	45 890	45 405	45 270
LGO	60 268	60 372	60 372	60 372	61 724	60 320	60 669	60 734
HGO	49 266	48 557	48 562	48 527	50 862	49 985	50 372	50 679
Vacuum overhead	218	221	221	221	212	218	214	213
LVGO	7599	7591	7591	7591	7625	7603	7623	7623
HVGO	32 276	33 079	33 071	33 113	30 195	32 078	31 002	30 655
Vacuum residue	54 420	54 330	54 330	54 300	54 630	54 420	54 553	54 591
Furnace duty	-1333	-1333	-1333	-1333	-1333	-1333	-1333	-1333
Profit	3538	3115	3122	3102	4194	3490	3320	3337
Per unit crude flow	5.0	4.4	4.4	4.4	6.0	5.0	4.7	4.8

Table 5

cleaning any one exchanger, the profits can increase significantly. The profit value per unit flow of crude for fouled exchangers was about \$3.6/t/h, which has increased by approximately \$1 for each case. Such an analysis also helps us in deciding which exchanger to prioritise for the purpose of cleaning and maintenance.

Conclusion

An ideal case with all clean heat exchangers in a preheat train with the right conditions is extremely hard to achieve in real life except when the equipment is brand new. A maximum fouling case with no restrictions on furnace and condenser duties was modelled but not practical in real life. Therefore, a case with realistic duty values and fouling conditions has been discussed in this article which shows that fouling cannot only adversely affect energy use but also the profits of the refinery. In the case of a preheat train, cleaning each exchanger has a marginally different impact on

improving the economics of the process and one of them has the largest impact. This particular exchanger can be different for a different process layout or even different pricing conditions. The hot side fluid could

The economic analysis showed that at least \$1/t of crude could be saved every hour by cleaning an exchanger

also potentially affect the outcome of the simulation as it is recycled back to the distillation column.

The economic analysis showed that at least \$1/t of crude could be saved every hour by cleaning an exchanger, especially in cases where equipment limitations result in reduction in crude flow or creation

of higher value products and higher energy consumption. This amount could add up to a huge value when considering the annual income of the plant.

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Hiren Shethna is the Founder and Director of Anukoolan Solutions which specialises in developing and deploying model based optimisation solutions across the chemical industry. With more than 25 years' experience in refining and oil and gas systems modelling, he previously worked with Saudi Aramco and Aspen Technology as an expert contributor in modelling and optimisation. He holds a PhD in chemical engineering from the University of Manchester, UK and a master's degree in chemical engineering from Indian Institute of Technology, Bombay, India.

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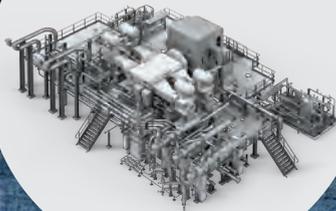
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Planning to counter economic turbulence

Synchronising engineering and planning models should be a key aim to support the resilience and agility needed for economic recovery

RON BECK
AspenTech

Global economic disruption has upended the refining industry. Not only are the dynamics of the situation difficult, but they seemingly change on a weekly or even daily basis.

In this territory of future price and demand uncertainty, refinery planners and schedulers are in the hot seat. Refinery executives and managers are forced to examine new scenarios daily, and each scenario needs to be evaluated for safety, logistics, and economics. The organisation's planners are at the nexus of this.

They will be the key to a refinery's economic resiliency and agility in the future. They require advanced technology to ensure the accuracy of their digital models in non-standard operating regimes, and ability to examine many scenarios quickly to optimise across a wide envelope of options and opportunities.

The business challenge

Refineries are typically set up to produce predominantly a mix of gasoline, diesel, naphtha (as gasoline and petrochemicals feedstock), and jet fuel. In today's market, with gasoline and jet fuel in slowly recovering demand and over-supply, and diesel the preferred transportation fuel output, planners and engineers are being asked by executives to rapidly develop refinery plans that maximise diesel. In tomorrow's market, with the energy mix in transition, most rapidly in Europe, planners can be strategic in advising executives as to the best capex and process strategies to achieve agility and resilience in the face of uncertain future market evolution. Both questions are being asked now.

Today, a wider range of crudes are

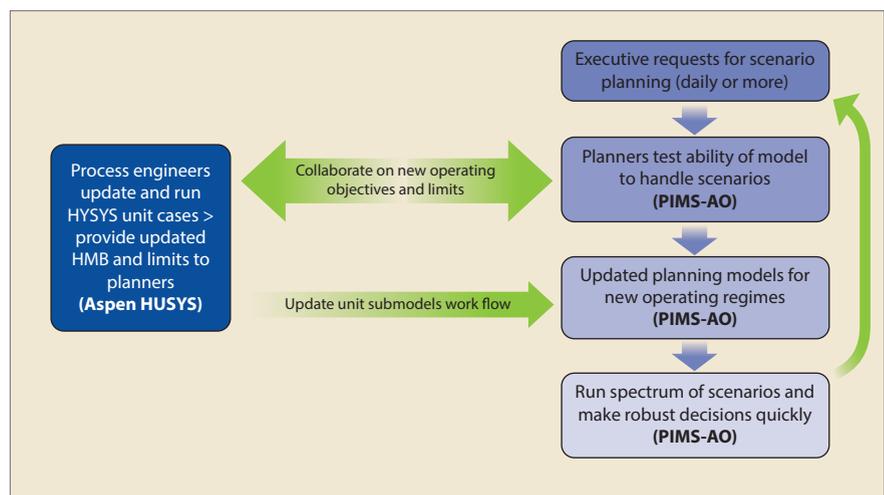


Figure 1 Collaborative planning and engineering for scenario planning in today's environment

available at low prices, which can be enticing, but future demand and pricing are uncertain, and refineries can potentially lose a lot of money if wrong choices are made. With diesel prices holding better than other product prices, maximising diesel is, in the short term, a key objective. Jet fuel demand is likely to be the slowest to come back. This focuses attention on several key refining units, especially the CDU and VDU, where the fractions that yield diesel can be maximised. Further, with maintenance crews having been largely taken out of the asset for health reasons, the integrity and safety of the process units must be reassessed when flows and parameters are changed significantly. This calls for engineering advice relative to scenarios that may look advantageous to planners.

It is now clear that assets may need to be operated in a new normal, with lower staff density on site. This requires looking at the interaction between production, catalyst lifetime, and asset health and integrity.

There are many cascading, related refining operational questions that planners and engineers are asked to answer. What is our lowest throughput safe operating level? Should we order catalysts early due to supply chain interruption? Can we make minor process reconfigurations to better utilise our intermediate products? What other moves can we make to take advantage of crudes that may be available at lower prices? Which operating plans give us better flexibility in face of extreme volatility of prices, supply, and demand?

Collaboration to respond to the challenge

Close collaboration between planners and process engineers is required to answer these questions. A digital solution is the best enabler of rapid response to this challenge. The modelling systems (for instance, the Aspen PIMS submodels used in about two-thirds of all refineries) used in planning a typical refinery were not originally implemented or tuned for the kinds

of eventualities being encountered dynamically today. Before the scenarios can be run with accuracy, the models of these key economic units must be changed to reflect accurately the proposed operating regimes. The engineering digital twin models of key units are a crucial competitive advantage to obtain a fast, actionable answer. And an automated workflow to enable the engineering model prediction to inform the planning submodel, without significant manual time, provides a critical advantage.

Figure 1 shows the collaborative work process required to respond rapidly to the need to scenario plan in this environment of volatility, uncertainty, complexity, and ambiguity.

The following are typical steps needed to answer executives' questions about scenario planning for increased diesel, low jet demand, rapidly changing prices, and flexibility for the future.

Address dramatically different product mix scenarios (maximising diesel and minimising jet and gasoline cuts; be prepared for increased naphtha demand as olefin feedstock).

The CDU and VDU submodels most importantly, but also hydro-

cracker, hydrotreater, and/or FCC submodels in the planning model were most probably not developed with the requirement in mind to look at these 'extreme' situational plans with any accuracy. When these linear submodels are pushed to outside the expected limits, the accuracy of the prediction will go way down. The scenarios are outside the existing model's range of accurate predictions. These model elements need to be quickly and efficiently rebuilt based on a new range of expected operating limits.

First, the simulation (Hysys Refining or similar) models need to be quickly updated, to match current operating data, and the process alternatives for maximising diesel cuts and minimising jet and gasoline cuts need to be created and modelled. Working remotely, as most are today, the engineer sets himself up for cloud access to the models, then obtains current data sets to recalibrate and update the model. The calibration can be accelerated using today's technology, with recent innovations in performing calibration assisted by data science, step-by-step widgets, and in-software advice. This needs to be done with constant collaboration with the

planner while working remotely. By running a sensitivity analysis of the planner's desired options, Hysys will inform the safe operating limits for the CDU and VDU and physical properties that need to be used for these new operating regimes.

Next, those CDU and VDU model results must inform an updating of the planning submodels. This can be done by communicating to planning the new safe operating limits, correct assay information, and new base delta vectors for the PIMS-AO (or similar) submodel. AspenTech has available a convenient and efficient workflow for updating the various PIMS submodels and is progressively automating that.

Using the PIMS-AO planning model, a wide range of crude and pricing products and demand scenarios can be run, to identify the optimal operating plan. Leveraging high performance computing, many scenarios can be run, and in this economic environment the planner may wish to run thousands of sensitivity cases across a range of possible scenarios on a daily basis.

Address low maintenance operating scenarios (running without heat exchanger cleaning and other routine maintenance):

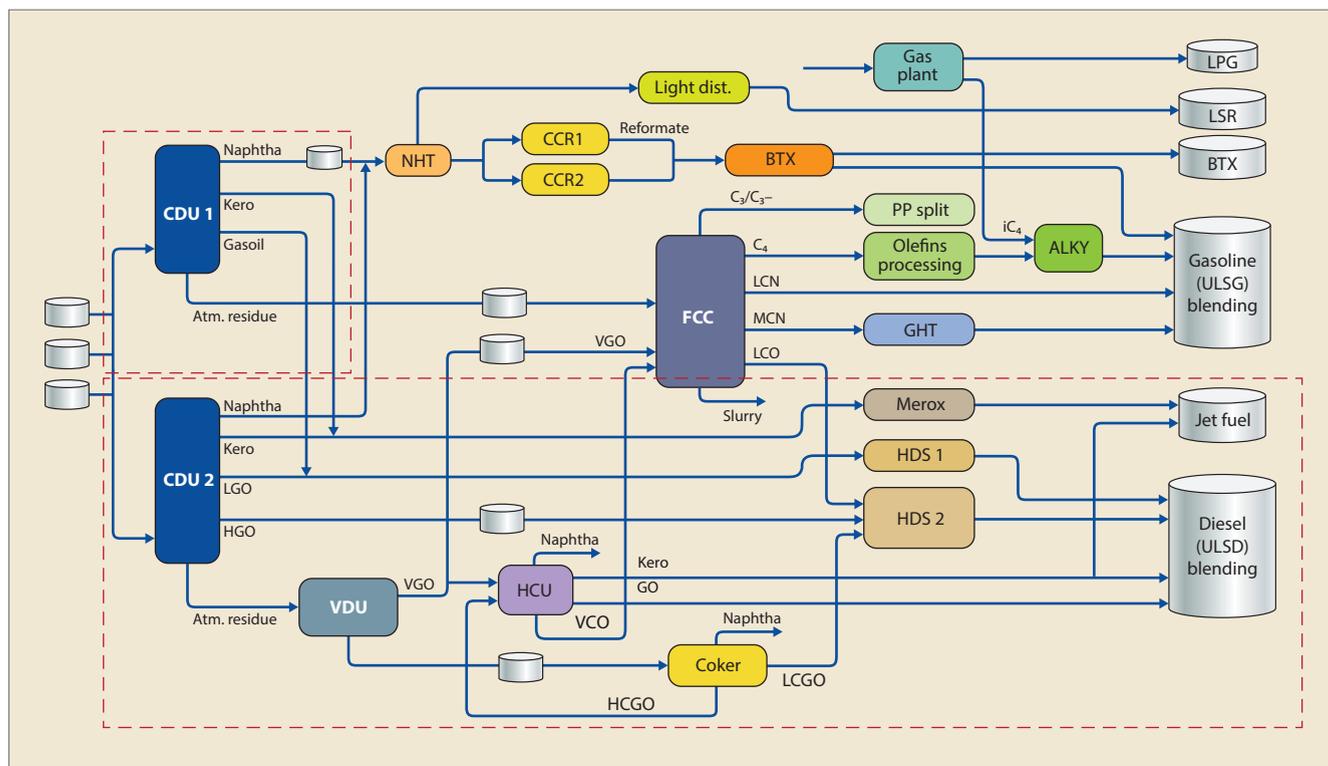


Figure 2 The CDU, VDU, HCU and cokers are all involved in rebalancing a refinery to produce more diesel

- The engineering team runs Hysys through a range of reactor/pre-heat train modelling scenarios to identify operating yields attainable under different heat exchanger fouling cases consistent with different lengths of time that may be necessary to run while deferring all but the most essential plant maintenance.

- Update planning models with a new operating yields model.
- Run refinery operating scenarios under different maintenance and production scenarios.

Use cases in a volatile pricing and demand environment

Here are a few typical use cases in which collaboration between engineering and planning can provide rapid scenario planning for a refinery's executive team:

- Maximise diesel production while minimising kerosene and gasoline output. Using Hysys and PIMS-AO together, quickly update the planning model, identify safe operating limits, understand feasible changes to the CDU, VDU, and kerosene hydrotreater, and understand the impact on catalyst life (see **Figure 2**).
- Evaluate crudes that are available at low prices and have not been used in the refinery previously.
- Evaluate multi-plant economics to make decisions about which refineries to run at which turndown levels, and product mix options across the circuit of plants.
- Evaluate catalyst lifetime and or substitutions that will better fit the new operating objectives, and make catalyst decisions with the best economics.
- Thorough scenario planning, advised on lowest feasible operating levels: PIMS-AO scenarios can identify the economics of different operating levels; HYSYS can identify safety and operating risk issues.

Case studies

Here are a few typical case studies to spur your thinking on the opportunities and possibilities that are available today to improve decision-making. None of the organisations we are working with during this current economic disruption time period wants to be named yet,

but these two earlier cases will give a strong indication of the benefits available.

The Korean refiner, Hyundai Oilbank, found that as feed quality had changed from when their planning models were built, due to changed crude slates or changed process conditions, the accuracy of their planning models when back-casted against their actual monthly operations had fallen as low as 90%. The refiner diagnosed the problem as being centred on the main FCC unit and worked with us to build and calibrate a Hysys FCC digital twin engineering model of this economic unit and then, through a semi-automated workflow, updated their PIMS-AO planning submodels of the same unit. The accuracy of the FCC planning submodel was improved to 98%, resulting in better plans increasing the ability to operate the FCC with a higher effective capacity and with a net annual margin benefit of \$36 million.

Energy producer and refiner Shell operates a network of over 15 major global refineries, international trading markets, and many associated assets, (for example, in Canada alone the planning network includes upgrading, blending, refining, chemicals, CCS storage, and terminal operations spanning multiple pathways to market). Employing the high performance computing capabilities of PIMS-AO planning technology implemented in the cloud, Shell has applied an agile value chain decision-making approach spanning operations and markets. The company's multi-asset model runs at high speed to enable better operational efficiencies, can anticipate movements of crude and products through their network, and is able to run a complete scenario in minutes to react to dynamic conditions. By optimising this model, Shell has achieved improved optimisation at each facility, enabled workers to focus on more strategic work, make better crude purchases and sales, improve planning across facilities, and better react to volatile and unexpected market conditions, as well as maximising economic performance across the global and seasonal variability they work within,

in particular volatile demand and economics.

This ability to optimise across multiple assets at speed is a strategic advantage with multiple future scenarios for recovery of hydrocarbon product demand over the next 12-18 months.

Conclusion

Technology can help refining companies to evaluate more scenarios faster in a time of economic transition. In these unusual circumstances, technology providers are working more closely than ever with the refining industry.

Here are some things companies could be doing in the short term:

- Putting both planning and engineering models in the cloud to enable remote working scenarios and to empower planning and engineering teams to collaborate.
- Taking advantage of e-learning opportunities to help knowledge workers improve their skills in some of the advanced optimisation techniques. Uncertainty in the market will continue for some time and skilled workers will empower organisations to conduct better analysis.
- Review your coverage of your key economic units with digital twin models. Construct or update those key models that are current gaps in your digital arsenal.
- Provide the incentive for better planning-engineering collaboration. Through the types of collaborative efforts discussed in this article, your organisation's agility will be supported by an accurate and flexible planning model.

At the highest levels, an awareness of the key technology tools in your arsenal is key to achieving competitive advantage. If the engineering digital twin and planning models are not synchronised and working accurately, this should be a key target for digitalisation to support resilience and agility in 2020 and 2021.

Ron Beck is the Industry Director of AspenTech. He has over 20 years' experience in providing software solutions to the process industries and 10 years' experience in the commercialisation of chemical engineering technology.

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IMO 2020: meeting the challenge

Developments in fuel additive technology address challenges and uncertainties raised by the IMO 2020 regulations

KERSTIN MÜLLER
Clariant

In one of the largest changes to environmental regulations in the shipping industry for decades, new rules reducing the sulphur content of marine bunker fuels came into force, beginning 1 January 2020.

Before these rule changes, shippers used low grade bunker fuel, the world's dirtiest diesel and a byproduct of the refining process. This bunker fuel had high sulphur content and was a major contributor to air pollution, as the exhaust from sulphur that is burned can be harmful to both humans and the environment. Now ships are required to use fuels with sulphur content capped at 0.5% compared to the previous limit of 3.5%. As the biggest reduction in the sulphur content of a transportation fuel that has ever been undertaken at one time, this move will drastically improve air quality and human health, particularly for those living close to ports and coastlines.

More broadly, the new regulations are part of a more ambitious, and longer term, sustainability strategy by the International Maritime Organization (IMO), the United Nations shipping agency. For the IMO, the year 2020 marks the beginning of the Sustainable Shipping for a Sustainable Planet initiative. This includes the goal of reducing greenhouse gas emissions from shipping by at least 50% by 2050 compared to 2008, whilst pursuing efforts towards phasing them out totally.

Leading up to the introduction of the new regulations, industry experts and analysts tried to forecast the impact on the shipping and bunker fuel industries – from cost implications and potential shortages of low sulphur fuel oil (LSFO) to oil comingling challenges and regional impacts, for example in Africa,

given the mix of lower and higher sulphur in oil production across that continent.

Six months in, questions still remain as to how the balance between environmental improvements and the potential impact on the bunker fuel and shipping industries is going to be achieved and, furthermore, how this first move to LSFO will be implemented in the longer term.

Though it is still early, concerns have already been raised. Since

Questions still remain as to how the balance between environmental improvements and the potential impact on the bunker fuel and shipping industries is going to be achieved

the new regulations have come into force, Standard Club, a specialist marine and energy insurer, says that it has been notified by some concerned members of the non-availability of compliant fuel at some ports, although it was not specific as to which ones.¹ Likewise, ship owners have warned of complications around LSFO, particularly in relation to sediment and wax formation.² In addition, the ISO Standard 8217 that specifies the requirements for fuels for use in marine diesel engines does not provide specific guidance on the composition of low sulphur fuels,

causing these LSFOs to vary greatly in composition and quality.

Before the new IMO 2020 regulations came into force, the main blend component for high sulphur fuel oil (HSFO) was high sulphur residue. The residue was blended with various cutter stocks to create the final HSFO composition. With the new regulations, high sulphur components will need to be replaced. In principle, refiners have three options available to them to accomplish this: additional desulphurisation, blending with low sulphur distillates, or the use of low sulphur crude oils as feedstock. Which option is preferred is dependent on the set-up of the individual refinery and the availability of blend components and crude grades.

Crudes and heavy fuel oils are complex mixtures of various hydrocarbons ranging from paraffins, aromatics, naphthenes, and resins to asphaltenes. While aromatic type LSFO bears a higher risk of instability, and incompatibility, when comingled with other fuel types, paraffinic type LSFO might show cold flow challenges like increased pour points. Put simply, paraffins will precipitate when cooled down whilst asphaltenes will precipitate when destabilised. Diluting high sulphur streams by using low sulphur distillate streams like marine gasoil will also have an effect on the cold flow characteristics.

So what are the key challenges with fuels that contain paraffins? Paraffins in the fuel tend to crystallise when cooled down, leading to severe increases in viscosity and solidification. They could be redissolved through heating; however, this requires a tremendous effort in terms of cost and time. Changing

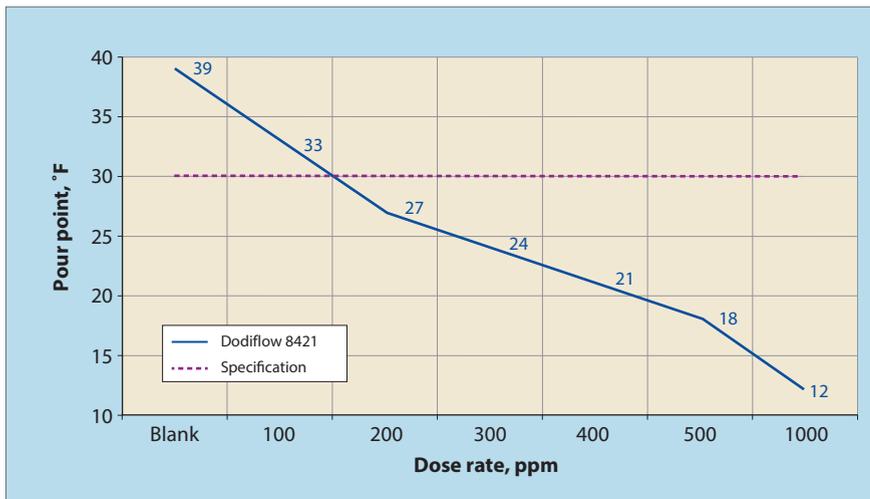


Figure 1 Pour point response of very low sulphur fuel oil with Dodiflow 8421

Characterisation of LSFO		
Pour point, °C	ASTM D 97	39
API@15°C	DIN 51757	17.3
WAT, °C	In-house method	38.5
WDT, °C	In-house method	42.4
SARA-Analysis		
IP 469		
Saturates, %		52.0
Aromates, %		26.0
Resin, %		18.0
Asphaltene, %		4.0
GC-Analysis		
Paraffin content, %	In-house method	31.4
<C10		0.02
C10-C17		0.79
C18-C35		22.3
C36-60		8.32
>C60		0

Table 1

the crude slate towards low sulphur crudes like 'sweet light' will ultimately also increase the amount of paraffins processed. Hence a higher pour point of the resulting fuel oil can be expected.

A pour point is the lowest temperature at which a fuel or oil will pour and, through additives called pour point depressants (PPDs), the pour points of fuel oils can be significantly reduced without changing the combustion behaviour of the LSFO. PPDs are polymer-like additives which are dosed to the LSFO ideally right after the blender fuel outlet, when the temperature of the fuel is high.

PPDs do not change the temperature at which wax crystallises or the amount of wax that builds up. Their application relies on the PPD co-crystallising with the targeted paraffin species present in the oil,

thus modifying the wax crystal structures to one more favourable to flow. Further, the wax crystals are kept isolated by the PPD backbone and, because of this steric hindrance, the wax crystals are no longer able to form the 3D structures responsible for gelation and flow inhibition.

Crucial to its application is that the PPD is dosed above the 'wax appearance temperature' (WAT) of the fuel. The WAT describes the temperature at which the first paraffin crystals start to form when a fuel is cooled down. The WAT can be determined by different methods like differential scanning calorimetry or viscosity measurements; however, such methods usually do not exist in refinery laboratories. A general rule of thumb is to dose the PPD 20°C above the pour point of the fuel; for example, if the fuel has

a blank pour point of 39°C, it would be recommended to dose the PPD at 60°C.

As a leading provider of marine fuel additives, Clariant Refinery Services has developed two PPD additive solutions for new types of marine fuels including Dodiflow 8421 and Dodiflow 6087, to ensure that the bunker industry can be confident in low sulphur blended fuels being compliant and safe.

Dodiflow 8421 is a specialised pour point depressant designed to improve cold flow properties of 0.5% sulphur fuel oils and has been tested to lower the pour point of the LSFO to the specification of 30°C. For the test results provided here, the LSFO and PPD had a temperature of 50°C. Considering the high blank pour point of the LSFO sample, Dodiflow 8421 showed an excellent response behaviour with a very low dose rate to achieve the target. Using only 200 ppm of Dodiflow 8421, the pour point of LSFO was reduced from 39°C to 27°C, allowing the ISO 8217 specification of 30°C to be achieved. The tests found that increasing the dose rate continued to improve the PPD response, up to 12°C at a dose rate of 1000 ppm (see Figure 1 and Table 1).

Dodiflow 6087 is a premium fuel additive pour point depressant designed specifically to improve the cold flow properties of low sulphur marine distillate to the required specification. Table 2 shows the characterisation of the marine diesel including the cold flow properties. In testing, the used marine distillate had a blank pour point of 12°C. The summer and winter specifications, which are required by ISO 8217, were easily met with dose rates of 65 ppm and 75 ppm, respectively. Figure 2 shows that increasing the dose rate leads to further improvement of the pour point, which leaves additional options for the refiner to blend heavier components into the marine diesel.

In addition to pour point challenges, mixing paraffinic and aromatic fuels can lead to fuel instability and incompatibility that can cause bottom sludge formation and increase the risk of engine failure.



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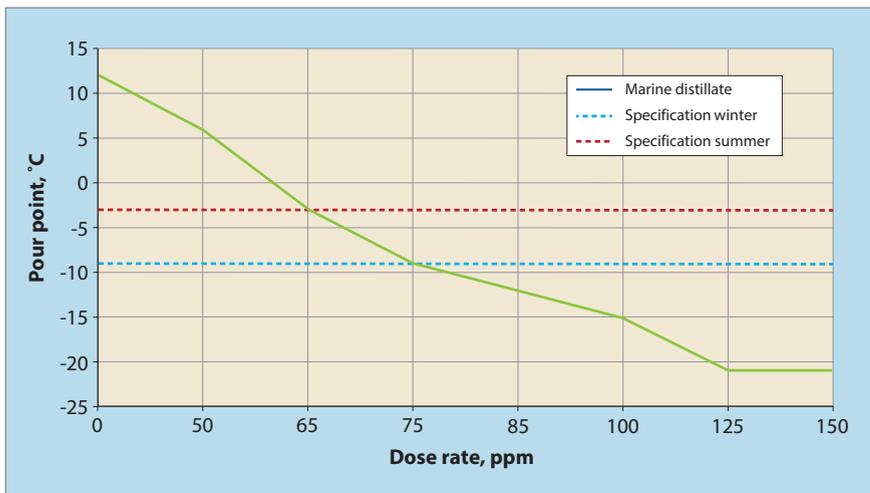


Figure 2 Pour point response curve of marine distillate with Dodiflow 6087

Characterisation of marine diesel (DMA 89 type)		
Properties	Method	Result
CP, °C	EN 23015	+15.5
CFPP, °C	EN 116	+15
PP, °C	ISO 3016	+12
Density, g/cm ³	ISO 12185	0,876
Aromatics, wt%	EN 12916	41.3
n-Paraffin content, wt%	Gas chromatography	23.4

Table 2

Clariant's LSFO compatibility enhancer Dispersogen 2020, formulated for the IMO 2020 regulations, is an additive designed to improve the stability of aromatic low sulphur marine fuel. When aromatic fuel compositions are comingled with more paraffinic blends, bottom sludge can form, destabilising the fuel. This destabilisation has the potential to do serious damage to engines. As well, asphaltenes can separate, also forming a sludge inside engine filters and separators, with the potential for loss of propulsion and auxiliary power. As there is no universal refining method for LSFO, neither ship owners nor fuel suppliers will know when, where or how different LSFO qualities have been mixed.

By dispersing asphaltenes and other fuel oil components to support the compatibility of fuel oil mixes, Dispersogen 2020 is used as a preventative measure to ensure that global refiners can meet new standards with fuel oil blends that will remain stable and compatible.

Recent testing of the asphaltene dispersion of an aromatic LSFO

blend containing Dispersogen 2020, measured according to ASTM D 7061 using a Turbiscan MA 2000, showed a consistent transmission throughout the test tube, indicating homogenous distribution of parti-

In addition to pour point challenges, mixing paraffinic and aromatic fuels can lead to fuel instability and incompatibility that can cause bottom sludge formation and increase the risk of engine failure

cles and a low separability number. This test demonstrated the success of Dispersogen 2020 in preventing sludge from forming and keeping the LSFO blend stable. Using the

same test, untreated blank LSFO showed an increasing transmission over the length of the tube, reflecting precipitation of insoluble matter and indicating the formation of sludge.

Both the pour point depressant and marine fuel compatibility enhancer solutions have been the focus of research and development at Clariant's new Crude and Fuel Oil Center of Excellence in the UK. The new laboratory is equipped with advanced technology, a wide selection of testing regimes, modern methods of crude oil analysis and performance testing, and the ability to replicate field conditions within the laboratory.

Specifically, Clariant has adopted the use of high throughput experimentation (HTE) methods for scientific experimentation alongside advanced analytics. Originally developed for use in pharmaceuticals, the HTE method rapidly improves upon classical experimentation methodology. Over the last three years, Clariant has utilised its HTE laboratories to perform feasibility studies to prove that this new research approach is useful in formulation development for the oil and gas industry. Using HTE, Clariant can identify more precise chemical formulations that go through the application development far quicker than traditional manual laboratory methodologies.

HTE methods have been particularly important in developing new pour point depressants. The first development step for a PPD is to measure the interaction it has with the viscosity of crude oil. The classic way to measure viscosity in a laboratory is with a technician operating a viscometer or rheometer. This method takes 30 to 40 minutes per measurement.

At the heart of HTE is a mixture of robotics, data processing, control software, liquid handling devices, and sensitivity detectors. Its development comes on the back of advances in smart automation, miniaturisation, parallelisation, and statistical design. It decreases time to market, enabling faster discovery of new technologies, and delivers greater understanding of existing

technology. In the laboratory for PPD development, a series of robotic arms enable the movement of crude oil samples to miniaturised and parallel viscometers. As this machinery will continuously work day and night, the testing process is accelerated while datapoints can be provided that otherwise would not be possible.

When HTE is combined with computational experimental design software, it becomes even more effective. The Design of Experiment software mathematically analyses the space in which fundamental properties are being measured. Instead of having to make 100 measurements to cover this space, it mathematically deconvolutes the data so that fewer measurements are required as it predicts the white space it leaves behind.

Although the software is commercially available, Clariant's process of taking existing technologies and combining them in novel solutions is unique for the development of PPDs. It is now possible to explore multiple options for potential for-

mulation using HTE by quickly disseminating formulations from one another. The result is a high degree of accuracy and, speed enabling customised formulations to be developed for every application that requires it.

Ship owners and refineries understand that they face potential quality issues in the near term from the impact of mixing together LSFOs that still have not been fully tested on ships' engines for composition, compatibility, and performance. Clariant's research and product development advances are helping to overcome this nervousness and uncertainty around solutions, and has led to increased interest from refiners to use PPD and other fuel stabiliser technology, as these are critical additives for ships without scrubbers to prevent pour point problems, fuel incompatibility, breakdowns, and significant financial losses.

Ship owners and the marine bunker fuel industry will continue to assess the impact of the IMO 2020 regulations for some time to come.

There will be ongoing challenges within the framework of this 'new normal', as well as new additives and solutions that will ensure that ships can continue to sail.

DODIFLOW and DISPERSOGEN are marks of Clariant.

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Kerstin Müller is Clariant Refinery Services' Product Expert in Pour Point Depressants, supporting refiners and fuel trading companies with their crude and fuel oil additive challenges. She coordinates product development, field trials, as well as research projects related to crude and fuel oil additives specifically related to transport and storage. Currently, she focuses on the fuel stabilisation and compatibility issues that have arisen due to the recent IMO 2020 standards introduced for bunker fuel and holds a PhD in polymer chemistry from the University of Marburg, Germany.

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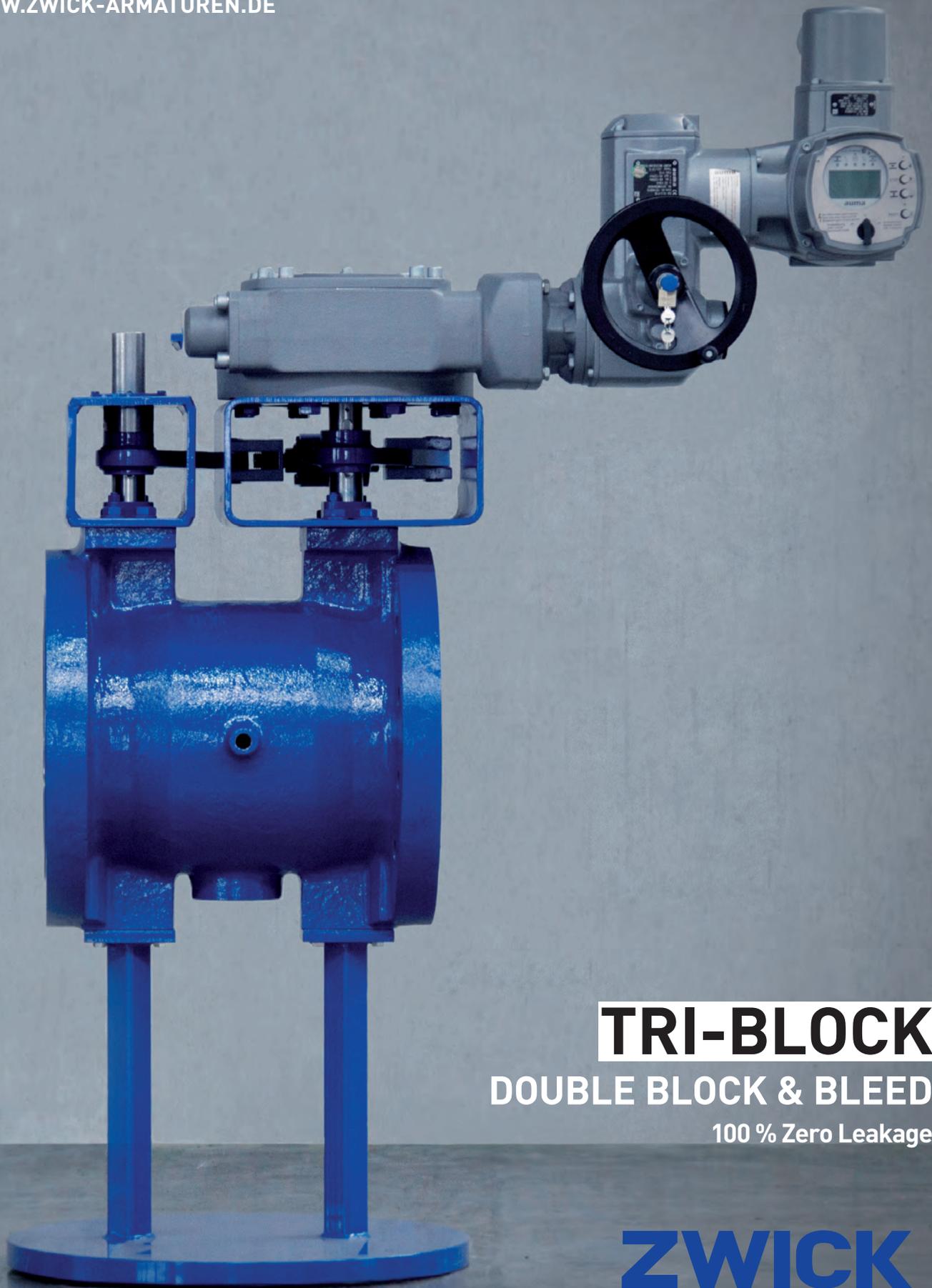
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Protect control valves when production slows

With many plants running at reduced rates or on shutdown, control valve operation faces severe challenges to maintain throughput. Solutions are at hand

ZANE BODENSTEINER and MATT GULLEEN
Emerson

Covid-19's effects have forced many petrochemical and refinery units to run at reduced rates or shut down temporarily. Abnormally low production rates, extended shutdowns, and reduced staff all create significant challenges for continued control valve reliability. This article will focus on the problems that each of these situations cause and offer solutions to deal with the issues in a cost-effective manner.

Falling output and rising problems

Most petrochemical and refinery units are designed to run at maximum rates, and many have undergone numerous debottleneck projects to push capacity even higher. However, decreased demand now calls for many units to produce just enough to keep the plant operating. Such abnormal conditions can have unexpected effects on the control valves that are crucial for plant operation. The following problems may arise.

Poor control

A control valve is normally sized to operate around 40-60% open, with a minimum opening of 10-15% and a maximum opening of up to 90%. Under these conditions the valve will provide consistent, stable flow control. However, low production rates can drop the minimum opening to 10% or less, forcing the valve to control with the plug very close to the seat. Under this condition, the flow will be erratic and difficult to control since a minor stem movement can generate a very significant and non-linear flow response. Additionally, extremely low travel operation under a clearance flow condition may cause additional damage to the seat. Clearance flow



Figure 1 Valve cavitation often occurs at low production rates and can cause significant damage to valve internals

occurs below the minimum controllable flow because the plug is not fully seated.

Cavitation

At low production rates, line pressure losses may be significantly reduced and a larger than normal pressure drop could appear across the valve. This condition tends to create or exacerbate cavitation in the valve, which can cause significant damage to the plug, seat, and valve internals (see Figure 1).

Anti-surge valves

During normal plant operation, a compressor anti-surge valve runs closed since the flow through the compressor is well above surge conditions. Low production rates often reduce the compressor load and force the anti-surge valve open to maintain flow through the compressor stages. These continuous high flow, high noise, and high pressure drop conditions can damage the anti-surge valve over time and force an unexpected outage should the valve fail.

Low flow rates rarely extend critical valve maintenance

It is easy to assume that reduced production rates will extend critical

valve maintenance cycles, but this is rarely the case. Valves exposed to corrosive conditions will continue to corrode at the same or even accelerated rates. Flow phenomena, such as cavitation and flashing, can also cause accelerated erosion. SIL-rated safety valves will still require periodic testing regardless of the production rate, and high pressure drop valves may sustain damage faster than normal. Therefore, critical valves should continue to be inspected, maintained, and tested at the same frequency as they were during normal production rates to avoid unexpected downtime.

Extended shutdown issues

When a plant shuts down temporarily, the operational condition of the control valves must be maintained and preserved so the unit can come back online quickly when product demand recovers. If specific precautions are not followed, many of the critical valves may not operate as expected when recalled to duty. Any or all of the following situations can occur during an extended outage.

Damaged valves will not fix themselves

When a unit is shut down, there is often little incentive to focus

on the current state of the equipment. Leaking and/or poorly performing valves are often forgotten until the unit is restarted, and the same problems reappear. In many cases, the valves may perform even less effectively than prior to the shutdown.

Bad instrument air

If the instrument air system is shut down during an outage, dust, rust, and water can collect in the air headers. When the air pressure is restored, the collected particulates and water will often be blown through the tubing, plugging valve positioners and damaging sensitive pneumatic valve components.

Stuck valves

If a valve is left in a closed position for an extended length of time, this can damage the seat, or corrosion may set up on the trim and keep the valve from opening.

Packing leaks

When a valve stem does not move for a prolonged period of time, the packing can lose elasticity and leak when process pressure is restored.

Diaphragm problems

When a valve actuator is immobile for an extended time, the diaphragm can become brittle and may leak when brought back into service. Similarly, O-ring seals in the actuator, positioner, and/or the valve body can become brittle with age.

During difficult economic times, management tends to reduce staff to cut operating costs. However, the effort required to run and maintain the plant at low production rates is often nearly the same as required to run the plant at full capacity. Under such conditions, the staff can only do so much and maintenance activities are deferred or eliminated. To keep the plant operating, the remaining staff must focus on the most critical issues, leveraging the product and application expertise of the control valve vendor whenever necessary.



Figure 2 The Fisher FlowScanner QL valve diagnostic system can be used to analyse a control valve's dynamic response, trend valve performance, and isolate repair needs. The system is used to evaluate current operating conditions without having to disassemble or remove control valves from the process

Providing solutions

While difficulties are significant, there are a number of ways to mitigate or eliminate these issues and keep control valves operating reliably when running at reduced rates or when service is resumed after a shutdown. Solutions include the following.

If a plant is going into a shutdown (extended or otherwise), diagnostic and leak tests should be run in advance

Improve control

Sometimes poor control can be resolved by simply retuning the loop to operation under the new flow conditions, with existing tuning constants saved for return to full production. However, if the valve is throttling too close to the seat, it may require a reduced trim for reliable operation. Valve vendors can evaluate troublesome valves and offer solutions.

Prevent cavitation

If a valve was already cavitating at normal rates, then the valve has likely been selected for those conditions and there is little that must be done, other than occasionally inspecting the valve. However, if a valve was not cavitating significantly before rates were reduced, then it is wise to have the valve vendor perform an evaluation to determine if the valve can handle the new service conditions. Cavitation can severely damage control valve internals, and special valve designs and/or hardened materials are required to avoid catastrophic failure.

Ensure anti-surge valve performance

Anti-surge valves are designed to take the full pressure drop at full flow, so operation in a throttled condition should not be a problem in the short term. Plants should inspect these valves more often if the valve is running at a throttled state continuously, as long term damage is inevitable under these conditions.

Provide effective maintenance

Do not assume that critical valve inspections can be delayed and extended just because the plant is running at reduced rates. It is best to inspect critical valves, safety valves, and severe service valves on the same frequency if at all possible.

Prepare for restart before shutting down

If a plant is going into a shutdown (extended or otherwise), diagnostic and leak tests should be run in advance (see **Figure 2**). Test systems are available to run a variety of tests on control valves supplied by different vendors, including dynamic scan, static point scan, step change, stepped ramp, stepped study, and sine wave response. This type of expert diagnostic data analysis helps identify problems and determine appropriate maintenance.

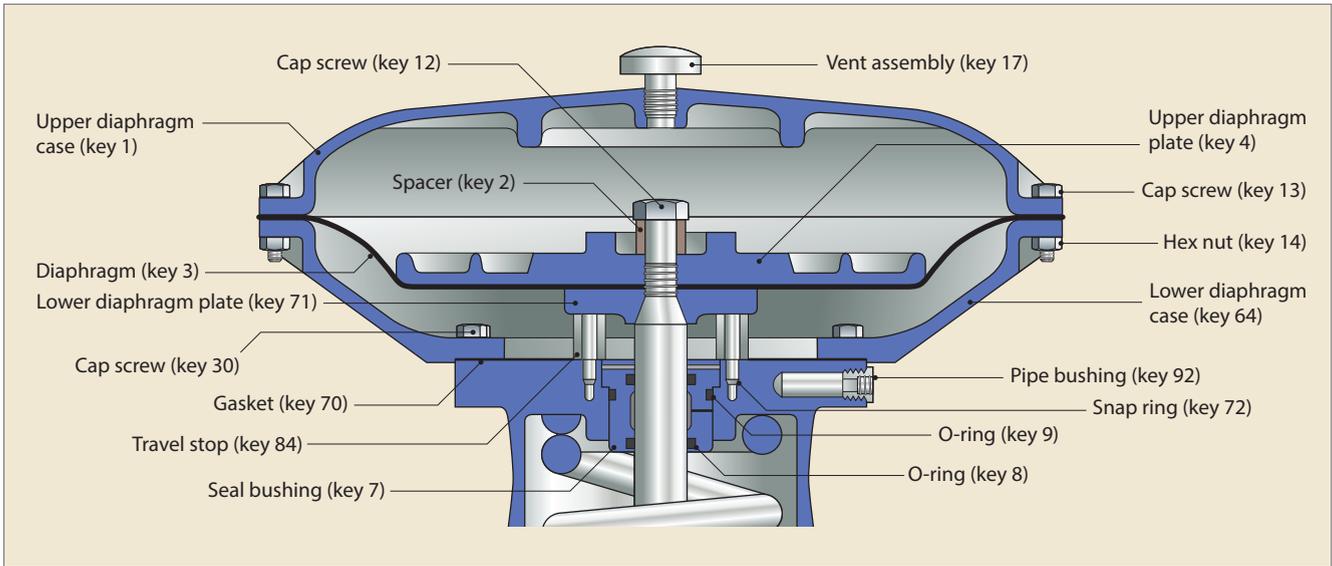


Figure 3 Actuator diaphragms and associated O-rings (above), as well as O-rings and packing in the valve body, can become brittle over an extended outage. Plant personnel should plan for thorough testing and possible replacement before bringing the equipment back online

Many of these tests can be conducted without impacting operations, and the data generated can be analysed to prevent significant financial impact. By focusing maintenance efforts on pulling and repairing the valves in need of service, instead of simply pulling every valve, the turnaround budget can be significantly reduced. Diagnostic tests also provide an 'as-left' valve signature that can be used to identify deteriorating valve performance in the future. Outsourcing the diagnostic and valve leak detection effort may be a wise option as it requires special equipment and expertise to interpret the test results.

Address instrument air issues

If at all possible, plant personnel should leave the air system pressurised during an extended outage to keep moisture and other particulates out of the system. If this is not possible, then the entire system should be drained and blown down before opening the air supply to the control valves. Failure to do so will likely damage the valve positioners, adding costs and time delays upon restart.

Set correct valve position

As many control valves as possible should be left slightly open and off their seat during an extended outage. This avoids long term seat damage, and it helps reduce the

possibility of the valve plug and seat corroding and becoming stuck to each other.

Test for leaks

Well in advance of any start-up, plant personnel should pressure test as many valves as possible and ensure any required replacement packing is available. Personnel should check to make sure parts are on-hand or can be readily acquired from valve vendors.

Deal with diaphragms

Similar to packing, diaphragm failures in the actuators should be anticipated after an extended outage (see **Figure 3**). Plant personnel should stroke valves well in advance of a restart to confirm there are no problems, and make sure spare parts are readily available if an actuator leak has developed.

Many of these solutions can be resource-intensive at a time when plants are light on staff. However, advanced diagnostic tests and leakage tests can reduce shutdown valve repair costs significantly and help plant personnel focus on the most critical items. Most of these recommended actions can be outsourced if plant personnel are unavailable. The cost of an unexpected production outage upon return to full production or a restart from shutdown will quickly eclipse the cost of implementing many of these solutions.

Conclusion

The current economic environment has forced many manufacturers to operate in unfamiliar territory. Rather than pushing for maximum plant capacity, many units are running at very low production rates, or even taking extended shutdowns. In these times, the unit has to run as efficiently as possible, or restart from suspended operations with limited issues. An initial identification of needs within the plant, a critical asset review, a comprehensive plan for valve preservation, and an understanding of key start-up actions are essential for efficient operation and maintenance.

Control valves are critical for plant operation and product quality. Taking the time to address valve problems or anticipate issues brought on by running at reduced rates or temporarily shutting down will pay huge dividends upon return to full production.

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Real-time crude and desalter monitoring

An analyser array supports corrosion management through continuous insights into changes in crude quality

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To maximise profits and remain competitive, refineries regularly reoptimise their crude slate with changing market conditions. As a result, crudes change frequently, and the plant is driven towards processing cheaper, heavier, and lower quality crudes. Many of these lower quality crude oils contain higher levels of salts (chlorides), organic chlorides, sulphur, nitrogen, metals, tramp amines, as well as high solids and acidity. All of these factors can drive up corrosion within the crude processing complex without proper conditioning which, in turn, can be hampered by the difficulty in determining the precise crude mix hour-by-hour (inadequate tankage for proper segregation, layering, tank heels of unknown composition, slops reprocessing, tight crude oil inventory controls to minimise working capital, and the frequency of crude tank changes). Many refiners report crude changes as often as every two to three days.

A critical element of corrosion control within the crude complex is the desalter (see **Figure 1**). The desalter serves several purposes:

- Reduces the salt (inorganic chloride) content of the crude oil
- Dehydration
- Solid separation
- Recovery of phenols from wastewater

Salt occurs naturally in crude oil, so a certain amount of brine is produced with crude which is separated in the field and relatively dry crude oil is sent to the refinery. Chlorides introduced into an oil well during a workover or well stimulation will also appear in the produced crude. Salt can also enter crude oil from seawater during

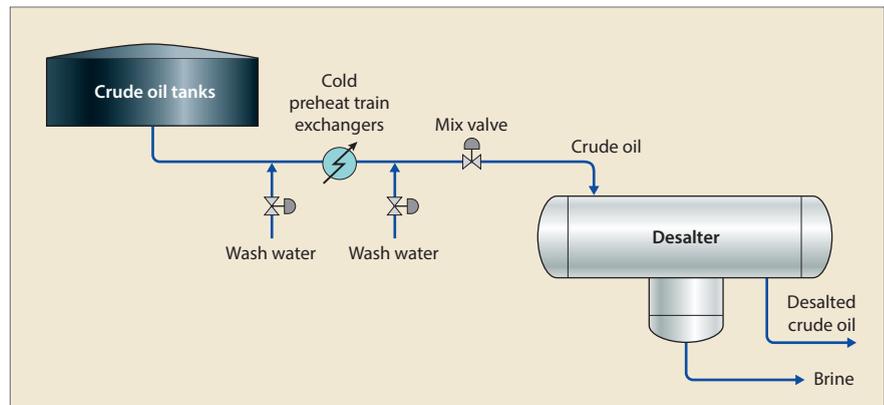


Figure 1 Typical crude unit cold preheat train and desalter configuration

transportation. The salts in crude oil consist primarily of sodium, magnesium, and calcium chlorides.

While some of these lower quality crudes can be priced at a \$2-\$3/bbl discount to Brent, most refiners would not be able to process these at more than 25% of their total crude slate – implying a commercial incentive of approximately \$0.50-\$0.75/bbl or \$37-55 million/y for a typical 200000 b/d refinery. Recent studies have suggested that the annual cost of corrosion in refining is approximately \$15 billion or

\$0.45-0.50/bbl of total global crude oil processed. Processing of these lower quality crude oils is concentrated within a subset of the global refining population, so there is clearly considerable commercial risk to processing these crudes without adequate monitoring of contaminants, operations, and corrosion rates to mitigate the potential for integrity problems.

Magnesium and calcium chlorides have a higher tendency to remain in the oil phase than sodium chloride, so sodium chloride removal by

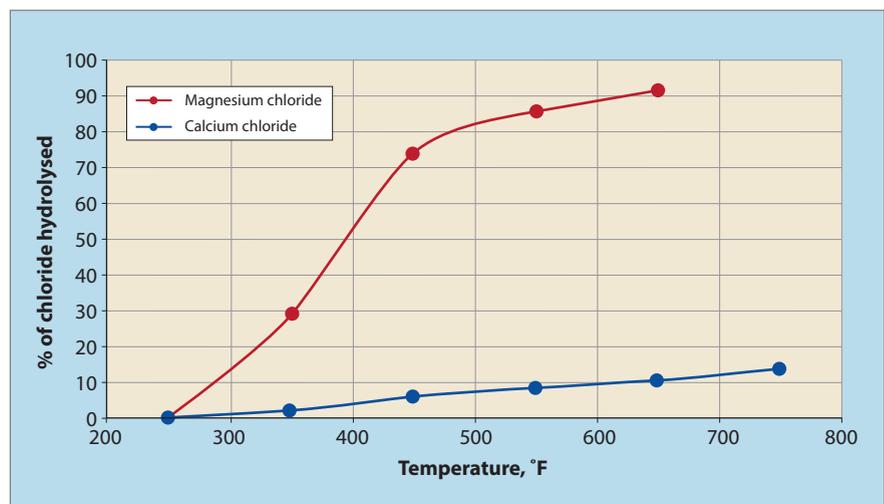


Figure 2 Hydrolysis of magnesium chloride and calcium chloride with temperature

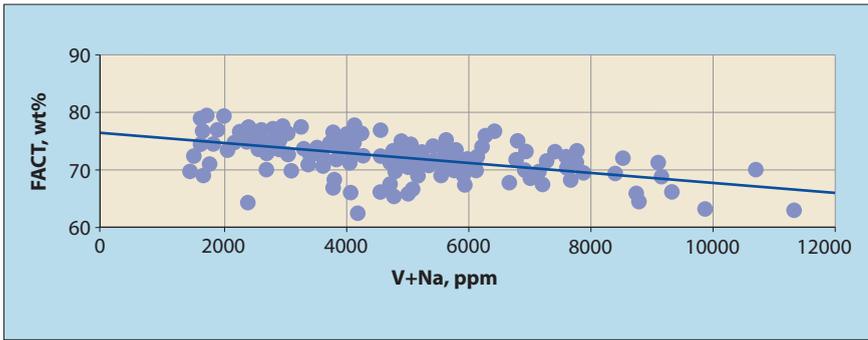


Figure 3 FCC catalyst activity, Ecat wt% vs Ecat V+Na

Source: BASF

effective desalting is usually nearly complete. In most cases, magnesium and calcium chloride levels in crude are low.

As crude is processed through the crude tower and then the vacuum unit and downstream residue upgrading units such as delayed cokers, residual magnesium or calcium chlorides will hydrolyse in the presence of trace water, releasing hydrogen chloride. The hydrolysis to temperature relationship is illustrated in Figure 2.

Sodium chloride will not decompose to any significant extent, but passes into the atmospheric residue where it can accelerate coking in the vacuum unit and downstream residue conversion units (visbreaker, delayed coker, and so on), shortening the run length between heater decokes. In addition, sodium in the FCC feed serves to exaggerate the conversion impact of any vanadium in the FCC feed, with implications for fresh catalyst use and yield performance (see Figure 3).

Hydrogen chloride generated from the magnesium and calcium salts will move upwards in the distillation columns until it finds ammonia or amines to combine with, or until a liquid water phase forms, or until the hydrogen chloride is drawn into a product. The corrosive impact of the chlorides will then be observed in the crude tower and the overhead heat exchangers. Therefore good control of the desalter can substantially reduce corrosion within the crude tower overheads, as well as fouling in the pre-

heat exchanger train and oil content of the desalter effluent water. However, many refineries have increased processing capacity over time and are running a progressively heavier crude slate, without making the corresponding modifications to their desalters, with the result that desalting and dehydration efficiencies have declined, thereby driving up the risk of downstream reliability issues.

In addition, normal build-up of sediments in the bottom of the desalter during the run (see Figure 4 for typical desalter internals) can also serve to reduce residence time, so desalting efficiency can reduce across the cycle. Within these tight net margin environments, it is surprising that the operation of many crude oil desalters is not rigorously adjusted following changes in the crude slate, and there has been limited investment in tracking desalter operating performance in real-time to provide advance warning of sub-optimal performance and potential downstream issues.

Clear understanding of the chlo-

ride content of the desalter effluent crude oil is therefore critical to mitigating corrosion. Chlorides (NaCl , MgCl_2 and CaCl_2) in excess of 20 ppm are known to cause serious corrosion issues due to the liberation of chloride ions which travel to the top of the crude tower (see Figure 5) and condense with the first drop of water at the water dewpoint, with a very low pH (1-3). This highly localised point of corrosion can move around within the overhead system, depending on the water content, top temperature, functioning of the condensers, and vapour flow rate. Refiners inject ammonia or amines into the overhead system to neutralise the acid, as well as filming amines which cover the internal surfaces of the exchanger tubes to prevent the acid from reaching the metal surface. Frequent crude changes and variations in desalter performance can result in under-dosing of neutralising amine. Filming amines can also be stripped by high vapour velocities or may fail to coat all surfaces evenly. As a result, dewpoint corrosion remains an ongoing issue within many crude towers.

This difficult situation is further exacerbated by two other factors:

- The declining demand for gasoline, particularly in European and Asian economies where refiners typically aim to maximise middle distillate (jet fuel and diesel) production. This drives down the optimum temperature for the crude tower overhead, further raising the risk of dew point corrosion, as well as the exposure of larger areas of the crude overhead system to the potential of dewpoint corrosion, such as the tower dome itself.
- Presence of organic chlorides in the crude oil, from upstream oil production chemicals, particularly with ageing oil fields. Organic chlorides are not removed in the desalter, preferring to remain in the oil phase, but can release chloride ions in the crude distillation tower just the same. These chloride ions usually appear in the

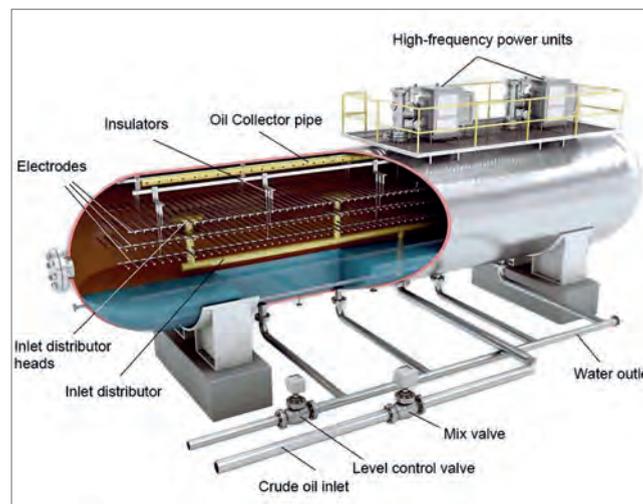


Figure 4 Desalter schematic

naphtha streams and react in the naphtha hydrotreater(s) to release hydrogen chloride, causing corrosion and fouling problems. The contamination of the Druzhba crude oil pipeline network with organic chlorides in April 2019 is a case in point which caused severe disruption to refinery operations in Central and Eastern Europe.

Real-time corrosion management

Good single-stage desalter performance achieves a desalting and dehydration efficiency of more than 90%. More than 95% salt removal can be achieved with double desalting. Absolute performance depends on various key parameters such as:

- Crude oil properties (API, asphaltene content, and so on)
- Desalter temperature
- Desalter pressure
- Wash water pH
- Oil residence time
- Effectiveness of the demulsifier chemical
- Wash water mixing

With relatively low levels (>20 ppm) of chloride content in desalted crude having the potential to lead to significant corrosion issues in the overhead condensation system of the crude distillate unit (Palash Kumar Bhowmik, 2012), the Hobr  solution employing the C-Quand XRF analyser comes into play. The C-Quand XRF analyser provides on-line measurements of crude contaminants (such as total chlorides, sulphur, magnesium, iron, nickel, vanadium, arsenic, and other elements) to enable the realisation of a real-time corrosion management strategy for the crude distillation unit, by:

- Ensuring effective crude desalting, by enabling reporting of desalting efficiency in real-time and alerting any exceptions caused by performance degradation during and following crude switches or due to slops reprocessing (with an undetermined and highly variable chloride content).
- Alerting to changes being required in overhead chemical dosage (ammonia or neutralising amines and filmer) by real-time measurement of the chloride content in the overhead

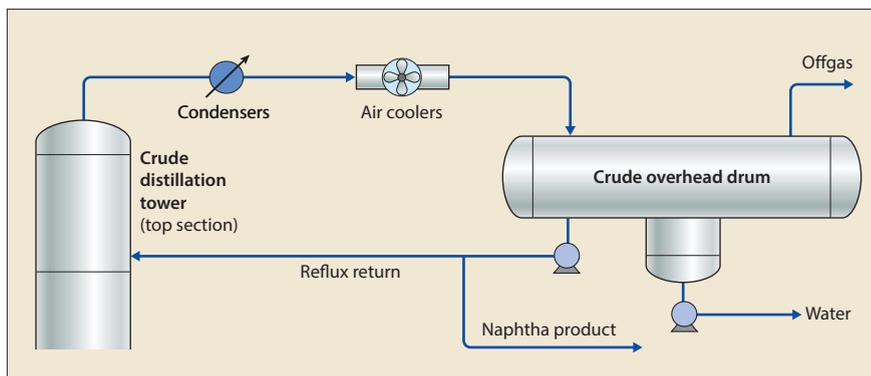


Figure 5 Typical crude unit overheads configuration

water. This enables tighter tracking of chemical injection rates in case of unit upsets, fluctuations, during start-up, or processing of crude oil with high organic chloride content.

In addition, real-time measurement of metals in crude oil can bring considerable value in predicting imminent changes in downstream unit feeds, where contaminants are either poisons or key final product quality specifications (such as chloride load to naphtha hydrotreating units, FCC feed nickel, vanadium, iron or delayed coker feed nickel, vanadium, sulphur). The system can also provide insight into incoming iron in crude, which is a problem widely observed during processing of light tight oils, to enable optimisation of iron removal chemicals.

With over 40 years' experience in designing and engineering online process analysers, Hobr  Solutions offers a turn-key total package solution tailored to specific layouts. The proposed solution consists of a set of C-Quand ED-XRF non-destructive analysers (and optionally sample handling, shel-

ters, and additional measurements for oil-in-water and water-in-oil analysis), providing the measurement of chlorides in real-time, offering the potential for continuous corrosion control (see Figure 6).

By accurate, sensitive, and continuous measurement upstream (Position 1 in Figure 6) of the desalter, the analyser enables operators to track changes in total chloride levels, to proactively adjust desalting operating conditions and chemical addition rates to ensure good desalting and dewatering performance.

A second analyser downstream of the desalter unit (Position 3) tracks the desalted crude chloride content to verify desalting performance and minimum chloride entering the crude tower.

For systems employing double desalting vessels, the desalted crude C-Quand analyser in Position 3 could be multiplexed to measure chloride entering the second desalter.

To provide a complete picture of desalter performance, installation of a water-in-oil analyser at Position 2 provides early warning

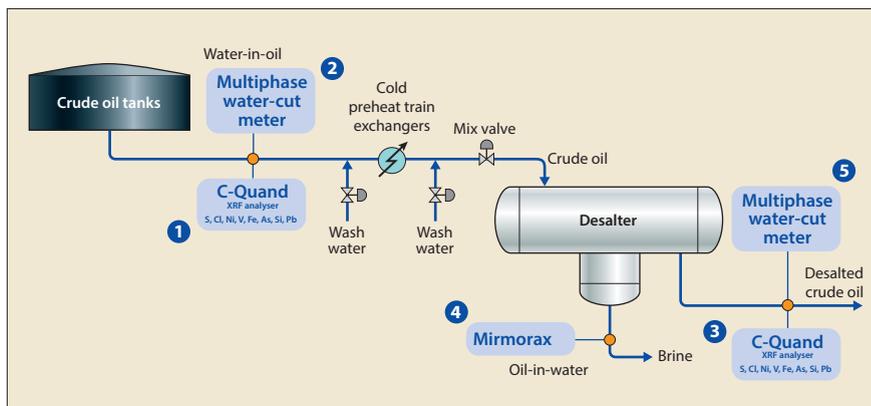


Figure 6 System for real-time desalter chloride measurement for corrosion control

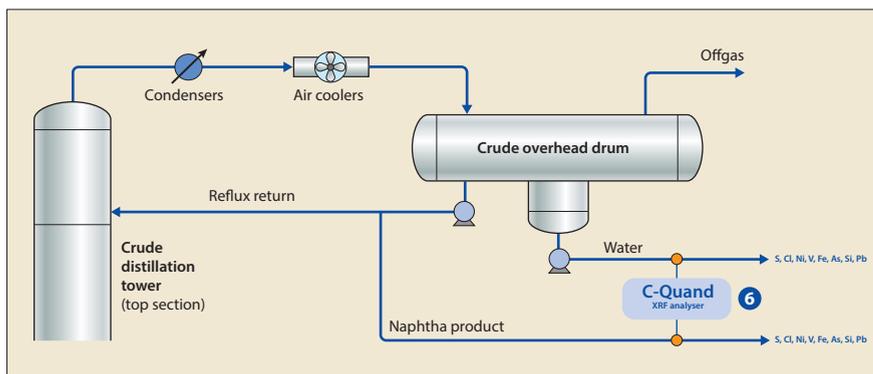


Figure 7 Proposed system for real-time desalter chloride measurement for corrosion control

of excessive water levels coming from crude tankage, in the event that the crude oil has not had sufficient settling time. Operators can use this measurement to anticipate an increase in water by trimming the wash water rates to avoid overloading the desalter and could be incorporated into a closed-loop control scheme.

A second water-in-oil analyser is proposed for the desalted crude (Position 5) to ensure that the unit is performing to optimal dehydration levels. Next, an oil-in-water analyser is recommended for the desalter effluent water ('brine') to ensure that this is minimised (Position 4), to avoid losses of crude oil to the effluent water treatment system that then consume crude processing capacity when they are later reprocessed.

Finally (see **Figure 7**), a C-Quand analyser measuring the chloride content of the crude overhead drum water (Position 6) enables real-time tracking of chloride excursions and, particularly, any organic chloride breakthrough, providing guidance to optimise filming and neutralising amine dosages. In addition, the analyser provides measurements of metallic corrosion products such as iron. This analyser can be multiplexed to also survey chlorides in the naphtha product, to provide early warning of carry-over into the naphtha hydrotreater feed. Tighter understanding of the total chloride balance across the desalter and the tower overheads, in combination with an on-line overhead corrosion monitoring system, allows operators to drive the top temperature to a minimum, thereby driving up commercially attractive middle distillate

yields at the expenses of naphtha/gasoline, without unnecessarily risking increased corrosion rates.

Economic justification

For a mid-sized refinery of 200 000 b/d, the estimated annualised costs due to a crude overhead failure caused by corrosion alone are of the order of €1 to €2 million/y (five-year run between turnarounds). A single 10-day shutdown event would cost approximately €5-10 million in lost processing capacity, replacement equipment (often ordered at short notice with premium pricing for rapid delivery), subcontract personnel, staff overtime, and crane costs. This figure would be further increased by an amount of the order of €4.5 million/y, comprising:

- Reduction in crude tower overhead temperature ($\approx 0.5^{\circ}\text{C}$) to increase jet kerosene production by 0.1 vol% (at the expense of naphtha) without increasing the risk of dew point corrosion ($\approx \text{€}3.6$ million/y for a 200 000 b/d refinery)
- Demulsifier over-dosing costs ($\approx \text{€}20\text{k}/\text{y}$ for a 10% saving)
- Filming and neutralising amine over-dosing costs ($\approx \text{€}7000/\text{y}$ for a 10% saving)
- Preheat exchanger network fouling increasing energy costs and/or increased preheat train antifoulant dosage ($\approx \text{€}300\text{k}/^{\circ}\text{C}/\text{y}$)
- Costs for reprocessing of recovered oil from effluent water treatment ($\approx \text{€}300\text{k}/500$ b/d/y)
- Savings in laboratory analysis, equipment and consumables costs ($\approx \text{€}100\text{k}/\text{year}$)
- Impact of chloride carry-over into the naphtha hydrotreater feed from corrosion, heat exchanger fouling,

catalyst fouling and deactivation, and increased reactor pressure drop (not evaluated)

- Shorter run lengths between heater decokes on the vacuum heater and any downstream residue conversion units (not evaluated)
- FCC yield impacts from higher Na+V in the feed, requiring higher fresh catalyst addition to restore yields, and/or economic penalty from yield degradation ($\approx \text{€}100\text{k}/\text{year}$ for a 1% increase in fresh catalyst usage)

A fully installed and operating analyser system, as specified in **Figures 6** and **7**, would generate a payback within just two to three months of operation, based on the operations savings evaluated above. A much shorter payback would be achieved if the system prevented an unplanned shutdown caused by crude overhead corrosion.

C-QUAND is a mark of Hobr  Analyzer Solutions.

Further reading

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- 2 American Petroleum Institute, *Understanding crude oil and product markets*, Digital Media, 2014.
- 3 Palash Kumar Bhowmik M E, *Corrosion and its control in crude oil refining process*, Dhaka: IMEC&APM- ABS-000, 2012.

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Improving turnarounds and operations with online cleaning

Case histories illustrate the financial and operational gains achieved by replacing mechanical cleaning with online, closed-loop operations

MARCELLO FERRARA and CRISTINA FERRARA
ITW

The conventional perception of the cost of mechanical cleaning is that it amounts simply to the cost of cleaning or hydroblasting. In reality, the cost of mechanical cleaning is more than 30 times the cost paid to the mechanical cleaning company.

Consider a preheat train to be cleaned in a major turnaround when it is usual to replace gaskets and bolts after bundles are extracted and cleaned. In a 40-exchanger preheat train, this alone can amount to more than \$200 000. This amount could be saved simply by not opening the bundles during cleaning.

However, not opening the bundles will mean a saving in downtime. A 100 000 b/d refinery can make a profit of around \$2 million/d, so a saving of seven days in downtime equals a preserved \$14 million of profit.

We believe that a reduction in overall costs and an increase in margin can be achieved by a shift in refiners' approach to operations. Recovery of losses will allow operators to meet and even reduce their budgets.

The online cleaning approach

ITW Online Cleaning is a patented technology for cleaning heat exchangers and process equipment in a closed loop, in the hydrocarbon phase. The technology includes a cleaning method and process steps, chemicals, and a monitoring system, all covered by patent. The technology cleans an entire production unit in as little as 24 hours on a feed-out/feed-in basis, thus reducing downtime during a turnaround.

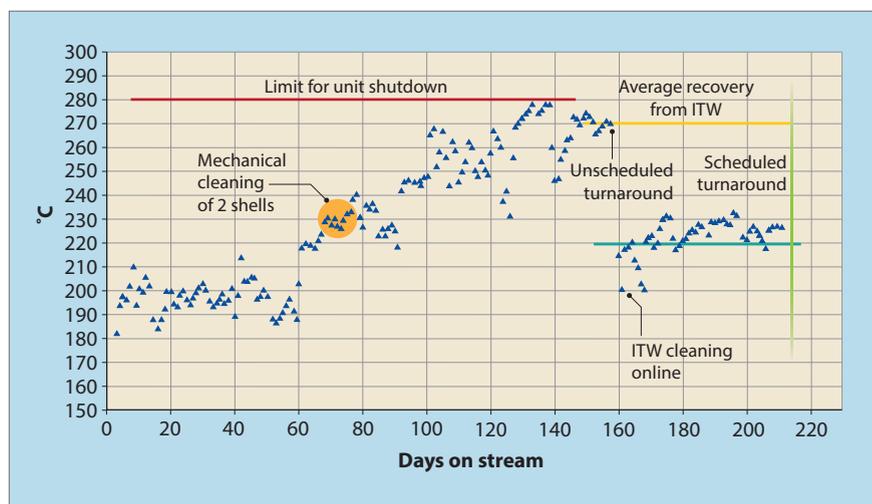


Figure 1 Avoiding an unscheduled shutdown and increasing the run length of a visbreaker

The washing fluids arising from ITW Online Cleaning are fully reusable/reprocessible, which means no waste will be generated by the cleaning operations. By operating on a closed loop basis, the process generates no airborne emissions during cleaning.

A reduction in overall costs and an increase in margin can be achieved by a shift in refiners' approach to operations

The gains in value which can be achieved with online cleaning can be identified by measuring key performance indicators before and after the cleaning operation and loading into a spreadsheet all of the cost items which would have impacted

the run by using conventional mechanical cleaning.

For instance, if a 1°C furnace inlet temperature (FIT) loss in a 100 000 b/d crude distillation unit costs, say, \$1 million/y, the recovery of 10°C FIT will have a value of \$10 million/y. If fouling is impacting the capacity of the unit (by increased delta P, for instance) then the gain in value is given by the recovery in production. And if the crude unit has reduced capacity by 5% and is making \$8/bbl, the daily recovery in margin (over losses) will be \$40 000.

This does not take into account the savings achieved through many other factors, including reduced pumping costs, reduced energy consumption, and avoiding the many costs of preparing and implementing a mechanical cleaning operation.

Online cleaning of refining plant

In the refining industry, most fouling is related to the precipitation of asphaltenes. This occurs because of



Figure 2 Vacuum tower bottom



Figure 3 Vacuum tower bed #4



Figure 4 Vacuum residue heat exchanger just opened

destabilisation of the asphaltenic micelles, which can be driven by chemical or thermal factors.

Among the causes of chemical destabilisation, the most common is the incompatibility of different feedstocks. It is well known that when a paraffinic feed is blended with an asphaltenic feed, asphaltenes will precipitate out of the blend and will deposit in the equipment.

The current trend in the refining industry of processing opportunity crudes (which are normally heavy crudes) makes this problem even more evident in that refineries cannot have enough storage capacity to segregate the many crudes which are processed on a daily basis.

Another type of fouling occurs when processing tight oils, which are basically very light oils, mostly of a paraffinic nature. In this case, heavy paraffins may separate out and precipitate, together with the relatively small amount of asphaltenes which are present in the oil.

Online cleaning technology can effectively address both types of fouling. The following case histories will better illustrate the results achievable by ITW Online Cleaning.

Case history: avoiding unscheduled shutdown of a visbreaker

ITW Technology has been applied on the vacuum section of a visbreaker unit. The refinery layout features a CDU, VDU, VBU, the vacuum section of the VBU, storage for visbreaker residue, and an integrated gasification combined cycle unit.

The problem was related to an increase in vacuum section bottom train outlet temperature (tag TI1826). The refinery's procedure was to clean the exchangers when the outlet temperature was approaching 280°C. During a run, the refinery normally mechanically cleaned two exchangers in order to reach the targeted run length.

Before the application of ITW Technology, mechanical cleaning did not help in recovering the tem-

Among the causes of chemical destabilisation, the most common is the incompatibility of different feedstocks

perature, so there was a steady increase of outlet temperature values, reaching the shutdown limit six months before the scheduled turnaround.

The visbreaker unit therefore required an unscheduled shutdown to clean all of the vacuum section bottom. To solve the problem, ITW Online Cleaning was applied in the vacuum section, and the visbreaker resumed production immediately afterwards.

Outlet temperature recovery was an average 45°C, which remained stable (see Figure 1). The unit could run easily for five more months without any issues up to the scheduled turnaround.

Case history: eliminating mechanical cleaning during a turnaround (1)

The atmospheric and vacuum distillation units of a refinery had scheduled a turnaround and the refiner wanted to validate ITW Online Cleaning and ITW Improved Degassing/Decontamination on the vacuum section. The units were under end-of-run conditions.

Cleaning took place during shutdown operations. Cleaning all of the vacuum section required about 16 hours, excluding filling and emptying operations. The wash fluids were sent to a slop oil storage tank and reprocessed with no issues at unit start-up.

On completion of ITW Online Cleaning, the unit was deinventoried. After removal of the hydrocarbons, ITW Improved Degassing/Decontamination took just seven hours and safe entry conditions were achieved (for instance, LEL=0%, H₂S = 0 ppm, benzene = 0 ppm).

Upon inspection, the vacuum tower bottom, wash bed grid, bottom packing, bottom packing pre-distributor, VEP distributor and vacuum residue exchangers were in a clean condition (see Figures 2-4).

The refinery checked the most critical vacuum residue heat exchanger and decided to eliminate mechanical cleaning of the vacuum tower and the vacuum residue loop from the turnaround scope, even if it was already scheduled. This helped the refinery to reduce downtime.

Case history: eliminating mechanical cleaning during a turnaround (2)

A refinery wanted to validate ITW Online Cleaning to use it strategi-

cally for future turnarounds/slow-downs and during the run, for itself, and for other refineries in the group. The scope of work was to avoid mechanical cleaning of the preheat train during the turnaround.

Online cleaning was performed on the entire crude unit over a period of about 24 hours.

Based on ITW's proprietary model, about 20 000 kg of fouling was removed from the unit. Washing fluids were routed to slop, then fully reprocessed at unit start-up. There were no quality or operational issues during reprocessing. The CDU started up with no mechanical cleaning of the exchangers which were cleaned online by ITW, with the following results:

- Average FIT increased by 21°C (see Figure 5)
- Normalised FIT increased by 37°C
- Specific fuel consumption decreased by 0.011 Gcal/d/t of feed
- Feed rate increased by 780 t/d

The cleaning operation resulted in the same furnace duty (even slightly lower) to process about 10% more feed, with no waste produced.

Case history: eliminating mechanical cleaning during a turnaround (3)

A refinery needed to perform a quick shutdown of its amine (MEA) unit to make repairs to parts of the system. The refiner chose ITW's cleaning and decontamination solution because it does not require tube bundles to be removed for cleaning. The lean/rich heat exchangers are in a tight space so removing the bundles for cleaning is difficult and dangerous for maintenance and contractor personnel.

Management decided to clean the regenerator as well as the lean/rich exchanger to improve unit efficiency upon restart. Online/in-situ cleaning and decontamination were successfully completed in less than 24 hours, significantly faster than the usual mechanical cleaning.

Upon resuming production, the following immediate benefits were observed:

- Reduced steam consumption at the regenerator reboiler by about 500 kg/h (see Figure 6)
- Increased delta T (about 10°C, see Figure 7) in the lean/rich exchangers

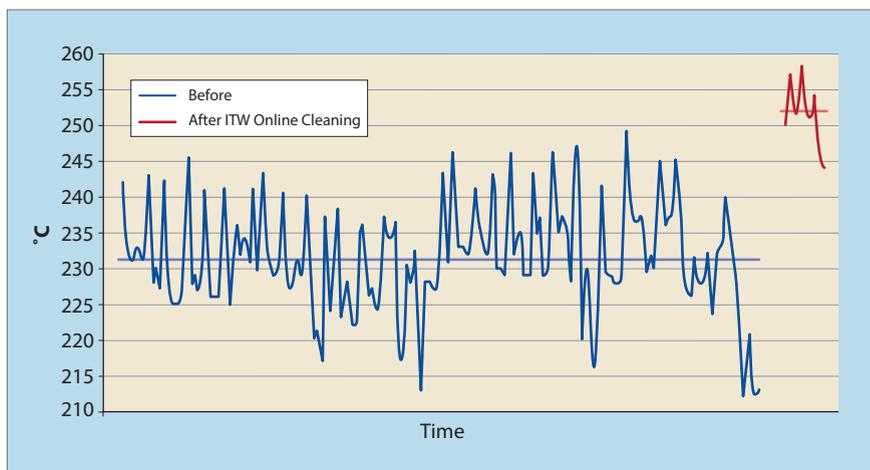


Figure 5 Furnace inlet temperature increased following online cleaning (end-of-run conditions)

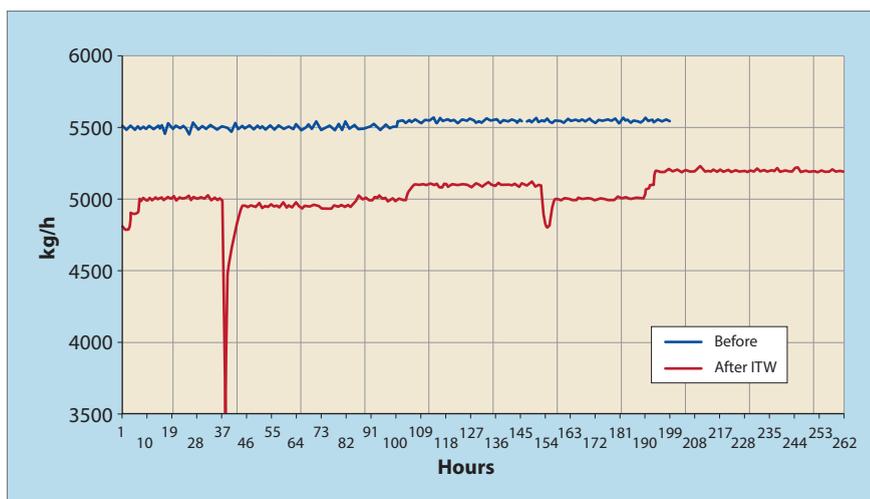


Figure 6 Steam consumption at regenerator reboiler

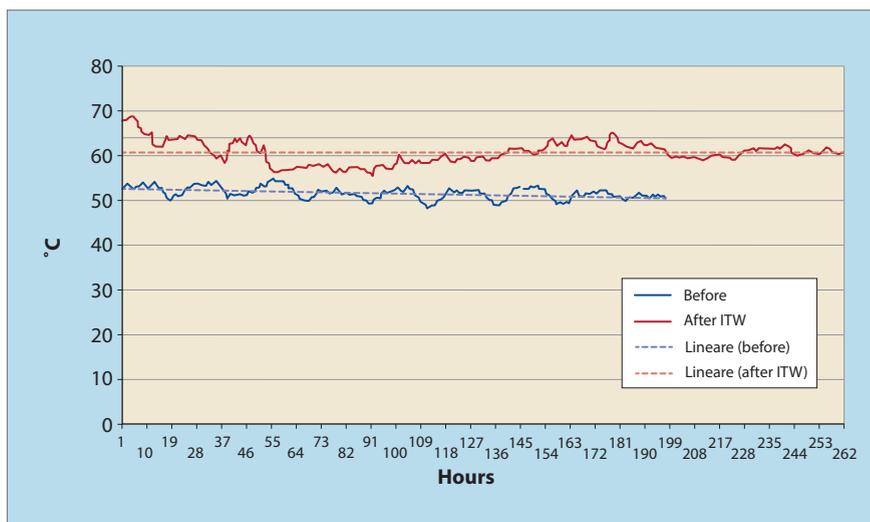


Figure 7 Lean/rich exchangers delta T

Case history: recovery of vacuum unit performance

A refinery was experiencing severe fouling problems in the preheat train of its vacuum unit. The unit processes atmospheric residue from

opportunity crudes and other crudes with a high fouling propensity. In addition, the vacuum unit processes unconverted paraffinic oil from the hydrocracker. This particular processing is performed in dedicated

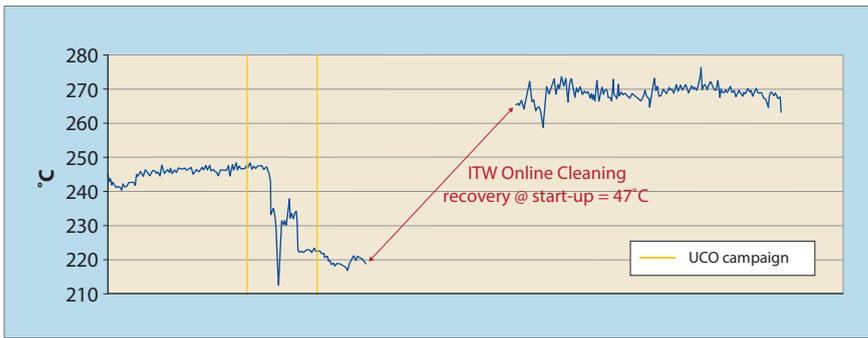


Figure 8 Normalised recovery in furnace inlet temperature

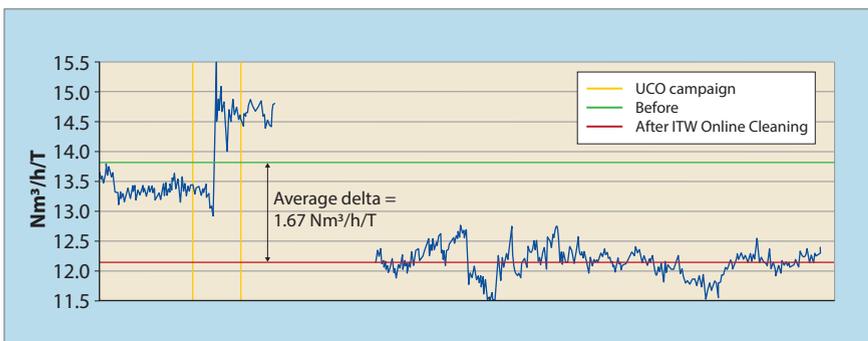


Figure 9 Specific fuel gas consumption

around so it turned to ITW to apply it as a process optimisation tool that replaces mid-run mechanical cleaning shutdowns and slowdowns.

ITW Online Cleaning of the entire VDU was performed in 24 hours on an oil-to-oil basis and the VDU altogether went from spec-out to spec-in within 48 hours.

Upon resuming production, the following performances were recorded:

- Normalised FIT increase at start-up = 47°C (117°F, see Figure 8)
- Average specific fuel gas reduction = 1.67 Nm³/h/t of feed (3.4 MMSCFD/lb, see Figure 9)

Another accomplishment was that the overhead temperature of the vacuum tower decreased from 160°C (320°F) down to 70°C (158°F) and wild naphtha production decreased from 2500 kg/h (5500 lb/h) down to 200 kg/h (440 lb/h); diesel production was increased accordingly. This further validates our consolidated results on the cleaning of the vacuum tower. Furthermore, no waste was generated and all of the washing fluids were routed to a fuel oil tank with no quality or operational issues.

Based on the natural gas price delivered at the refinery, there was a saving in fuel consumption exceeding \$25 million on an annual basis. Additional returns came from reduced payment of emission taxes, and from the avoidance of lost opportunity for profit. If online cleaning had not been performed, the refinery would have experienced an additional capacity reduction with related loss of margin and opportunity.

Online Cleaning in the oil and gas industry

Online cleaning can address all fouling in the oil and gas industry. In particular, a specific proprietary chemistry is used to dissolve/modify polymers in the petrochemical industry, which makes possible the cleaning of almost all petrochemical plants.

Online cleaning is also applicable for cleaning storage tanks, thereby enabling recovery and reuse of sludge. Application at oil and gas fields includes the cleaning of

Mechanical cleaning vs ITW Online Cleaning: operational items (CDU)			
	Mechanical	ITW Online Cleaning	Delta value (100 Kbbt @10 \$/bbl)
Effectiveness	Proven	To be validated by new users	0
Downtime	15-20 days	1 day	14-19 MM\$
Required manpower	50+	1	0.3-0.6 MM\$
Equipment	Massive	Negligible	0.3-0.6 MM\$
Preparatory jobs	Massive	Negligible	0.3-0.6 MM\$
Organisation	Massive	Negligible	0.1-0.2 MM\$
Co-ordination	Massive	Negligible	0.1-0.2 MM\$
Control	Massive	Negligible	0.1-0.2 MM\$

Table 1

Mechanical cleaning vs ITW Online Cleaning: turnaround case (CDU)			
	Mechanical	ITW Online Cleaning	Delta value (100 Kbbt @10 \$/bbl)
Decontamination	Always necessary	Only for turnaround	0.2-0.4 MM\$
Reliability	Concerns	No concerns	0.4-4 MM\$
Pyrophorics	Need to be addressed	No need to be addressed if applied proactively	0.2-0.4 MM\$
Equipment opening	Necessary	No need if applied proactively	0.5-1 MM\$
Weather/contingency	Impacting	Not impacting	0.5-10 MM\$
Applicability	Turnaround	Proactive or turnaround	0.5-10 MM\$
Cleaned equipment	Straight tubes/flat surfaces	Any, including packings	0.5-10 MM\$

Table 2

campaigns wherein the VDU is fed with 100% of the feedstock.

As a result, the FIT decreased dramatically at a rate far greater than the 'normal' downward trend (which is very steep) as a result of

processing the high fouling residues. The unit was limited by furnace duty and had to reduce capacity accordingly.

The refinery had already validated ITW Online Cleaning during a turn-



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Mechanical cleaning vs ITW Online Cleaning: HS&E (CDU)

	Mechanical	Online Cleaning	Delta value (100 Kbb l@10 \$/bbl)
Safety	Concerns	No concerns	0.5-10 MM\$
VOC emissions	Concerns	No concerns	0.1-0.2 MM\$
Waste	Fully disposed	No or minor	0.5-1 MM\$
Hazards	Concerns	No concerns	0.5-1 MM\$
Handling	Waste	Chemical	0.2-0.4 MM\$
PPE	Special needs	Normal	0.05-0.1 MM\$
Confined space entry	Required sometimes	Not necessary for proactive application	0.2-0.4 MM\$

Table 3

production units as well as tanks, FPSOs, FPOs, and so on, while in the maritime industry, use of the technology in oil tankers and product tankers is particularly useful to reduce downtime and to improve operational HSE.

The value of online cleaning

Tables 1-3 summarise some of the key items to be evaluated when considering online cleaning against mechanical cleaning. A full evaluation should be run (including reliability, safety, loss of opportunity, proactive application, energy costs, and so on) in order to capture the value and opportunities offered by the technology.

Improved degassing/decontamination

During turnaround operations, safe entry conditions for maintenance and inspection personnel are required and safe entry of the equipment is mandatory. ITW's decontamination and degas-

ing chemical is introduced to the steam-out line connected to the equipment, then the steam-out operation is performed. This patented chemistry is injected into the unit, together with the steam, to

During turnaround operations, safe entry conditions for maintenance and inspection personnel are required and safe entry of the equipment is mandatory

remove hydrocarbons and to decontaminate the equipment. Chemical injection together with steam will avoid water circulation and related pitfalls.

The chemistry temporarily solubi-

lises hydrocarbons in water, thereby removing them from metal surfaces and achieving LEL = 0%. Whilst quickly removing hydrocarbons from the equipment, the chemical will simultaneously:

- Eliminate H₂S/mercaptans emissions/noxious odours
- Eliminate hydrocarbons emissions/noxious odours
- Reduce benzene inside the equipment down to <1 ppm
- Eliminate pyrophoric solids problems

The chemistry is capable of transforming steam/water into a temporary 'solvent' for hydrocarbons and is designed to be carried by the steam. Importantly, it does not create emulsions with hydrocarbons and is biodegradable. This means that no additional de-emulsification step is needed and water can be routed directly into the oily sewage.

The effects of the patented chemistry are shown in Figures 10 and 11.

In Figure 10, note that the water containing the patented chemistry is bright and clear (pouring beaker) and the hydrocarbons are 'solubilised' (lower beaker). In Figure 11, the hydrocarbons are clearly separated and the water which separates after some seconds is bright and clear.

As a comparison, Figure 12 shows the effects of using an emulsifier: water containing the emulsifier is itself emulsified (pouring beaker), and the hydrocarbons become emulsified (lower beaker).



Figure 10 Applying an aqueous solution of the patented chemistry



Figure 11 Separation of hydrocarbons and water using the patented chemistry



Figure 12 Effect of emulsifiers

Operators have been known to use acid or strong bases to accomplish the task; some even use toxic permanganate, all of which oblige the user to dispose of the waste water and not to dump it in oily sewage.

ITW's patented chemistry also eliminates any problems related to pyrophoric solids ignition.

Therefore, no potassium permanganate or sodium percarbonate will be used after the use of the patented chemistry.

Note that the water containing permanganate is toxic and cannot be dumped in the oily sewage.

The above features are particularly important in that, by simply settling, a spontaneous and immediate separation of hydrocarbons from water will occur. No emulsion breaker or calcium chloride is therefore necessary to separate hydrocarbons from water.

Moreover, the wastewater treatment plant will not be overloaded by hydrocarbons, as they will be easily separated.

The chemistry is very fast acting

for removing hydrocarbons and contaminants and, therefore, the equipment will be decontaminated within a few hours.

The chemistry also contains compounds capable of neutralising the effects of sulphur compounds. Hydrogen sulphide and mercaptans will react with the patented chemistry and no noxious odours are released during steam-out and/or manway opening.

On-stream cleaning of oil and gas plants

A new patent has been granted to ITW for cleaning oil and gas plants during a run. The technology uses the chemicals that have proven to be effective for online cleaning.

The chemicals are completely safe for any equipment and/or for any catalyst and therefore can be injected while the unit is running. Under ITW's patent, some plant modifications need to be implemented to apply the technology.

Conclusion

Current methods for mechanically

cleaning equipment in the oil and gas industry create many concerns, including HSE issues and high overall costs. Evaluation of cleaning costs should include all of the items and activities involved in cleaning, not simply the cleaning cost.

This creates a new paradigm in the industry, in that the cleaning can be value driven rather than performing it after 'running to death', with related losses and inefficiencies.

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Molecular management for refinery- petrochemical complexes

Designing a digital twin for process simulation of an integrated complex enables enhanced molecular management to deliver higher margin

JITENDRA CHELLANI and SACHIN SRIVASTAVA
KBC (A Yokogawa Company)

The future comprises a world of fuels refineries, refinery-integrated petrochemical complexes and crude oil to chemicals. Through the energy transition, the latter two will no doubt be more resilient toward future demand- and/or supply-side dynamics.

The potential for incremental improvement with increased conversion capabilities of a fuels refinery with added petrochemical integration is \$1.5-2/bbl of crude processed. The value gained from effective molecular management is significant. Key objectives of molecular management for the overall complex are:

- Improvement in gross product worth by maximising high value products
- Reduced cost of feedstock by replacing expensive imports with low value streams

However, with the increase in complexity of refinery-integrated petrochemical complexes, a gap has developed in the tools needed to effectively drill down to the stream carbon number level on a continuous basis. Traditional tools used for refinery optimisation rely on bulk properties such as cut point for stream optimisation. Such methods have been found to have limitations in fully achieving the objectives of molecular management. The latest process simulation tools address this by enabling detailed carbon number breakdown from crude assays through to blending and petrochemical units, for the whole integrated complex. These enhanced capabilities enable identification of site-wide optimisation opportunities across the integrated complex,

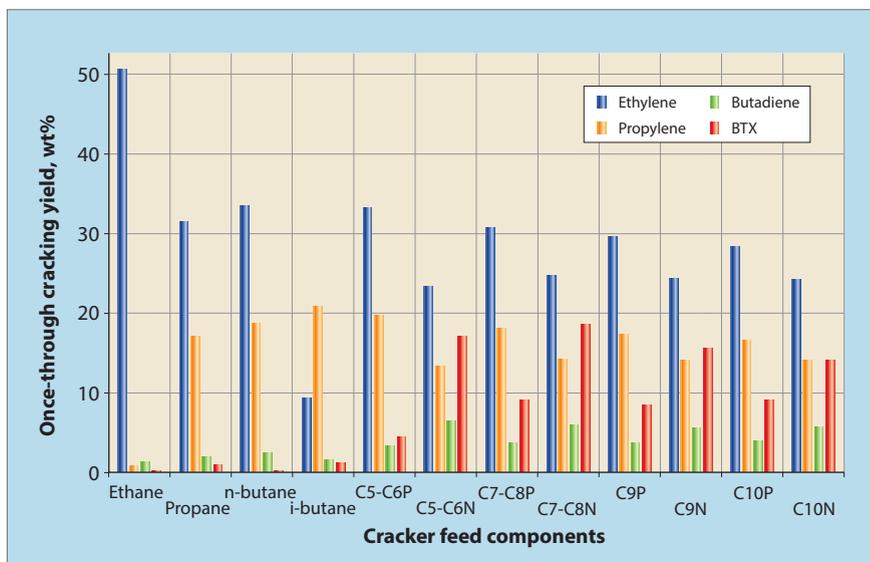


Figure 1 Once-through steam cracking yield for feed components

as well as ongoing sustainment of benefits through real-time monitoring and re-optimisation.

Why manage molecules?

To recognise the need for molecular management and carbon number level simulation, it is important to understand the difference in nature of refining and petrochemical processes. The purpose of refinery naphtha processing units is to maximise octane barrels which can be blended into gasoline. Isomerisation and dehydrocyclisation reactions improve octane, with thermal cracking a side reaction that is minimised to prevent yield loss. However, for steam cracking in petrochemicals, thermal cracking of naphtha is optimised to produce olefins.

Due to differences in the units' reactions, selection of molecules to be processed is extremely important. Replacing molecules from one process unit to another can improve

yields from both the specific units as well as reducing operating expenses such as energy consumption, other utilities, catalyst, and chemicals.

The yields from a steam cracker can vary extensively depending on the feedstock carbon number and different isomers (see Figure 1).

Yield of ethylene and propylene is expected to reduce while yield of heavier products is expected to increase with an increase in the feed carbon number. Even for feeds with the same carbon number, cracking yields change with changes in C/H ratio, for instance paraffinic feeds have higher ethylene yield. Different feeds can be cracked separately or co-cracked, all having an impact on the cracking yields and furnace run length. Aromatics components in the feed rarely crack to produce ethylene and propylene, but these may be too costly to separate prior to processing.

The profitability of the aromatics

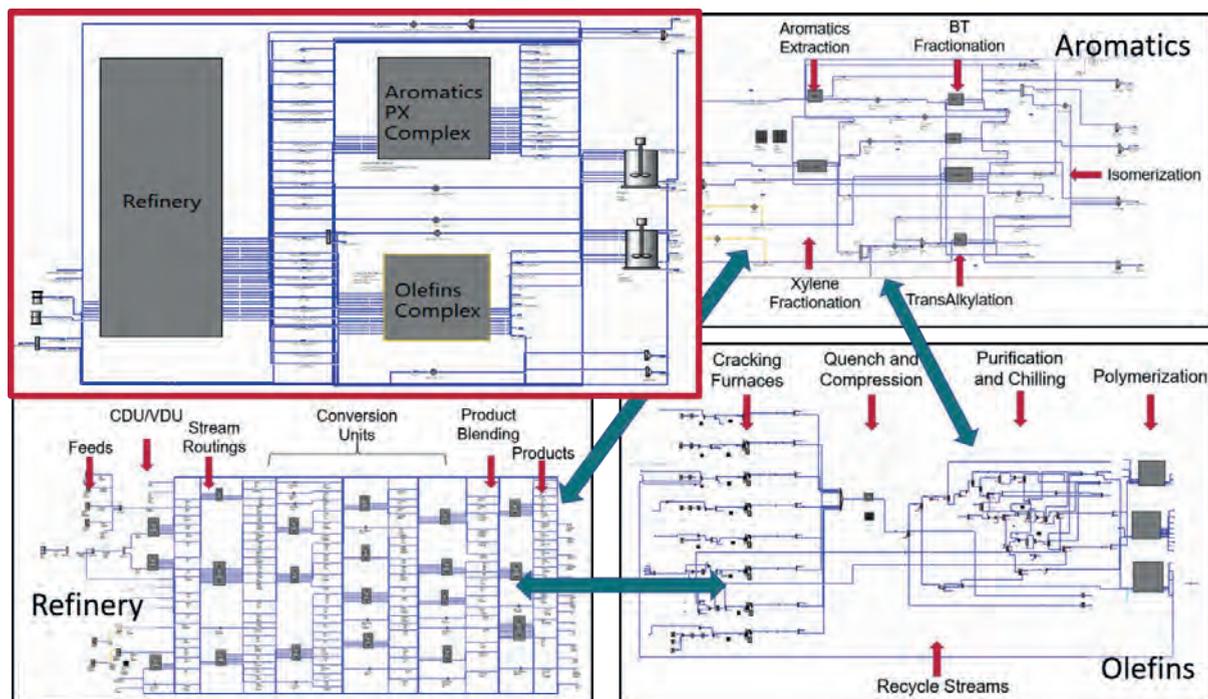


Figure 3 Petro-SIM model of an integrated refinery-petrochemical complex

erroneous results, for instance feed quality parameters in the form of bulk PNA, which do not capture the effect of carbon numbers in the steam cracking operating parameters. Also, a significant fraction of components are continuously recycled in aromatics units, which has an impact on unit opex and the maximum feed that can be processed. Very few refiners simulate these recycles in an LP based model.

Proven basis of the digital twin

KBC has developed and improved Petro-SIM models for refinery-petrochemical integration over many years, working on design configuration and optimisation engagement with clients. Petro-SIM has a seamless transition from bulk properties to component based simulation and vice versa. Information for components available in crude assays, as well as generated from the refinery reactor models, is carried through to petrochemical models using Petro-SIM's infrastructure. Reactor models are calibrated based on the performance of the operating unit, which allows process engineers to track information at a molecular level that is rarely available at the operating unit.

The main function and value of the complex-wide process simu-

lation model is understanding the interaction between different process units and product yield. This can be quickly and easily done, as the equilibrium and kinetic based models for all the refinery, steam cracker, and aromatics units are in a single Petro-SIM simulation flow-sheet (see Figure 3).

This combination holistically and seamlessly captures the effect of feed molecules. The integrated process model carries detailed composition and non-linear kinetics and can be used to augment the LP model to boost profitability through effective molecular management. LP models are still required for bigger optimisation problems, however an integrated process model is needed to routinely validate the optimised solution estimated by an LP. The optimised solution analysed through the integrated process model should be used to validate various constraints and to estimate operating targets.

Various process streams are exchanged between refinery and petrochemical units in the complex-wide model. Apart from feeds to cracker and aromatics, many other streams are also mapped, for instance off-gases and propylene from a refinery, integration of the hydrogen network, and so on.

KBC has deep experience of using integrated models for refinery-petrochemical complexes for identifying and implementing opportunities for profit improvement for the parties involved: re-routing of streams, changing unit severities, and modifying the degree of fractionation. In joint venture projects, a single integrated model is valuable for transfer pricing of intermediate streams between respective parties, based on stream quality. After all, it is the streams' molecular nature which ultimately determines its value in use. The use of the integrated model extends to the cost side too, with integrated modelling of utilities.

The integrated model can be used to estimate transfer pricing, as well as optimise the overall complex for the mutual benefit of all parties involved.

Case study

A KBC client was planning to build a grassroots refinery-petrochemical complex. According to the design of the integrated complex, C₅ from a cracked gasoline hydrotreater was to be routed as a feed to the steam cracker. The C₅ material was highly olefinic and therefore would give poor cracking yields unless it was hydrogenated to saturate the ole-

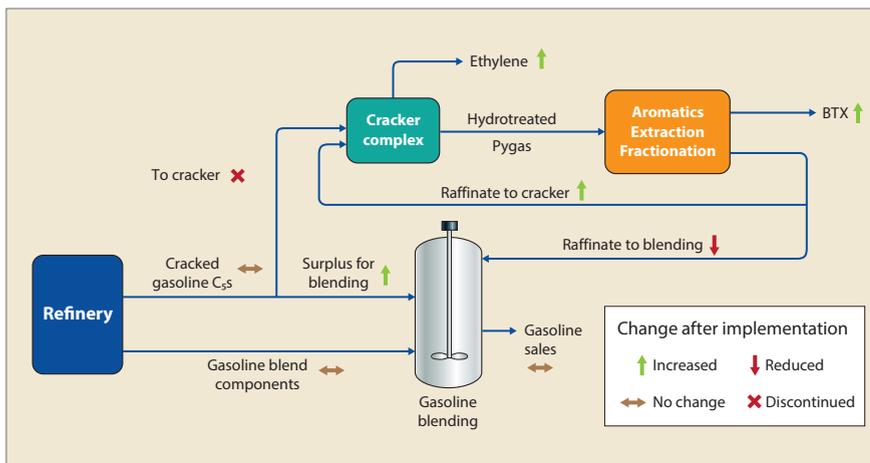


Figure 4 Case study for refinery and cracker complex integration

fin. Based on the relatively small quantity of C_5 , a dedicated hydrogenation system was not economically justified. The next best option was to blend C_5 into the gasoline pool as it had relatively high RON and would boost gasoline production owing to its lower specific gravity. However, routing this stream to the gasoline pool without any other change would have reduced petrochemical yield and would therefore have given lower overall margins. The other potential constraint was the high RVP of C_5 which would have caused issues with the RVP and VLI of gasoline.

KBC reviewed all available streams that can be used to replace C_5 as a cracker feed. Raffinate from the aromatics extraction unit was partially returned to the cracker as feed, with the balance sent to the gasoline pool to meet volume demand for gasoline. The raffinate was rich in paraffins with C_6 - C_8 components, an ideal feedstock for steam cracking. KBC proposed to replace the C_5 feed to the steam cracker with raffinate, routing the C_5 s to the gasoline pool.

A complex-wide model was used to capture the impact on the cracker yield for both feeds and changes in gasoline RVP/VLI. Due to differences in the product specifications, summer and winter operations were analysed and it was found that all of the C_5 could be absorbed in the gasoline pool. There was an overall increase in petrochemical yield due to better cracking from raffinate while maintaining gasoline target volume production. This

resulted in an economic benefit of almost 7c/bbl of crude. An overview of this case study is shown in **Figure 4**.

A digital twin for unit monitoring

Extending the availability of real-time unit operations data to refinery and petrochemical process engineers can transform their situational awareness of unit performance. With a greater understanding of the factors affecting unit performance, in real-time, deeper unit optimisation can be achieved.

Extending the availability of real-time unit operations data to refinery and petrochemical process engineers can transform their situational awareness of unit performance

Utilising the complex-wide Petro-SIM model, with detailed embedded reactor representations calibrated using operating data, allows the integrated model to represent true unit operations over a wide range. To constitute an integrated process digital twin for evaluating unit operations in real-time, the complex-wide process simula-

tion model can be put into operation with real-time operations data from sites' DCS, historian (OSIsoft, PI or other), and laboratory information systems (LIMS) to deliver real-time, high-fidelity virtual representations of hydrocarbon molecule transformation and associated operating conditions. This involves activating the in-built capabilities of the process simulation model without middleware being required.

To track unit performance, well-defined KPIs are used for ongoing scrutiny by unit operations engineers. For each KPI identified, actionable recommendations and procedures for correcting the poor or inefficient performance are developed. One of the key KPI measures is the comparison of reconciled data, with results from process simulation and the LP model used to validate the performance of these tools.

Petro-SIM's data reconciliation utility assesses the health of raw data available through the historian and LIMS. This includes raw mass balancing of sulphur and nitrogen for naphtha processing and petrochemical units, as well as carbon and hydrogen.

The digital twin can estimate parameters which require complex calculations such as cyclone velocity in a RFCC, chemical hydrogen consumption in each reactor, and remaining catalyst life in hydroprocessing units. Margin improvement indicators (MII) configured in the digital twin indicate the loss of margin or gap that needs to be closed to improve the profitability of the complex. The impact of MIIs on margin is estimated using complex-wide digital twin calculations and is configured in the digital twin of a process unit. Monitoring of MIIs ensures that the process engineers and operators continue to optimise the unit. Deviations from target and loss associated with this can then be reported on a continuous basis and acted on, thereby developing a culture of profitability in the organisation.

Case study

KBC worked with a refinery which was designed to produce light and

middle distillates for the domestic market. A new aromatics complex was commissioned near to the refinery which was operated and managed by a different organisation. Most of the feed for the aromatics unit was imported naphtha.

Although a part of the naphtha stream from the refinery was transferred to the aromatics plant, both the refinery and the aromatics plant maintained their own production accounting and reported financial performance using a naphtha transfer price. The refinery was using naphtha as low flash blendstock for middle distillates with the surplus sold to the aromatics plant. As the transfer price of naphtha to the aromatics plant was lower, blending in middle distillate was profitable for the refinery.

KBC compared the quality of imported and refinery naphtha and found that the quality of refinery naphtha was inferior to imported naphtha in terms of carbon number. The paraffin content of refinery naphtha was higher, and it was rich in C_7 whereas imported naphtha had higher C_8/C_9 content. With this comparison it was agreed that the refinery naphtha should be priced at a discount to imported naphtha.

The discount for refinery vs imported naphtha was validated using the integrated process simulation model. In a sensitivity case, a fraction of the imported naphtha was replaced with refinery naphtha. Both the refinery and the aromatics plant were considered as one holistic optimisation for this sensitivity, meaning that a transfer price was not required to estimate the economic impact of this change for the overall complex. This sensitivity case showed benefits of >\$5 million/y without any investment.

The model indicated that processing the different quality of refinery naphtha reduced p-xylene production and increased benzene yield. With the higher price of p-xylene compared to benzene, there seemed to be an economic penalty. The middle distillate production was also reduced. Even with all these changes, the sensitivity case indicated improvement in

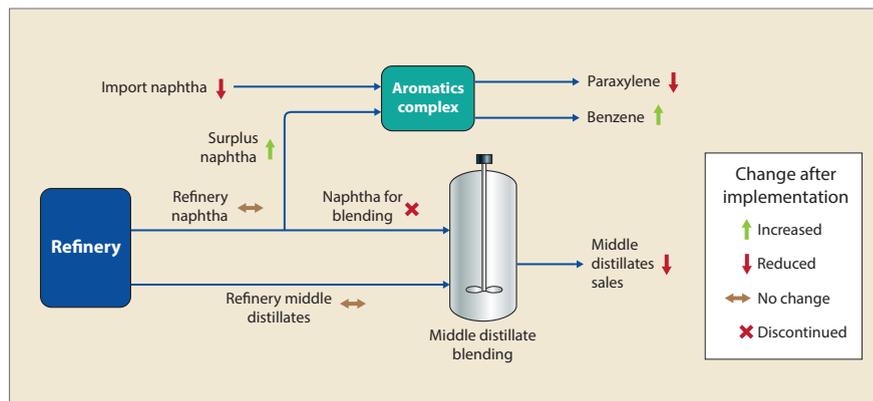


Figure 5 Case study for refinery and aromatics integration

overall profitability. This was due to the significant premium paid by the aromatics plant for imported naphtha.

The proposed opportunity was implemented by the refinery and the aromatics plant. The integrated process simulation model for the complex calculated the breakeven price of refinery naphtha. A discount to the breakeven price at which the aromatics plant would purchase naphtha from the refinery was agreed between the two organisations. With a revised transfer price, there was improved profitability of both organisations. With the integrated process model able to monitor the streams for quality changes, an update to the operating strategies of both plants was able to be implemented. An overview of this case study is shown in Figure 5.

Conclusion

A digital twin aims to be an accurate representation of an asset over its full range of operation and its full lifecycle. It is ideally created during the initial study to evaluate the feasibility of the asset. It is used and further developed during the design, construction, and commissioning of the asset. It facilitates the optimum design of the asset and the training of the staff who will operate the asset. It works in the present, mirroring the actual plant in simulated mode, but with full knowledge of its historical performance and accurate understanding of its future potential.

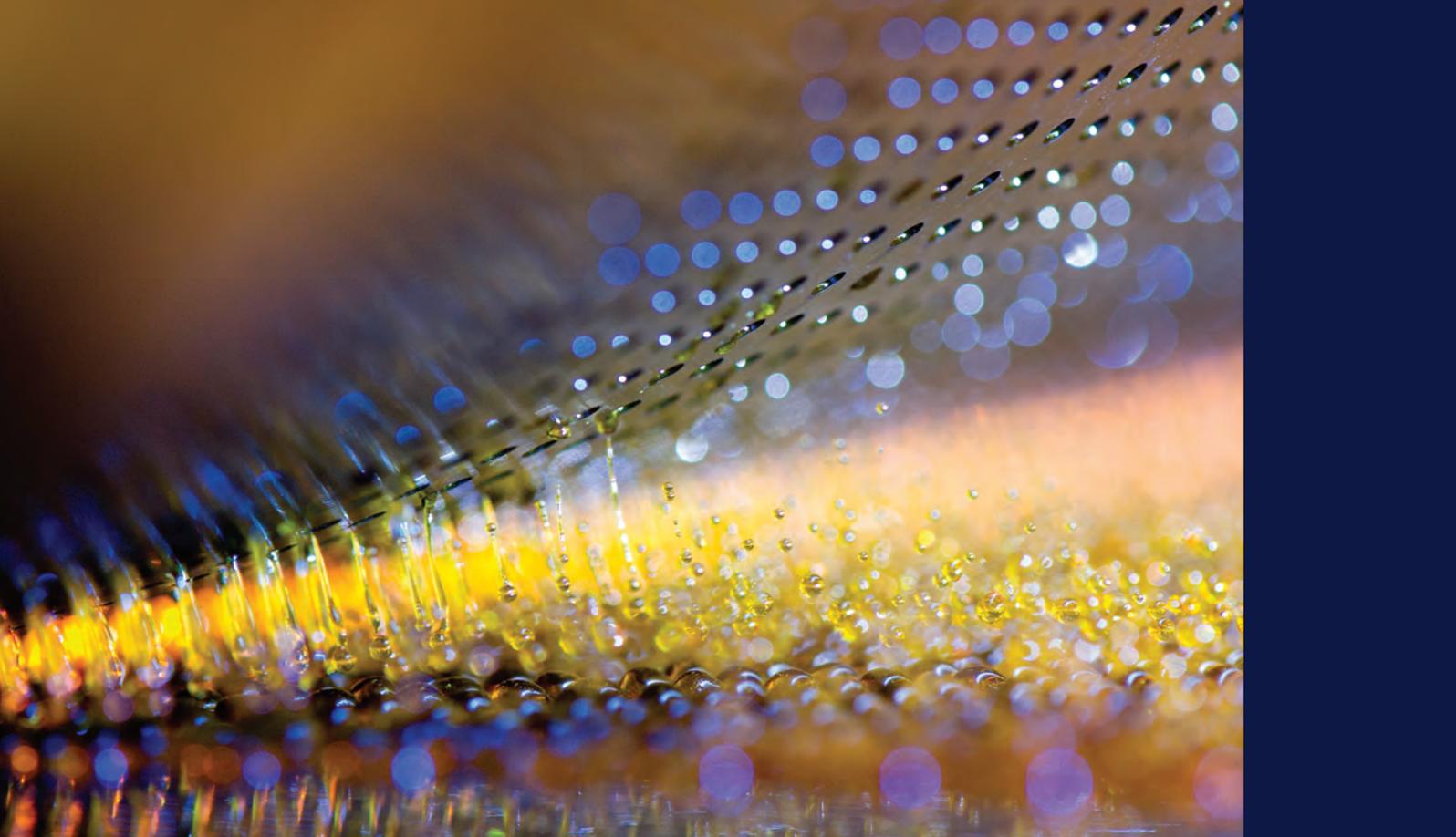
KBC's digital twin is built on our rigorous site-wide first principles simulator, Petro-SIM. The plant model inside the simulator

synchronises with the plant model inside the enterprise process historian to ensure their separate representations of the plant remain aligned. Data gathered from the plant in real-time is validated and statistically reconciled to ensure that all physical and chemical laws are respected; and electronic noise and dynamic effects are eliminated through filtering, thereby ensuring that data quality issues are identified and mitigated.

Petro-SIM enables identification of opportunities for site-wide improvements in performance, as well as benefit sustainment through real-time monitoring of the entire complex. The potential for improvement of an integrated refinery-petrochemical unit is significant and requires tools that are able to analyse accurately for all of the key optimisation factors. Additional benefits can be achieved through effective molecular management for a refinery and petrochemical complex aided with a detailed carbon number breakdown from crude assays through to blending and petrochemical units.

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Remote management of hydrogen production

Remote monitoring and control can improve safety, detect problems early, and promote efficient operations through modelling and analysis of hydrogen production

BRIAN BUMGARNER, MARCO MÁRQUEZ and JEFFREY SWANSON
Matheson, a Taiyo Nippon Sanso Corporation company

The use of hydrogen in petroleum refining is essential to the production of clean burning, low sulphur fuels, the hydro-treating of heavy feedstocks to yield more desirable products, and also for the production of second generation renewable (green) fuels, an area which has received considerable recent attention in the marketplace. Hydrogen production has increased significantly in recent decades as the demand for transportation fuels increases and environmental regulations and product quality considerations have become more critical for lower allowable sulphur content in gasoline, diesel, marine fuel oil (IMO 2020), and maintenance of high cetane in diesel.

Hydrogen can be produced in several ways including steam reforming, partial oxidation, autothermal reforming, gasification, and electrolysis. Of all these routes, steam reforming of natural gas, commonly known as steam methane reforming (SMR), is the most widely used process, primarily due to the efficiency, reliability, and lower cost and evolved experience base with the technology. Even though natural gas has the lowest carbon content of conventional hydrocarbons, it is important to maximise the efficiency of its use and minimise emissions from a sustainability perspective.¹ The importance of doing this is illustrated in Figure 1, which presents a simplified scheme with some actions that can be taken to minimise greenhouse gas emissions.² Focusing on the central column of Figure 1, the efficient operation of hydrogen plants – via optimised consumption and energy monitoring systems – can significantly contribute to reducing costs and emissions.

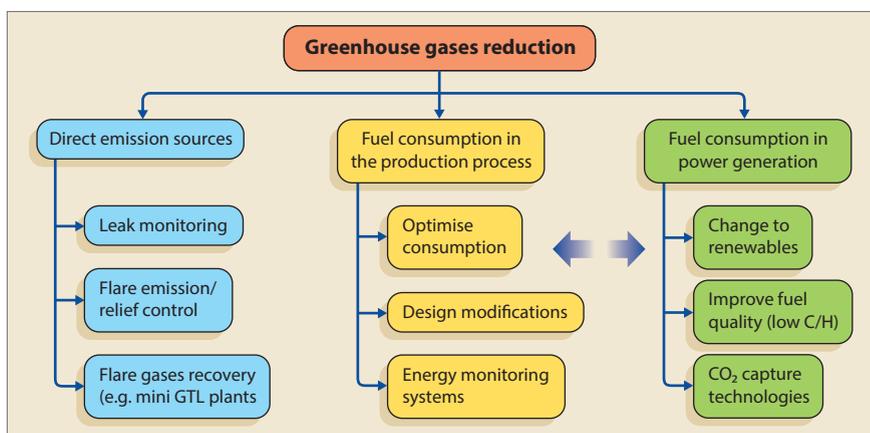


Figure 1 Roadmap to reduce greenhouse gas emissions²

Since the 1990s, many petroleum refiners have shifted the responsibility of hydrogen supply to industrial gas companies (IGC) through over-the-fence supply. Refiners understand that suppliers like Matheson own and operate multiple hydrogen plants worldwide and can benefit from their expertise and the associated advantages including a commitment to safety, guaranteed efficiency, improved reliability, infrastructure maintenance, and predictable and lower overall hydrogen cost. One of the many beneficial practices implemented by some suppliers is the use of remote monitoring and operations centres.

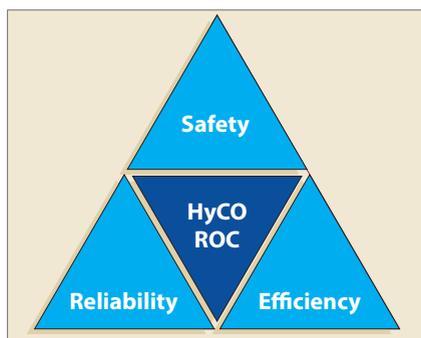


Figure 2 A remote operations centre promotes plant safety, reliability, and efficiency by monitoring plant operations

The role of remote process control and monitoring

Matheson's SMR based hydrogen plants worldwide are data-linked to the HyCO (hydrogen, carbon monoxide and syngas) Remote Operations Center (ROC) in La Porte, Texas. The fundamental role of the centre is to support local operations and promote plant safety, reliability, and efficiency (see Figure 2). It also serves as a training platform for current, incoming, and future operators. From the ROC, hydrogen facilities can either be controlled or monitored remotely, thus providing expert advice and troubleshooting to operators sitting at any of the local plant's control panels. The remote monitoring system enables continual observation, analysis, evaluation, and control of what is happening, while in-house developed simulation tools visualise what should be happening. Matheson has developed proprietary models that predict in real time how a plant should be running and compare those results to how it is actually running. An example interface screen associated with one of Matheson's models is shown in

Figure 3. This tool is used to identify potential problems.

The advantages that the ROC can offer rely on the expertise leveraged by owning, monitoring, operating, and maintaining multiple sites over time. Operators and supporting engineering staff have monitored and operated multiple SMRs with various configurations for years, gathering experience and data from real and simulated scenarios. They are able to intervene before minor issues escalate to become major problems. This adds up to better safety, improved reliability, and enhanced energy efficiency.

Safety, training & operational modes

Safety is the first and most important objective of plant process design and operations. The primary commercial goal of a business can be short and long term profit optimisation. Sometimes these two objectives can appear to be at odds with each other. The implementation of a remote operating centre can help achieve better overall performance with respect to all objectives and goals.

A key element of process safety is having well-trained operators. The ROC provides virtual and actual training platforms for the operations

staff. The centre is equipped with an in-house developed plant simulator that utilises the plant's control system logic and a human-machine interface. This means the operator can be trained on a generic plant simulator, before moving on to an actual operating plant. In-house calculation simulations have been developed to give realistic feedback to the operators so they can learn the effects of their actions. Our simulator is dynamic, allowing operators to train for scenarios involving start-ups, shutdowns, process upsets, and mechanical failures.

With proper automation measures installed at the local plant (instrumentation and controls), remote operation centres can maintain a high degree of operational safety, while complementing the headcount at the local site. The centre's support allows local staff to optimise plant operations on each shift. The centre is staffed with a collection of expert operators with knowledge across sites, who a site employee can use as a 'sounding board' in the event of an unusual occurrence.

Annual plant reliability

Annual plant reliability can be defined as the fractional volume of

hydrogen delivered to the customer versus the amount of hydrogen requested by the customer.

$$Reliability = \frac{\sum_{yr} Delivered\ H2\ Volume\ by\ IGC}{\sum_{yr} Requested\ H2\ Volume\ by\ Customer} \times 100 \quad (1)$$

(* include the periods of scheduled maintenance, force majeure, and any feedstock/utilities supply shortfalls.

A reliable supply of hydrogen is essential for refinery operation. Fuel processing, utilisation, and quality depend on hydroprocessing units to remove sulphur and other impurities and hydrocrack heavy feedstock. Days, or even hours, without hydrogen can represent significant monetary losses and operational and logistical challenges for a refinery. As such, IGCs typically guarantee high annual reliability of hydrogen supply to the end user.

Some of the key advantages associated with plant reliability that have been realised from remote monitoring and operation include:

- Reduced locally caused downtime
- Reduced cost of downtime
- Efficient operations
- Ability to ramp up and down automatically with customer demand while maintaining stable operations
- Improved operational performance
- Documentation and distribution –

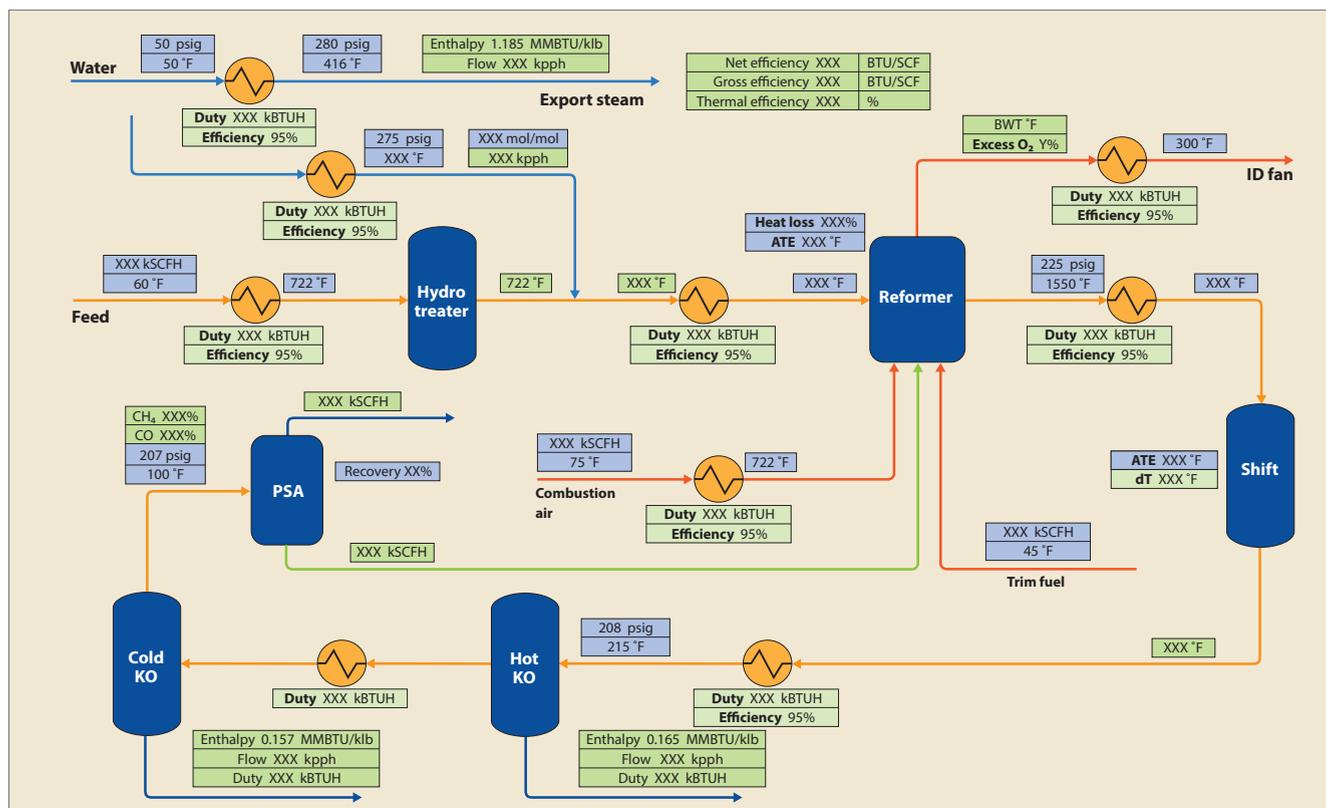


Figure 3 Sample output screen at Matheson's HyCO ROC

among the fleet of plants – of learnings (incidents, near misses) and best practices implemented to prevent future events

IGCs are in the position of operating SMRs with remote monitoring and control capabilities in a reliable manner due to the extensive experience gained from multiple plants. The ROC operations may be able to predict a plant trip before it takes place. Layers of security on top of the audio/visual alarms for operators are able to monitor and analyse an entire plant on a continuous basis. This has proven to be valuable in preventing plant trips. An example occurred when the signal from a combustion-air flow transmitter started to drift from actual flow. The ROC detected and notified local operations well before this was detected by alarms in the field. Had the ROC not alerted the operator of the issue, the combustion air measurement at the plant level may have continued to drift, in which case the excess oxygen level would have approached zero, thus causing large swings in fuel flows, which would have ultimately led to an unplanned, preventable plant trip.

The ROC has also improved reliability through the in-house calculations that have been developed to give realistic feedback to operators so they can learn the effects of their actions; they can be used to allow operators to train in start-ups, shut-downs, and process upset mechanical failure situations. The simulator can be used to write procedures, even before the plant is built, to enable a smoother commissioning process.

Maintenance

Preventive and major turnarounds are essential to preserve the integrity of plant equipment and preserve reliability and efficiency. Although standard maintenance is planned ahead of time, constant monitoring of plant performance can help anticipate if an additional specific maintenance task is required or if the maintenance plan should be modified. By monitoring certain parameters, for example boiler feed water pressure, flow rate, and output of knockout pots, it is possible to detect

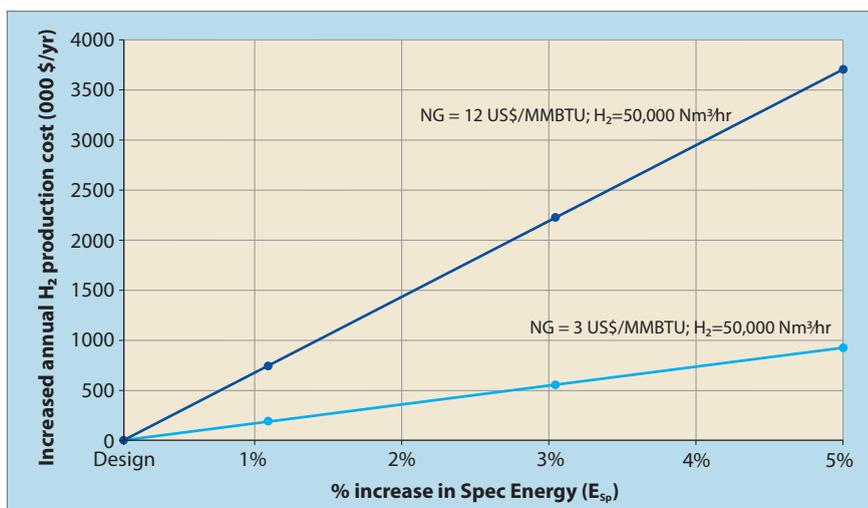


Figure 4 Effect of increased specific energy consumption (SEC) on annual hydrogen cost

the development of a heat exchanger leak. Pressure drops and approach temperatures can be used to predict when a specific heat exchanger may be experiencing fouling/plugging, and service can be planned and coordinated with the customer at a convenient time as opposed to fixing it on an emergency basis and negatively impacting plant reliability.

Plant efficiency (specific energy consumption) and emissions

The largest variable cost component of hydrogen production is the hydrocarbon feed and fuel, most typically natural gas in the Americas. Depending on the hydrogen product pressure requirement and the relative economic basis (utility pricing basis), the natural gas energy cost typically exceeds 80% of the variable hydrogen cost, after taking credit for any steam export. Depending on the underlying design, a modern 50 000 Nm³/h hydrogen plant will consume \$18-20 million per year in natural gas (after steam export credit, at \$3.00 per MMBTU HHV). The SMR hydrogen plant's efficiency can be defined as a specific energy consumption (SEC) and can be expressed as the net amount of energy utilised in the process divided by the amount of hydrogen produced:

$$SEC = \frac{(Feed + Fuel\ consumed - Steam\ exported)}{Hydrogen}$$

$$= \frac{Net\ energy\ used\ per\ day}{Hydrogen\ produced\ per\ day} \quad (2)$$

where the net energy is usually expressed in BTU, MW, MJ, Kcal,

and so on, and the volume in normal cubic metres (Nm³) or standard cubic feet (SCF).

The underlying hydrogen plant design (process parameters and topology) determines the specific energy consumption target (SEC Design). Once the hydrogen plant is commissioned and operating, the day-to-day or actual specific energy consumption (SEC Actual) depends on how well the plant is operated and maintained. Even small deviations from the target specific energy consumption (SEC Design) can have a significant impact on the annual cost of hydrogen production. Figure 4 shows that the economic impact of deviations in the SEC Actual (1-5%) can be in the order of millions of dollars per year, and increases with natural gas pricing. The cost impact increases proportionally as the plant capacity increases.

Similarly, the hydrogen plant's SEC has a direct impact on the hydrogen plant's emissions. Hydrogen production technology has evolved substantially over time on at least three fronts: plant front-end technology developments and commercialisation to reduce emissions; plant back-end optimisation and integration to improve efficiency and reduce emissions; and plant feedstock optimisation to use natural gas to minimise emissions. However, the plant is still a source of carbon dioxide emissions, despite this being at a much lower level relatively, and any scope for mitigating these impacts would be beneficial. Figure 5 shows the green greenhouse

gas emissions in a typical refinery;³ notice that the H₂ production accounts for about 6%.

The primary emissions from the SMR come from the reforming furnace stack as CO₂, SO_x, NO_x, particulates, and unburned hydrocarbons, with CO₂ emissions being the largest in magnitude and impact. All of the carbon that enters the hydrogen plant as natural gas feed and fuel ultimately leaves the hydrogen plant as CO₂. **Table 1** illustrates the effect that inefficiently operating an SMR can have on incremental CO₂ emissions. Similar to the effect on economics, the emissions are greater as the plant's capacity increases and the plant is less efficient. Proper monitoring of the plant's efficiency is key to minimising its emissions despite the improvements in design over the last two decades.

When refiners or petrochemical producers outsource the hydrogen supply to an IGC, the efficiency (effectively the hydrogen variable cost) is guaranteed; this protects the end-user from the operational efficiency risk. However, the risk to hydrogen production efficiency still exists and is merely transferred to the IGC. Therefore, it is necessary for the IGC to track, monitor, and adjust the operating parameters that influence the SEC.

Some of the key operating parameters that influence the SEC are:

- Feed and fuel gas composition
- Steam to carbon (S/C) ratio
- Key process temperatures (reactor inlets/outlets, combustion air, syngas, and so on)
- Excess oxygen in the flue gas exiting the reformer furnace
- PSA recovery and operating factor
- Hydrogen product purity

While these variables are locally monitored and controlled, the added connection and monitoring by the ROC provides significant additional benefit in the form of:

- Tracking and trending
- Modelling and simulation tools
- Lessons learned across a fleet of multiple SMRs
- Extra set of eyes on processes

Deep-dive plant analysis

In a case study at one of the plants in the Matheson fleet, the ROC's online

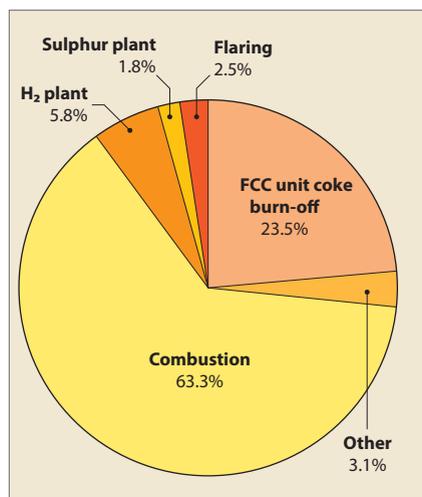


Figure 5 Greenhouse gas emission profile in refining units Source: EPA, 2010

modelling tools indicated that more hydrogen was being produced in excess of what was predicted based on the plant's operating parameters. By adjusting various inputs into the model, the ROC engineers identified that there was likely an error in the measurement of the process steam. Further investigation and troubleshooting determined that a tap for a pressure transmitter that was being used for flow compensation was plugged. The problem was corrected and the excess process steam was adjusted appropriately. The ultimate result was an increase in steam export to the refinery and an improvement to the plant's SEC. The local operators would have eventually detected the operational issue, as the problem grew worse, but the connection to the ROC and the fast response from its staff minimised any efficiency losses that would have amounted to approximately \$300 000 annually (plus any associated increased emissions).

Conclusion

A remote operations centre with staff who have expertise on the specific

Effect of increased specific energy consumption on annual CO ₂ emissions	
% increase in specific energy consumption (SEC)	Increase in CO ₂ emissions (MT/yr) H ₂ capacity = 50 000 Nm ³ /hr
Design	Base
1%	3290
3%	9870
5%	16 445

Table 1

hydrogen plant fleet of the operator is a valued asset for plant operations and its fundamental role is to support the local operation, promoting plant safety, reliability, and efficiency. Remote monitoring and control can improve the safety of field personnel, detect problems early reducing downtime hours, and can promote efficient operations through modelling and analysis, lowering the annual cost of production. The ROC also provides a dynamic platform for virtual and in-person operator training. Mechanical failures can often be anticipated with tools that help predict and plan for equipment maintenance during lifecycle operation.

Industrial gas companies like Matheson have leveraged their extensive operating experience in hydrogen plant through the use of the ROC successfully for the last decade, providing the end customer with safe, reliable, and cost efficient hydrogen supply. Constant monitoring of plant performance contributes to the refiner's bottom line by optimisation of feed and fuel consumption to reduce cost and emissions.

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More petrochemicals with less capital spending

Even in nations with exceptional dependence on transportation fuels like Brazil, better integration with petrochemicals production is essential for refiners

MARCIO WAGNER DA SILVA
Petrobras

Recent market forecasts indicate a trend of reduction in the proportion of transportation fuels in the energy matrix at the global level. Faced with this, refiners have been looking at closer integration with the petrochemical sector, taking into account growing demand for petrochemicals intermediates (see Figure 1).

The current scenario presents major challenges for the crude oil refining industry: the price volatility of raw materials; pressure from society to reduce environmental impact; and refining margins increasingly lower. The newest threat to refiners is a reduction in the consumer market with news of countries that intend to reduce or ban the production of vehicles powered by fossil fuels in the medium term, mainly in the European market.

The search is on for alternative products to ensure the survival and sustainability of the refining industry. Better integration between refining and petrochemical production processes appears an attractive alternative. The production of petrochemical intermediates, beyond opening new markets for refiners, enables more added value in view of the higher product prices of these products when compared with streams dedicated to transportation fuels.

Petrochemical production has been growing at a considerably higher rate when compared with the transportation fuels market in recent years. Additionally, it represents a future for crude oil derivatives that is less environmentally aggressive. The technological bases of the refining and petrochemical

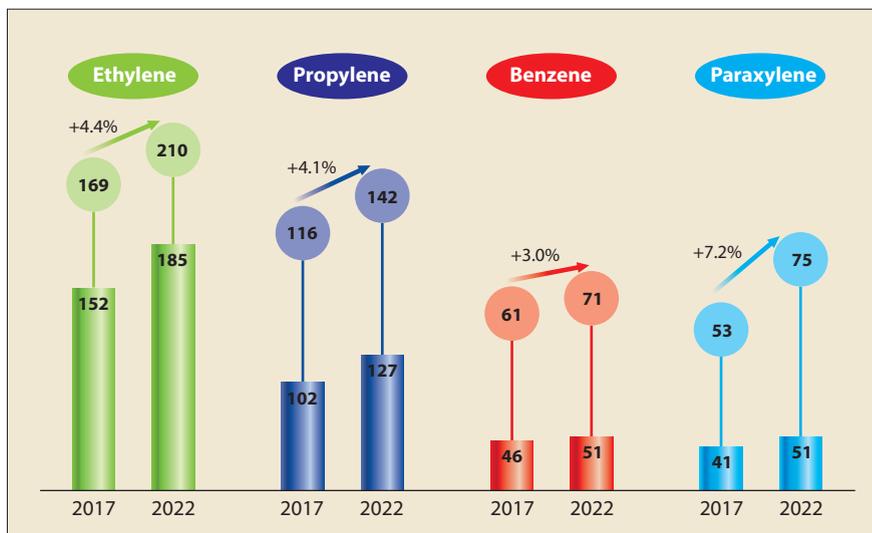


Figure 1 Growing trend in demand for petrochemical intermediates (million metric tonnes) Source: Deloitte, 2019

industries are similar, which leads to possible synergies to reduce operating costs and add value to derivatives produced in refineries.

Figure 2 shows some possibilities for integration between refining and the petrochemical industry.

Process streams with low value for refiners like fuel gas (C₂) are attractive raw materials for the petrochemical industry, just as streams considered residual by petrochem-

ical producers (butanes, pyrolysis gasoline, and heavy aromatics) can be adapted by refiners to produce high quality transportation fuels. Table 1 shows some chief characteristics of the refining and petrochemical industries and the potential for synergies.

The potential for integration and synergy between processes relies on refining schemes adopted for the consumer market; for instance,

Characteristics of the refining and petrochemical industries	
Refining industry High feedstock flexibility High capacities Self-sufficient in power/steam High hydrogen consumption Streams with low added value (unsaturated gases and C ₂) Strict regulations (benzene in gasoline, for instance) Demand for transportation fuels declining	Petrochemical industry Raw material from naphtha/NGL Higher operation margins High electricity consumption High availability of hydrogen Streams with low added value (heavy aromatics, pyrolysis gasoline, C ₄ s) Strict specifications (hard separation processes) High demand for products

Table 1

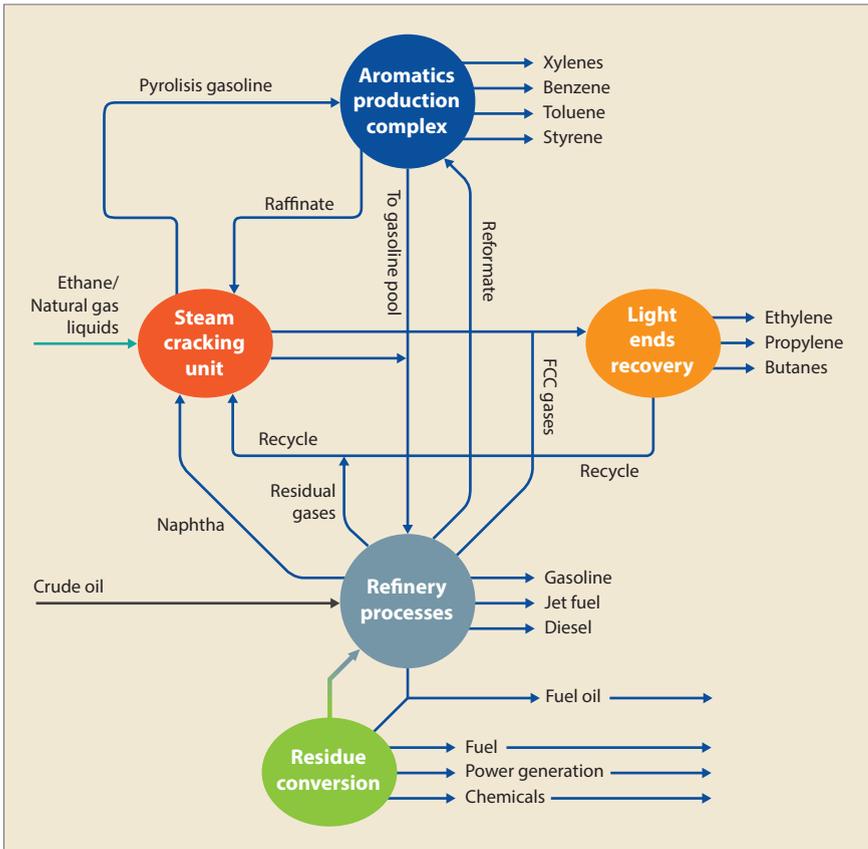


Figure 2 Possible synergies between refining and petrochemical processes

process units such as fluid catalytic cracking (FCC) and catalytic reforming can be optimised to produce petrochemical intermediates to the detriment of streams that are incorporated in the fuels pool. In the case of FCC, units dedicated to produce

petrochemical intermediates (petrochemical FCC) reduce the generation of streams to produce transportation fuels. However, capital investment is high since the severity of the process requires the use of expensive metallurgy for construction.

Refining technologies and low cost alternatives to integration

Historically, the refining industry has optimised its operations and developed technologies in the spirit of maximising production of transportation fuels to meet high demand. Figure 3 shows a typical configuration for a high complexity refinery focused on the production of transportation fuels.

The trend towards falling demand for transportation fuels, together with a growing petrochemical market, have led refiners to search for ways of optimising their hardware to raise the yield of petrochemicals to the detriment of fuels, thereby promoting closer integration with the petrochemical sector.

In this sense, flexible refining technologies such as FCC and catalytic reforming have gained prominence in the downstream industry since they are able to maximise the production of high added value petrochemical intermediates (olefins and aromatics, respectively). However, some refiners have seen the high cost of capital as a barrier to further integration with the petrochemical industry in view of the greater need for investment associated with units to maximise petrochemicals. The installation of units dedicated to the production of pet-

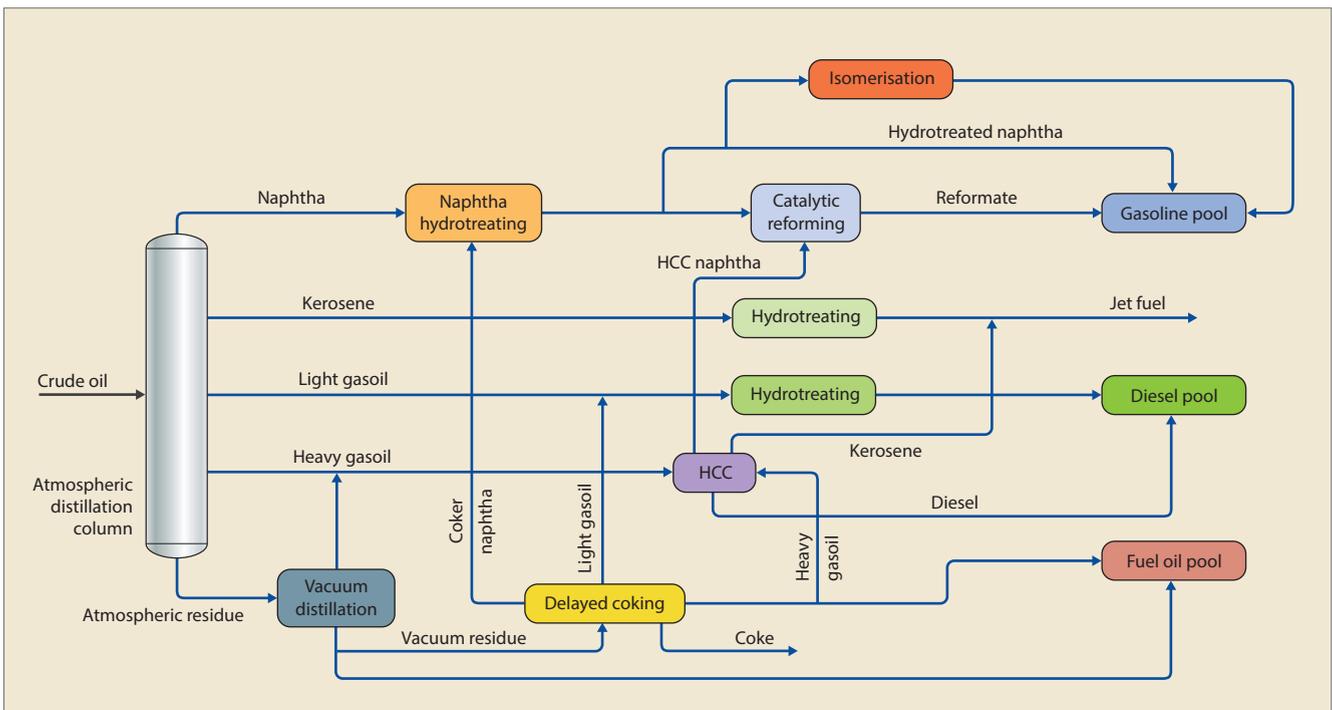


Figure 3 Refinery with a coking/hydrocracking configuration

rochemical intermediates requires high capital investment in high severity FCC units, or complex separation units dedicated to the production of light aromatics in the case of catalytic reforming units.

Despite the restrictions of capital investment, there are some alternatives to maximising petrochemical intermediates through refining hardware with relatively low capital investment. Fractionating straight-run naphtha can be an attractive alternative (see **Figure 4**).

In this case, the light fraction of naphtha may be directed to the market for higher value added petrochemical intermediates while the heavier fraction may comprise the gasoline, diesel or jet fuel pool, according to local market demand.

A conventional FCC unit can have its process variables optimised for the production of petrochemical intermediates (see **Figure 5**).

By changing the reaction severity, it is possible to maximise the production of petrochemical intermediates, mainly propylene, in conventional FCC units (see **Figure 6**).

The use of ZSM-5 in FCC catalysts can increase the unit's propylene production by up to 8%, although recovery of propylene produced by the unit requires the installation of a dedicated separation unit (see **Figure 7**).

Despite the higher operating costs, higher revenues from derivatives should lead to a positive financial result for the refiner, according to current market projections. A relatively common strategy also applied to improve the yield of LPG and propylene in FCC units is the recycling of cracked naphtha, leading to over-cracking of the gasoline range molecules.

Another alternative for refiners with low capital availability is the installation of units dedicated to the recovery of olefins from refinery off-gases (see **Figure 8**).

The off-gases from deep conversion units such as FCC and delayed coking have a high olefin content (>20%). In markets with a high availability of natural gas, the installation of olefin recovery units tends to be economically viable for a refiner.

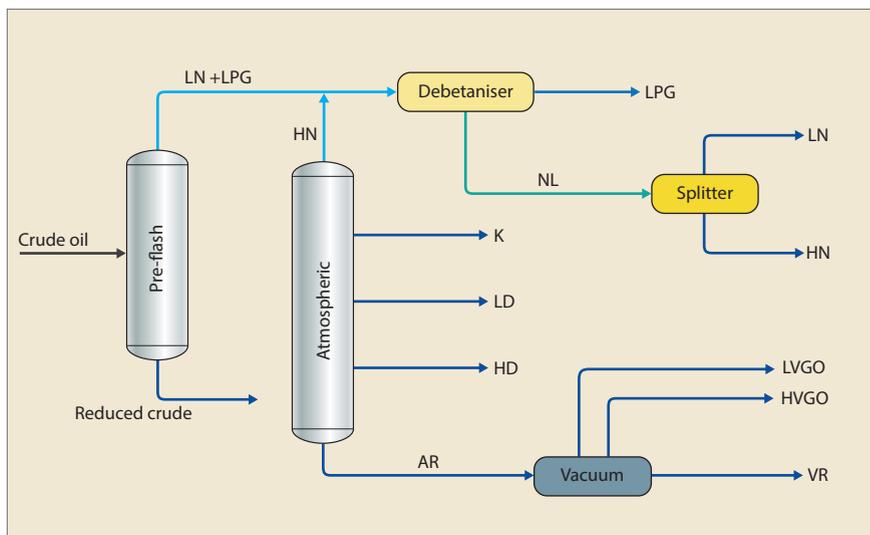


Figure 4 Crude oil distillation scheme based on fractionating straight-run naphtha

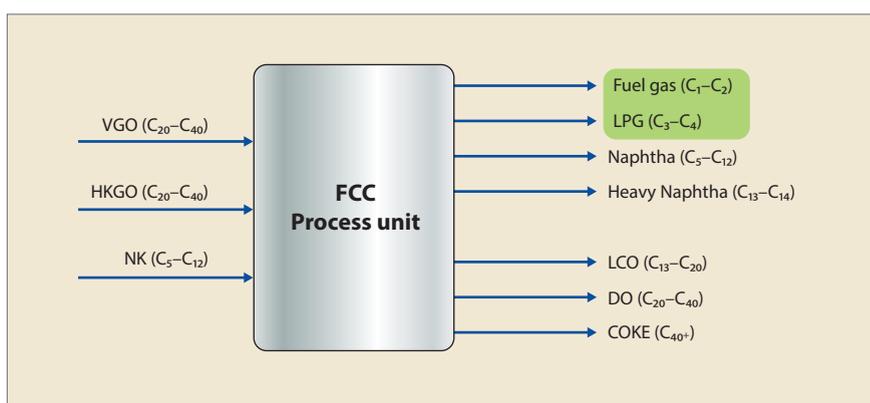


Figure 5 Possible feedstocks and derivatives produced by FCC units

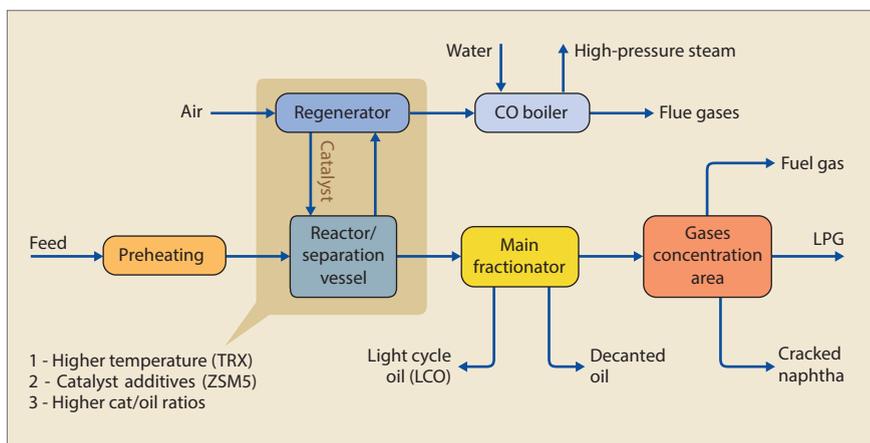


Figure 6 Optimisation of process variables in FCC units to improve the yield of petrochemical intermediates

The off-gases from thermal or catalytic cracking are sent to a compression unit, then pass through a nickel catalyst bed where acetylene, which contributes to coke deposition in petrochemical reactors, is hydrogenated to ethane. Due to their low olefins content, the gases from separation or treatment units such as distillation and hydrotreat-

ing are not used as petrochemical intermediates and are normally directed to the fuel gas refinery pool with the natural gas supply.

After removal of acetylene, the off-gas stream is directed to amine treatment to remove sour gases, H_2S , and CO_2 , which can poison the catalysts used in petrochemical conversion and also raise the

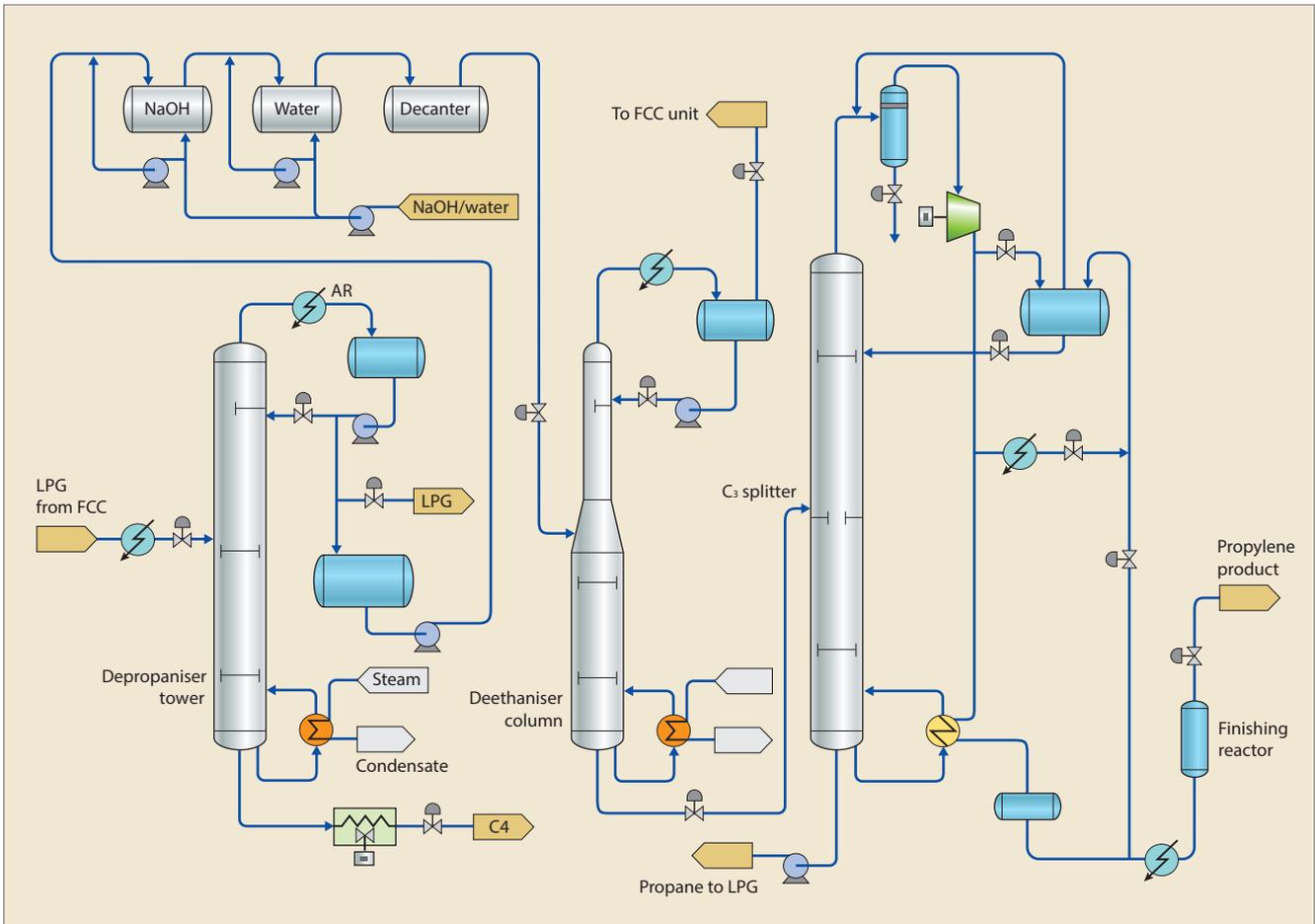


Figure 7 Typical arrangement of a propylene separation unit

level of corrosion in transfer pipelines. Other common contaminants in refinery residual gases, mainly in streams from FCC units, are nitriles, mercury, arsine/phosphine, oxygen, ammonia, and nitrogen oxides. These contaminants, which also poison petrochemical conversion catalysts, need to be removed.

The petrochemical FCC alternative

The majority of catalytic cracking

units are optimised to maximise transportation fuels, especially gasoline. However, those units which have been optimised to maximise the production of light olefins (ethylene, propylene, and butenes) have operating conditions which raise the cracking rate. A reaction temperature of typically 600°C and a higher catalyst circulation rate raises the production of gases, which requires a scaling up of the gas separation section. Higher thermal demand

means operating the catalyst regenerator in total combustion mode, leading to the need to install a catalyst cooler system.

Installation of a catalyst cooler raises the unit's profitability through enhanced conversion and selectivity to products such as propylene and naphtha, rather than gases and coke. When the unit is designed to operate in total combustion mode, heat is released at a much higher rate, hence the need for a catalyst cooler:

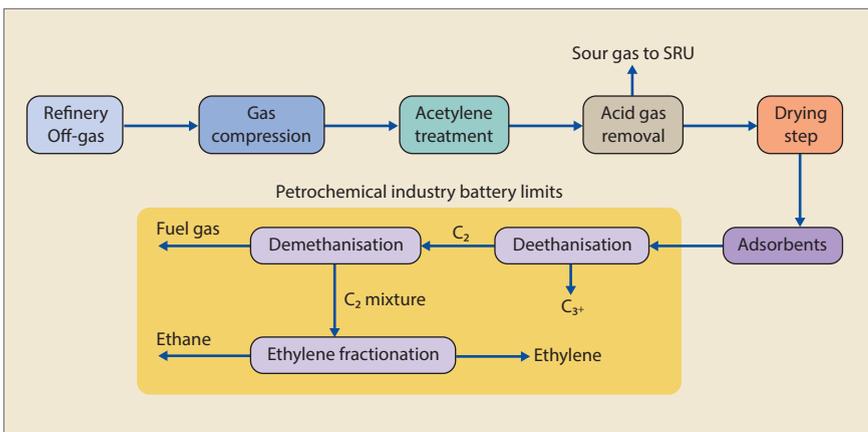
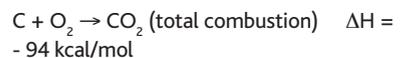
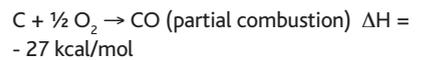


Figure 8 Typical arrangement to recover olefins from refinery off-gases



In such a case, the temperature of the regeneration vessel can reach values close to 760°C, leading to a higher risk of catalyst damage which a cooler avoids. The total combustion mode option needs to allow for the refinery's thermal balance. Moreover, higher tempera-

tures in the regenerator require high specification metallurgy, which raises installation costs significantly.

Petrochemical integration in Brazil

Despite the trend of reduced demand for transportation fuels at the global level, some markets are still strongly dependent on them to sustain economic development. This is especially true of developing economies like Brazil's.

Brazil is a country of continental dimensions that depends on road transport to meet its logistical needs. It is the world's seventh largest consumer of crude oil derivatives, the major component of which is transportation fuels. Hence the nation is the third largest consumer of transportation fuels, mainly middle distillates (diesel and kerosene). According to the Brazilian Petroleum Agency (ANP), national demand for crude oil derivatives will rise 19% up to 2026 from a current 2.4 million b/d. **Figure 9** shows the distribution of crude oil derivatives by end use in Brazil.

As a result of the internal market's characteristics, Brazilian refineries are optimised to maximise the yield of transportation fuels rather than petrochemical intermediates. The crude oil refining sector has an installed processing capacity of 2.3 million b/d of which 98% comprises state company Petrobras's assets. The infrastructure of the Brazilian downstream sector is composed of 17 crude oil refineries, four petrochemical plants, 51 biodiesel plants, 382 ethanol production mills, and close to 5000 km of pipelines to ensure the distribution of derivatives throughout the country.

Despite the Brazilian downstream sector's focus on transportation fuels, some relatively low cost options have been adopted in recent years to improve the yield of petrochemical intermediates in refineries. The higher capacity refineries installed propylene separation units, to recover the petrochemical from LPG produced in FCC units. Installed capacity to produce propylene from FCC LPG in Brazil is 1 300 000 t/y. Of 17

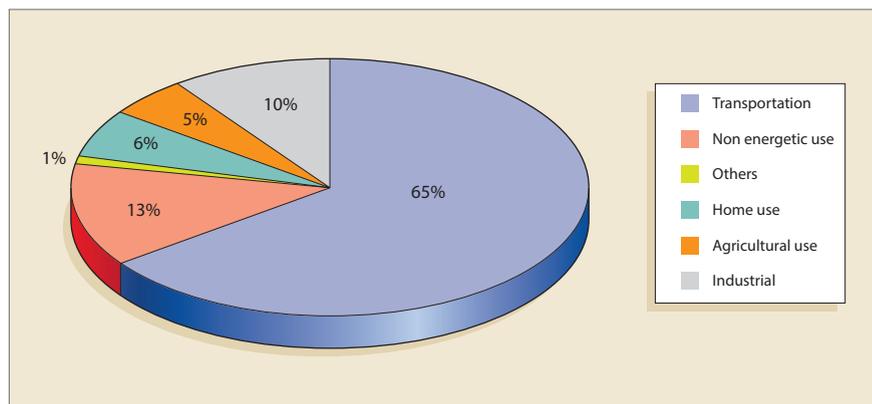


Figure 9 Consumption of crude oil derivatives by final use in Brazil's domestic market
Source: EPE, 2019

Brazilian refineries, eight rely on propylene splitter units.

Brazil's refineries rely on straight-run naphtha fractionating systems. Normally, the light naphtha is directed to the petrochemical industry while the heavy naphtha is blended to diesel or jet fuel according to market demand and restrictions in derivative specifications. In São Paulo state, the biggest Brazilian market, there is a refinery off-gas recovery unit with capacity to process 1 million Nm³/d to recover ethylene.

Conclusion

Synergy between refining and petrochemical processes raises the availability of raw material for petrochemical plants and makes the supply of energy in these processes more reliable, while at the same time ensuring better refining margin through the higher added value of petrochemical intermediates compared with transportation fuels. Another advantage is the reduced risk of over-supply of transportation fuels during the current decline in demand and restrictions in the supply of fossil fuels.

It is important to consider that integrated processes lead to higher operational complexity. However, given the current and medium term scenarios facing the refining industry, integration between refining and petrochemical processes is fundamental to the economic sustainability of the downstream industry.

Recent forecasts indicate that the production of petrochemical intermediates will account for most crude oil consumption in the

medium term. In this case, maximising petrochemical intermediates from refining hardware, and closer integration with petrochemical assets, should be a downstream industry trend in the coming years. Refiners with capital investment constraints risk losing market share and competitiveness, hence action at low relative cost to maximise petrochemical output should be economically attractive.

Further reading

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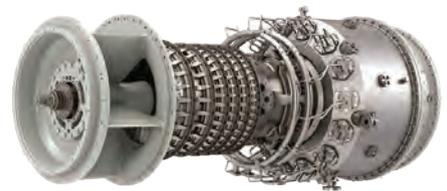
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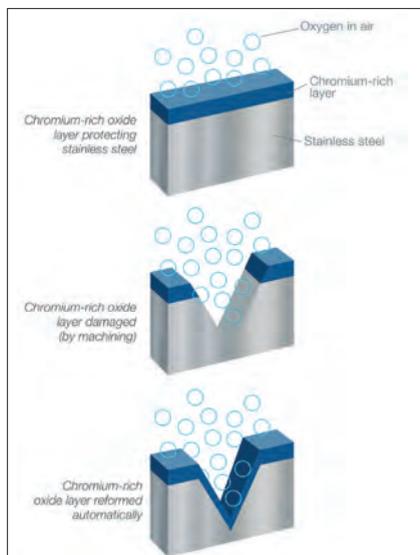
Types of corrosion and materials to combat them

A review of corrosion problems in fluid systems and how to prolong their life in one of the oil and gas industry's most challenging environments

GERHARD SCHIROKY
Swagelok Company

Large offshore platforms feature thousands of installed fluid system components and miles of tubing. Valves, tubing, and fittings are used in process facilities, seawater systems, and utility lines. These components face many corrosive threats, which can come from internally contained fluids or externally from seawater that forms chloride-rich deposits on equipment upon drying. Corrosion, if not detected in its early stages, can lead to costly shutdowns, repairs, and, in worst case scenarios, accidents. Therefore, regular inspections should be performed to assess the integrity of fluid systems. Systems should be constructed with readily available materials, have optimal corrosion resistance to the particular environment in which they are used, and be cost effective.

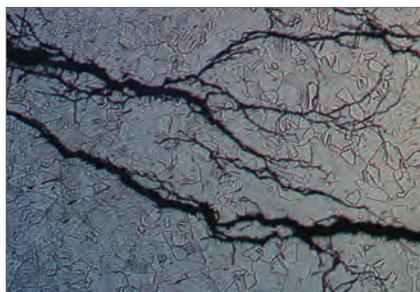
Historically, 316/316L stainless steel (SS) has been the preferred choice for constructing typical fluid systems. However, as more assets began operating in hot and humid climates, the limitations of this material became increasingly evident – most notably in the form of pitting corrosion on tubing, which can lead to perforations and leaks. When the advent of deep water well injection technology required fluid systems to operate at higher pressures, it became evident that alloys with better mechanical properties than 316/316L SS became preferred candidates for the material of construction of components. Finally, the production of oil and gas from increasingly sour reservoirs has led to the use of nickel alloys as preferred materials of construction.



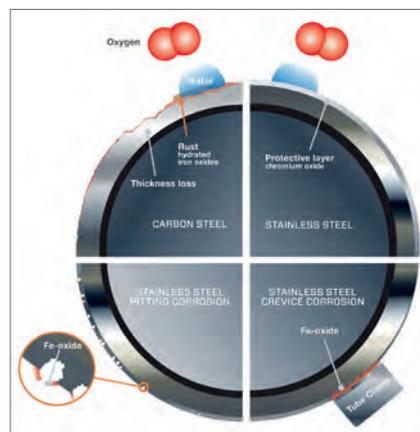
a. In stainless steels, a passive, chromium-rich oxide layer automatically forms on the surface in ambient air (top), protecting the material from corrosion. If this outer layer is damaged by machining or in the field (middle), it will reform automatically (bottom)



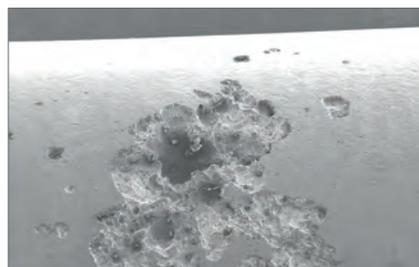
c. General (uniform) corrosion



f. Stress corrosion cracking



b. Corrosion occurs when a metal atom is oxidised by a fluid, leading to a loss of material in the metal surface. It may appear in the form of general corrosion (rust), pitting corrosion, crevice corrosion (all shown), or a variety of other types of corrosion



d. Localised pitting corrosion

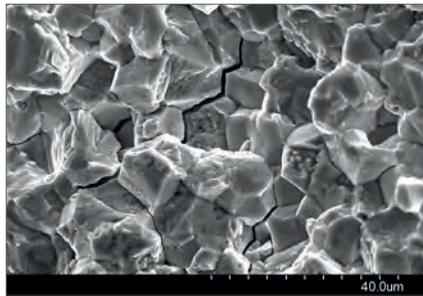


e. Localised crevice corrosion is likely to form between tubing and tubing supports (shown), as well as when tubing is installed close to other surfaces, due to accelerated reactions that take place within the confines of a crevice

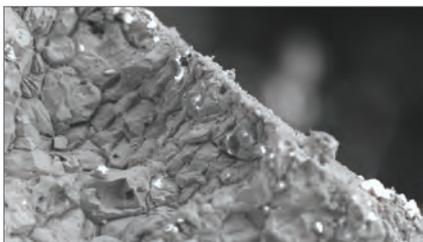
Figure 1 Types of corrosion
All images Swagelok



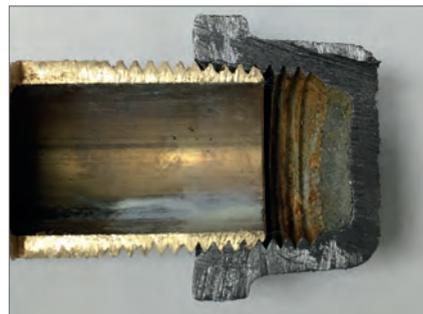
g. Sour gas or sulphide stress cracking corrosion



h. Intergranular corrosion of hydrogen embrittled Inconel X-750 diaphragm



i. Intergranular corrosion



j. Galvanic corrosion of carbon steel cap attached to a brass pipe containing a sodium chloride solution

Figure 1 Continued Types of corrosion
All images Swagelok

Stainless steels and many nickel alloys consist of roughly 10 different elements, each of which provides the material with a distinct characteristic or property. The most important alloying additions to iron are nickel, chromium, and molybdenum – and, in some cases, nitrogen. The importance of chromium is illustrated in **Figure 1a**, which shows how this element reacts with ambient air to form a very thin, adherent, and protective oxide layer on stainless steel.

Various forms of corrosion, which are described in this article, threaten the integrity of materials. To select optimal materials of construction for fluid systems on offshore platforms, it is important to first understand the internal and external environments the components will see. Then, candidate materials can be identified and evaluated against different corrosive threats.

Identifying types of corrosion

Corrosion is a natural phenomenon

that takes place as a metal physically degrades due to interactions with its environment. It occurs when a metal atom is oxidised by a fluid, leading to a loss of material in the metal surface (see **Figure 1b**). This loss reduces the wall thickness of a component and makes it more prone to mechanical failure. Many types of corrosion exist and several are detailed in this article, with each posing a threat that must be evaluated when selecting optimal materials for platform applications.

General (uniform) corrosion

General, or uniform, corrosion (see **Figure 1c**) is the easiest to spot and predict. It forms relatively uniformly across the surface of carbon or low alloy steel and appears as iron oxide scale, or rust, as the surface begins to break down. General corrosion rarely leads to disastrous failures – but it is not unheard of – and therefore is often regarded as an eyesore rather than a serious problem.

When protective paint no longer protects the structural carbon steel components of a platform, steel oxidises quickly. Water may transport rust and redeposit it on stainless steel parts. In such cases, stainless steel parts themselves may appear to have corroded, but they actually have been contaminated with the corrosion products of carbon steel. Excessive contamination may ultimately initiate corrosion of stainless steel.

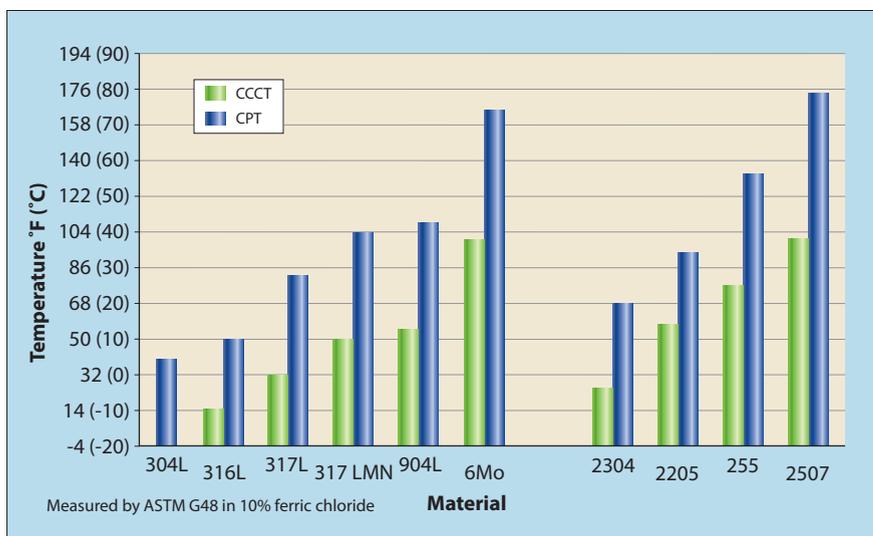


Figure 2 Crevice corrosion can occur at lower temperatures than pitting corrosion. For instance, for 316L SS in a 10% ferric chloride environment, pitting corrosion can start to occur at 10°C (50°F), whereas crevice corrosion can begin at -10°C (14°F)

Localised corrosion: pitting and crevice corrosion

Localised corrosion occurs in a concentrated area where the metal's protective layer breaks down when exposed to fluids that contain chlorides. It is common in chloride containing acidic environments and in installations with crevices between metals or between a metal and a non-metal. Localised corrosion may occur in the form of pitting corrosion (see **Figures 1b** and **1d**) or crevice corrosion (see **Figures 1b** and **1e**), both of which are more difficult to detect than general corrosion. As a result, these types of corrosion can be more challenging to identify, predict, and design against.

Materials with higher critical pitting temperatures (CPT) and critical crevice corrosion temperatures (CCCT) are more resistant to localised corrosion. Potential solutions to combat both pitting and crevice corrosion include using 6-moly stainless steel, 2507 super duplex stainless steel or nickel alloys 625, C-276, or 400 (see **Figure 2**).¹

Pitting corrosion

Common in high-chloride environments at elevated temperatures, pitting corrosion causes small cavities, or pits, to form on the surface of a material (see **Figures 1b** and **1d**). It begins when the passive oxide layer on the metal's surface breaks down, making the metal susceptible to the loss of electrons. When an electron from the metal escapes, iron in the metal dissolves into a solution in the bottom of the pit, diffuses toward the top, and ultimately oxidises to rust. As the pit gets deeper, the iron chloride solution concentration in the pit can increase and become more acidic, which in turn accelerates the pit growth. Eventually, the corrosion may lead to perforation of tubing walls and leaks.

Pitting corrosion is best prevented by selecting alloys with higher pitting resistance equivalent number (PREN) values. Different metals and alloys can be compared using their PREN, which is calculated from the chemical composition of the material (see **Figure 3**). PREN values increase with higher levels of chromium, molybdenum, and nitrogen, and higher values indicate greater pitting corrosion resistance.

Crevice corrosion

In a typical fluid system, crevices exist between tubing and tube supports or tube clamps, between adjacent tubing runs, and underneath dirt and deposits on component surfaces. The breakdown of the material's protective oxide layer in these areas leads to the formation of small pits, which grow larger and deeper until they cover the surface of the entire crevice (see **Figures 1b** and **1e**). Crevice corrosion can occur at far lower temperatures than pitting corrosion.

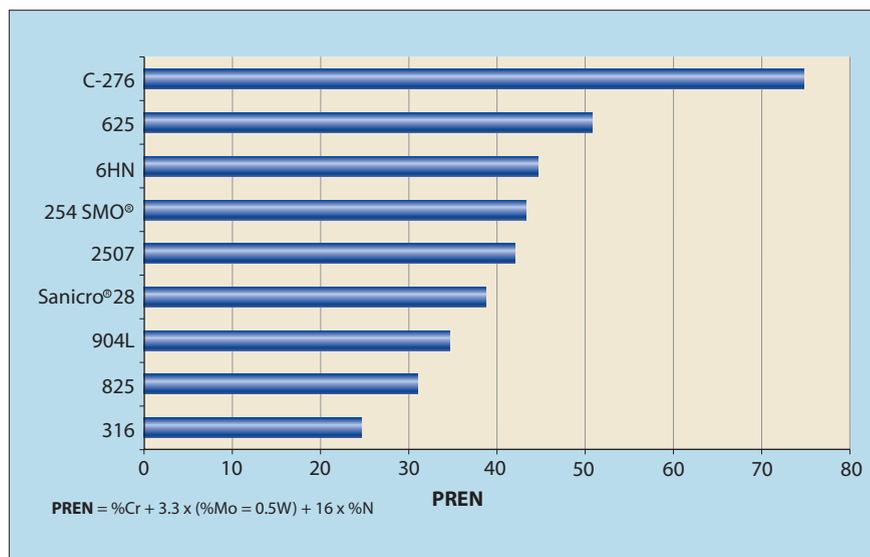


Figure 3 Higher PREN values indicate greater pitting corrosion resistance. 6HN denotes 6-moly alloy UNS N08367

Crevice corrosion occurs due to accelerated reactions that take place within the confines of a crevice. When seawater diffuses into a crevice, some positively charged ferrous ions dissolve and cannot rapidly diffuse out of the tight area, attracting negatively charged chloride ions from seawater into the crevice. As the chloride concentration increases,

Stress corrosion cracking can destroy a component at stress levels below the yield strength of its material of construction and may cause the material to fail suddenly

the crevice solution becomes more corrosive, causing more iron to dissolve, which in turn attracts more chloride ions to diffuse into the crevice. Ultimately, the crevice solution turns into an acidic and highly corrosive solution.

Stress corrosion cracking

Stress corrosion cracking (SCC, see **Figure 1f**) can occur when components that are under tensile stress

are exposed to corrosive media. It can be induced by chlorides on austenitic stainless steels, alkalis on mild steel, and ammonia on brass. The ions interact with the material at the tip of a crack where tensile stresses are highest, making it easier for the crack to grow. SCC is a dangerous form of corrosion because it cannot be detected visually and can be difficult to detect with non-destructive testing methods. SCC can destroy a component at stress levels below the yield strength of the component's material of construction and may cause the material to fail suddenly.

SCC-resistant materials include 6-moly alloys and alloys 2507, 825, 625, C-276, and 400.

Sour gas cracking or sulphide stress cracking

Sour gas cracking (see **Figure 1g**),² also known as sulphide stress cracking (SSC), is very similar to SCC. The primary difference is that the metal deteriorates due to exposure to hydrogen sulphide (H₂S) and moisture. SSC may occur in new sour reservoirs and aging reservoirs where seawater has been injected for enhanced oil recovery.

In the presence of water, H₂S becomes severely corrosive, which can lead to embrittlement of metal and subsequent cracking under the combined action of tensile stress and corrosion. SSC poses an increased risk when the metal has a higher material hardness/tensile

strength, when the environment has a higher hydrogen ion concentration (which equates to a lower pH value), and when the H₂S partial pressure is high. In addition, higher total tensile stress, which includes applied and residual tensile stress, longer exposure times, and lower temperatures contribute to an increased potential for SSC.

The NACE MR0175/ISO 15156 standard describes requirements for the condition of many materials used in sour environments in oil and gas production, including 316 and 6-moly stainless steel, super duplex stainless steel 2507 and nickel alloys 825, 625, C-276, and 400. This standard also describes the environmental limits – maximum temperature, chloride concentration, and H₂S partial pressure – to which these alloys can be used.

Hydrogen embrittlement

Hydrogen atoms can diffuse into metals, causing them to become brittle (see **Figure 1h**).³ The dissolved hydrogen atoms can cause changes in the mechanical properties and behaviour of the metal, including reducing its ductility, impact strength, fracture toughness, and resistance to failure by fatigue. Subjected to sufficient static or cyclic tensile stress, the embrittled metal is at a greater risk of failure.

Hydrogen embrittlement can be avoided by selecting materials that are resistant to hydrogen. For example, austenitic stainless steels (such as 316/316L SS and 6-moly) with nickel content between 10% and 30% show relatively little embrittlement. Conversely, ferritic alloys with very low nickel contents can become significantly embrittled when hydrogen atoms diffuse into these materials.

Intergranular corrosion

Common in welding operations, heat treatments, and high temperature applications, intergranular corrosion (IGC) may occur when chromium and carbon react to form carbides on the metal's grain boundaries (see **Figure 1i**). The latter are the microscopic interfaces between the individual grains in a metal. The carbide formation affects the uniform

Volts vs SCE	Surface classification	Material
-1.60	Active	Magnesium
-1.00		Zinc
-0.95		Aluminium
-0.70		Cadmium
-0.60		Steel
-0.50		Type 304 (Active)
-0.40		Type 316 (Active)
-0.35		Naval brass
-0.30		Muntz metal
-0.30		Copper
-0.30		Manganese bronze
-0.25		90-10 Cu-Ni
-0.20		70-30 Cu-Ni
-0.20		Nickel
-0.15		Lead
-0.10		Type 304 (Passive)
-0.05	Type 316 (Passive)	
0.00	E-BRITE® alloy	
0.00	AL 29-4C® alloy	
0.00	AL-6XN® alloy	
0.05	Alloy 625, alloy 276	
.010	Noble	Titanium
.025		Graphite

Figure 4 Highly noble materials with 'passive' surfaces are not as susceptible to galvanic corrosion as less noble materials or as noble materials with 'active' surfaces. In this anodic index chart, magnesium is the least noble material, and graphite is the most noble material. SCE = saturated calomel electrode

distribution of elements within the metal by robbing material adjacent to grain boundaries of important elements, such as chromium. When corrosive fluids attack the chromium-depleted regions, intergranular cracks can form. Such cracks can propagate throughout a material and remain undetected, making IGC a dangerous form of corrosion.

Selecting a stainless steel with low carbon content, such as 316/316L, will help to minimise the potential for IGC.

Galvanic corrosion

When two dissimilar metals are combined in the presence of an electrolyte, galvanic corrosion (see **Figure 1j**)³ can occur if the potential (voltage) difference between the materials is too great. Too high a potential difference causes the passive layer of the less noble material to break down, leading to its corrosion. A more noble material has higher resistance to corrosion and oxidation than a less noble one.

The anodic index (see **Figure 4**),⁴ which describes the potential or

voltage difference of metals measured in seawater against a standard electrode, is helpful for determining the compatibility of metals. Highly noble materials are not as susceptible to galvanic corrosion as less noble ones. Likewise, a material with its passive surface intact has higher resistance to galvanic corrosion than the same material with an active surface. An active surface of a metal is present when its passive, protective surface oxide film is removed by erosion or fretting.

To avoid galvanic corrosion, choose materials with a voltage difference that does not exceed 0.2V. For example, a 316 SS fitting (-0.05V) combined with 6-Moly tubing (0.00V) would result in a voltage difference of 0.05V between the two alloys. This voltage is significantly less than 0.2V, so the risk of galvanic corrosion is low.

Selecting materials

Selecting the proper materials can help mitigate corrosion and promote asset longevity and safety. Selections include stainless steels and nickel alloys, as well as titanium alloys and engineered combinations of components made from two different materials.

Stainless steels

In austenitic stainless steels, chromium and nickel are critical for corrosion resistance and ductility, respectively. Adding more than 10% chromium to steel transforms it into stainless steel, as the chromium creates an adherent and invisible passive oxide layer on the metal's surface. This oxide layer forms when chromium in the alloy reacts with oxygen in ambient air, giving steel its stainless characteristics and its corrosion resistance. The addition of nickel provides good ductility and ease of forming and welding.

The following stainless steels are commonly specified for corrosion resistance:

316 SS

Among stainless steels, 316/316L SS is a widely used material with satisfactory resistance to various types of corrosion in moderately corrosive fluids. Most raw materials and

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products contain not much more than the minimally required concentration of 10% nickel and 16% chromium. However, components featuring a more highly alloyed material with at least 12% nickel and 17% chromium resist corrosion far better. The greater nickel content provides the austenite with added stability against the undesirable formation of martensite when the material is cold-formed, for instance by cold-drawing, machining, and burnishing. The higher chromium content translates into a higher PREN value, giving the material added resistance to localised corrosion. The lower carbon content of the dual-certified 316/316L SS material provides for higher resistance to IGC as compared to a 316 alloy with high carbon content.

6-Moly alloys

Significantly higher levels of chromium, molybdenum, nickel, and nitrogen provide 6-moly super austenitic stainless steels with much higher resistance to various types of corrosion than 316 SS. The 6-moly alloy 6HN (UNS N08367) has been found to have better corrosion resistance in chloride containing media than 6-moly alloy 254 SMO (UNS S31254).^{5,6} Considered super austenitic stainless steels, 6-moly alloys contain at least 6% molybdenum and have a PREN value of at least 40. Their yield strength is 50% greater than that of 316 SS.

2507 super duplex

As another option, 2507 super duplex, ferritic-austenitic stainless steel is well suited to service in many very corrosive environments. Its composition includes chromium, nickel, molybdenum, and nitrogen, which provide the material with excellent resistance to general corrosion, localised corrosion, and SCC. The material is weldable, but proper procedures must be followed. Duplex stainless steels have a two-phase microstructure of austenite and ferrite grains, which lead to high strength, good ductility, and good resistance to chloride-ion induced SCC. The use of a super duplex alloy as material of construction brings about many advantages:

- Its high yield and tensile strength allow for the construction of products with much higher pressure ratings, especially when compared to 316 SS.
- Alternatively, the wall thickness of a product such as tubing can be decreased, which allows for increased fluid flow.

Nickel alloys

Nickel alloys feature nickel as an important element and commonly offer ductility, toughness, and strength. Some nickel alloys offer exceptional mechanical properties at very high temperatures, while others feature superior corrosion resistance in concentrated acids at elevated temperature. Nickel alloys that offer outstanding corrosion resistance in offshore environments include the following:

Alloy 825 is a nickel-iron-chromium-molybdenum alloy designed to

Titanium and its alloys are highly resistant to oxidising acids over a wide range of concentrations and temperatures

resist general corrosion, localised corrosion, SCC, and SSC in a wide range of media. Stabilised with titanium, alloy 825 is resistant to IGC. In addition, it has high chemical resistance to sulphuric and phosphoric acids.

Alloy 625 is a nickel-chromium-molybdenum alloy with a small quantity of niobium to reduce the risk of IGC in a wide variety of severely corrosive environments. It also resists hydrochloric and nitric acids, providing protection from localised corrosion in high temperature uses, as well as SCC and SSC.

Alloy C-276 contains nickel, chromium, and molybdenum. Its high

molybdenum content makes it exceptionally resistant to localised corrosion. It is one of only a few materials that can withstand the corrosive effects of wet chlorine gas, hypochlorite, and chlorine dioxide. In addition, it is suitable for highly sour gas environments. Alloy C-276 is resistant to oxidising and reducing media, as well as SSC and IGC. It is not recommended for use in highly oxidising environments such as hot and concentrated nitric acid.

Alloy 400 is a nickel-copper alloy known for its exceptional resistance to hydrofluoric acid. It is also resistant to SCC and pitting in most fresh and industrial waters; stagnant seawater, however, can induce localised corrosion. Alloy 400 offers strength and corrosion resistance in a wide range of temperatures and media and retains mechanical properties at sub-zero temperatures.

Titanium alloys

Titanium alloys have excellent resistance to microbiologically induced corrosion (MIC). Titanium and its alloys are highly resistant to oxidising acids over a wide range of concentrations and temperatures. Common acids in this category include nitric (HNO₃), chromic (H₂CrO₄), perchloric (HClO₄), and hypochlorous (Cl₂ gas dissolved in water) acids. However, titanium will sometimes corrode in aqueous chloride environments.

Engineered combinations

In marine installations in which 316/316L SS fittings have performed well but the surface of 316/316L tubing has experienced crevice corrosion where it was in contact with tube clamps or tube supports, it may be cost effective to use 316/316L fittings in combination with tubing from a more corrosion resistant alloy instead of using the more expensive alloy for all components. Such engineered combinations of 316/316L tube fittings with tubing made from alloys 254 SMO, 904L, 825, or Tungum (copper alloy UNS C69100) would reduce the cost of fittings throughout the installation, while maintaining the

overall performance of this more economical combination by reducing the risk of crevice corrosion of tubing where mounted in tube supports (see **Figure 1e**).

Selecting materials and maintaining systems

The risk of fluid system components being negatively affected by various forms of corrosion in offshore environments can be reduced substantially by selecting optimal materials of construction. Regular inspection of installed components is a highly recommended practice. In some cases, in which stainless steel components appear discoloured by rust, corrosion has not occurred, but the corrosion products from carbon steel structural elements of a platform have been deposited on stainless steel. In this case, the affected stainless steel components should be cleaned and protected from further contamination. In some cases, especially when stainless steel is exposed to many cycles of salt fog deposition and drying, pitting corrosion may

be detected. Tubing clamps should regularly be opened to inspect the tubing for signs of crevice corrosion. When pitting or crevice corrosion is detected, the use of an alternate material of construction should seriously be considered.

The use of optimal materials will lead to substantial long term payback for owner companies and operators

Conclusion

This article provides a range of candidate materials with high resistance to various forms of corrosion. The use of optimal materials will lead to substantial long term payback for owner companies and operators through assured system integrity, avoidance of lengthy shut-downs for maintenance and repair,

the overall longevity of assets, and improved operational safety.

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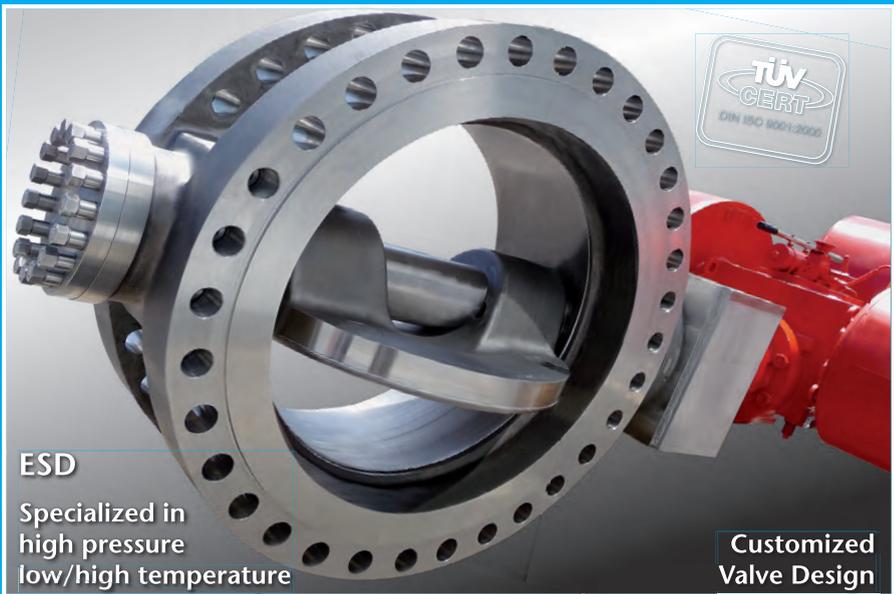
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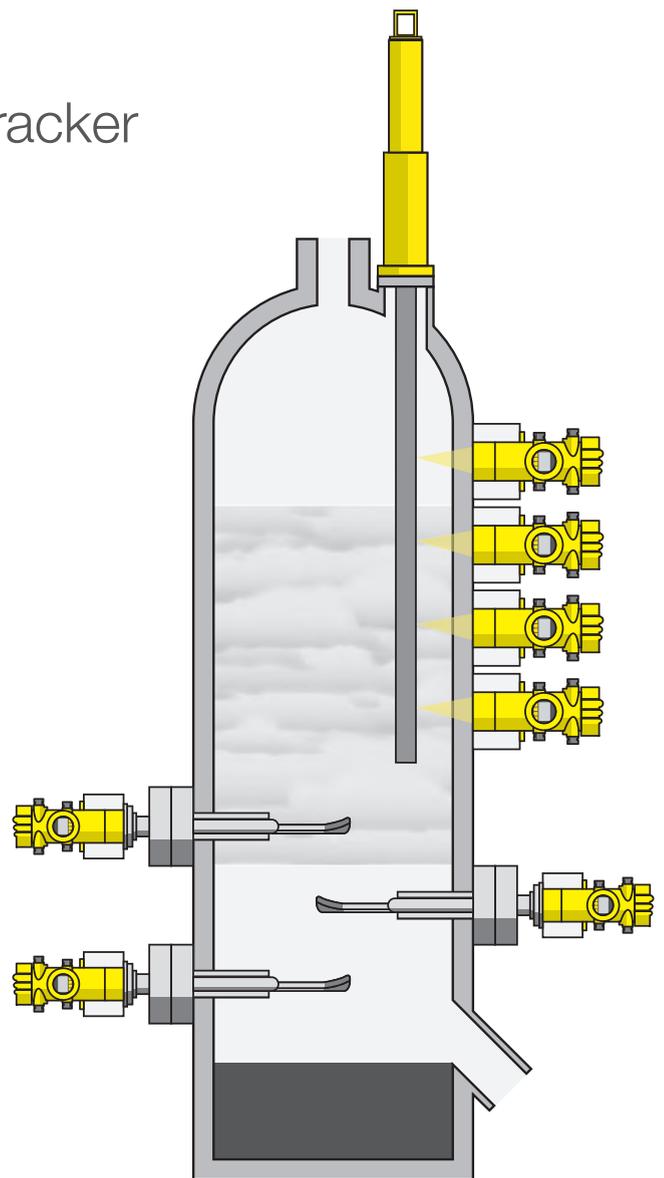
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Measurement in the Hydrocracker

Hydrocracking is a process used to process heavy feedstock residues, such as atmospheric and vacuum residue. Fresh catalyst is continuously added and used catalyst is withdrawn, improving product quality over time. To promote safe and efficient heavy oil processing, a reliable measurement and density profiling is needed for control of critical process stages.

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Boosting mild hydrocracking performance

Optimising its mild hydrocracking operations using new catalyst developments enabled a refinery to meet more complex targets for fuel quality

XAVIER ENRIQUE RUIZ MALDONADO *Haldor Topsoe A/S*

CARLOS MOSTAZA PRIETO, JOSE CARLOS ESPINAZO UTRERA and JAVIER PIERNA RODRIGUEZ *CEPSA*

Due to more complex refinery targets, increasing demand for high quality fuels, and reduced refinery operating margins worldwide, many refiners are looking for opportunities to expand (either with new units or via revamps of existing units), or are considering innovative, high efficiency catalyst solutions for their current processes.

Implementation of new International Maritime Organization regulations (IMO 2020) has also pushed refineries to operate under more stringent conditions in order to produce bunker fuels with less than 0.5 wt% sulphur, while balancing the refinery yields of middle distillate and the feed streams to fluid catalytic cracking (FCC) units.

For many years, the mild hydrocracking (MHC) process has been a key conversion technology used to increase yields of middle distillates and improve downstream conversion and product quality in FCC operations. However, the continued development of new, improved catalysts for hydrotreating and hydrocracking is crucial in making it possible to comply with sulphur specifications in gasoline and ultra low sulphur diesel (ULSD). Improved hydrocracking technology and catalyst solutions are emerging all the time to help refineries overcome these challenges.

Background

A conventional MHC unit operates at a design hydrogen partial pressure of 50-100 barg and a space velocity of 0.5-1.2 h⁻¹ normally provides a true conversion within the 5-30% range. However, high operating temperatures are required to achieve any specific conversion target, resulting in overtreatment of the heavy products

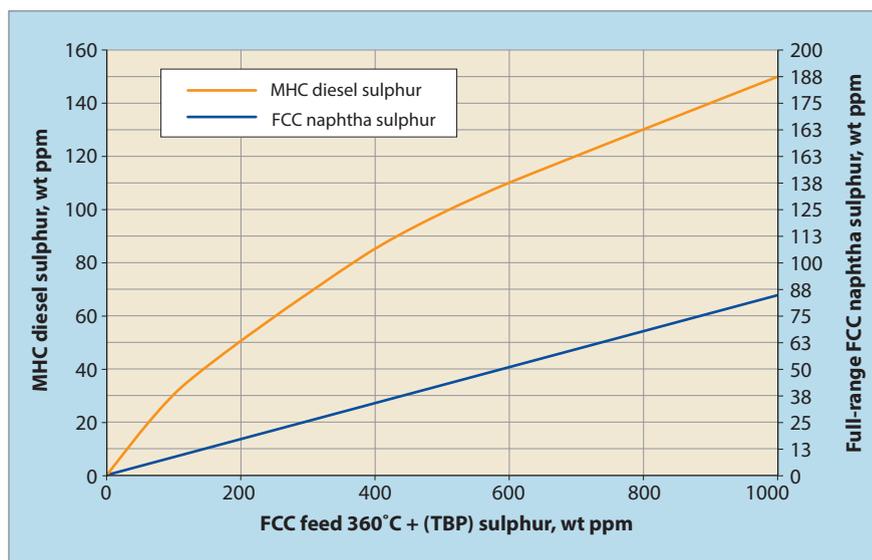


Figure 1 Relationship between MHC diesel, FCC naphtha and FCC feed sulphur content

and a less than ideal density for the middle distillate fractions.

Recently developed MHC technologies have become available to counterbalance this requirement as well as to minimise capital requirements and operating costs compared to a conventional MHC unit.

This article presents ways to optimise MHC operations as well as providing an overview of industrial and research experience within the field of MHC.

The article also examines the practical results obtained from an MHC revamp using Topsoe catalyst technology undertaken in 2019 by a European refinery company – Compañía Española de Petróleos S.A. (Cepsa) – and explains the significant new conversion capabilities that have been achieved with this set-up.

Process limitations in MHC

Partial conversion – also known as MHC – has been the main source of feed preparation for refinery FCC units for many years. Figure 1

illustrates the feed sulphur requirement to meet MHC diesel and FCC naphtha specifications. This also clearly shows the need for a deep hydrodesulphurisation (HDS) conversion (>99%) for a medium to high VGO sulphur feed (>2 wt%) in order to comply with the 10 wtppm ULSD specification.

Furthermore, when a refinery is targeting Euro V product specifications, the operating pressure has a huge impact on reaching the required maximum density of 845 kg/m³.

A minimum conversion of 40% and a hydrogen partial pressure above 110 barg are required to obtain a minimum specific gravity of 0.845 in a full-range diesel product (see Figure 2). If the refinery's diesel hydrotreating capacity makes it possible, blending the MHC diesel with a low density diesel is normally feasible. However, doing so would then be at the cost of reduced kerosene (Jet A-1) output and the ability to meet specifications for the smoke point.

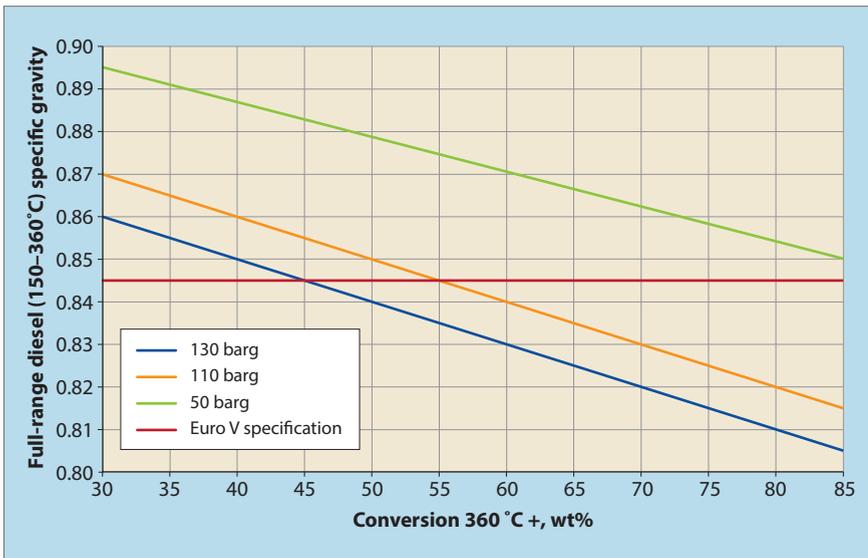


Figure 2 Full-range diesel specific gravity mapped against conversion

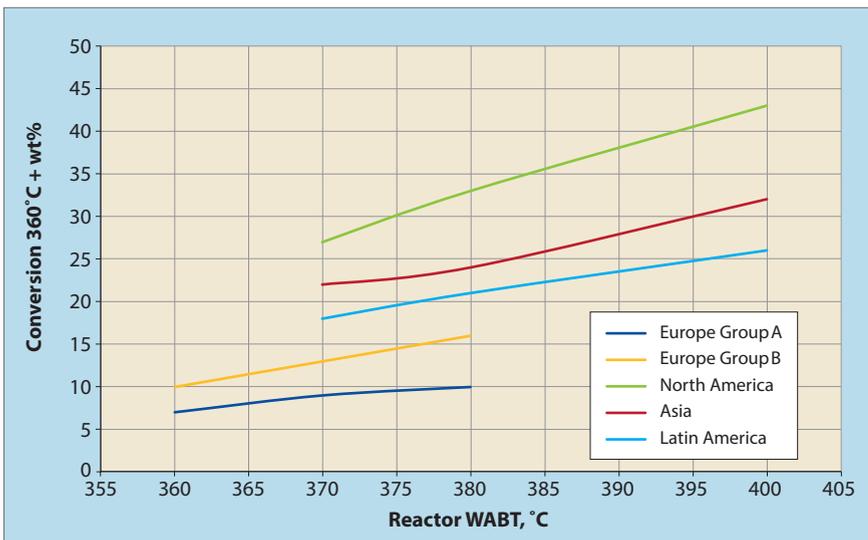


Figure 3 Conversion performance in commercial MHC units used in different parts of the world

Comparison between a conventional MHC and Topsoe technology

Feed composition	HVGO	
Specific gravity, sg	0.913	
Sulphur, wt%	1.33	
Nitrogen, wt ppm	1122	
Distillation D-1160°C		
IBP	315	
10%	378	
50%	434	
90%	505	
FBP	548	
Reactor conditions	Conventional MHC	Topsoe technology
Reactor hydrogen partial pressure, barg	100	100
Gross conversion, vol%	30	30
Overall LHSV, h ⁻¹	0.63	0.7
PT/HC catalyst, vol%	75/25	65/35
Kerosene, 150-250°C, vol% FF	8	10
Diesel, 250-360°C, vol% FF	23	18
UCO, 360°C, vol% FF	8	10
Kerosene smoke point, mm	15	20
Kerosene specific gravity, sg	0.84	0.825
Diesel specific gravity, sg	0.874	0.845
Diesel cetane index, adim	46	48

Table 1

Technical and geographical differences abound

MHC units are all designed differently, especially in terms of space velocity and hydrogen partial pressure. The crude slate and feed quality also vary considerably. Any refinery's ability to reach desired product specifications depends heavily on factors that include crude availability and refinery location.

The differences in operating parameters for MHC units frequently encountered on different continents are shown in Figure 3. European Refineries Group A is normally characterised by low feed sulphur and high space velocity, which makes it difficult to achieve MHC mode, while European Refineries Group B has good potential for increased conversion due to the designed-in low space velocity. North American refineries are usually configured for a low space velocity and high pressure, while aiming for low sulphur (<300 wtppm) FCC production. This enables these refineries to achieve high conversion. Refineries in Asia and Latin America usually process mid-to high sulphur vacuum gasoil (VGO >1.8 wt%), paving the way to increases in conversion despite the low space velocity design.

Topsoe catalyst and technology solutions

Conventional MHC technology targets a higher cetane index and better kerosene properties, which can only be achieved in a MHC conversion if the hydrogen partial pressure increases by 60%.

Topsoe, on the other hand, has invested significantly in developing innovative catalyst technology solutions for MHC processes. Topsoe configurations are able to maximise the diesel uplift, while still maintaining the HDS requirement at lower conversion levels and with lower hydrogen consumption than any conventional high pressure MHC technology. A typical comparison is shown in Table 1.

Topsoe provides selective, top tier catalysts that enhance catalyst stability in a wide range of operating conditions. The ratio between hydro-treating catalyst and hydrocracking

catalyst is also a factor to take into consideration when selecting the most effective catalyst loading for a particular unit, because an optimised loading will determine levels of profitability in the refinery complex as a whole – and specifically the operating synergy between the MHC and FCC units.

The HDS and hydrogenation capacities of the catalyst are crucial to keep product sulphur levels low for as long as possible. When a hydrocracking catalyst is required in this process, nitrogen slippage and ammonia partial pressure are the deciding factors. High nitrogen slip hinders aromatic saturation capability, which considerably suppresses the capabilities of the cracking catalyst. An illustrative example of optimal hydrotreating vs hydrocracking utilisation in a low to medium range hydrogen partial pressure is shown in **Figure 4**.

This is why Topsoe has launched new catalyst formulations based on the HyBRIM and HySwell technologies, including individual products such as TK-564 HyBRIM and TK-6001 HySwell to enhance catalyst activity and stability along the targeted cycle.

Case study

The following case study is based on the MHC unit at the Cepsa-owned Gibraltar San Roque refinery. This particular MHC unit was originally designed with a single reactor for an

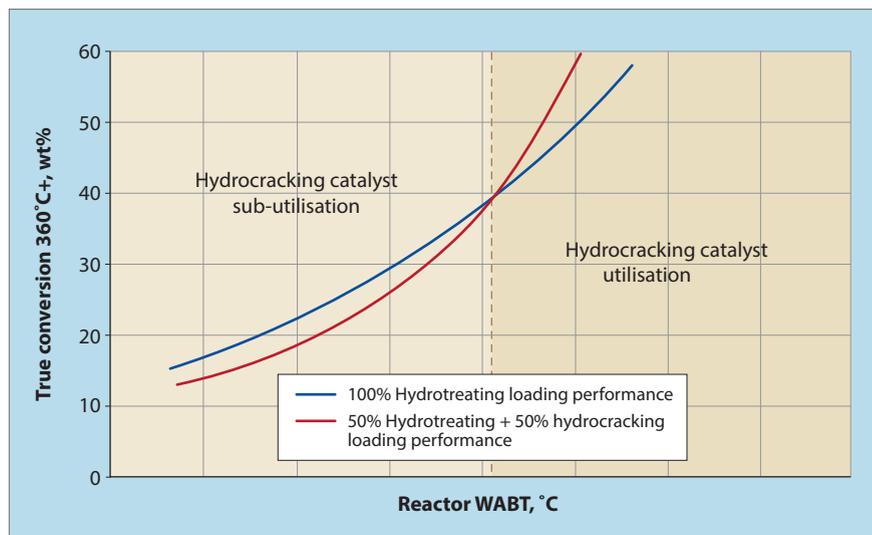


Figure 4 100% Hydrotreating vs 50% hydrotreating – 50% hydrocracking loading performance in a low to medium pressure MHC unit

hourly liquid space velocity of 1.3 h⁻¹ and hydrogen partial pressure of 50 barg, aiming at a maximum true conversion of 12 wt%. The unit has operated using Topsoe catalysts for more than 10 years.

Due to an increase in market demand for middle distillates, Cepsa launched a project to investigate how to maximise conversion. This resulted in a revamp, consisting of installing a new reactor in series with the existing reactor, along with other modifications in order to adapt the unit to the new middle distillate yield. The installation of a second reactor also made it possible to reduce the space velocity from 1.3 to 0.65 h⁻¹, paving the way to an increase of true conversion at 383°C+

from 12 wt% to 27 wt% with 1.8 wt% sulphur in the feed.

The unit installed at Gibraltar San Roque is designed to process 4900 t/d of a blend of 20 vol% heavy gasoil (HGO) from an atmospheric distillation unit (ADU), 15 vol% light VGO (LVGO), and 65 vol% heavy VGO (HVGO) from a vacuum distillation unit (VDU). The layout of the new MHC unit at the Gibraltar San Roque refinery is shown in **Figure 5**.

The main heater only heats the treat gas phase, so the unit is configured with a stripper downstream from which naphtha and kerosene cuts are drawn, while the diesel and sweet VGO fractions are drawn from the vacuum tower. The naphtha cut produced from the MHC is sent to

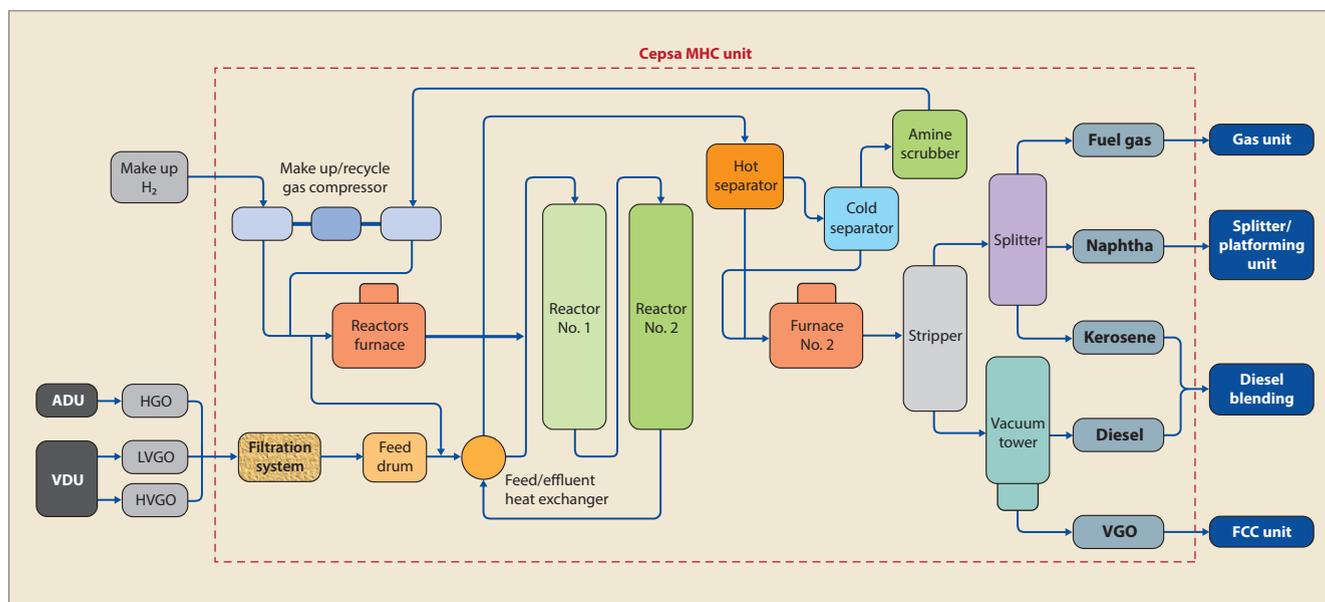


Figure 5 Layout of new MHC unit at Cepsa Gibraltar San Roque refinery

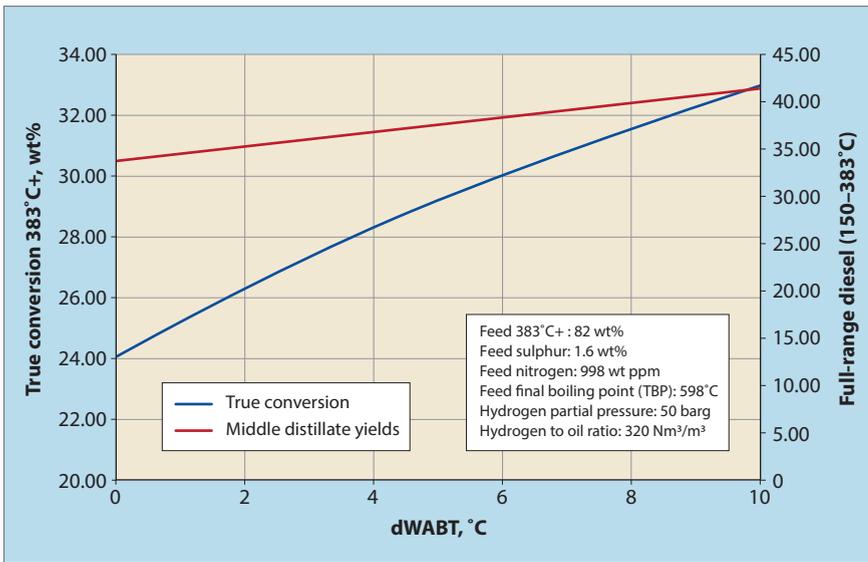


Figure 6 Revamped MHC unit with fully hydrotreating Topsoe catalyst

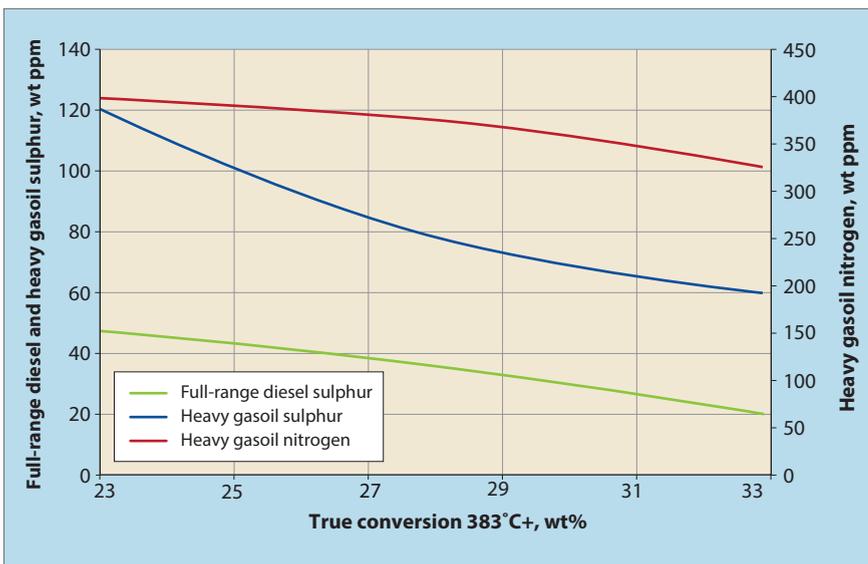


Figure 7 Product sulphur from the different fractions

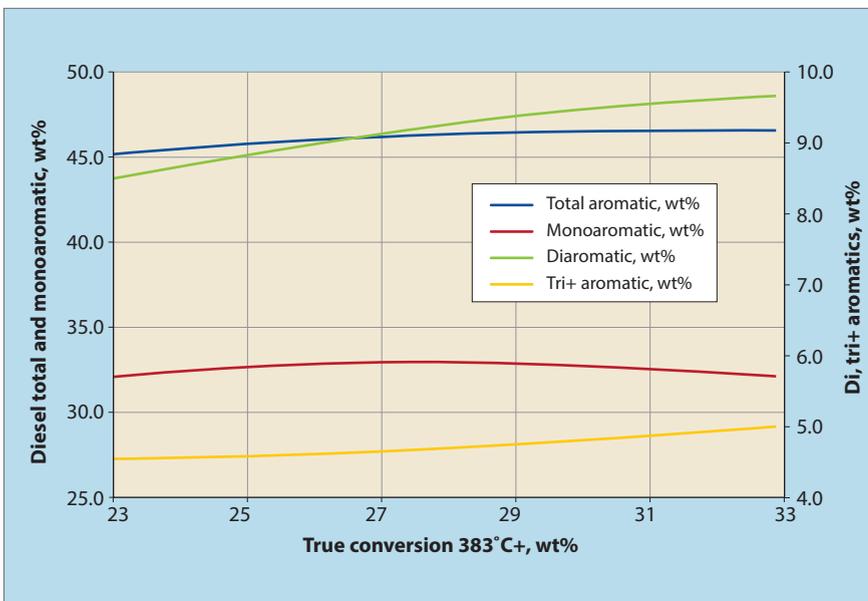


Figure 8 Diesel aromatic distribution mapped against true conversion

the platforming unit after the lighter part is drawn, while the diesel and kerosene cuts are sent to the blending pool. Pretreated VGO from the unit is combined with straight-run VGO from the storage tank and processed in the FCC.

After the revamp, Cepsa had two catalyst loading options to choose between: a 100% hydrotreating loading or a loading split between hydrotreating and hydrocracking catalysts. Cepsa evaluated the Topsoe catalyst proposal against those from several competitors, resulting in Topsoe being awarded the contract for the full hydrotreating solution for two consecutive cycles.

This technical decision was based on pilot plant tests conducted at the Cepsa Research Center in Madrid, where the full hydrotreating configuration proposed by Topsoe was found to provide the required true conversion at 383°C+, which was comparable to the combined hydrotreating and hydrocracking option from other catalyst suppliers. The full hydrotreating loading provided lower naphtha yields, while the sulphur and density in the diesel and HGO fractions were slightly better.

The overall findings are that in units that operate with a hydrogen partial pressure below roughly 80 barg, the zeolite and amorphous silica-alumina catalyst are largely affected due to organic nitrogen slip and generated ammonia partial pressure, which together lead to a high deactivation and loss of conversion.

Once the new unit had been commissioned and operating steadily for several weeks, Cepsa and Topsoe conducted a performance test run guarantee (PTRG) in order to secure a detailed evaluation of the catalyst performance in terms of conversion and selectivity at the closest design condition.

The true conversion and total middle distillates (full-range diesel) results are shown in Figure 6. The catalyst performance was as expected from the pilot plant test and technical recommendations from Topsoe. Significantly, the unit was able to exceed the predicted true conversion targeted by Cepsa (27 wt%) and to achieve much higher true conversion (33 wt%). This result

provides an indication that Cepsa is now able to produce approximately 4 wt% higher middle distillate with a small reduction in cycle length, amounting to a couple of months.

Furthermore, the unit was able to achieve total product sulphur below 100 wppm in the heavy fraction and less than 40 wppm in the full-range diesel at the targeted conversion (see **Figure 7**). The lower diesel sulphur content increased flexibility in the refinery's diesel pool because it is now possible to blend MHC diesel with low density diesel in order to optimise the refinery's diesel hydro-treating capacity in accordance with current operating requirements.

A huge improvement was also observed in HGO nitrogen, which was less than 400 wppm, resulting in a notably positive impact on FCC conversion results.

Aromatic distribution as a function of applied true conversion in the various fractions was also carefully monitored during the test run. Details of the results are shown in **Figures 8-10**.

A slight increase in the total aromatics wt% was observed in the diesel fraction (see **Figure 8**). This increase is mainly the result of an accumulation of polyaromatics caused by the thermodynamic equilibrium between paraffins/naphthenes at a given unit operating pressure and temperature. However, the mono-aromatic content remains similar – as expected – due to equilibrium limitation.

The density penalty due to the increase in aromatics was found to be approximately 1.5 kg/m³ per 1% conversion. However, the diesel density was lower than before the revamp.

The kerosene fraction shows a more significant increase in the total aromatics wt% (see **Figure 9**). The accumulation of diaromatic is the result of the polyaromatic content being higher than 10 vol%, which creates a challenge to produce A-1 quality jet fuel. The density penalty was observed to be approximately 1 kg/m³ per 1% conversion.

In the VGO fraction, low product nitrogen promotes monoaromatic saturation, which in turn reduces the density of the fraction by a factor

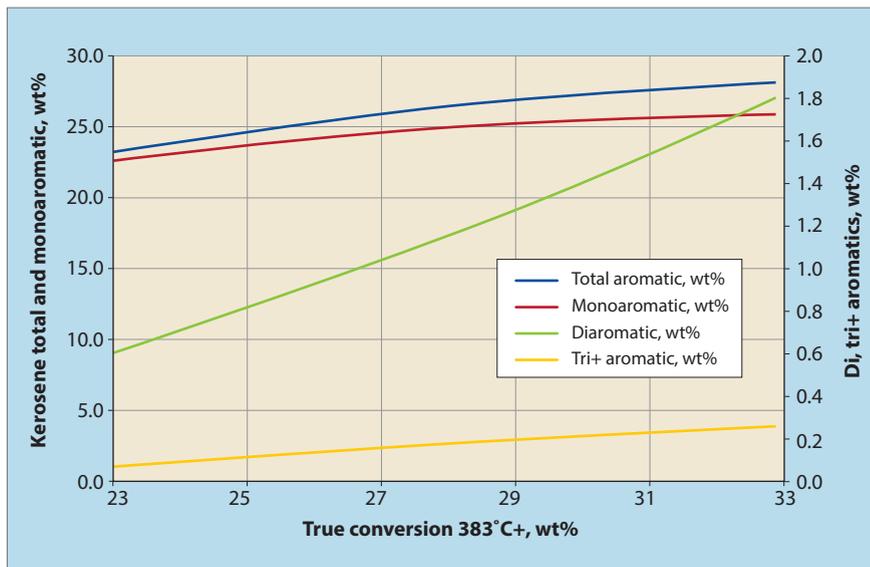


Figure 9 Kerosene aromatic distribution mapped against true conversion

of 0.6 kg/m³ per 1% conversion (see **Figure 10**).

The observed reduction in monoaromatic is crucial in the development of new catalysts to boost hydrodenitrogenation (HDN)/HDS activity in order to remove the most refractive compounds and maximise aromatic saturation.

Cepsa MHC operation and its impact on FCC conversion

After the PTRG had been carried out, operation of the MHC unit was alternated between three different modes, in accordance with the refiner's day-to-day planning optimisation:

- **Primary mode** – maximum conversion mode, aiming to maximise middle distillate production. In this

mode, the unit achieves the best delta product value per barrel per stream day (b/d) in comparison to before the revamp. This amounts to approximately \$0.75/b/d, based on average 2019 prices, due to the higher middle distillate added value versus HVGO products.

- **Secondary mode** – HDS mode, aiming at middle distillate sulphur specification and maximising pretreated FCC feed flow rate. In HDS mode, a slightly lower basic nitrogen compared to before the revamp was observed. This also provides benefits for FCC operations.

- **Alternative mode** – maximum hydrodearomatisation/hydrodenitrogenation mode (HDA)/HDN, aiming at the optimal MHC conversion range to maximise FCC total

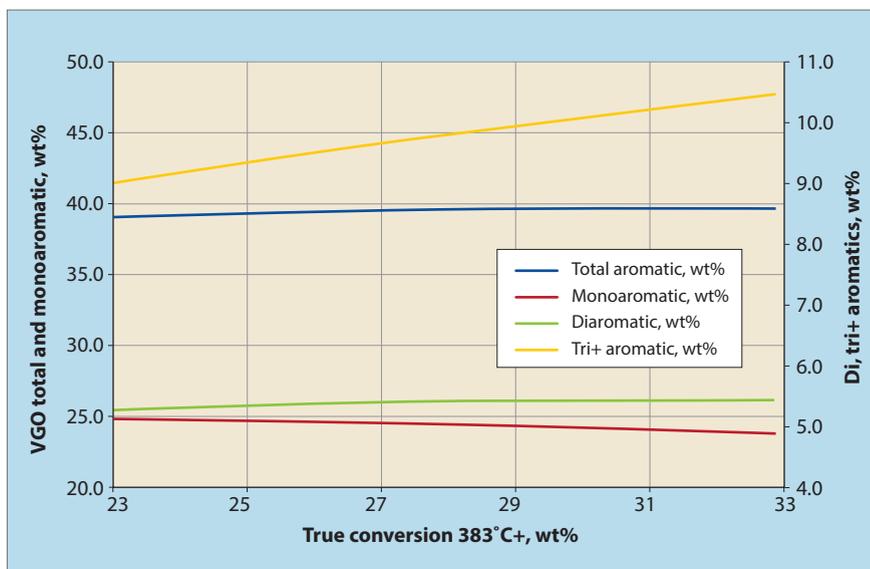


Figure 10 HGO aromatic distribution mapped against true conversion

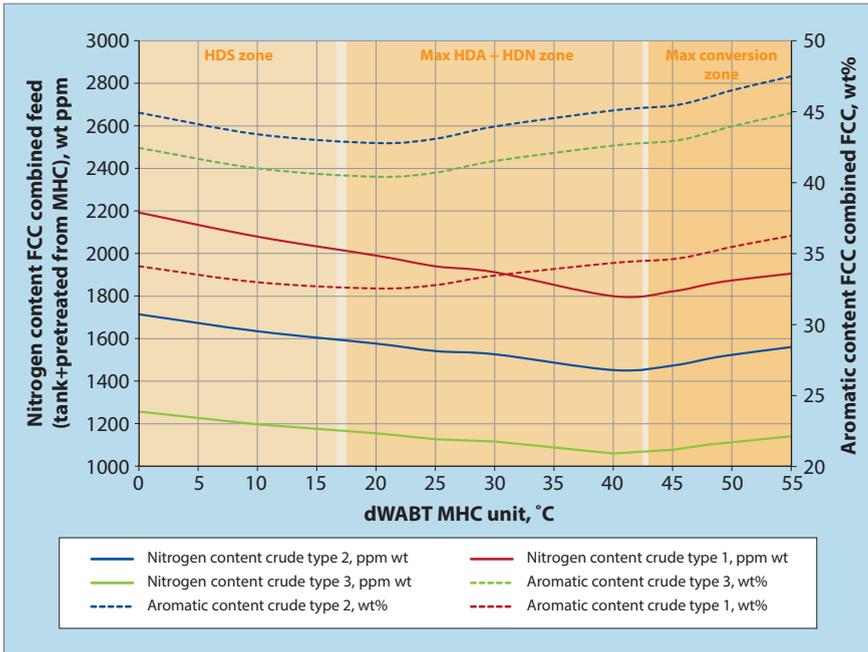


Figure 11 Correlation between feed nitrogen and aromatic content to the FCC with respect to different MHC operating mode zones

conversion. In light of the implementation of IMO 2020 requirements featuring low sulphur and high nitrogen crudes, a third operating mode was considered by taking into account FCC total yields versus MHC performance.

The compromise between FCC feed nitrogen and aromatic content (combined straight-run VGO from the tank and pretreated VGO from the MHC) and the required reactor

delta WABT (dWABT) are shown in Figure 11. Three different typical crudes (types 1, 2 and 3) that were processed in the unit had different levels of nitrogen and aromatics. The lowest combined feed nitrogen and aromatic content are directly dependent on the feed content from the tank and the applied MHC gross conversion. MHC product nitrogen removal is driven by kinetics, while aromatic saturation at unit hydrogen

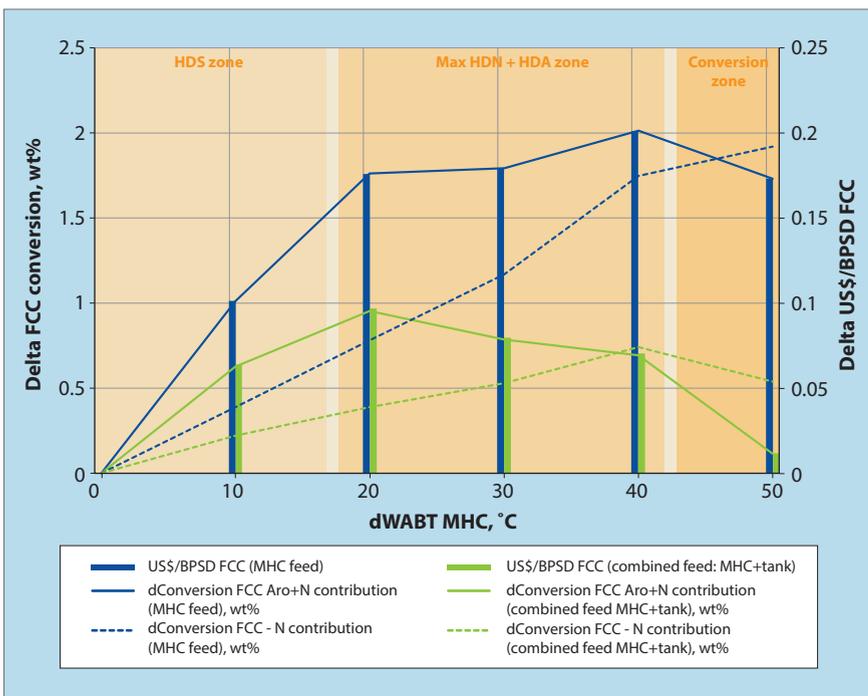


Figure 12 Correlation between FCC conversion and FCC delta profit with respect to different MHC operating mode zones

partial pressure is clearly affected by equilibrium constraints at different temperatures.

As Figure 11 shows, the reactor dWABT has to be increased by approximately 55°C in order to switch from HDS to MHC mode – which substantially affects removal of both nitrogen and aromatics.

Optimised MHC and FCC operations therefore depend strongly on the combination of nitrogen and aromatic content. To deal with this, Cepsa has developed three specific customised FCC correlations, as a function of the following parameters:

- Feed total aromatic content, hydrogen content, UOP K factor
- Feed total nitrogen, FCC conversion
- Feed UOP K factor, FCC conversion

An example is shown in Figure 12 for crude type 3, showing the correlation of FCC conversion and delta FCC profit (b/d) against different operating modes and two different FCC feed quality cases. The blue lines consider a pure feed from MHC, while the green lines correspond to the combined straight-run VGO from tank and feed MHC.

The dotted lines show the isolated nitrogen impact on FCC yields. On the one hand, the green case presents maximum FCC conversion at the highest HDN range, where the combined feed nitrogen balance to FCC is the lowest. On the other hand, when only MHC feed is processed, the data shows maximum FCC conversion at the highest MHC WABT, corresponding to maximum nitrogen removal.

The straight lines show the combined nitrogen and aromatic impact on total FCC yields for the two cases explained here. Maximum FCC conversion is seen at the higher MHC WABT over the HDA/HDN zone. By contrast, the combined feed case gives a best result at the lowest WABT range within the HDA/HDN zone, as the result of the impact of lower aromatic balance content on FCC yields.

The best delta FCC profit (b/d) for each mode corresponds to the same observed peaks, showing an optimum operational MHC WABT window for the following scenarios

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Logam lumayan
Vyuma vya Thamani
Ädelmetaller
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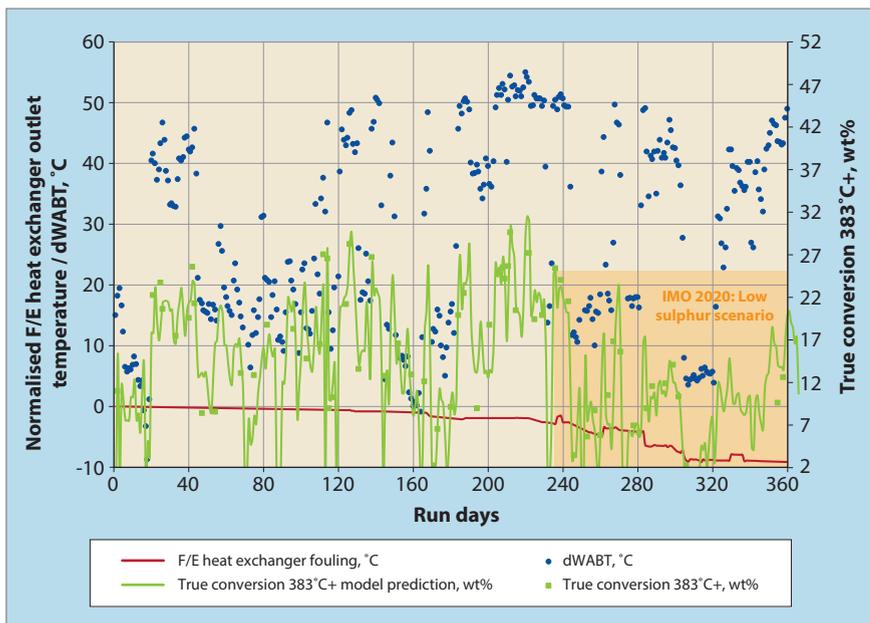


Figure 13 Delta WABT change and true conversion at 383°C + cut point

at the Cepsa Gibraltar San Roque refinery:

- Maximise FCC conversion depending on FCC/MHC margins and VGO prices/availability
- Maximise nitrogen removal when processing high nitrogen content crudes, avoiding basic nitrogen in FCC products with minimum FCC yields impact.

Under the current scenario and with installation of Topsoe catalysts after the revamp, a huge benefit is seen when MHC and FCC units are operated integrally. Cepsa has registered a benefit from lowering the basic nitrogen by 150 wt ppm and the aromatic content by 1.6% wt on average over 2019. The FCC unit performance shows 1.5–2 wt% higher conversion compared to before the revamp, equivalent to approximately \$0.15–0.2/b/d in refinery delta profit.

In addition, the lower sulphur content observed in gasoline from FCC has relaxed the hydrotreating requirements to meet the sulphur specification gasoline pool. Lower NO_x and SO_x were also observed.

IMO regulations and their impact on MHC unit operation

Since the new IMO regulations came into force in 2020, crude baskets at Cepsa refineries have shifted significantly, from medium sulphur to very low sulphur feeds. As a result, the average sulphur content of the

MHC feed blend has fallen from 1.8 wt% to 0.8 wt%. This feed change has been a challenge in maximising the unit's profit margin because of its impact on general unit performance, product yields, and product quality. The lower sulphur content has also reduced the conversion to middle distillate as a result of less HDS contribution. Moreover, lower mean average boiling range shift in the feed had forced the refinery to operate the unit at a higher severity in order to compensate for conversion losses.

The temperatures involved in operating the unit at a higher severity had a negative effect on the cycle length, especially when processing heavy feed blends due to the higher risk of coking, and has forced the reactor furnace to operate near its design limits. As Figure 13 shows, increased fouling of the feed/effluent heat exchanger (resulting in lower normalised heat exchanger outlet temperature) was observed with the low sulphur scenario in compliance with IMO 2020. This imposes a new operational limit that prevents the unit from reaching the required end-of-run temperatures.

This new scenario – along with more complex refinery targets due to the demand for higher fuel quality, volatile oil prices, and reduced refinery margins worldwide – represents a key challenge with regard to meeting refinery targets. This in turn

compels refineries to look for new solutions.

In this respect, Cepsa is working on the following alternatives:

- Co-processing of high sulphur and cracked feed to compensate for the low sulphur scenario, which will lead to a higher deactivation rate.
- Collaboration between Topsoe, Cepsa Refinery, and the Cepsa Research Center to consider loading new catalyst formulations based on Topsoe HyBRIM technologies in order to boost HDN/HDS activity and to be able to remove the most refractive compounds, while maximising aromatic saturation at the same time.
- Evaluating new, sweeter crude blends – such as CPC, Azeri light, Bonny light, Saharan, and Eagle Ford – in order to identify those that cause severe fouling problems in feed/effluent heat exchanger networks.
- Developing different customised correlations in the fluid catalytic cracker in order to identify the MHC operations that are most effective for maximising FCC conversion under different feed scenarios.

Future considerations

In order to overcome potential refinery limitations resulting from implementation of the new IMO regulations, refiners need to optimise MHC units to maintain or maximise refinery operating margins.

Simply switching to sweeter crude slates to meet the new bunker fuel limitation within the new sulphur specification (0.5 wt%) represents a high cost in refinery opex, because the lower middle distillates yields thus obtained are heavily affected by:

- More frequent heat exchanger fouling
- Heater and heat exchanger limitations in units that depend on heat integration
- Higher deactivation rates when processing high density crudes

This makes it important to implement innovative catalyst and technology strategies to buffer the impact of the IMO 2020 regulations and ensure long, uninterrupted operation in order to remain profitable in the volatile oil market, while

complying with all appropriate environmental and safety regulations.

Decision-makers want clear answers to questions such as:

- What is the most difficult feed I can process in my existing unit, without needing to revamp it?
- Do I need to incorporate a hydrocracking catalyst if my unit operates at 60–70 barg?
- What is the minimum capex if I wish to maximise our conversion rates?
- What is the maximum conversion I can obtain with low sulphur by only using hydrotreating catalysts?

For instance, careful consideration of the following aspects is highly recommended:

- **New catalyst and technology solutions:** new catalysts, in optimal combinations, are available for a broad range of operating conditions and specific feed compositions. In the MHC field, Topsoe provides technologies and catalyst solutions to meet refineries' targets with the ideal capex/opex balance in a challenging era where new investments in either expansions (greenfield installations) or unit revamps are required in order to overcome increasing operating limitations.

- **Challenges from processing new feed blends within design boundaries:** processing a new feed can be highly beneficial and yield a higher internal rate of return (IRR). However, there are also lots of benefits to be gained from factoring in consequences in terms of fouling, higher deactivation, and catalyst volume requirements, in addition to process impacts at the back end. To deal with these concerns, it is important to collaborate with suppliers of the most effective technologies and catalysts in order to achieve the best results.

- **In-depth experience with the practical details of refinery operations:** every refinery works differently due to the specifics of unit integrations. This almost always means that there is a strong need for customised solutions in order to maximise refinery operating margins.

Despite refineries currently navigating unprecedented market uncertainties and with unknown future operating scenarios throughout all forms of business derived from fossil fuels, an optimised refinery integration, stream management, and working side by side with an experienced, expert catalyst supplier should all be taken into consideration in order to stay ahead in a fiercely competitive market.

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Troubleshooting premature tower flooding

Thorough analysis of field data and tray hydraulics together with gamma scanning were key factors in the successful troubleshooting of premature flooding in a debutaniser

LOWELL PLESS *Tracerco*

ANDRÉ PERSCHMANN, DAVID BRUDER and THOMAS WALTER *Linde AG*

Flooding is defined as an operating condition where liquid accumulates in a column. It is the most common cause of capacity limitation of a separation column.¹ The build-up of liquid in a column can initiate from a variety of mechanisms, for instance jet flooding, downcomer choking, and backup flooding. Flooding is usually revealed by a sudden increase in the column differential pressure. Several reasons for column malfunctions have been reported in the literature. Many column malfunctions related to flooding are caused by fouling.²

This is a case study of successful troubleshooting of the premature flooding of a debutaniser in a steam cracker unit. The column has been operating well for decades and usually did not have serious problems during the typical five-year turnaround cycle. However, during a recent cycle the column had been in operation for only two and a half years since its last shutdown when flooding was detected.

A rapid rise in pressure drop was measured by the plant owner in October 2017. Shortly after that, the bottom product purity deteriorated, followed by the overhead product purity deteriorating and the column operation became unstable. The feed rate to the debutaniser had to be reduced to achieve steady-state operation again. Due to this, the column ultimately became a bottleneck, limiting ethylene production to approximately 80% of plant capacity. Thus, it was necessary to urgently identify the root cause of premature flooding and to develop a solution to overcome the capacity bottleneck.

As **Figure 1** shows, the debutaniser is equipped with 20 two-pass

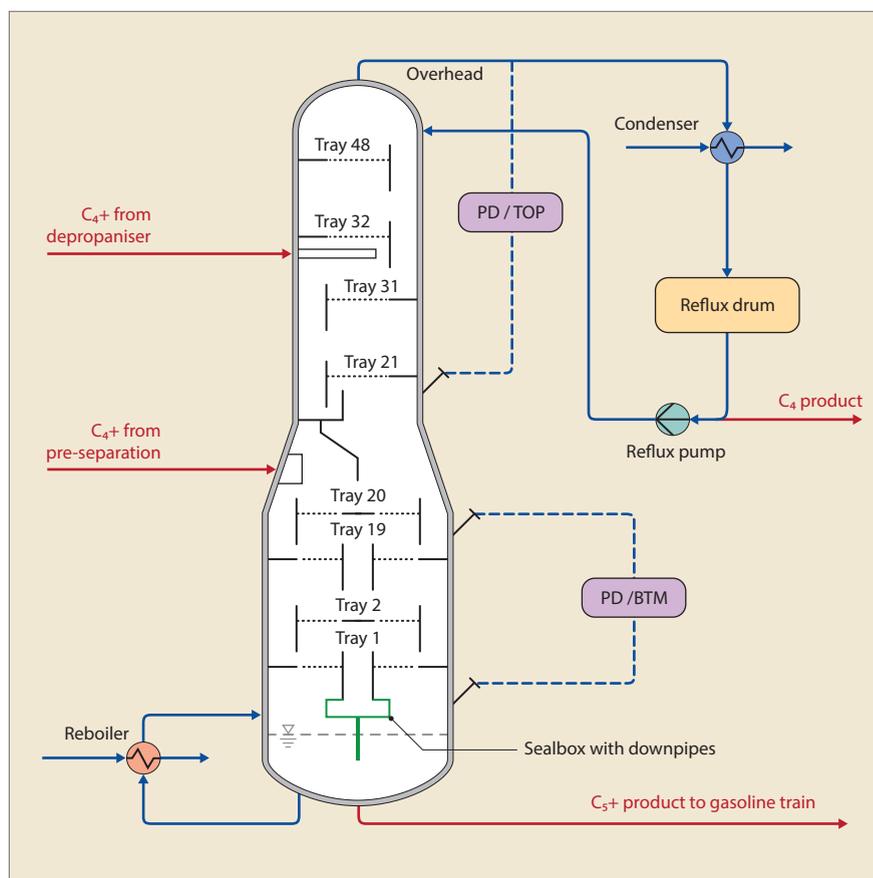


Figure 1 Simplified process scheme of the debutaniser (courtesy of Linde AG)

standard valve trays in the bottom section below the lower feed inlet, 11 one-pass standard valve trays in the middle section below the upper feed inlet and 17 one-pass standard valve trays in the top section. Each section has straight downcomers on a tray spacing of 600 mm (~24 in).

A C_4+ fraction from an upstream pre-separation column is fed to the debutaniser's lower feed inlet and a C_4+ fraction from an upstream depropaniser is introduced to the debutaniser's upper feed inlet. The feeds are separated into a C_4 overhead product and a C_5+ bottom product. The column is normally operated at an overhead pressure

of 4.75 bara (68.9 psia) and a bottom temperature of 105°C (221°F). The debutaniser is instrumented with two differential pressure (ΔP) measurements: one ΔP measurement covering the top trays, Trays 21-48, and the other covering the bottom trays, Trays 1-19. Polymerisation inhibitor is fed to the upstream fractionators to avoid polymer fouling in the debutaniser.

Root cause analysis

First, the plant owner analysed the operational data to better understand the flooding phenomena. A sudden increase of the differential pressure across Trays 1-19 in

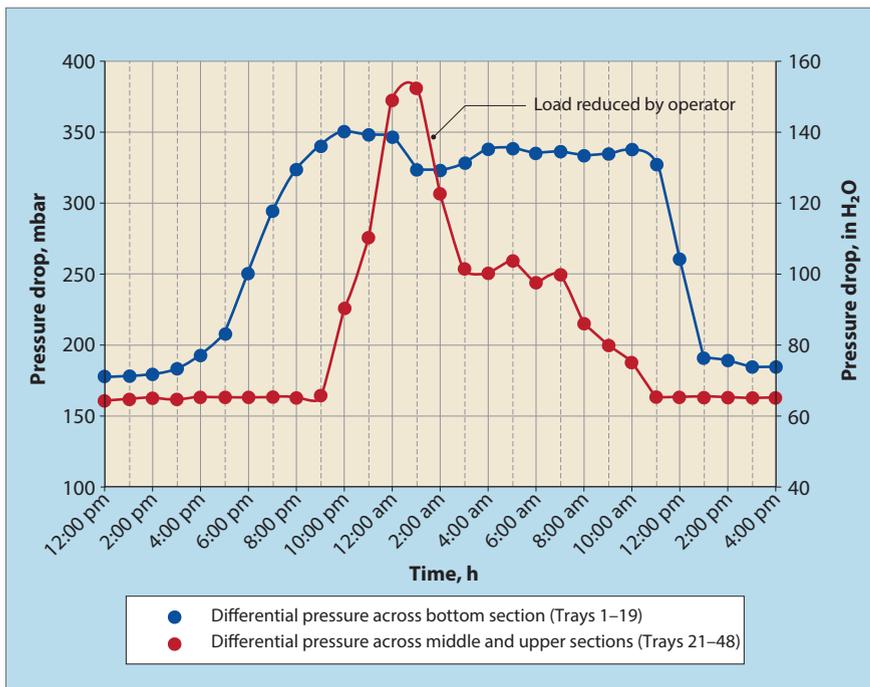


Figure 2 Differential pressure measured 4-6 October 2017 (courtesy of Linde AG)

the bottom section was noticed in October 2017 (see Figure 2). Shortly after the bottom pressure drop had established a plateau, the pressure drop across the middle and upper sections, Trays 21-48, started to increase significantly. As Figure 2 shows, the pressure drop in the bottom section went from 180 mbar to 350 mbar (72 in H₂O to 141 in H₂O), followed by the pressure drop in the middle and upper sections which rose from 160 mbar to 370 mbar (64 in H₂O to 149 in H₂O). After the feed rate to the column was reduced, liquid build-up on the trays appeared to have immediately stopped and then receded. The pressure drop in the middle and upper sections decreased until the initial value was reached again. Shortly afterwards, a reduction in the pressure drop in the bottom section was seen. Steady-state operation and a normal pressure drop were achieved after all the accumulated liquid receded from the trays.

Investigation of the pressure drop data was the first indication that the root cause of the premature flooding was in the bottom section of the column, the reason being that liquid accumulation and hence an increased pressure drop always take place above the liquid flow restriction. The debutaniser is well known for butadiene polymerisa-

tion fouling. Hence, this observation was a strong indication that polymer fouling in the bottom section

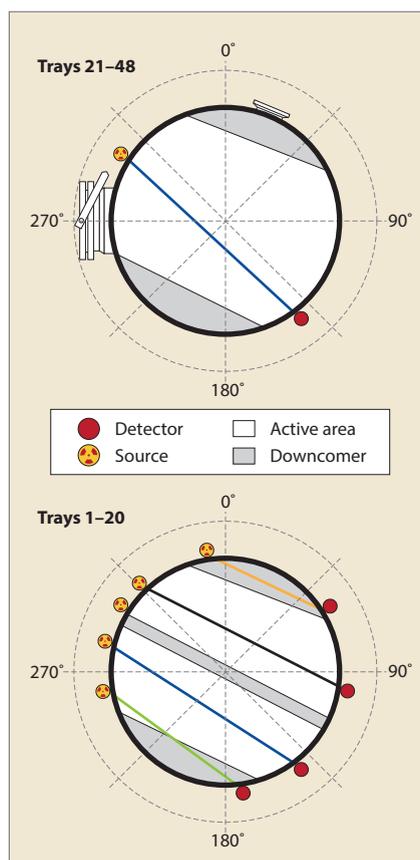


Figure 3 Scanline orientations: August 2017 baseline and December 2017 flooding scan – blue scanline; December 2017 east active area and downcomer scans at normal conditions – black, orange and green scanlines

could have caused blockage of the tray active area and/or plugging in the downcomers. Nevertheless, several aspects of the tray design were studied before the entire investigation was focused on flooding caused by fouling.

Second, a hydraulic rating of the trays was performed using plant data from a past high load operation of the column. The results proved that the valve trays have sufficient capacity to accommodate the normal flow rates when no plugging occurs. The calculated overall pressure drop, including the static head and the pressure drop of the overhead nozzle, matched the measured pressure drop of 290 mbar (116 in H₂O) for the high load operation and hence proved the validity of the simulation. It could be concluded that the valve tray design was not limiting the capacity of the column. However, there was still the possibility that the trays were collapsed, which could only be verified by gamma scanning.

Gamma scanning is a non-intrusive investigative technique to diagnose malfunctions of process equipment while it is in operation. During the measurement, a gamma ray emitting radioactive source, along with a radiation detector, are synchronously lowered down opposite sides of the column. The radiation beam passes through the process equipment and its intensity is measured by the radiation detector in terms of a count rate. Interaction of the gamma ray beam with the column shell, internals, and the process fluid cause attenuation of the gamma ray, correlating to the average material density.³

A baseline scan had already been conducted by Tracerco on behalf of the plant owner under normal operating conditions in August 2017, three months before premature flooding occurred for the first time. All trays were scanned, but only the western active areas of the two-pass trays in the bottom section were scanned. The orientation of the scanline is shown in Figure 3.

The results of the baseline scan are shown in Figure 4. All 48 trays were holding adequate levels of aerated liquid, hence the good

mechanical condition of the trays was confirmed. The one-pass trays in the top section were uniformly loaded, with tray froth levels ranging from 31-48% of the tray spacing. In the lower section, Trays 3 to 20 and Tray 1 were holding uniform froth levels ranging from 33-41% of the tray spacing. But another observation was noticed by Linde AG – a higher froth height was detected on Tray 2 compared to the other surrounding trays, particularly Tray 1. Tray 2 appeared to hold a froth level approximately 66% of the tray spacing. An isolated high or low froth height detected on a single tray is very frequently a result of a measurement anomaly caused by obstructions in the scanline, most typically an external interference such as a support ring, pipe support, weld pad for a manway, or nozzle. However, no notation of potential external interference was made by the scanners in the vicinity of Tray 2. In fact, the same higher froth height on Tray 2 was observed by Linde AG in a previous troubleshooting scan. In this earlier investigation, the cause was physical blockage of Tray 2's downcomer clearance due to fouling causing liquid to stack on the tray active area.

A normal froth height was detected on Tray 1 due to specific sealing of the centre downcomer. A seal box was attached to the centre downcomer of Tray 1 instead of a commonly used seal pan (see **Figure 1**). Downpipes bolted to the seal pan and submerged below the liquid level routed the process fluid into the column sump. Unlike a seal pan, a seal box does not have a clearance under the downcomer. Accumulation of fouling material in the downcomer exits of Tray 1 was not possible since all the solid material was washed away via the downpipes. Therefore downcomer backup flooding would start from Tray 2 or the above trays only. Further gamma scans were performed in December 2017 at flooding conditions to prove the proposed hypothesis. The scan results for this operation are shown in **Figure 5**.

For the December 2017 scan, the scanline orientation used for

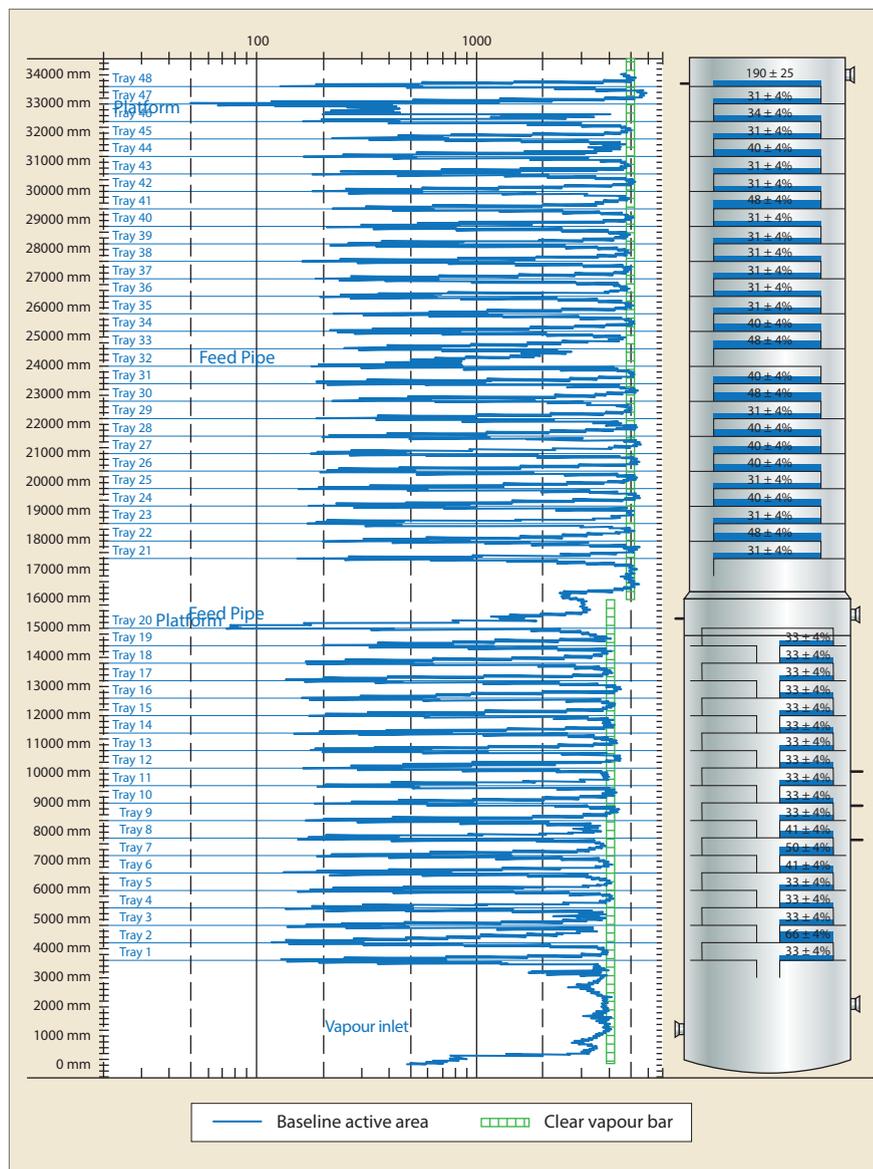


Figure 4 August 2017 baseline scan of tray active areas at normal operating conditions

the baseline scan of the entire column was repeated (blue scanline in **Figure 3**) under flooding conditions. The scan results are shown in **Figure 5**. The blue scan data curve represents the baseline scan results while the red scan data curve represents the flooding scan results. The red scanline revealed that the column was flooding, starting from Tray 2. Tray 1 still showed a normal froth height. This conclusively proved that the flooding originated at Tray 2.

Feed rates were reduced to alleviate the flooding. Another gamma scan, but of the eastern active area of the two-pass trays, was performed at normal operating conditions to finally confirm the mechanical integrity of all trays. These scan results are shown with

the black data curve in **Figure 6**. The east side active area of Trays 1-20 showed the trays holding adequate froth levels, thus tray damage was not causing the column to flood. As observed in the baseline scan from August 2017 on Tray 2's western active area, an increased froth height was also detected on the eastern active area of Tray 2, approximately 80% of tray spacing.

Additionally, scans were done at normal operating conditions through the outside downcomers in the bottom section. These scanlines are shown in **Figure 3** as the green and orange scanlines. Depicted in **Figure 6** by the green and orange data curves, the downcomer scans showed that the side downcomers of Tray 2 were liquid full, further proof that the flooding was originating at

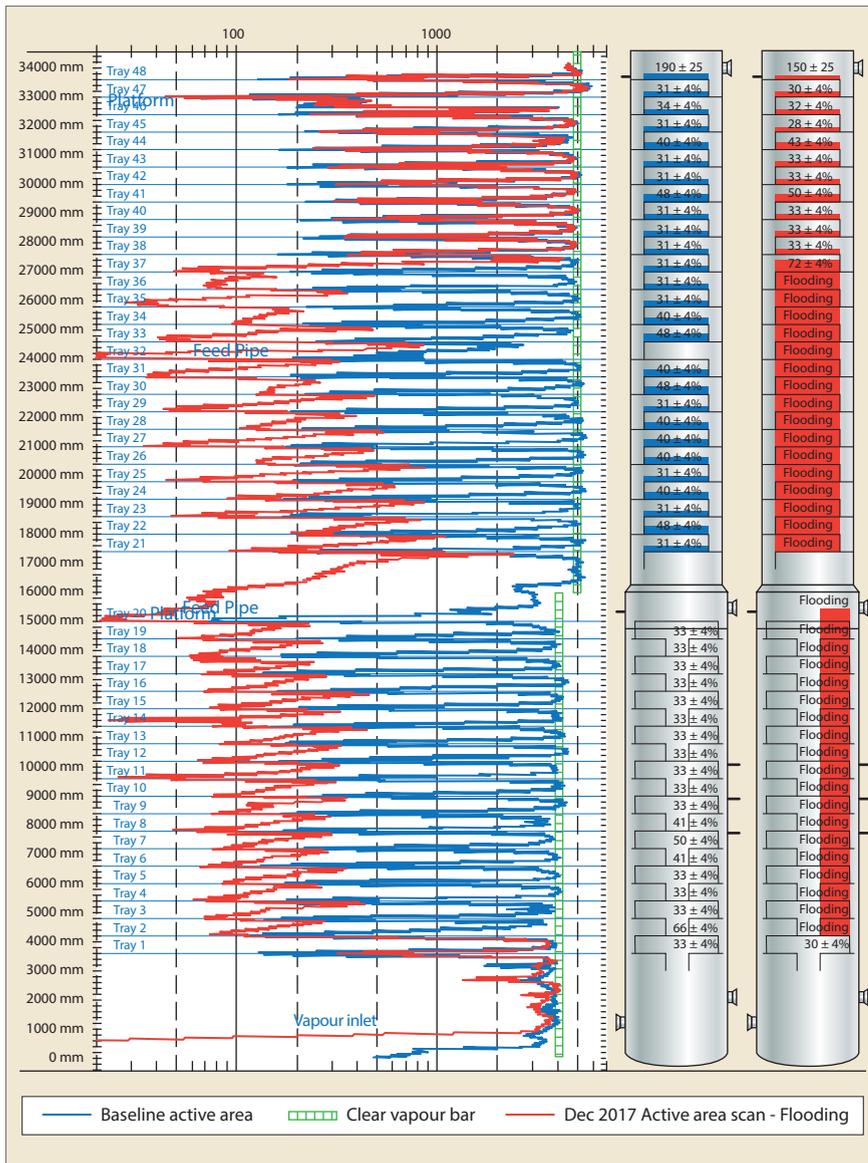


Figure 5 December 2017 scan of tray active areas under flooding operating conditions. Blue curve is the baseline scan; red curve shows flooding started at Tray 2 and had propagated up the column to Tray 38

Tray 2. The downcomers from Tray 4 also appeared to have high liquid levels, the east side outside downcomer appearing liquid full; the west side outside downcomer appearing to hold an 80% liquid level. The other outside downcomers in the lower section appeared to hold liquid levels at 50-58% full.

The observations described from these scans provided strong evidence for plugging of the trays and downcomers caused by polymerisation fouling. However, cleaning the trays and downcomers was not a viable option since this would have required a costly shutdown of the entire steam cracker unit. Therefore, the load in the bottom section needed to be reduced. Linde

AG and the plant owners decided to investigate a liquid bypass around the problem area.

The observations described from these scans provided strong evidence for plugging of the trays and downcomers

The relative froth density, the height of the liquid on the tray deck, the pressure drop due to liquid flow under the downcomer, and

the total tray pressure drop contribute to the liquid backup in the downcomer.⁴ A downcomer backup of 326 mm (13 in or approximately 53%) was calculated for the aerated liquid. This was the observed downcomer liquid load from Trays 6-20, presumably not affected by fouling. The gamma scans showed that the downcomers from Trays 2 through 4 were close to or already full under these loading conditions. In other words, the aerated liquid backup in the downcomers was approaching the 600 mm (~24 in) tray spacing. This meant that increased tray pressure drop contributed only partially to the overall liquid backup in the downcomers. Hence the remaining liquid backup was mainly caused by plugging of the clearance under the downcomer. Reducing the liquid load would reduce the downcomer backup. This was the rationale for installation of a liquid bypass line. A process simulation was conducted by Linde AG to demonstrate that the desired bottom and overhead product specifications could still be achieved, while bypassing a portion of the liquid into the sump.

Solving the flooding problem

The column should be capable of working at desired plant load conditions after installation of the bypass. Therefore, two different actual operating cases of the column were simulated. Case one represented the recent highest load operation of the column. Case two simulated the normal operating conditions of the column at the time of the downcomer gamma scans, just below the flood point. As is typical for a distillation column, the process simulation showed that the highest gas and liquid loads occur in the bottom section, especially on Trays 1 through 5. The liquid load that could not be processed by the column due to plugging of the clearance under the downcomer was determined to be 20.9 m³/h (92 gal/m). It was necessary to overcome the column bottleneck by bypassing at least this amount of liquid around the affected trays.

Figure 6 shows that at normal operating conditions the outside

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ring. In total, four hot taps were installed on the pressure shell, two in the side downcomers of Tray 8 and two below the normal liquid level in the column sump.

The bypass lines were put into operation in mid-2018. The steam cracker unit operating rate could be increased to 97% ethylene production capacity. On-specification overhead and bottom products were produced while the bypass was in operation. The debutaniser was opened in a later turnaround and severe polymerisation fouling was found on the bottom tray active areas and in their downcomers (see **Figure 7**).

Conclusion

In summary, thorough analysis of field data and tray hydraulics together with gamma scanning were key factors for a time- and cost-efficient troubleshooting. Close collaboration between the plant owner, Tracerco scan experts, and engineering company personnel made the troubleshooting discussed here a success.

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Thomas Walter heads the Equipment Process Design & Computational Mechanics department of Linde Engineering where his group is responsible for the process design of static equipment for petrochemical, natural gas, air separation, and hydrogen/synthesis gas plants. He holds a master's degree in process engineering from the Technical University, Dresden, Germany.

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Managing the life cycle of coke drums

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ABBY KING, N CHITHRANJAN and MITCH MOLONEY
Becht

Coke drums are fatigue machines. Fatigue damage accumulates with every cycle and cannot be reversed. Fatigue damage is not easily measured like corrosion, and will manifest in cracking over time, occurring first at the highest stress areas. The location and rate at which this fatigue damage occurs is different for every coker and is dependent upon numerous factors such as the design and operation of the drums (see **Figure 1**). Understanding how much fatigue damage has accumulated along with how quickly it will continue to accumulate and when to take action is critical to managing the life cycle of coke drums.

As fatigue accumulates in coke drums, more frequent inspection and repairs are needed. There is no true 'end of life' for coke drums, instead there is a turning point when outages for inspection and repair or unplanned downtime with reactive repairs outweigh the cost of replacing the drums. Predicting the point when these costs will increase allows time to weigh the economic benefits of the repair and/or the replacement options. Without this forward looking assessment, many sites have found themselves having to react by making very costly repairs, not necessarily because they are the best option but to buy time to plan for drum replacement.

For these reasons, it is critical to know where in the life cycle coke drums are, although this step is easier said than done. Coke drums fall outside of programmes that are used for other pressure vessels, tanks, and piping, such as risk based inspection. Recognising this gap, Becht developed a coke drum reliability assessment tool, BechtCokers, and associated work



Figure 1 Two drum coker unit

process to save clients the time and expense of other methods of analysis to understand the current phase of life of their drums (see **Figure 2**). As part of this assessment, a life cycle view is created for the coke drum from the day that it is placed in service. That allows proactive optimisation of the economic trade-off between coke drum fatigue life and operating costs and the margin value realised.

Since this approach directly links design, condition, and operation of the drums, Becht's team includes process, mechanical, materials, inspection, and reliability subject matter experts. The work process also facilitates multi-disciplinary

discussions between site personnel. Reliable operation of coke drums requires good communication across disciplines to understand the impact of operational changes to the life cycle of the drums and the resulting changes that need to be made to the inspection and maintenance plans.

Becht's approach uses a ranking of critical factors to benchmark drums at a single site or across several sites' drums versus the historical performance of other drums in industry. This benchmarking allows us to establish the phase of life and the estimated life fraction consumed to date as a percentage. This approach also provides a predictive model for estimated remaining life in number

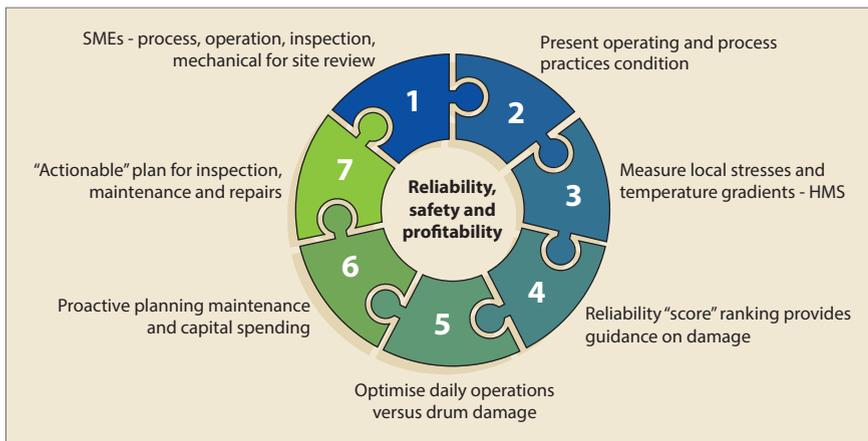


Figure 2 Becht's coke drum reliability assessment work process

of cycles and years, depending upon current and future operations.

Equipped with this knowledge, an owner can plan inspection and maintenance activities that will help ensure reliable operation of the drums by reducing the likelihood of through wall cracks, and structural skirt damage. As the end of life approaches, economic analysis can be applied to the factors that affect the life of the drum, such as operational changes, skirt replacements, structural weld overlay, and drum replacement to make the best financial decisions. In some cases, owners have found they can defer significant coke drum replacement capital investment with the right strategies.

Life cycle analysis

When projecting the life of coke drums, we evaluate individually three parts of the drum: shell girth seams, cone, and skirt. This helps identify the limiting component and customise the mitigation plans for different life profiles. The evaluation includes classifying the drums into one of the following three phases of life:

- **Phase 1: Minor problems**
 - Proactive minor maintenance
 - Baseline and routine inspection, as justified
- **Phase 2: Predictable crack growth**
 - Increased inspection
 - Planned repairs
 - Optimised repairs during planned shutdowns
- **Phase 3: Maintenance intensive**
 - More frequent shutdowns
 - Higher risk of unplanned outages
 - Repair vs replace economic evaluation

For the purposes of this article, we will focus on the critical factors used to evaluate the shell girth seams. The two major categories of factors that affect the life of girth seams are the design and operation of the drums. The design is a fixed condition, so let us first examine the critical factors of design that have the greatest impact on drum life.

Material of construction

The most common materials for the shell and cone of coke drums are 1 Cr – ½ Mo and 1-1/4 Cr – ½ Mo, with almost all drums being constructed in low chrome alloys. The vast majority of drums in industry have a 410 SS lining. The BechtCokers tool is calibrated for those materials as well as carbon steel, C – ½ Mo and 2.25 Cr, although they are less common in industry. For materials outside this envelope, materials engineers are consulted for additional calibration as necessary to determine the effects on the fatigue life of the drums.

Effects of drum thickness and changes in thickness

In simplistic terms, the thicker the shell is the longer the fatigue life the drums will have. This is due to a number of factors but can be summed up by saying that once cracks are initiated they will take longer to propagate through a wall. The BechtCokers tool gives credit for thicker shells and reduces the number of estimated cycles in life for thinner wall drums.

Some drums have a constant thickness which is the case for most recently constructed drums.

However, historically a large number of drums had been built with thickness transitions, sometimes several of these. In this case, the thickness transitions from thicker material at the bottom of the shell to thinner sections nearer the top of the drum. This was done to minimise materials manufacturing cost and to reduce the weight of the drums, reducing structural steel costs. The stress risers due to the thickness changes results in a greater propensity for cracking than in drums of consistent thickness.

Feed inlet design

Traditionally, the feed entered a coke drum at the bottom of the cone. This configuration is referred to as true centre feed. This design was typical for coke drums in the 1940's to 1970's, since sponge coke was produced and there was very little safety risk of coke fallouts or incomplete drains. As the industry shifted to shot coke production, the risk of injury during bottom head removal increased.

To reduce the risk to operators, slide valve technology was introduced, which eliminated significant safety risks during opening of the coke drum. This technology requires that feed come in from the side, above the slide valve. There are now three typical feed entry arrangements: single side entry, dual side entry, or centre feed.

The centre feed configuration results in the most uniform filling, heating, and cooling of the drum, thus minimising thermal gradients that cause high localised stresses. Symmetric dual-opposed designs can produce similar results. Single side entry configurations generate preferential asymmetric flows into the drum. Depending upon coke morphology, this can result in high thermal stresses and what is called the 'banana effect', when drums will bow to one side during operation. Localised high thermal stresses also commonly cause localised bulging.

Asymmetric flow entry can result in preferential flow channels in shot coke beds. When this happens, there is a higher probability of cold quench water contacting hot metal,

creating high thermal stress which reduces the fatigue life of the drum.

The BechtCokers tool accounts for the configuration of feed inlet nozzle and adjusts the projected cycle life accordingly. The largest debit to life is for single side entry; the next largest is for dual side entry, and the least is for centre feed (see **Figure 3**).

Delayed coker operations

Cycle time

The coking cycle time is the time during which the feed is filling up the coke drum. Coke drums operate in pairs, with one drum being filled at a time, while the coke in the other drum is being quenched, cut, and emptied from the drum. The coking cycle is roughly half the time of the complete operation. Cycle times vary from 12 hours to over 24 hours.

The difference in the cycle time is accounted for in BechtCokers, with faster cycle times resulting in a shortened life, and the longer the cycles the longer the life. In the absence of stress data, the model uses a correlative approach to relate fatigue life to cycle time (see **Figure 4**).

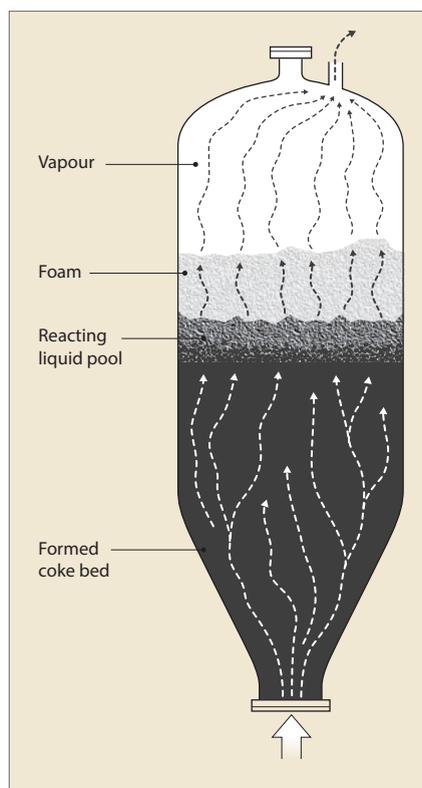


Figure 3 Coke drum with centre feed

The feed nozzle configuration and type of coke produced can greatly affect the amount of stress seen

in the drum during the quench. Directionally, the higher the initial quench rate is, the higher the stresses will be, resulting in a shorter projected drum life. Reducing the initial quench rate either by lengthening the quench duration or maximising the flow rates later in the quench, depending upon the operational constraints, is beneficial for prolonging the life of the drum.

Initial quench rates vary from <50 gpm to >300 gpm for up to an hour, with rates increasing to the maximum output of the pumps towards the end of quenching. Most quenches are automated to ensure consistent flows and duration for the quench portion of the cycle. Becht benchmarks quench rate data by comparing the rates to over 50 other coking units worldwide (see **Figure 5**). As we will discuss later on, quantifying the stress levels in the drum during the quench significantly improves the accuracy of the life estimate significantly and enables a more accurate understanding of how the changes in operation can affect the drum life rather than

Operations and current condition

Quench

Quench is when water is introduced to the drum through the feed nozzle, and sometimes above the coke bed, in order to cool the coke. There are two key areas where stress manifests itself:

- Skirt-to-shell weld area
- Coke drum shell circumferential welds

The skirt-to-shell weld area is the most responsive and sensitive area, since it achieves the lowest warm-up temperature and can rapidly see the effects of early quench water flow rate. The drum shell life is most greatly affected by quench water stresses and secondarily by extent of warm-up in the coke drum cylinder. Stresses during quench can be as high as twice the yield stress of the material. The initial rate at which the water is introduced plays an important role in the accumulation of damage, especially in the cone, lower drum, and skirt. The overall rate of quench water flow increase is also very significant, and primarily affects cylinder life.

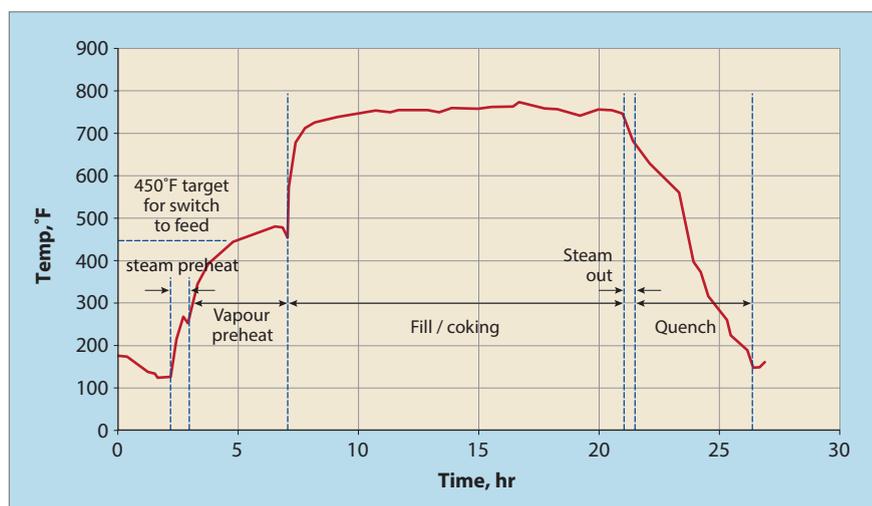


Figure 4 Example of a coker cycle (14 hours)

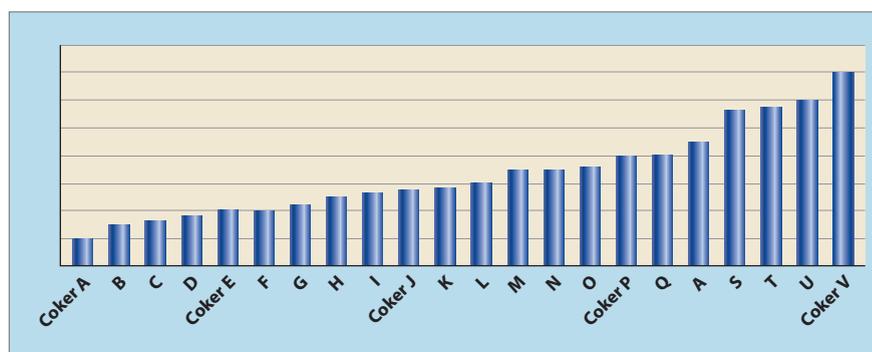


Figure 5 Benchmarking initial quench rate

providing a directionally 'good' or 'bad' assessment.

Switch temperature

Switch temperature is the target temperature at which the drum is heated before introducing hot feed into the drum. The higher the switch temperature, the lower the thermal stresses will be when introducing the feed. The impact of switch temperature is greatest at the skirt-to-shell junction. Optimisation of switch temperature is often intended to mitigate cracking in the skirt to shell; however, when cycle times need to be reduced, there is often a trade-off between the time allotted to warm-up and to quench.

Coke morphology

The two most commonly produced types of coke are shot and sponge. Sponge coke is a porous material and shot coke resembles small pebbles. Shot cokers in industry typically have at least a ~20% shorter life than sponge cokers. This is most commonly attributed to the porous nature of the sponge coke that results in an even distribution of quench water, allowing steam to more likely contact the metal before water, which reduces the stress, when water arrives (see **Figure 6**). Metal temperatures in the drum will cool more evenly than in shot cokers, reducing the thermal gradients that produce high stresses



Figure 6 Sponge coke

and rapid accumulation of fatigue damage.

Shot coke beds can result in what is called 'channeling'. The number of flow paths is greatly reduced in comparison to sponge coke. This results in quench water either flowing preferentially to certain areas of the coke drum or in cold water contacting hot metal. This results in either a higher frequency of high stress in preferential areas or rapid quenching of metal throughout the circumference with large temperature gradients and high stresses.

The cycle life of delayed coke drums in industry varies between 4000 and 14 000 cycles. Shot cokers have an average life of 8000 cycles, while a sponge coker's average life is 10 000 cycles.

Condition assessment

With a wide range of cycle lives in industry, our estimate takes into account the current known condi-

tion of the drums to determine if the rate that damage is occurring is faster or slower than the norm. The inspection history of the drums is reviewed to determine if cracking or bulging has occurred and, if so, to what extent. If damage has been found, what repairs have been made and what is the quality of those repairs?

Common inspection techniques on coke drums include laser scans and high definition video on the internal diameter of the drum. These scans document the size and depth of any bulges and will document the rate at which the bulges are progressing, if the inspections are done regularly.

Visual and other types of NDT are used, including advanced ultrasonics to identify and size cracks at welds. Depending upon the rate and extent of damage, the team will adjust the cycle life estimate accordingly to ensure as accurate an estimate as possible.

If little or no inspection is done, the band of uncertainty around the estimated cycle life increases. The higher the number of cycles without collecting inspection data, the greater the band of uncertainty.

Operational changes

It is common in industry to change the operational parameters of a coker unit. These changes can include almost any variable, from the type of coke produced, the length of the cycle, the switch temperature, to the initial quench rate. These changes can have a significant impact on the cycle life of drums. BechtCokers takes this into account by reviewing the historical changes and bucketing the cycles into different periods of operation. This enables accounting for periods of time when more or less damage has accrued. The output of the tool shows the life fraction consumed for each of the periods of operation, and projects behaviour into the future, allowing planning for upcoming major events, typically the next two turnarounds (see **Figure 7**).

Some coker units have been in service for many years. As a result, a site's historian may not have operational data for the whole life of the

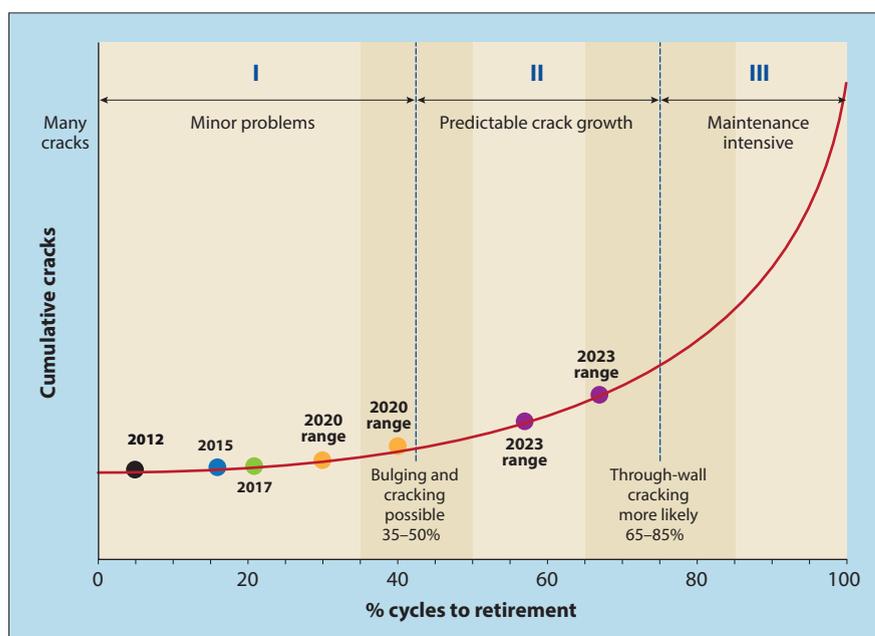


Figure 7 Coke drum life curve

drums. This is one of the important reasons for engaging with experienced operators on the unit. They can provide valuable input on the history of operations and repairs to the drums.

Mitigation of risk and life extension

Understanding where the drums are in life is the stepping stone to mitigating the risks of through wall cracks and unplanned outages, as well as steps that can be taken to extend the life of the drums if this is economically justified.

Phase I drums

For drums that are in phase I of their lives, there is ample opportunity for developing proactive inspection and maintenance plans and applying life extension actions. The earlier that life extension steps are taken the more successful they will be. For example, optimising the warm-up and quench steps utilising data gathered from a health monitoring system (HMS) that includes strain gauges and thermocouples installed on the drum can easily extend the life of drums for two turnaround cycles if it is applied early and the data is utilised. If HMS is applied during phase III, the goal is more likely to be reliable operation up to the next opportunity for drum replacement and helping with the design and operation of new drums, rather than life extension. Optimisation of the cycle includes gathering data for base case operations and for adjusted cases to quantify the reduction (or increase) in stress levels and to minimise fatigue damage. Often, these optimisations can be made within the normal cycle time without affecting the throughput of the unit.

Common inspection activities in phase I include laser scanning, which can be done between cycles, visual inspections of the skirt, and NDT of common areas of failure such as thickness transitions.

Phase II drums

Phase II is when inspection activities increase, with the progression of tracking of bulges over time and follow-up inspection on the more severe bulged areas. Laser scanning

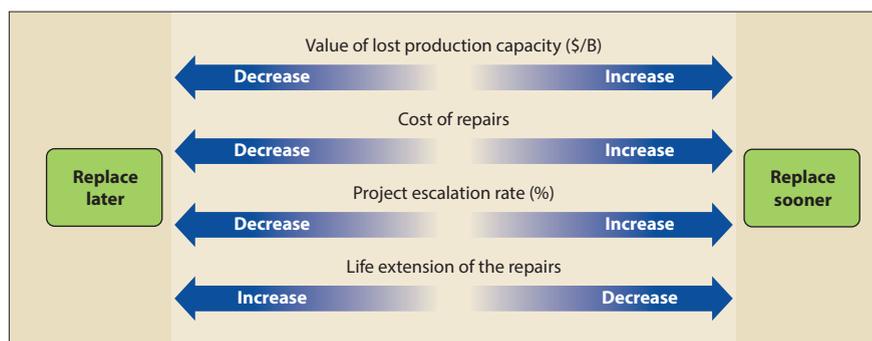


Figure 8 Sensitivities on repair vs replace

in advance of turnarounds can be used to develop inspection scope and repair estimates to minimise discovery work. Phase I is also when proactive inspection of weld seams is recommended to identify cracks. Developing repair criteria before cracks are found is a useful way to manage discovery work during turnarounds. Once cracks are identified, they can be sized using NDT, allowing a proper repair rather than a monitoring decision to be made.

Optimising operations during phase II can still make a significant impact on extending the life of the drums, and data from HMS can inform the timing and extent of inspection. There is an economic trade-off for changes in operation. As an example, when cycles are shortened to increase throughput, this should be expected to shorten the life of the drum. Understanding the impact on drum life versus economic gains is critical to the decision making process, and again data from HMS can be used to directly measure the effect on drum life.

Phase III drums

As drums progress into phase III of life, which is the maintenance intensive phase, inspection and repair activities should be expected to increase. Aggressive inspection plans and proactive repairs will be required to prevent unplanned shutdowns from through wall cracks. This phase of life is about managing end of life. Economic analysis is a powerful tool to inform repair versus replace decisions (see Figure 8).

Conclusion

It is not a question of will your coke drums crack, but when. The

life cycle of any drum depends on the design, operation, inspection, and maintenance of the drum and requires a multi-disciplinary approach to reliability.

Understanding the fatigue life of coke drums and where they are in the life cycle is the key to optimising the cost and margin trade-offs. Without this knowledge you are essentially flying blind and are risking costly unplanned downtime and repairs. Proactively assessing the life cycle of drums enables planning for the most cost effective scope and timing for inspection, repairs, and replacement. The reliability assessment using BechtCokers and a work process implemented with subject matter experts accomplishes this through industry benchmarking and analysis of site specific factors.

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Mitch Moloney supports Becht's delayed coking area. He graduated from Princeton University with a bachelor's degree in chemical engineering and is a registered PE in Texas.



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Revamp raises crude flexibility and profits

Hyundai Oilbank (HDO) has been operating an atmospheric residue desulphurisation (ARDS) unit, producing feed for the RFCC unit, at its Daesan, South Korea, refinery since May 2011. The unit consisted of two identical reactor trains (modules), with each module having a fully independent, high pressure section, but with a common work-up section. HDO recognised that the ARDS process was constraining both the refinery crude diet and capacity and requested Shell Catalysts & Technologies to implement an expansion revamp to increase crude flexibility, especially to heavier, lower cost crudes, to make the refinery more competitive in the marketplace, creating an opportunity for increasing profits.

The technical team at HDO determined that they could leverage the combined power of SDA (the biggest C5 SDA globally) plus deasphalted oil (DAO) in mild hydrocracker (MHC) technology to increase conversion of residue in the refinery. They looked to their long-time technology provider, Shell Catalysts & Technologies, which has offered reliable technical service and the delivery of process and catalytic solutions in several previous refinery projects, to work with them on the necessary improvements.

The project's goal was to increase the overall unit capacity and at the same time enable the refinery to process more difficult crudes. The project has been successfully executed over a series of expansion revamps.

The first phase revamp began in 2016, where Shell Catalysts & Technologies provided the technical support for HDO to expand the capacity of ARDS Module 1 and revamp Module 2 to a DAO MHC, with a combined capacity increase of 50%. The project achieved an increase in capacity needed to process the additional vacuum residue generated from a change to a heavier crude diet. Overall, an increase in capability was achieved for upgrading high sulphur residue into low sulphur fuel oil and more valuable light products (such as distillates) from heavy crude processing.

It took only 16 months from the beginning of the feasibility study to start up in September 2018.

HDO began phase two of the revamp in 2018 with Shell Catalysts & Technologies, starting with a feasibility study plus basic engineering design package, with completion in 15 months. This revamp will accomplish the following in the two modules:

- **Module 1** – capacity will be further increased by 30% with revamp of the existing single train to two parallel trains. The design cycle length will be increased by 50%
- **Module 2** – capacity will be further increased by 10%. The design cycle length will also be increased by 50%. The revamp project will also enable further integration of the refinery with the new heavy feed petrochemical complex (HPC)

Both expanded and revamped modules enable the refinery to upgrade low value hydrocarbons, vacuum residue in this case, into valuable products which are expected to deliver higher margin/profit to HDO. The revamps will help HDO to achieve several objectives:

- Increase crude processing flexibility with the ability to process cheaper, heavier crudes as a lever to increase refinery profit margin
- Capability to meet IMO 2020 by producing marine low sulphur fuel oil (<0.5 wt% sulphur)
- Provide sustainable feedstock to HPC
- Maximise RFCC feedstock and produce more valuable products such as propylene, gasoline, and distillate

Since the first phase revamp, HDO has had success in improving refinery margins by significantly reducing its crude acquisition costs by processing very difficult heavy crudes. A third revamp phase is in development, designed to fully support the competitive crude sourcing objectives by further optimising the unit's performance.

Changduk Cho, Manager of Business Development Team of Corporation Planning Office, Hyundai Oilbank

John Baric, Hydroprocessing LTM, Shell Catalysts & Technologies

Chee Long Hoh, Principal Sales Manager Licensing APR, Shell Catalysts & Technologies

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Analyser delivers fast quality checks for biorefinery

The demand for biofuels has increased in recent years, with the EU requiring that 10% of the total transport fuel in its member countries is to come from a renewable energy source in 2020.¹ In addition, the US Energy Information Administration anticipates between 18% and 55% growth in biofuels production over the next 30 years.² While biodiesels typically contain little sulphur, they are still required to meet compliance specifications for fuel quality, either for use in vehicles or as a blending feed for traditional refinery fuels. As such, biorefineries must measure the sulphur in their product to ensure it is below regulatory limits, typically less than 15 wtppm. In addition to this, due to the variety of feedstocks online, analysis of biofuels can be challenging due to changing sample composition.

XOS's Sindie 6020 online total sulphur analyser uses monochromatic wavelength dispersive x-ray fluorescence (MWDXRF) to measure a sample stream continuously and non-destructively, and to deliver results at user defined intervals. The analyser uses a dynamic window module (DWM) to automatically replace the sample window, which effectively eliminates any drift and significantly reduces the frequency of required



Figure 1 ecoMotion biodiesel plant in Malchin, Germany

calibrations. This, in addition to the rugged design of the analyser, reduces the time and frequency of required maintenance, leading to an uptime as high as 98%.

In August 2019, a Sindie 6020 online total sulphur analyser was installed at the Malchin biofuels refinery of ecoMotion GmbH by 360KAS, XOS's exclusive distributor in north-west Europe. This site is one of the first biodiesel pilot plants built in Germany and has been in operation since 2001. The primary feedstocks for this plant are animal fats, vegetable oils, and waste cooking oil. The site produces 10 000 tonnes of biodiesel annually (see Figure 1).

The core process in biodiesel production is transesterification. In this chemical exchange reaction, the glycerine contained in the primary material is replaced with methanol. This leads to the formation of fatty acid methyl ester (biodiesel) and glycerine. When converting animal fats and waste frying fats, the production process has two additional steps that are not required in conventional biodiesel production. In the first step – prior to transesterification – the free fatty acids contained in the primary material are esterified. After transesterification, the product is distilled. The result is a pure, crystal-clear and almost colourless product.

The expectation was to continuously measure the sulphur concentration in the biodiesel to confirm that the site was producing a product compliant with the climate protection targets set by the European Union. Previously this required the site to send samples to a remote lab which introduced delays and uncertainty in their production. By installing Sindie 6020 online sulphur analyser, the site obtains a measurement every five minutes, enabling operators to optimise their production, be confident their product is compliant and of high quality, and reduce their gas consumption by 5%.

Almost a year after installation, the site has reported that expectations for the performance of the analyser continue to be met, the analyser continues to operate without any problems, and the measured values match laboratory cross checks.

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XOS

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Automated level measurement cuts desalter upsets

The path from crude oil to high quality, usable products involves complex technical production and processing procedures in refineries, whereby several challenges have to be mastered, not only those of process measurement technology. Before the crude oil passes through the various process steps, starting with distillation, it must be desalted. Therefore, desalting is the first stage treatment in a refinery, whereby the correct and efficient performance is essential to ensure smooth operation in all subsequent process steps.

With refiners trying to maximise their margins, they turn to the use of lower cost opportunity crudes. The increased use of such opportunity crudes can cause issues with the proper operation of the desalter and leads to the formation of greater emulsion layers inside the vessel. This emulsion robs the operator of valuable volume inside the vessel used to separate the oil and water. In turn, this decreases residence time inside the vessel, leading to increased carry-over of water, salts, and minerals. However, these can cause various issues downstream from tray damage, fouling of heat exchangers/furnaces, corrosion issues, and catalyst deactivation. In addition, large quantities of expensive chemicals are often added to prevent the excessive formation of emulsion. For these reasons, control of the emulsion layer is of great importance. With a reliable interface measurement, it is possible to react better and faster to the formation of the emulsion and thus to optimise the desalting process, which saves high consequential costs. Various technologies can be used for level and interface measurements on desalters. These include, for example, differential pressure, RF absorption probes, and radiation based density profile measurements.

Radiometric based multiphase level measurements are among the most reliable and durable measuring methods for an application under extreme conditions such as those prevailing in desalters. Berthold's measurement solution EmulsionSENS consists of several detectors mounted on the vessel's outside and multiple sources inserted into a dip pipe (see Figure 1). A shield mounted

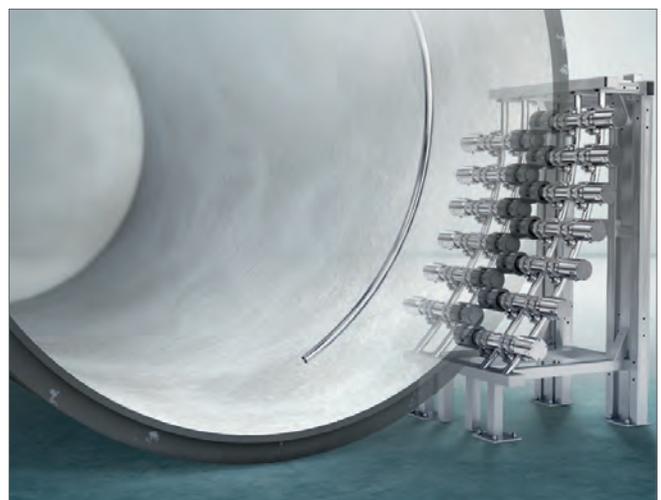
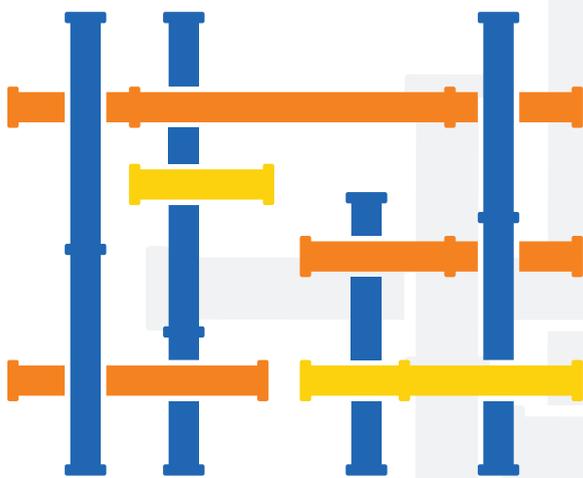


Figure 1 Measurement with EmulsionSENS



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on the top of the dip pipe ensures safe handling and storage of the sources, not only during transportation but also during maintenance where entering the vessel is unavoidable. EmulsionSENS is available in two different arrangements and can therefore provide exactly the values needed. With the so-called aligned arrangement, you obtain very precise density information on each detector elevation. Using the so-called staggered arrangement provides not only the density values in the area between the detectors but also the position and thickness – in other words, the level values – of all the layers. In the desalter process, level monitoring is of great importance, especially in the area of the water outlet.

Refiners have experienced a decrease in the number of upsets in the desalters from two to six upsets per year to none in the two years in which they operate with a nuclear density profiling system. The main reason for this reduction of upsets is the ability to provide automatic control and a continuous adjustment of the water outlet valve to maintain proper control and minimise the risk of having salt, water, or mineral carry-over. Another advantage of level measurement is the monitoring of chemical usage, its optimisation, and the associated cost savings. In addition to reducing the number of upsets and the chemical savings, a refiner can greatly increase the reliability of downstream equipment of the desalters by severely limiting corrosion caused by salt carry-over and extending the catalyst life by increasing the efficiency of the desalter. All in all, the profitability of a refiner can be significantly increased.

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Captured knowledge delivers expertise on demand

Refining and petrochemical companies around the world are asking the same question; how do we institutionalise knowledge that is quickly retiring? The challenge stems from a wave of retirements with nearly one-quarter of the sector's workforce being age 55 or older. The energy industry has worked diligently to deal with an aging workforce through early awareness, knowledge transfer, retention and productivity maximisation, and boosting of recruitment. An energy industry survey by The Manufacturing Institute found that firms seeking to enhance knowledge transfer implemented three best practices: establish and strengthen mentorship and apprenticeship programmes; collect and archive older workers' knowledge using centralised electronic records; and hire older workers with needed knowledge.¹

One US refinery selected the Knowledge-on-Demand Network as a platform to capture and institutionalise knowledge throughout its facility and access an experienced third party workforce. Its objective was to have quick access to the right experts while capturing both external and internal expert opinions on an ongoing basis. War stories were shared during preliminary discussions with the refiner: who has seen the senior engi-

neer retire and everybody wonder where are her notes and learnings? The unfortunate reality is that prior experience would say the majority of knowledge leaves when that person departs. This is the real problem that this refiner was seeking to solve.

The Knowledge-on-Demand Network is a web based platform for capturing and institutionalising knowledge, share learnings between plant sites and keep us from learning lessons of the past. The platform is built with easy searchability based on plant discipline (for instance fixed equipment), technology (such as FCC), and equipment type (for instance drum) tagging. Becht travelled onsite to meet with key representatives from process technology & operations, maintenance & reliability, turnaround & projects and other departments to educate them on the tool and methodology. Especially important was alignment with the refinery's IT department on a single-sign on (SSO) solution which allowed the client to build access directly into their Intranet.

The client engaged Becht directly as an outsourced central engineering organisation through the platform. Requests for support are entered either by email or through the web platform with responses typically provided in less than 24 hours. In one instance, the client had significant vibrations associated with boiler observations; a multi-disciplined team of burner, boiler, and rotating subject matter experts was assembled to review plant operational data and provide guidance. The team reviewed past and current operation including fuel gas variability, air flow control, burner operation, support design, and other aspects. Practical guidance was issued capturing the primary and secondary causes with actionable advice on how to mitigate vibration.

All responses and technical writings were documented in the platform. History would tell us that this issue will repeat itself within 5-10 years and the people who previously solved it will either have rotated to new roles within the refinery or moved externally. This refiner wanted to make sure that did not happen to them.

Reference

1 www.themanufacturinginstitute.org/Research/Aging-of-the-Manufacturing-Workforce/~/_media/7C49C34926E14737A9029C77F758EE0E.ashx

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Slug catcher debottleneck protects downstream processing

Effective separation of oil and gas from different impurities in upstream operations is a matter of paramount importance. All downstream activities and the processing equipment's service life depend on the purity level obtained in these first steps. When three slug catchers at a major oilfield were struggling to effectively process crude oil, Sulzer Chemtech promptly created a designed solution to restore peak performance. The revamp was completed quickly during a planned downtime period and minimised future regular maintenance.

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Located between the outlets of pipelines and processing units, slug catchers are the first stage in upstream processing trains and plants. The fundamental purpose of such large vessels is to hold the slugs temporarily and then direct them into downstream equipment and facilities at a rate at which the separated gas and liquid stream can be properly handled. In addition, they support degassing and bulk solid removal from the liquid phase as well as the delivery of a more even supply of liquid to downstream facilities. This in turn prevents any overload in the plant's gas/liquid handling capacity, especially during pigging operations.

Key components of slug catchers are mist eliminators. These may be pushed to their limits by increasing the unit's capacity, because of the arrival of a liquid slug or gas surge, or when fouling materials accumulate on them. In these situations, the slug catcher's demisting devices may be exposed to fouling as well as corrosion and become inefficient. As a result, downstream facilities may be exposed to high liquid and solid entrainment in the gas outlet stream.

When liquid droplets get away from separators

One of the world's top 10 oil producers was experiencing these issues in three identical high pressure slug catchers at one of its oilfields. The liquid carry-over from the slug catchers was impacting downstream separation processes such as the company's amine unit. Simultaneously, the entrained solid particles were causing fouling of demisting mesh pads and other downstream components.

To minimise the impact of these negative effects, the company had to drain liquids being accumulated in a downstream scrubber every 13 hours. In addition, the overall production capacity had to be reduced to minimise liquid carry-over and solid particle entrainment.

The oil producer contacted Sulzer to develop a suitable solution that would address these issues and debottleneck its operations. In particular, the company wanted a revamped system to keep the liquid carry-over from the slug catchers equal to or below 0.1 USgal/MMSCF (14 lt/MMNm³).

Designing mist elimination

Sulzer's specialised engineers began by conducting computational fluid dynamics (CFD) simulations. These would support root cause analysis (RCA) and identify key improvements in the slug catchers' design that could lead to enhanced separation performance.

This investigation revealed that the demisting capabilities of the existing wire mesh pads could be improved by using additional pieces of equipment, one of them being a T-shaped, half-open inlet device. While other items commonly installed in such vessels might be based on vane packs, Sulzer's CFD study revealed that two perforated inlet distribution baffles, coupled with a horizontal flow axial cyclone deck at the outlet nozzle of each slug catcher, would provide a better demisting performance.

While vane packs work properly under normal atmospheric conditions, they are generally not recommended for hydrocarbon processing at high pressures, such as

in the slug catchers we were investigating, which operate at 72 bar (464 psi). In these situations, they tend to feature lower separation efficiencies. Conversely, axial cyclones are ideal as they can withstand these harsh operating conditions better.

The ideal horizontal flow axial cyclone was identified to be the Shell VersiSwirl, which is a high-capacity system able to remove all liquid droplets while withstanding fouling. To further increase the slug catchers' performance, Sulzer's team suggested equipping the top section of the second baffle with its Mellachevron vane pack pre-conditioner. This supports demisting operations by coalescing the liquid droplets to form larger aggregates that are easier to capture.

Happy with the design suggestions proposed by Sulzer's engineering team, the oil company asked the specialists to plan the installation of the three demisting devices. Key requirements for this phase of the project were the completion of the revamp within the plant shutdown period, two weeks for each slug catcher, and the avoidance of any welding activity on the vessels.

As the slug catchers operate at high pressure, welding would require post-welding heat treatment and vessel rectification. These would not only result in prolonged downtime but would also need large volumes of water for hydrotesting that would not be easily accessible to the plant due to its remote location. To address this issue, Sulzer's engineers utilised support expansion rings that would not require any welding and could be installed quickly.

After the first slug catcher was successfully upgraded, the downstream scrubber needed to be drained only once a week rather than every 13 hours. In addition, the performance tests, conducted by an external independent laboratory, showed that the total carry-over was way below 0.1 USgal/MMSCF, exceeding the expectations of the oil company.

Fully satisfied with the results obtained, it asked Sulzer to repeat the same revamping activities on the remaining two slug catchers. After completion, draining intervals further lengthened, requiring interventions only every one or two months.

The revamp project conducted for this oil producer showed comprehensive capabilities as a full-service provider of mass transfer and separation solutions and specialised field services.

Shadi Aoun, Head of Sales & Technology – Upstream Components, Sulzer

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New boilers lower emissions, raise reliability

Refineries are under constant pressure to lower emissions. This includes National Ambient Air Quality Standards, New Source Performance Standards (NSPS), and National Emission Standards for Hazardous Air Pollutants (NESHAP). Additionally, new or upgraded refinery equipment and technology is often subject to

requirements such as lowest achievable emission rate (LAER), best available control technology (BACT), and maximum achievable control technology (MACT). 2015 EPA regulations, for example, require refineries to conduct analyses of the causes of the toxic emissions, then take action to reduce the level of toxins such as benzene.

Faced with an aging infrastructure, some parts dating back more than 70 years, one US refinery decided to up its environmental game via a series of upgrades. This included replacement of critical items such as fluid catalytic crackers and boilers. Management decided to introduce the latest technology to eliminate unscheduled outages and bring emissions levels well below current standards.

The facility processes over 100 000 b/d of crude oil for gasoline, diesel, jet fuel, and petrochemicals. It wanted boilers that would combine high efficiency and reliability with low emissions. Accordingly, it specified a furnace and steam drum that were larger than its immediate needs. Further, the refinery demanded a design that could operate in tandem with selective catalytic reduction (SCR) technology and Coen LoNox burners as a means of minimising NOx production. Facilities operating a larger furnace and steam drum find it easier to meet or exceed NOx requirements. More conservative sizing also helps to minimise problems with flame impingement. When augmented by Coen LoNOx burners and SCR, NOx production from boilers has been brought down below 5 ppm in some cases.

Additionally, a large steam drum allows better separation to remove water from the steam before it goes to the superheater. This is an important aspect of refinery reli-

ability: too much water carry-over from the steam drum can eventually blow out the superheater. In addition, if there is a loss of feedwater flow to the boiler, the larger drum gives personnel more time to take corrective action before steam levels drop – specify too small a steam drum and refinery operators might only have a minute or so from the time of loss of feedwater flow to prevent a trip.

The Rentech boiler design also minimised the amount of refractory. This means that operators do not need to worry about replacing refractory seals or rebuilding refractory walls. By placing the superheater behind the convection section, they are more protected from the high temperature of the exhaust gas. This extends the life of the superheaters and boosts reliability.

The boiler burns refinery gas, supplemented by pipeline gas. This 250 000 lb/h unit was designed to follow steam load. It can fire up and reliably run at low fire then ramp up or down when needed, in accordance with demand, producing steam at around 750°F (400°C) at a pressure of 450-650 psi.

According to the plant manager, the new boilers increased efficiency from around 85% to 92% and meet BACT standards. He added that they have been operating reliably since installation, providing the required steam. Unplanned shutdowns due to aging boiler issues have been eliminated. Overall efficiency has been increased while helping the facility to conform to stricter environmental standards.

Rentech Boilers

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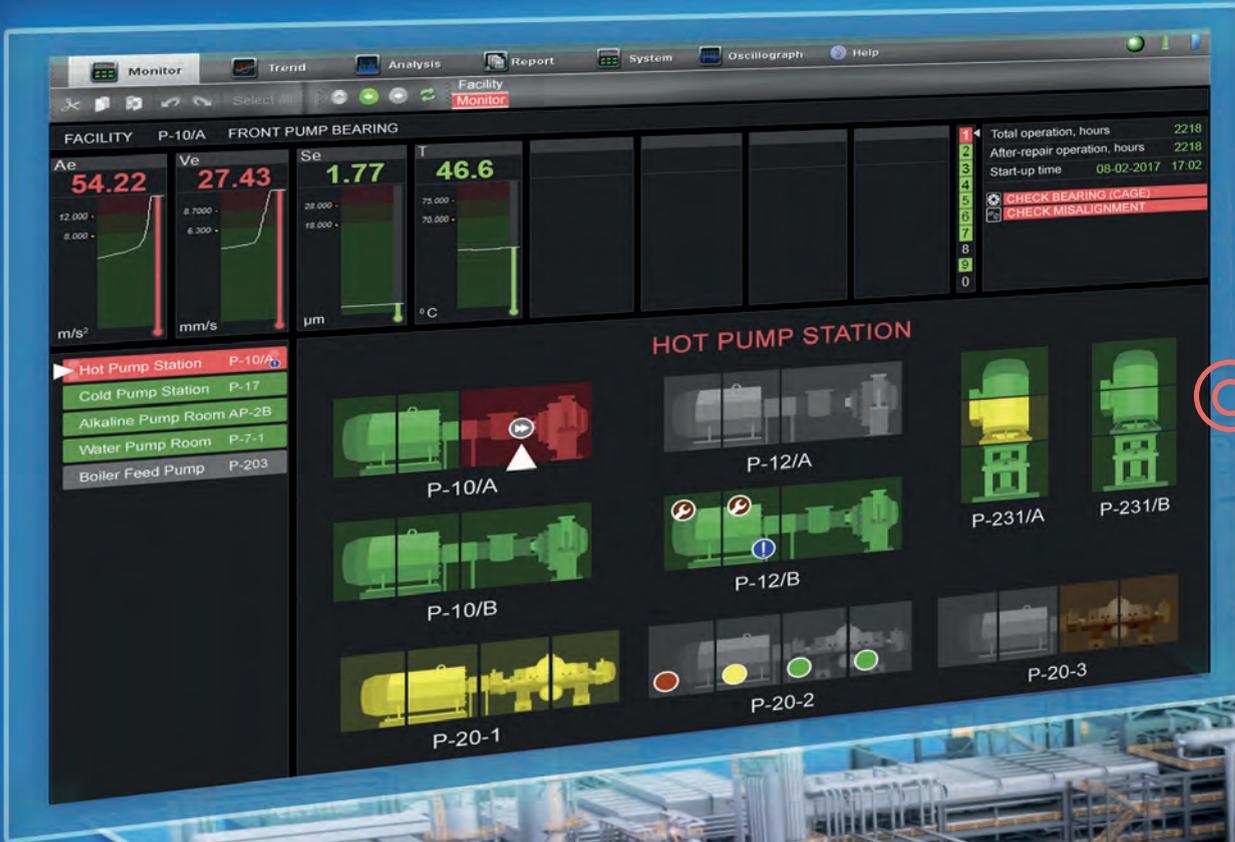
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