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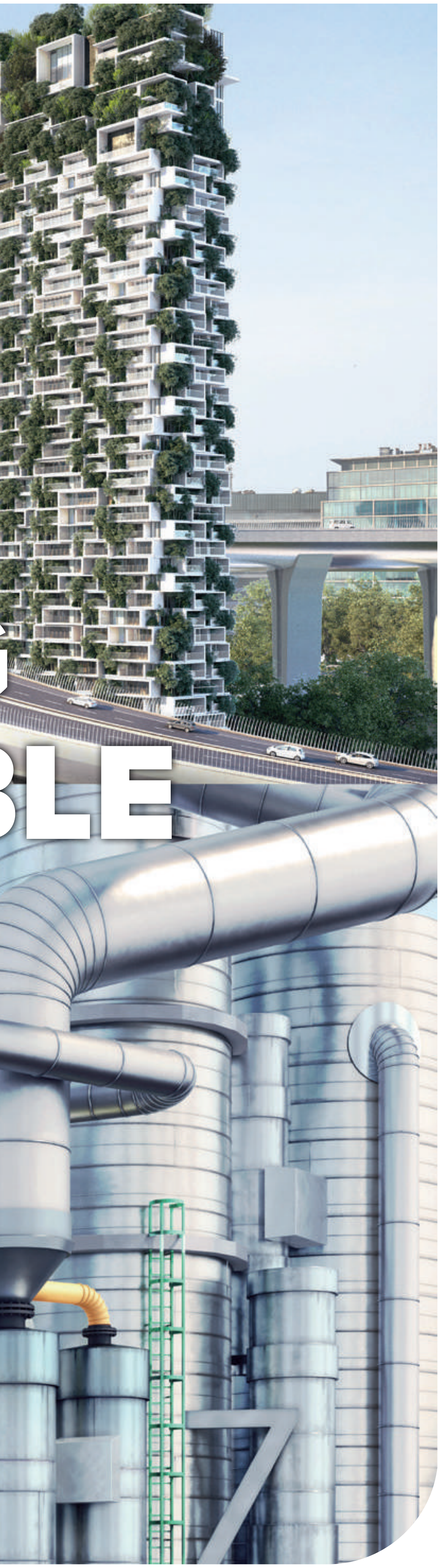

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Cover
Neste's Porvoo refinery includes two NEXBTL units producing MY renewable diesel
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As you were – almost

After a full year of Covid, you might expect an impression of how the world's petroleum processing industry is developing to be confused. Although the pandemic slowed production everywhere except China, and has accelerated closures that were anyway inevitable, the bigger emerging story appears to have changed little, with China and India quickly expanding their roles in world markets while Europe's refiners can barely make any money from their operations.

India's refineries have largely recovered their utilisation rates from pandemic levels. The nation's biggest site, Reliance's Jamnagar complex, was reporting a combined throughput for its domestic and export production of around 98% early this year, still a little below the level it reached at the same point in 2020.

However, percentage rates in the high 90s and beyond are fairly typical of Indian refining performance, a clear indicator of further expansions and new refining capacity in the coming years. A forum organised by S&P Global in February heard that India sees peak oil arriving much later there than elsewhere in the world and that the scene is set to continue its refining industry as the global epicentre of expansion. For instance, Bharat Petroleum is planning to raise capacity at its Numaligarh refinery to 9 million t/y by 2025, from a current 3 million t/y.

The story of growing domination of global oil refining also continues in China where the industry is set to take over as the biggest producer, perhaps within the coming year. This would be the first time ever that US refining has not held the top spot.

With increasing capacity, China's refiners are, like India's, becoming preferred customers for crude exporters and are, in turn, increasing their hold on international markets for fuels.

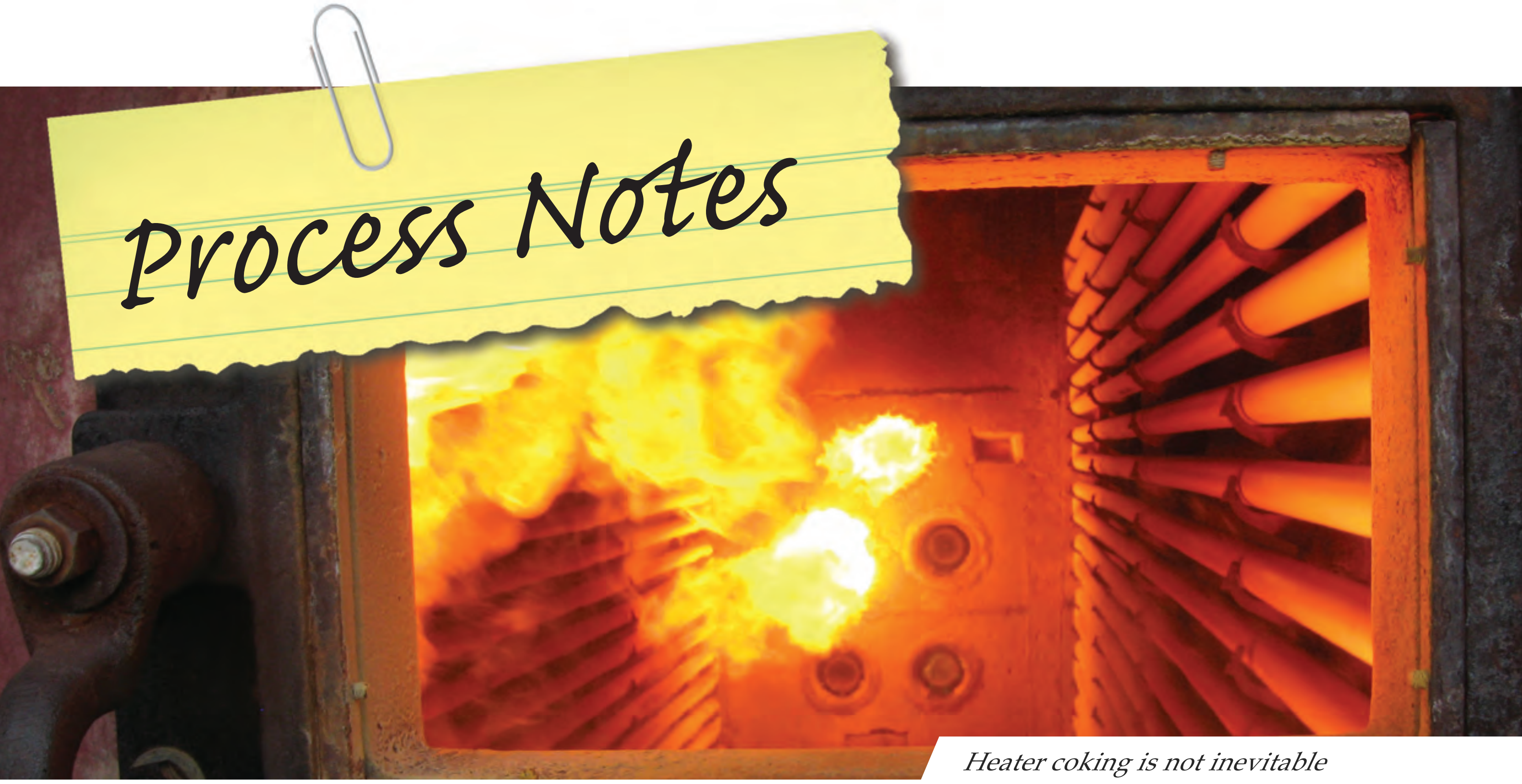
A clearer picture of the status of US refineries should begin to emerge in the second quarter of the year. Percentage rates had been running in the low 80s before a winter storm battered the Gulf Coast region. In February, utilisation had hit a rock-bottom 56% before recovering to 63% in early March. Nonetheless, some major units were not expected to be fully on-line until later in the spring. Logically, the resulting draw on stocks combined with refinery closures should boost throughput, if not refining margins, as the year develops.

Oil refining in Europe declined throughout 2020 and seems unlikely to change trajectory any time soon as the pandemic continues to bite. Projected refinery closures aside, the biofuels factor is also changing the shape of European fuels production. Italian major Eni has so far converted two of its refineries to produce biofuels and is considering conversion at Livorno in the north west of the country. The company aims to be producing 5 million t/y of biofuels by 2050.

Neste is shutting down its Naantali refinery in Finland with a switch to terminal operations, while the company's Porvoo refinery will be revamped to focus on co-processing renewable raw materials, continuing a policy that began with production of renewable diesel at its Singapore and Rotterdam, Netherlands sites.

In Portugal, Galp will finally shut down production at its 100 000 b/d refinery at Matosinhos in response to the combined impact of the pandemic and the need to upgrade operations. The company will confine operations to its other, larger site at Sines.

CHRIS CUNNINGHAM



Heater coking is not inevitable

Avoid Fired Heater Coking

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

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

Mass flux is king

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

Heat flux can surprise

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

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

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

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Q We would like to explore oil to chemicals routes. Any process ideas for VGO/resid conversion?

A Bani Cipriano, Segment Marketing Manager, Light Olefins, W. R. Grace & Co., Bani.Cipriano@Grace.com

The fluid catalytic cracking (FCC) unit provides an excellent opportunity to increase the yield of petrochemical products from the refinery. Specifically, the FCC is the unit that generates the highest yields of propylene in the refinery. Propylene is a valuable petrochemical feedstock, the majority being converted to polypropylene while the remaining finds use in production of cumene and acrylonitrile among other end uses. Under suitable conditions of hardware, operating conditions, and catalytic system, FCCs can process VGO and/or resid feeds.

Conventional FCCs generate propylene yields in the range 4-5 wt%. FCCs can operate in max $C_{3=}$ mode and can reach upwards of 12 wt%. Commercially proven high olefin yield catalytic cracking processes exist that can achieve propylene yields of >20 wt%. One such example is PMcc process technology available through a joint effort of Technip Energies and Grace.[1,2]

The propylene yield depends in general on three key aspects[1,2]:

- Hardware configuration: as examples only, (i) regenerator design is different for resid vs VGO feeds, and (ii) addition of a secondary, external riser for cracking naphtha can increase the yield of propylene.
- Process conditions: in general, higher ROT and lower hydrocarbon partial pressures in the reactor will increase the yield of propylene.
- Catalyst for propylene maximisation: these catalysts in general (i) include the shape selective ZSM-5 zeolite to crack gasoline olefins into propylene, (ii) are designed to tolerate and retain their catalytic activity in the presence of harmful metals such as V, Ni, and Fe to name a few, and (iii) have engineered macro and mesoporosity to facilitate the upgrading of the largest feed molecules into valuable products.

It is also important to consider $C_{3=}$ and LPG olefin recovery constraints (wet gas compressor, splitting capacity). In Q2 2020, during the COVID-19 pandemic, many FCCs were processing lower than customary rates and this freed up $C_{3=}$ recovery capacity. Refiners turned to strategies to maximise propylene (ZSM-5 usage and higher ROT). If operating at full rates, refiners may need to invest in additional recovery and splitting capacity if operating in max $C_{3=}$ mode.

Finally, operating in max $C_{3=}$ mode can be very profitable for refineries. We recently estimated that the PMcc process can deliver approximately $2.60/bbl in uplift over an FCC processing a similar rate[1], the uplift being the result of higher values for propylene over gasoline and fuels.

References

1 For information about high olefin catalytic cracking including hardware configuration, process conditions, and catalyst design for high olefin yields, the reader is referred to Singh *et al*, Conventional FCC to maximum propylene production, *Hydrocarbon Processing*, Sept 2020, and Dharia *et al*, Introducing PropyleneMax Catalytic Cracking (PMcc®), *Grace Catalagram*, Vol 125, 2020.

2 For more information about refinery strategies in the aftermath of COVID-19, the reader is referred to Roundtable Session: Turbulent Markets Getting the most out of the FCC during COVID-19, Hunt *et al*, AFPM 2020 Annual Meeting.

A Mel Larson, Strategic Consulting Manager, Becht, mlarson@becht.com

The world is moving away from pure residua conversion; RFCCs are out of favour considering the demand for low sulphur products. The shift has been to some version of hydrogen addition to bottom of the barrel. On the FCC front, east of Suez has focused on high conversion/propylene-making FCCs with recycling of a portion of FCC naphtha to recrack as diesel. This trend will continue by maximising the cracking of VGO to petrochemical feedstocks.

Q What is hydrogen embrittlement, where could it occur in our refinery, and how do we avoid it?

A Collin Cross, Senior Product Analytics/Support Manager, SUEZ – WTS, 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 which 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 specific 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, the 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 as a result of welding practices, cleaning practices, metal manufacturing processes, and so on. 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 oftentimes are the most at risk.

For HE to occur, generally three factors are necessary: high concentrations of hot (<300°F, 150°C) gaseous hydrogen, alkaline conditions, and poisoning agents that slow the recombination of monoatomic hydrogen into molecular hydrogen. Examples of common poisoning agents are cyanide, arsenic and sulphides. The type of corrosion that favours the conditions above is called wet H_2S corrosion and most frequently occurs in cracking units such as FCC and hydroprocessing units, cokers, amine units, sour water service units, and HF alkylation units.

To avoid HE, there are many strategies that should be employed. Routine inspection and monitoring help the detection and mitigation of HE. Proper alloy usage is also an important factor. 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, which are 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 ammonium or sodium polysulphides. 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 in use today, they have several negative side effects that have caused their use to decline in recent decades considering the development of newer and less problematical 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 services. While filmers do not directly eliminate the cyanide (or other poisoning agents) as do polysulphides, they do effectively 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, favorable economics, and strong ability to prevent HE.

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

Hydrogen embrittlement is a complex process. A simple way to describe the cause is by the diffusion of atomic hydrogen into metal followed by recombination to molecular hydrogen in voids or impurities in the metal, causing local areas of high pressure inside the metal. It can occur during welding or in a sour wet environment if conditions are such that atomic hydrogen can be generated and diffuse into the metal. The units with wet sour environments that can be most susceptible to embrittlement in a refinery are normally the FCC, thermal cracking units such as cokers and visbreakers, and downstream amine units.

Hydrogen embrittlement can be avoided by using steels that are less susceptible and the use of proper welding procedures for equipment in sour service. Monitoring the composition of sour water can help determine the risk for hydrogen embrittlement for a certain part of a unit while in operation. If conditions are such that there is an increased risk, actions can be taken to reduce the risk. These can include reduction of corrosives by water wash or scavengers or the use of a corrosion inhibitor. Failure of equipment by stress corrosion cracking due to hydrogen charging can be a very drastic event with severe consequences and all possible means should be used to prevent this. Nalco Water can help manage the risk for hydrogen embrittlement with analytical capabilities, monitoring, and the use of patented Pathfinder corrosion inhibitors.

A **Andrew Layton, Principal Consultant, KBC (A Yokogawa Company),** Andrew.Layton@KBC.global

There are a number of embrittlement corrosion phenomena which are sometimes confused. A brief clarification of three of the most common is given here before talking specifically about hydrogen embrittlement:

- Temper embrittlement of steels, which is a high temperature long term phenomenon related to higher alloy materials especially when used in thick wall reactor vessels.
- H_2 embrittlement of steels which is a low temperature phenomenon usually related to absorption of H_2 generated from cathodic corrosion reactions like Wet H_2S corrosion
- High temperature H_2 attack (HTHA) of steels is a relatively high temperature phenomenon impacting more the low alloy materials like CS or C ½ Moly. This is often discussed in recent years because it is related to significant incidents on hydrotreaters or naphtha reformers. This has resulted in the updating of the Nelson curves which identify when HTHA is a concern as a function of temperature, H_2 partial pressure, and material type.

H_2 embrittlement of steels is created by absorption of H_2 into the steel at low temperatures. It has several forms and there are many mechanisms proposed. Important factors contributing to the phenomena include high hardness, the presence of stress, and water. Typical examples are:

- Poor welding procedures where moisture may be present
- Localised dissimilar metals, allowing a corrosion cell to be created in the presence of moisture; this will also generate H_2 at the cathode. This can happen in many locations where there are dissimilar materials in the presence of water. One example could be dissimilar bolt/washer/structure materials on jetty or any external supports.
- Wet H_2S corrosion, which is perhaps the most common example of H_2 embrittlement, especially if any cyanides and high ammonia levels are present in the presence of H_2S and water. Cyanides are a particular problem even at low ppm levels as they can remove the sulphidic protective layer which helps prevent the corrosion cells being set up.

Typical location examples for H_2 embrittlement are:
- Poor welding and in hardness zones
- FCC/coker overheads and light ends systems where H_2S/cyanides and moisture are present
- Hydrotreater reactor effluent and stripper systems where H_2S/moisture/ammonia is present and sometimes cyanides, which is a particularly bad actor
- Gas treating systems such as amine systems
- Alkylation units
- Sour water systems
- Some crude and VDU systems dependent on crude type

Typical mitigations are:
- Good welding practices
- Improved steel fabrication standards and selection for equipment going into wet H_2S service
- Dilution of corrosion precursors by water washing with a focus on good mixing design as well as dilution
- Use of chemical additives such as polysulphides
- Stress relieving of critical equipment after construction or mechanical/welding work
- Good inspection programme
- Good positive materials identification to prevent dissimilar materials issues

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

Hydrogen embrittlement is an insidious type of failure, often driven by bisulphide ions (HS^-) as high pH corrosion. Refinery units with high pH operations are hydrotreaters, amine units, sour water strippers, and FCC light ends. Hydrocrackers, visbreakers, and coker fractionators are occasionally affected, while H-Oil units (LC Finers) or reformers are only infrequently affected.

Hydrogen embrittlement is a form of corrosion, where high-strength steel becomes brittle and fractures following exposure to hydrogen. Often this form of corrosion is not recognised, which can lead to unexpected and sometimes catastrophic damage. The complete mechanism is not completely understood, because hydrogen embrittlement is not a permanent condition. It starts with hydrogen atoms diffusing through the metal. When these atoms recombine to form hydrogen molecules, they can create extremely high pressure from inside the cavity they are in. When this occurs, the metal ductility is significantly reduced, leading to cracking and brittle failures.

Hydrogen sulphide ions are known to promote hydrogen embrittlement by allowing more time for the atomic hydrogen to become absorbed. This inhibits the recombination reaction of atomic hydrogen to molecular hydrogen.

The degree of embrittlement can be influenced by the amount of hydrogen and microstructure of the metal. Ferritic steel is more susceptible to hydrogen embrittlement than high quality steels such as austenitic stainless steels, aluminum, and nickel alloys with different crystal structures. The best method of controlling hydrogen damage is to limit the contact hydrogen has with the metal. Film forming inhibitors reduce the potential for corrosion. They are absorbed to the metal through its polar group. The non-polar tail of the inhibitor is oriented vertical to the metal surface, then the atomic hydrogen reacts with the corrosion inhibitor forming a barrier to the metal surface.

A Henk Helle, Corrosion Engineer and Reliability Expert, Petrogenium, henk.helle@petrogenium.com

Hydrogen embrittlement (HE) is the obstructing effect of dissolved atomic hydrogen on the plastic straining of metals. On elastic straining there is no such effect. Since refinery equipment is nominally designed to be stressed elastically, there is generally another factor at play: stress raisers, such as cracks or sharp notches, which induce local plastic zones.

This redefines the problem: HE is the cause, but hydrogen stress cracking (HSC), or the propagation of cracks under the influence of dissolved atomic hydrogen, is the consequence.

HSC can occur in a range of metals such as alloyed or unalloyed ferritic steels and nickel-base alloys. Cracking occurs when atomic hydrogen diffuses through the metal lattice to highly stressed points such as notches, inclusions, weld defects or crack tips, and hinders the capacity of the metal to deform plastically, causing it to crack instead. This effect will be stronger at lower temperatures where the diffusion of hydrogen is low enough to become trapped in a stressed zone. The severity of HE depends first on the concentration of dissolved hydrogen. HSC is a quick process: when the conditions are right, crack growth is a process of hours rather than years, although cracking may stop when conditions change. In higher strength materials, the HSC rate tends to be higher and potentially more catastrophic than in ductile metals.

So, where in the refinery can HSC occur? It requires three ingredients: dissolved hydrogen, susceptible metal, and plastic strain. Hydrogen dissolves in metal when in contact with hot hydrogen gas, such as in hydroprocessing units, or when aqueous corrosion reactions form cathodic hydrogen in the presence of H_2S, HCN, or HF. This form of hydrogen charging may cause HSC known by another name: sulphide stress cracking or SSC. Aqueous H_2S solutions are found in numerous locations in a refinery from storage tanks to the sour water stripper, basically all wet and ambient temperature locations. This is pretty much everywhere in the refinery if the shutdown condition is considered as well. HF exposure is generally limited to HF alkylation units.

The stresses that produce local plasticity can have several causes: weld stresses and other fabrication stresses, thermal stresses, internal pressure, and external forces. Regarding design, installations are elastically strained, but in practice they often are not.

Susceptible metals are ferritic materials or duplex stainless, or Ni based alloys, and the critical property is hardness. The reason that hardness determines susceptibility is that crack tip blunting in softer metals gives a lower stress intensity, whilst a sharper and more highly stressed crack tip zone in harder metals is prone to brittle cleavage failure. An empirically derived hardness limit for ferritic steel is 22 HRC, below which HSC is less likely (though not impossible). The finer points of HSC encompass an elaborate standard defining hardness limits and other specifications of metallic materials in relation to SSC in refineries.

Avoiding HSC requires the following main principles:

- When shutting down, slow-cool hot pressurised hydrogen-containing equipment in accordance with the specifications.
- Follow the materials specifications as given in NACE Standard MR0103.
- Fastidiously adhere to MOC procedures.

A **Craig Harclerode, O&G Industry Principal, OSIsoft,** charclerode@osisoft.com

Hydrogen embrittlement, also referred to as high temperature hydrogen attack (HTHA) or methane reaction, is a widely documented corrosion phenomenon in petroleum refining and petrochemical processes that can be best described by using intent search engines like Google and articles like: AICHE Engage, Preventing HTHA, by Lauren Grim (8/15/2016 post) or articles such as ASTM F519 and ASTM G142. In short, the Nelson Index correlates the impact of hydrogen embrittlement on various high strength material such as in the case of carbon steel alloys at high temperatures and high hydrogen partial pressures.

An example of using advanced analytics can be found in the 2016 EMEA OSIsoft Users Conference in a presentation by MOL's Tibor Komróczki (Delivering Business Value from Digital Transformation) which describes how MOL developed HTHA advanced corrosion analytics by using PI Asset Framework (PI AF) to configure a HTHA template that was then rapidly deployed to over 50 nodes across four refineries.

Many companies like MOL are using advanced analytics and methods to monitor for HTHA with associated operational alerts in addition to gathering intelligence to aid in the determination of preventive measures such as the need to inspect or replace certain nodes with different alloys or change operations.

An additional reference can be found in Leveraging the PI System in the Processing of Opportunity Crudes by MOL's Gábor Mucsina in the OSIsoft UC2017. This presentation discusses the use of integrity operating windows (IOW) in areas including HTHA to aid in the safe processing of opportunity crudes.

Q **We have fuel performance issues when we blend low sulphur marine fuels from different sources. How can we resolve this?**

A **Marcello Ferrara, Chairman, ITW Technologies,** mferrara@itwtechnologies.com; **Domenico Ferrara, Process Engineer, ITW Technologies,** dferrara@itwtechnologies.com

The difficulty for marine engines to keep up with the times has been severely tested by the new IMO 2020 regulations which require the use of low sulphur fuels which may create deposits and fouling inside the combustion chamber and consequently cause severe damage to the pistons, liners and pistons rings, and in the worst cases lead to a sudden stop of the engine. Additionally, all of the system upstream of the engine will suffer from fouling issues.

While lower sulphur in fuels will mean fewer harmful emissions, the loss of lubricity that sulphur brings can also make engine operations more challenging.

Distillate ageing also contributes to increasing issues. The percentage of distillate blend components in VLSFO often come from complex secondary refinery streams where much of the natural stability has been removed or weakened.

Distillate ageing is a chemical process that produces sludge in the presence of elevated temperature, oxygen, or by a catalyst present in the fuel (for instance, a metal). These processes can be prevented by the use of proprietary additives.

Unstable distillates oxidise (most commonly under elevated temperatures and pressures), forming sand-like sediments which block injector nozzles, while gums become impregnated with inorganics (catalyst fines, metals, sediments), creating a grinding paste on small tolerance contact surfaces (fuel pumps, injectors, and so on).

Long chain paraffins present in many fractions of VLSFO are also responsible for wax formation in fuels. Injector blockages and separation failures indicate aged distillate material.

The major problem when blending VLSFO comes however with asphaltene stability. It is well known in the industry that, by blending different stocks, asphaltene stability will be impacted and finally asphaltene will associate into larger molecules and precipitate. Additionally, the paraffinic matrix of the VLSFO will make asphaltene naturally unstable as it will dilute the resins that keep asphaltene in solution. These larger asphaltenic molecules require more time and oxygen than is available within one combustion cycle to burn. These unburnt residuals deposit on liners and pistons in the combustion chamber; or burn later and contribute to poor ignition and airborne emissions.

Adding proprietary chemistries for chemically rebalancing the fuel and restoring stability is king for improving fuel performance and for avoiding all of the operating issues, as asphaltenes can be kept in solution and sustain inappropriate blending.

Both ship owners and fuel suppliers have no chance of controlling the blending in that a ship can bunker at any place in the world and the fuel makers receive their feeds from any place in the world.

The problem can therefore be addressed only by enhancing asphaltene stability in situ, either while bunkering or at the fuel supplier tank.

ITW has a long track record in asphaltene stabilisation, ranging from blending incompatible stocks to getting out-of-range values of sediments back on-spec by hot filtration, as well as dissolving precipitated asphaltene and coke-like materials.

Additionally, ITW has a long track record in reducing airborne emissions in engines and in power stations firing any type of fuel oil, including the ones with very high asphaltene content.

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

A known problem with fuel oils, including low sulphur fuel oils, is instability. In an unstable fuel oil, asphaltenes precipitate so the fuel oil will have solids present. Asphaltenes are a heavy (high molecular weight) component so are found in the heaviest hydrocarbons on a refinery; lighter streams (cutters) are used to blend with the heavy streams so that the resultant fuel oil meets the specification. Some hydrocarbon species have a tendency to precipitate asphaltenes whereas others will keep them in solution; generally speaking, the more paraffinic cutters are the more likely they are to precipitate asphaltenes, whereas the more aromatic they are the more likely that asphaltenes will stay in solution. Refiners will blend fuel oils such that they are stable, thus avoiding asphaltene deposition. However when fuel oils are mixed they can become unstable; the fuel oils are said to be incompatible.

Low sulphur fuel oils may have a tendency to be incompatible with each other as they may have more light material in them than higher sulphur specification marine fuel oils. This is because sulphur is more likely to be a constraining property than it is in higher sulphur fuel oils. Thus it becomes necessary to blend for sulphur as well as other parameters such as viscosity. A higher mass or volume of cutters may be used to achieve the sulphur specification than is the case in a higher sulphur fuel oil. These lighter materials may have a relatively high paraffin content (this is not always the case, there are some aromatic cutters such as FCC LCO) and thus be more likely to precipitate asphaltenes.

There are numerous tests that can be performed and algorithms that can be used to predict whether a fuel oil blend, or mix of blended fuel oils are likely to produce a stable or unstable fuel oil.

A **Jari Marci, Distillation and Thermal Conversion Expert, Petrogenium,** jari.marci@petrogenium.com

I assume that the performance issue is related to unstable blends of fuel oil, and thus to a total sediment potential exceeding the allowable limit of 0.1 wt%.

A very common approach to producing residual low sulphur fuel oil (LSFO), since the advent of IMO 2020, is to blend low sulphur vacuum residue with desulphurised gasoil. Such fuels are common on the market and are characterised by good stability (ASTM D7112) in terms of their P-value (P-value approx. 2.0-3.0). The P-value is a measure of the blend stability and a ratio of two parameters: P0 and FRMax.

P0 is the available aromaticity of the non-asphalthene phase, and FRMax is the required aromaticity of the asphalthene phase – so long as P0 > FRMax, the blend is stable and all asphalthenes are kept in solution. The individual components of P0 and FRMax could be, for example, 46 and 20 respectively. Furthermore, these oils have a low asphalthene content.

In the past and in some cases today, marine residual fuel is produced by processing of residue in a visbreaker. Visbreaking is a mild thermal conversion process by which the viscosity of a residue is substantially reduced. Producing fuel oil from thermally cracked residue still requires external diluent, but much less (-50%). One effect of the thermal conversion is that the P0 of the non-asphalthene phase is reduced, while the FRMax of the asphalthene phase is strongly increased.

When blending to fuel oil viscosity specification, the residual stability of such a blend can be as low as 1.1 with e.g. a P0=68 and a FRMax=62. Furthermore, these blends are high in asphalthene content. When blending LSFOs from straight run origin with LSFO made with thermally cracked material, the largely different FRMax of the individual components leads to instability.

By contrast, the FRMax is dominated by the cracked material, and the P0 is an intermediate value between the straight run and cracked component. Even with minor additions of cracked material, the blend becomes unstable and asphalthenes are rejected from the oil.

Fundamentally, there is no cure for this problem other than to identify the source and quality of different fuel oils and to keep them separate. Limiting the quantity of cracked base material to low levels (10-15%) may help and result in stable blends. This depends on the respective LSFOs properties. Dedicated blending tests or calculation (pending availability of stream stability data) can be conducted to determine stability limits and maximum allowed fraction of thermally cracked component.

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

Blending different fuels to make IMO 2020-compliant VLSFO blends can create unstable mixtures that cause sedimentation and sludge. Sedimentation can occur in these blends because paraffins are an antisolvent (or non-solvent) for highly aromatic asphaltenes. Sometimes the sedimentation is immediate, particularly if the blend components are highly incompatible, but often the sedimentation is much slower and may only be observed after a prolonged period of time or after exposure to external stress such as elevated temperatures.

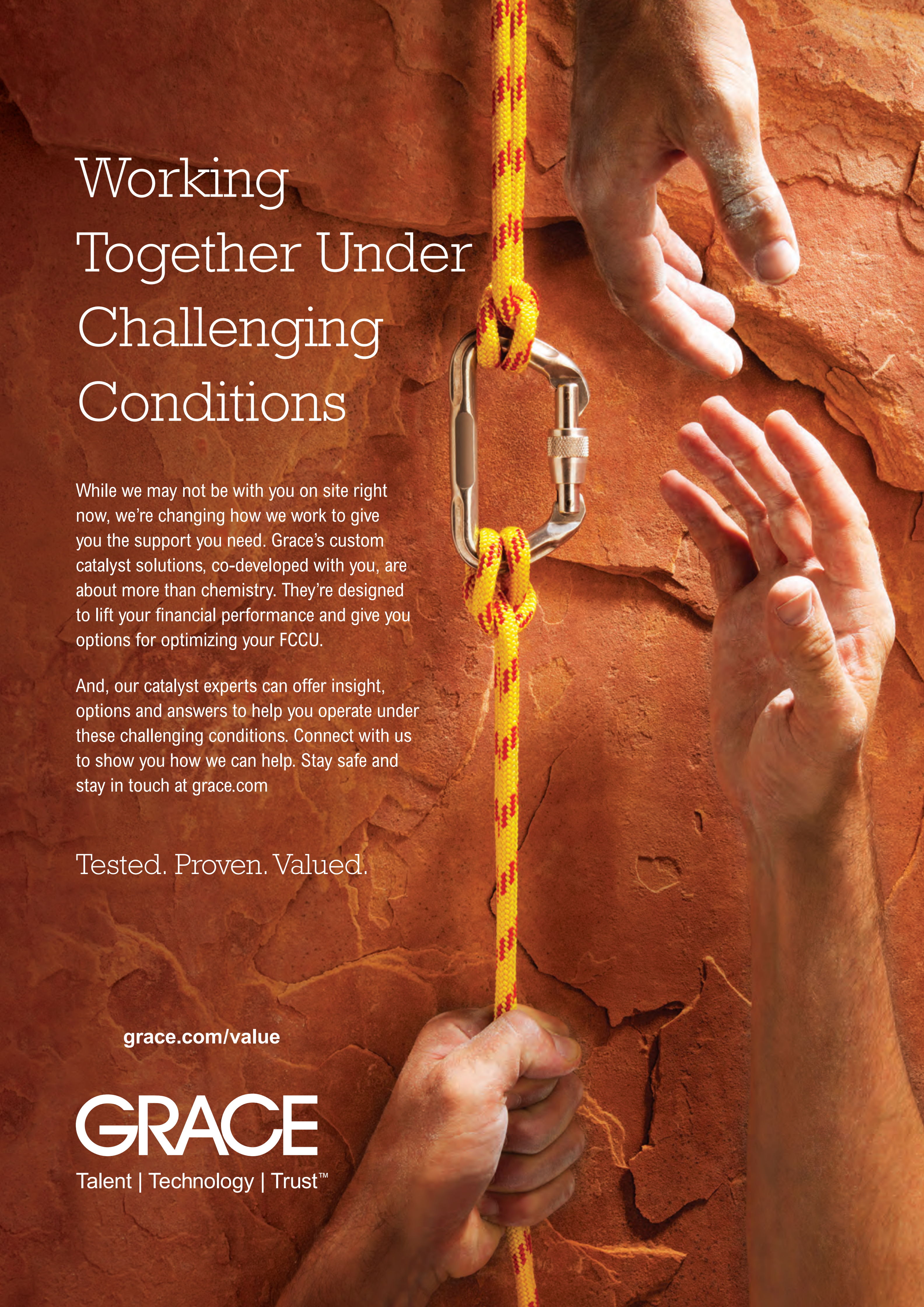
These challenges can be addressed by treating with Nalco Water additives that stabilise the asphaltenes in the final blend.

The principal function of the Nalco Water stability additives is to prevent flocculation and/or maintain the asphaltenes in a dispersed state in the fuel blend. By stabilising the asphaltenes in the blend, the additives will ultimately reduce the amount of sediment formed from otherwise incompatible or unstable VLSFO blends.

The stability of a blend and the potential need for a stability additive can be predicted with a proprietary Nalco Water blending model.

A **Mel Larson, Strategic Consulting Manager, Becht,** mlarson@becht.com

This may be more of an issue of the engine than the fuel. The historical marine engine was built and tuned for CCAI values of 850. In order to meet the lower sulphur VLSFO specification, less residua with less carbon content is being delivered as well as different viscosity. Each component in the bunker fuel blend should be assessed for compatibility as well. Globally, there has been an


Working Together Under Challenging Conditions
While we may not be with you on site right now, we're changing how we work to give you the support you need. Grace's custom catalyst solutions, co-developed with you, are about more than chemistry. They're designed to lift your financial performance and give you options for optimizing your FCCU.
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increase in light sweet crude consumption to meet the VLSFO specification. Light sweet and unconventional crudes tend to be more paraffinic in composition. The blending of highly paraffinic and conventional oils may result in precipitation either in the tank or throughout a system lacking a homogenous fuel to the engine.

Q What are the likely causes of and solutions for severe fouling in a vacuum unit's preheat section?

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

Fouling in vacuum unit preheat trains is often associated with the higher temperature section of the preheat train though not exclusively so. There are numerous potential causes of fouling. Some of these are:

- Low velocities can lead to fouling. These are often addressed by design changes to either the exchanger internals or by changing the arrangement of the exchanger (e.g. from parallel to series).
- Corrosion deposits can cause fouling.
- Heavy cracked slop oil can end up in the vacuum unit, particularly if there is a risk of oxygen contamination (for instance being stored in un-blanketed tanks). These are often better processed in a unit that has cracked streams such as a visbreaker or FCC. Alternatively, blanketing the tanks they are stored in can reduce the risk of fouling. Some refiners have had success with oxygen scavengers.
- Asphaltene deposition can occur in the vacuum unit preheat train.
- Inadequate desalting can lead to fouling, often because solids are not effectively removed. If the vacuum units are fed only with atmospheric residue from the refinery's crude unit, this is more likely to be problematic in the crude unit. If the vacuum unit is fed with imported residue then either consider desalting it or, if it is desalted, then review the desalter operation.

Analysis of the deposits helps in identifying the problem and the solutions to alleviate them. Antifoulants and/or corrosion inhibitors may help and there are commercially available programmes, such as KBC's HX monitor, for heat exchanger monitoring, advice on which exchangers to clean, and estimating the cost of the fouling (such as increased energy consumption and CO_2 emissions, yield reduction, and throughput reduction). All these will help decide how much investigation is warranted and in justifying remedial action.

A Jérémy Provost, Senior Technology Expert, Process & Technologies Division, Technip Energies, Jeremy.Provost@technipenergies.com

There are few severe fouling root causes in a vacuum unit's preheat section. Their relative impacts depend mainly on the refinery's strategy and objective (processing Middle East crude oils, heavy Canadian blendings, capture opportunity crudes on the market, and so on). These choices help determine the operation, (required flexibility) of the preheat train and its design. Nevertheless, the main causes which lead to severe fouling are identified below.

Severe fouling in a vacuum unit's preheat section is generally linked to asphaltene precipitation and even coking. This phenomenon is strongly governed by product temperature. Too high a wall temperature in a heat exchanger of the preheat train will be prone to fouling development. This can later spread through the whole train by reducing heat transfer. For instance, too cold a desalter inlet temperature, resulting from a poor performing and fouled cold train part, will jeopardise the desalter performance and result in a higher corrosion risk in the hot train part. A similar performance cut in the hot train part will impact consumption of the fired heater prior to the distillation column as well.

In the early 2010s, Technip Energies, in partnership with Total and CEA, co-developed a dedicated test loop named BEECH (Fouling Exchanger Test Loop in French). Several measurement campaigns and studies have been performed showing the importance of wall temperature, shear stress, and heat exchanger design on the fouling mechanisms in a preheat train. The main outcomes to limit fouling development are:

- Reduce the wall temperatures as low as possible by promoting a high heat transfer coefficient on the cold fluid side.
- Maximise shear stresses at the wall on both exchanger sides to limit deposits and improve heat transfer coefficients. This can be done by combining high regime flow rates (for instance, above 2.0 m/s on the tube side) with well-chosen and proven turbulence promoter heat transfer solutions (grooves or corrugations on walls, inserts).
- Pressure drop should not be a 'target' but a 'consequence': Designs with higher energy consumption, using a more powerful pump will be paid back by a limited fouling development and hence a longer production lifetime.
- Manage pressure drop on the whole train and not item by item; pressure drop must be expended where it is needed.
- Avoid excess area applying standard fouling resistance design method and prefer a margin based method where a limited heat transfer area is allocated to manage fouling. When using resistance based design, up to 85% of the heat transfer area can be dedicated, from the design phase, only to manage future fouling. In general, this results in very low velocities, leading to lower heat transfer coefficients and higher tube wall temperatures, accelerating fouling development.
- Whatever the selected heat exchanger technology is, always take care of flow distribution in all the parts and avoid dead zone areas and bypass flows. These are starting points for fouling development. For instance, when designing a shell and tube heat exchanger, careful attention is given to the shell side to limit bypass and dead zone areas with relevant baffle type selection and arrangement.

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

The vacuum unit separates the heavier crude oil fractions to decrease the boiling temperatures with a lowering of the pressure. The boiling points are so high that thermal cracking would occur under atmospheric distillation.

Many experienced specialists are working on vacuum heater designs and revamps to improve the efficiency with less coke fouling. Vacuum heaters are typically cabin or box type heaters with four or six passes in a single radiant cell. Maximising the convection section duty will decrease the radiant section duty, which reduces the coke formation potential. The localised oil film temperature and oil residence time in the radiant section depend on the heat flux, tube mass flux rates, and bulk oil temperature. They are variables to minimise the rate of coking.

Some crude oils are less stable than others and have a poor thermal stability. Asphaltenes, maltenes, waxes, and resins are components that change the behaviour and structure with temperature, pressure, and the composition of crude oil. Asphaltenes are very sensitive to shearing forces and electrostatic interactions, which is why vacuum units are often affected by asphaltene fouling and coking. Crude oils with poor thermal stability begin to generate coke and gas at relatively low temperatures. Crude unit heaters with a high outlet temperature and high residence time in the crude column bottom decrease the oil stability with rapid coke and gas formation. Minimising the oil film temperature and oil residence time will help to decrease the potential for coke formation, which improves the run length of the heater.

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

There can be multiple reasons for this. If the preheat is continuously fouling it may be a design issue related to exchanger design or configuration. The fouling can also be related to crude blending, type of crudes processed, impurities or contaminants content such as solids and salts, desalter operation, and caustic addition. The use of intermediate storage of atmospheric residue and blending of other streams or imported materials can have a big impact and needs to be evaluated. Key is to have a good model of the heat exchanger train that can track the performance of the whole train by NFIT and of each individual exchanger such as Nalco Water's Monitor. This can help to correlate fouling events with feed composition and operational conditions. It is also important to have a good analytical programme in place to trend feed stability, composition and contaminant content. This, together with analyses of fouling material, can help determine the root cause and develop a mitigation strategy. The mitigation can be by elimination of problem crudes, improved contaminant removal in the desalters, and controlled blending for increased stability. This can be combined with the use of a properly selected antifoulant, such as Nalco Water's Thermogain which deals with the identified fouling mechanism.

A Mel Larson, Strategic Consulting Manager, Becht, mlarson@becht.com

This is a bit of an unusual question as most vacuum columns are fed directly from the atmospheric column. A 'pre-heat' section would indicate a standalone vacuum column before the furnace. On the feed side of a preheat system would be potential oxygen contamination and interactions of compounds that result in precipitation either in a tank or as the solution is heated with an increased propensity for precipitation. The challenge on the passing effluent stream in preheat service is the temperature difference between the passing fluids and the resulting tube wall temperatures. On the bottoms side of heat exchange, the tube wall engagement will be 'cooler' rising to a higher potential of 'adherence' to a surface and or cooling rapidly enough so as to enhance a precipitate dropping out (some call this asphaltenes, however it can be any maltene structure). The challenge in these services is to accurately identify the cause. Considering this may be an interaction that causes some type of precipitate formation, find an appropriate solvent that can keep the system flowing and in solution. In very severe services it is justifiable to install spare standby exchangers with rotation of cleaning and service to minimise the lost revenue from outages. Others have found that some chemical additives work, but careful consideration is required as to the impact on any downstream systems.

Q What is the optimum level of excess air in a natural draft heater?

A John Skelland, Senior Staff Consultant, KBC (A Yokogawa Company), John.Skelland@KBC.global

Aim to operate the heater at its original design excess air level in the first instance. A good performance in modern heaters is 10% excess air (2% oxygen in the flue gas) for heaters fired with fuel gas. Fuel oil fired heaters usually require 15% excess air (about 3% stack oxygen). This is often due to fuel oil burners being slightly more difficult to tune and operate. Operating at these low levels is made easier if automatic control is installed rather than relying on frequent attention from the operators.

It is sometimes possible to safely operate fired heaters at stack oxygen contents as low as 1% (~6% excess air) if an advanced control system such as Yokogawa's Combustion One is installed. This system, incorporating tunable diode laser spectroscopy (TDLS), gives fully automatic control and optimisation of the combustion process. It measures oxygen, carbon monoxide, and methane concentrations in the flue gas to prevent the risk of unstable combustion.

A Edwin Voeten, Furnace & Combustion Expert, Petrogenium, Edwin.voeten@petrogenium.com

Optimal value excess air should be evaluated on a case-by-case basis. However, as a design case 3 vol% O_2 in flue gas is typically used, which corresponds to some 15% excess air over the stoichiometric requirement.

The use of a forced draft fan is done for technical, economic, and/or historical reasons.

The incentive to lower excess air is economics. As a guideline, some 1% fuel efficiency can be gained for every 2 vol% of O_2 reduction in flue gas. Excess air is easier to control by use of a forced draft fan (together with other benefits from a forced draft arrangement). However, this requires additional capex.

Consequentially, a forced draft arrangement is typically used in larger heaters.

In a natural draft heater, for every process change or upset an operator may need to make changes to individual burner air registers in the field (and draft control/stack damper as well). Significantly, there may be an incentive to move towards forced draft where operation is expected to be less stable. Alternatively, in a natural draft unit a wider margin in excess air (a higher value than the design value) can be used to minimise the risk of sub-stoichiometric firing from any operational changes or upsets. This then has an economic penalty (see the numbers above).

As a result, it is not uncommon to see a natural draft unit in the field operate in the 4-5 vol% O_2 range, or higher. Although I should mention that this often is a consequence of operational staff having 'other priorities' and improvements are feasible.

Note that this refers to gas fired natural draft units, which is the standard. I know of less than a handful of oil fired natural draft units (in Turkey, Kazakhstan, and Russia). Such units should not have been designed with the combination of fuel oil and natural draft, as this is a continuous source of trouble. Last thing I heard, the unit in Turkey was to be converted to forced draft.

A Grant Jacobson, Division Manager, Fired Heater Services, Becht, gjacobson@becht.com

It depends on the heater design and operating objectives. For most applications, optimised excess air (or excess oxygen if discussing on just an O_2 basis) can be set between 15% and 25%. To confirm where this can be optimised safely it is important to conduct a CO breakthrough test and then set the optimisation targets based on where CO breakthrough is observed. An example of this would be if CO breakthrough occurs at 1.5% excess O_2; the target to operate normally would be set at 3.0-4.0% excess O_2. It is critical to not lose sight of keeping fired equipment stable and safe, and optimising to reasonable targets when able to do so.

Q What options are there for CO_2 capture from a SMR based hydrogen unit?

A Clément Salais, Associate Group Manager, Gas Business Group, Axens, clement.salais@axens.net

In a typical steam methane reforming (SMR) unit designed to produce high purity hydrogen, methane reacts with steam in a dedicated heater to produce a converted syngas which, after CO shift, contains mainly hydrogen and CO_2. The syngas is then purified through a PSA to produce hydrogen at 99.9% purity and a purge gas that contains CO_2, CO, and some hydrogen. This purge gas is routed back as a fuel to the SMR furnace. The SMR furnace produces a flue gas containing all of the CO_2 emitted by the SMR unit.

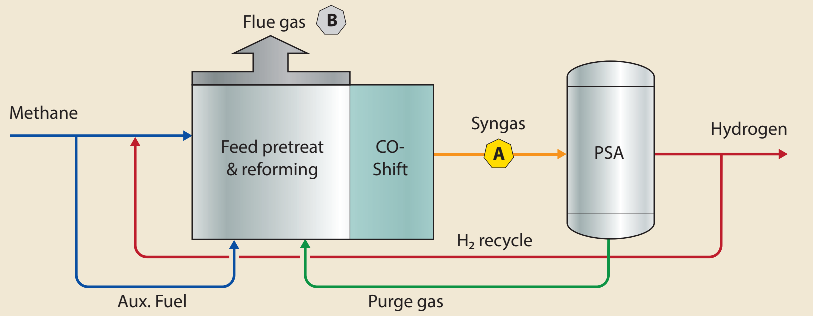
There are two main locations at which CO_2 can be captured: either the converted syngas identified as location A or the flue gas identified as location B in **Figure 1**. CO_2 absorption from syngas is much more favourable as it is at high pressure and there is consequently a large driving force to absorb CO_2. The syngas is quite pure and does not contain any oxygen but it contains only part of the CO_2 emitted by the SMR unit (up to 60% depending on the scheme and operating conditions).

Adversely, the flue gas contains all of the CO_2 emitted by the SMR and up to 90% of the CO_2 emitted can be absorbed there. But the flue gas conditions are harsh: low pressure, high temperature, and a few per cent O_2 in the gas.

In terms of technology, a typical amine based acid gas removal unit with activated MDEA can be used to absorb all of the CO_2 in syngas (up to 99%). Steam energy consumption can be reduced to about 1 GJ/t of CO_2 with an optimised process scheme which avoids about 57% of the CO_2 emissions of the SMR unit. The avoided CO_2 readily takes into consideration emissions of CO_2 due to energy consumption in the carbon capture unit. This gives a better insight into the amount of CO_2 that is effectively recovered in the overall process.

CO_2 emissions of a SMR unit can be significantly reduced by installing mature technology such as Advamine EnergizedMDEA technology which is licensed by Axens for syngas.

On the other hand, solvent based post-combustion carbon capture processes that are required to capture the CO_2 in flue gas are much more energy demanding. The steam energy consumption of a first generation carbon capture process such as a MEA solvent based process is up to 3.7 GJ/t of CO_2. The amount of CO_2 avoided is, as a consequence, only 67% considering the additional CO_2 emitted to regenerate the solvent. Post-combustion carbon capture from flue gas enables further reduction of CO_2 emissions from the SMR unit but requires the development of new solvents and new processes to be more energy effective.



	A Syngas	B Flue gases
Inlet gas pressure	30 bar	atm
Inlet gas CO_2 content	17.3%	18%
Inlet gas CO_2 partial pressure	5.2 bar	0.18 bar
O_2 in the inlet gas	No -traces	Few %
CO_2 captured on SMR	60%	90%

Figure 1 Steam methane reforming: where to capture CO_2?

Performance of post-combustion carbon capture processes			
	A	B	B
Technology for CO_2 capture	Syngas AdvAmine	Flue gases MEA process	Flue gases DMX process
Typical energy requirement (GJ/t CO_2)	1.0-2.5	3.7	2.9
CO_2 'avoided' in SMR, %	57.0[1]	67.0	72.0

1 Considering 1 GJ/t CO_2 as the energy requirement

Table 1

Axens is currently developing, with IFP Energies nouvelles, a new process for post-combustion carbon capture called the DMX process that is much less energy intensive than first generation processes. It is a solvent based technology but with a new solvent that has specific demixing capabilities under certain conditions of pressure and temperature. The energy consumption of the DMX process can be reduced to 2.3-2.9 GJ/t CO_2 compared to the 3.7 GJ/t CO_2 of the MEA process, leading to further reduction of CO_2 emissions from the SMR unit as the CO_2 avoided increases to 72% (see **Table 1**).

Its performance is proven at laboratory scale but needs to be demonstrated industrially in order to be ready for commercialisation. This demonstration is in progress through the 3D Project funded by the European Union (H2020 - Grant Agreement N°838031). It includes the construction of a demonstration unit at the ArcelorMittal Steel Mill in Dunkirk, France which is already in progress. Operation of the unit will begin in early 2022.

A **Elena Petriaeva, Technical Marketing Manager Middle East/Central Asia, BASF OASE Gas Treatment Excellence,** elena.petriaeva@basf.com; **Bernhard Geis, Industry Manager Europe/Africa/Russia, BASF OASE Gas Treatment Excellence,** bernhard.geis@basf.com

To meet the emission reduction targets required by 2050 under the Climate Change Act, energy sources will need to shift to an almost entirely carbon-free energy. That points to a larger role for hydrogen, which can be produced in low-carbon ways from electricity or with carbon capture and storage (CCS).

Syngas, a mixture of hydrogen and carbon monoxide (H_2 and CO), is produced on a large scale via steam reforming of natural gas and water. In the steam reforming process, carbon dioxide (CO_2) is produced as a by-product and emitted from two different sources: as part of flue gas and as part of process gas.

BASF's OASE white is a proven amine scrubbing technology for deep CO_2 removal from syngas and offers great energy efficiency and robust operation, achieving the minimum targeted process gas CO_2 capture rate of up to 99.97 mass%. The treated syngas can be further separated into H_2 and CO to be used as a key raw material for various products. OASE white technology has been successfully applied in many world scale ammonia plants, syngas plants for petrochemicals, and others such as steel production (see **Figure 1**).

Moving forward, the use of pure hydrogen (H_2) can support cleaner fuel for vehicles, whereas the high purity CO_2 captured by OASE white can support direct carbon capture and utilisation (CCU) to manufacture chemical products on a commercial scale. CCS is also possible.

For flue gas carbon capture, OASE blue technology was developed specifically as an optimised post-combustion capture technology with low energy consumption, low solvent losses, and a highly flexible operating range.

A core task for the design of carbon capture technology is to reduce solvent loss by reason of economic efficiency and environmental friendliness. The development programme of BASF with OASE blue for flue gas CO_2 emissions capture and OASE white for process gas CO_2 emissions capture is demonstrating that, by combining two effective technologies, the target of lowest CO_2 footprint overall is possible.

A **Ulrich Koss, Syngas & Syngas Conversion Expert, Petrogenium,** ulrich.koss@petrogenium.com

In a refinery, steam methane reforming (SMR) based hydrogen production represents one of the most prominent single-point sources of CO_2 emissions. It consists of three consecutive process steps. In the steam reformer, a mixture of natural gas and steam is 'reformed', which

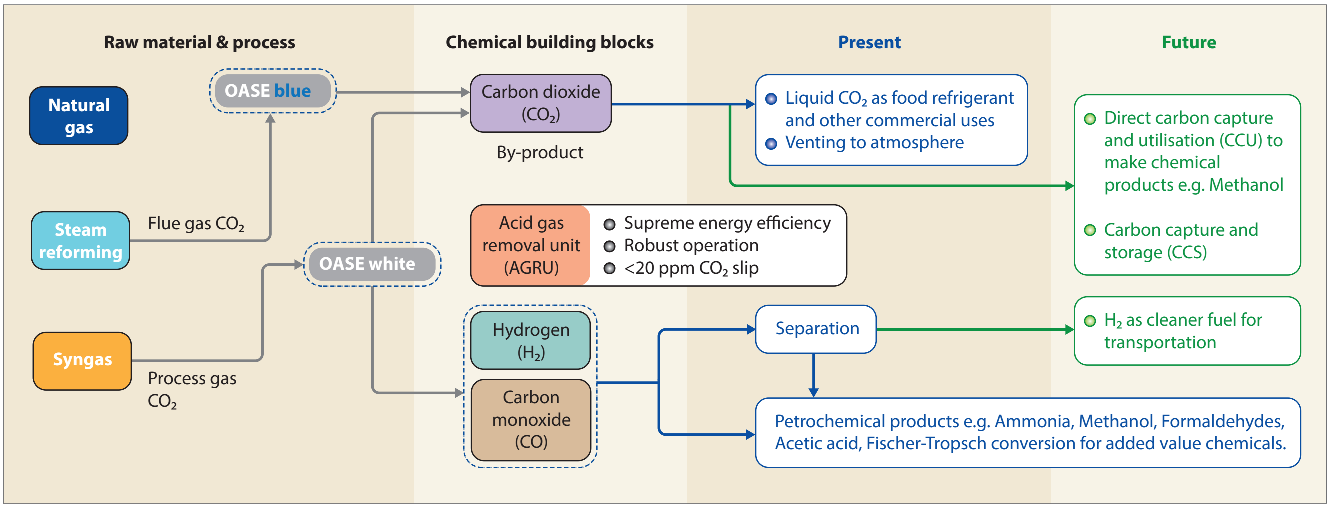


Figure 1 Applications of OASE white amine scrubbing technology

means it is converted to syngas – a mixture of H_2, CO, and CO_2. The reforming reaction is strongly endothermic and consumes a lot of heat, which is provided by combusting gas in the furnace of the SMR.

In the downstream reactor, the water gas shift (WGS) reaction converts CO and steam contained in the syngas to additional H_2 and CO_2. Third, a pressure swing adsorption (PSA) is used to separate a pure H_2 product from the converted syngas. The PSA accumulates all other components in an off-gas stream, consisting mainly of CO_2 but also containing unconverted CH_4, CO, and some H_2. This gas is added to the fuel to the SMR burners. Thus, all carbon contained ultimately ends up as CO_2 in the SMR flue gas. The aim is to upgrade this 'grey' H_2 production a to a 'blue' one, by adding carbon capture.

A first option is to add post-combustion CO_2 capture in the SMR flue gas path. This solution is successfully applied to fertilizer production, where natural gas is converted into H_2, then ammonia, and ultimately urea. For converting all ammonia into urea, more CO_2 is needed and can be extracted from the syngas. To close this gap, a handful of these plants source additional CO_2, extracting it from the flue gas of their SMRs using amine post-combustion capture technology. Oxygen and NOx present in the flue gas require amine technology specifically adapted to such service, to keep emissions, corrosion, and amine degradation under control. Most references use Mitsubishi's KS-1 technology. Other technologies available are BASF´s OASE blue, Aker's CleanCarbon, DOW's UCARSOL FGC3000, Fluor´s Econamine FG or Shell´s Cansolv. All consume considerable amounts of steam. Amine degradation and emission control so far have been a persistent problem and a relevant cost factor.

A second option is to add a compact amine wash between WGS and PSA. Such syngas amine wash selectively extracts all CO_2 upstream of the PSA, yielding a pure CO_2 stream and a CO_2-free PSA off-gas. Here, the well-referenced 'working horses' of gas clean-up are applied, among them BASF´s aMDEA, Dow´s UCARSOL, etc. This strategy is far more economical and easier to operate than the above post-combustion capture. The downside is that only the 'low hanging fruits', the CO_2 in the syngas, are captured. This is whilst the CO_2 generated in the SMR firing remains emitted, delimiting the capture rate to 60%. Higher rates are possible if the SMR is converted to H_2-firing. However, such a strategy will massively derate the SMR´s capacity, as it must produce the H_2 fuel additionally to the H_2 product.

Small-scale, electrically heated SMR (eSMR) technology exists, offering a hybrid between natural gas and electricity. Future large-scale eSMRs, implemented together with the syngas amine wash, boost the capture rate but require an alternative outlet for the PSA off-gas.

A third option is to apply oxy-firing, which basically means replacing N_2 in the combustion air by recirculated CO_2. Doing so, the flue gas will largely consist of CO_2 and water. After water condensing, the CO_2 remaining is purified and compressed. The principle is simple but requires an air separation unit (ASU), a quite sophisticated tail gas treatment, and a substantial revision of the SMR firing and safety concepts. To keep the combustion temperature reasonably low, the amount of CO_2 internally recirculated is 4-5 times larger than the amount finally captured.

Other (non-SMR):

If a new, large-scale blue H_2 production is planned, a different concept can be applied: in such a case, an ATR-solution is considered the optimum. Here, the SMR is replaced by a high pressure O_2-driven autothermal reformer (HP ATR), which does not require external firing. The converted syngas of this system offers a high CO_2 concentration at a high pressure. CO_2 extraction can be accomplished very efficiently not only by the 'working horse' amines but also using a simple cold methanol absorption/flashing loop. ATR technology is available from ThyssenKrupp Industrial Solutions, Air Liquide, Haldor Topsoe, and others. It requires an ASU to produce the O_2 for the ATR.

A newcomer among the technologies for the CO_2 emission-free production of H_2 from natural gas is the production of 'turquoise' H_2 by means of methane pyrolysis. Here, the natural gas is directly de-composed to H_2 and carbon black solids, where the latter can be used as a feedstock in tyre production or in any other industry consuming carbon black. The technology is being developed by BASF, Linde, and ThyssenKrupp Industrial Solutions, but it is not yet fully commercial.

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

CO_2 can be captured from SMRs at different locations and using different technologies. Nearly all installations use amine solutions as the technology to capture CO_2 and we are aware of one large scale cryogenic CO_2 capture plant.

In SMRs most CO_2 is generated at the process side, not by burning fuel in the reformer furnace. Therefore, it is possible to capture most CO_2 'pre-combustion' after the shift reaction step, prior to the PSA and the furnace. This has the advantage that pressure (and therefore driving force for amine capture) is high, which considerably reduces capital cost and plot space. However, it will not allow one to capture all CO_2 generated on the unit (even if capture would be 100% efficient) because CO_2 generated by the fuel of the furnace is generated after capture. Pre-combustion capture will enable capturing 5-6 tonnes of CO_2 per tonne of hydrogen produced while the total CO_2 emissions of the unit are at least 8 tonnes per tonne of hydrogen output.

Post-combustion capture of the CO_2 from the SMR furnace flue gas also has the advantage that it is a tail-end solution which in many cases will be easier to fit in. But it will be larger in size and require more capital investment. In short, the choice between pre- and post-combustion is the result of a trade-off between a number of advantages and disadvantages, the main ones being the investment cost and the amount of carbon captured.

A Mel Larson, Strategic Consulting Manager, Becht, mlarson@becht.com

Most modern SMRs have a means of hydrogen purification, commonly now it is either pressure swing absorp-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Crystaphase
Here's an idea: Let's get more out of your reactor.
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tion and or a prism system. The effluent or reject stream will be rich in CO_2 (40-45 mol%). This stream is the candidate to be processed further either with cryogenic or solvent systems to concentrate the CO_2. The concentrated CO_2 can be used for enhanced oil recovery. New technologies are being developed to consider absorption systems although not many have been taken to the commercial scale yet.

A **Sanjiv Ratan, Consulting Director, Zoneflow Reactor Technologies,** SRatan@zoneflowtech.com

For capture from a SMR based hydrogen unit, there are principally two CO_2 containing streams - the shifted process gas and the combustion flue gas. Typically, in a hydrogen plant, the CO_2 content of the shifted gas is separated (along with other components) in the PSA unit in the form of its low-pressure purge gas. The purge gas is usually utilised as primary fuel for SMR firing, which caters for the larger part of the SMR fired duty, and the remaining heat release is provided by the make-up fuel (also for firing control).

Accordingly, the flue gas ends up with the combined CO_2 from the hydrocarbon feed as well as make-up fuel.

Such a process configuration offers three options for CO_2 capture:

1. From process gas upstream of the PSA unit
2. From PSA purge gas
3. From combustion flue gas

Options 1 and 2 are pre-combustion CO_2 capture alternatives but only offer partial capture (typically around two thirds of the total load) whereas option 3 can be combined with options 1 or 2 or just by itself as post-combustion capture for higher CO_2 removal. Each option has its pros and cons.

Option 1 is the simplest, most cost-effective, and most proven in terms of solvent based CO_2 removal processes applied at process pressure on clean gas. It can be integrated in a new hydrogen plant as well as in a revamp project. The PSA purge gas volume reduces while its calorific value increases, which increases NOx in the flue gas. The flue gas volume reduces on account of a lower volume of purge gas as well as some make-up fuel savings in lieu of avoiding heating up the removed CO_2. Accordingly, the export steam quantity also goes down.

Option 2, though seldomly considered, may have more relevance for CO_2 removal retrofits in existing hydrogen plants since it has no impact on the performance and/or adsorbent adaptation of the existing PSA unit. However, it needs pressure boosting to overcome the pressure drop and involves higher energy consumption for CO_2 removal due to much lower CO_2 partial pressures. In new plants, a PSA design can be optimised for higher purge pressures versus reduced H_2 recovery. The effect on the material and heat balance is similar to option 1 for the same CO_2 removed.

Option 3, like any fired unit CO_2 capture, suffers from limited available and/or well proven technologies, apart from the capital and energy intensity of any post-combustion capture.

The choice and economics of CO_2 capture in a SMR-based hydrogen plant are usually driven by the target percentage reduction in emissions based on any CO_2 credit (for EOR or as by-product), or regulatory requirements and related credits or taxation going forward.

Q **Please explain the best approach to cutting NOx emissions from a gas turbine.**

A **Jan Zander, Energy Systems & Utilities Expert, Petrogenium,** jan.zander@petrogenium.com

A new gas turbine should have proven low NOx burners (nothing new here). Some attention should be given to the low NOx technology if a partial load of the gas turbine is required (such as in Oman LNG). For existing gas turbines it might be possible to retrofit low NOx burners. In extreme cases, steam injection may be required to reduce NOx. Water injection has been applied on gas turbines in refineries, but may cause higher maintenance costs (burners and blades).

A **Paul den Held, Rotating Equipment expert, Petrogenium,** paul.den.held@petrogenium.com

As an introduction, the NOx in the gas turbine combustion system is formed by the following three mechanisms:

1. Thermal NOx: this is formed during fuel combustion by oxidation of molecular nitrogen (N_2) in the combustion air. The formation of thermal NOx is highly dependent on the gas temperature.
2. Prompt NOx: radicals like CH and CH_3 can attack free N_2 in the air to form NOx.
3. Fuel NOx is produced by oxidation of nitrogen compounds contained in the fuel (up to 2% of the total NOx formed in the combustor).

Two key parameters are normally used to characterise the thermal NOx production during gas turbine combustion: equivalence ratio (fuel to air ratio) and adiabatic flame temperature. The relationship between the thermal NOx production and these two parameters is provided in **Figure 1**.

Selection of the appropriate NOx abatement design and the best approach for the gas turbine to reduce NOx depends on a number of factors:

1. Type of combustion system available, refit or new design
2. Type of fuel gas to be applied in the gas turbine
3. Diluent available (steam, water or nitrogen)
4. NOx limit requirements at the specific location
5. Manufacturers references on the typical fuel and fuel gas system

There are different primary NOx abatement options.

Conventional combustion systems

For a gas turbine using mainly natural gas as the fuel source and equipped with a conventional combustion system, the NOx abatement options are to apply a diluent and select either water injection or steam injection.

Each of these options has its specific issues. These include the impact on the maintenance factor, the reduced lifetime of the parts, and an obvious continuous loss of water or steam. This technique is applied on many gas turbines in operation that are not equipped yet with the dry low NOx systems. The diluent is applied

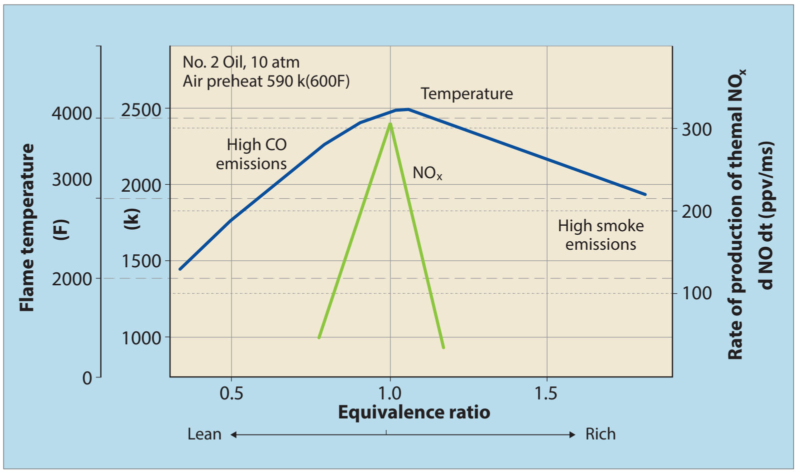

Figure 1 Equivalence (fuel to air) ratio and adiabatic flame temperature in thermal NOx production

to reduce the flame temperature and thereby reduce the NOx produced.

The application of a diluent needs certainly to be considered for gas turbines operating on low-Btu type fuels, syngas types of fuel gases with a high content of hydrogen and CO_2, and for coal gasification applications. For such fuel gas applications, the DLN systems may not be offered by the manufacturers. Petrogenium can offer experience in the evaluation of the designs offered by the manufacturers.

Dry low NOx combustion systems

Dry low NOx (DLN) combustion systems are significantly more expensive (hardware costs are 30-40% more) than the standard combustor, and require a more complex staged fuel gas system and more intrinsically complex fuel gas nozzles. Since NOx production increases exponentially with high adiabatic flame temperatures, the NOx abatement technologies focus on reducing the peak flame temperatures. This however conflicts with the desire to have higher firing temperatures required to achieve turbine efficiency. Modern DLN combustors manage this conflict by designing combustors that can have lower peak flame temperatures whilst keeping the same firing temperatures. Combustion near stoichiometric conditions (equivalence ratio = 1) increases NOx production. Therefore DLN combustors are designed around 0.5 equivalence ratio. This, however, brings challenges, as combustors operating at this equivalence ratio often face risks of lean blow out (flame extinction). Current gas turbine manufacturers each offer their specific DLN combustion systems.

Catalytic combustor (future systems)

The catalytic combustor is still in the 'proof-of-concept' phase and requires substantial efforts before it is offered by manufacturers. Realistically speaking, it will be another 5-10 years or more before it would be commercially available for heavy duty gas turbines.

Secondary NOx abatement options

Selective catalytic reduction works on the principle of removing NOx from the gas turbine exhaust utilising, say, ammonia injection and a SCR catalyst that converts NOx to molecular nitrogen. This system is only considered in the case of DLN combustion systems and the selection of a required diluent is not an option. The SCR has some distinct limitations.

In summary, the best approach to reducing NOx emissions from the gas turbine depends on the NOx emission levels to be achieved, the gas turbine hardware currently installed, the application of the gas turbine, diluents available and the type of fuel gas used for the combustion.

A John Skelland, Senior Staff Consultant, KBC (A Yokogawa Company), John.Skelland@KBC.global

NOx emissions can be reduced by injecting a small amount of water or steam into the combustion zone, known as wet low emission technology (WLE). This reduces the temperature in the combustion zone which reduces the rate of NOx production. However, this water or steam injection is a thermodynamic loss and so reduces the energy efficiency of the gas turbine. This technique also requires a supply of boiler feed water or steam to be provided. The technique has historically been the most common retrofit to existing gas turbines.

Alternatives to steam or water injection include:

- Dry low NOx combustion (DLN), a technology that uses staged combustion and lean premixed fuel/air mixtures. This requires that the gas turbine has several combustors rather than a single combustor. It is very effective in maintaining low NOx over the entire operating range. However, maintenance costs are generally higher than for a standard gas turbine and the control system is more complex. DLN upgrades are available as retrofits to some gas turbine models.
- Catalytic combustion: the turbine combines catalytic combustion of fuel and air in a catalyst bed followed by normal fuel combustion at a low enough temperature to prevent significant NOx formation. This technology is in the early stages of commercialisation.
- Post-combustion exhaust gas clean-up systems including selective catalytic reduction (SCR): this type of technology requires the use of NOx reducing chemicals (such as ammonia) in the presence of a catalyst. The advantages of this option include relatively low capital investment, a small footprint, and no need for modification to the gas turbine itself. However, operational expenses are high due to the cost of replacement catalyst. Also, the use of hazardous chemicals such as ammonia is required. This technology can usually be installed as a retrofit to existing gas turbines.

Of these, DLN is the most commonly used technology. DLN and SCR can be combined where really low NOx emissions are required.

A Greg Zoll, Manager, Power Generation Plant Services, Becht, gzoll@becht.com

The technology utilised for gas turbine NOx reduction is well proven. It is almost universally achieved by use of selective catalytic reduction (SCR) which utilises a vanadium catalyst to reduce NOx to N_2 and water. Ammonia is injected ahead of the catalyst as the reductant. For gas turbines operating in combined cycle applications, the SCR is embedded in the heat recovery steam generator to achieve the correct exhaust gas temperature. In simple cycle installations, cooling air is injected into the gas turbine exhaust ahead of the SCR. Alternatively, high temperature catalysts have been developed to eliminate or reduce the amount of cooing air required.

Q What is the most effective way to capture particulates in FCC flue gas?

A Raj Singh, High Olefins FCC Technology Manager, Technip Energies, Raj.singh@technipenergies.com; **Steve Shimoda, FCC Technology Director, Technip Energies,** Steve.shimoda@technipenergies.com

Today, refiners are taking a number of steps to reduce emissions across their operations to lower the environmental impact. FCC regenerators are the largest single source of particulate emissions in refineries. Capturing catalyst particles from flue gas is accomplished through a combination of equipment. The primary equipment utilised are regenerator cyclones. The catalyst losses from a FCC regenerator are generally in a range of 250- 450 mg/Nm^3.

The selection of equipment downstream of the regenerator depends on additional objectives besides the capture of catalyst fines. Typically, a third stage separator (TSS) provides a further reduction of catalyst in the flue gas. This is critical for units that include a turboexpander for power recovery. Depending on the underflow capture device, the TSS system can bring the catalyst loading to less than 150 mg/Nm^3 for a underflow cyclone, or 100 mg/Nm^3 for an underflow filter.

To get below 50 mg/Nm^3, either an electrostatic precipitator (ESP) or a flue gas scrubber is used. A flue gas scrubber (FGS) can also reduce SOx emissions. However, scrubbers require water, which can be a challenge for certain locations, although they do alleviate the safety concerns that have been associated with ESP use during transient operation.

An alternative to the ESP and FGS is a full flow barrier filter. These are offered by a couple of suppliers and have demonstrated the capability to reduce particulates to less than 5 mg/Nm^3. There are not many installations, but at least one has been in operation for over 15 years.

The barrier filter has demonstrated to obtain the lowest particle emissions (see **Table 1**). But, to properly answer the question of what is the "most effective", requires an examination of other parameters such as:

- What are the target emissions?
- What other contaminants need to be removed?
- What utilities are available?
- What is the available plot space?
- What is the importance of capital cost versus operating costs?

Summary of typical particulate emissions

Equipment	Effluent particle loading, mg/Nm^3
Regenerator cyclones	250-450
TSS with underflow cyclone	<150
TSS with underflow filter	<100
ESP	<50
Flue gas scrubber	<50
Barrier filter	<5

Table 1

A Mel Larson, Strategic Consulting Manager, Becht, mlarson@becht.com

The industry has two basic systems that maximise particulate removal from the FCC flue gas. In the US the EPA expanded the definition of particulate from catalyst by adding condensable particulates. This answer will concentrate on the catalyst element. The systems can be divided into wet and dry. A wet system is a flue gas scrubber where the flue is passed through a venturi chamber that has a solution which will trap catalyst, react with SOx, and make a slurry solution that can be used for other purposes. Scrubber systems often have a third stage catalyst separation system before the scrubber to assist recovery of catalyst.

A dry system is most often but not always a two stage system of third stage multiple cyclone separation followed by a electrostatic precipitator (ESP). The most effective system will be a function of location. In arid locations where water is a scare resource, using water may not be desired, even if the mass of loss is lower than in an ESP. ESPs have a narrower operating temperature range, allowing for some energy inefficiencies. Optimally, regardless of flue clean-up, always consider the most efficient means to extra value from the FCC flue gas, be it steam generation, power generation from pressure letdown, and or a combination of both to maximise the energy recovery.

A King Yen Yung, Fluid Catalytic Cracking Expert, Petrogenium, kingyen.yung@petrogenium.com

Before deciding on the most effective option, one should consider what the specifications are for the reduction of particulates in the FCC flue gas being ultimately released to the atmosphere.

Standard FCC units are equipped with two stage cyclones in the regenerator. Nowadays many countries prescribe that dust emissions be reduced to a level below 50 mg/Nm^3 which requires additional catalyst fines capturing capacity. The most cost effective and simple way to achieve this is the installation of third and fourth stage separators (for instance, TSS and FSS from Shell licensed through Dupont).

The TSS/FSS system enables separation of virtually all erosive particles and hence protects the power recovery expander and is fully contained in a single vessel of proven mechanically sturdy construction.

Only when a TSS/FSS system is not able to meet the dust emissions limit should someone consider the installation of a far more expensive and operationally cumbersome electrostatic precipitator or wet gas scrubbing system.

A smart approach to tank dewatering

A tank dewatering technology using smart sensors is designed to reduce hydrocarbon losses and raise the quality of crude supplies to the refinery without process interruption

FAWAZ AL SAHAN, OMAR AL ZAYED and FAWAZ AL HADLAQ
Saudi Aramco

Hydrocarbon tank dewatering is a crucial process in the oil and gas industry. It impacts safety, the environment, health, hydrocarbon losses, and crude quality. Improper tank dewatering can result in incidents, process interruption, tank corrosion, and customer claims. Traditionally, there have been two types of dewatering solutions: manual and automatic. Common automatic dewatering solutions include internally mounted microwave and capacitance sensors and externally mounted drain valves, microwave and capacitance sensors on the drain pipes.

For the first time in the oil and gas industry, three disruptive solutions for hydrocarbon tank dewatering have been deployed: a sound velocity dewatering system, internally mounted interface sensors, and a combination of the two – smart dewatering.

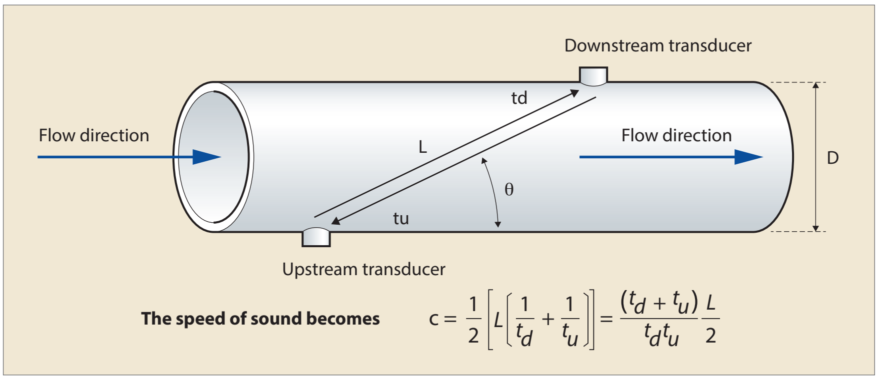

Figure 1 Sound velocity sensor principle of operation *Source: efunda*

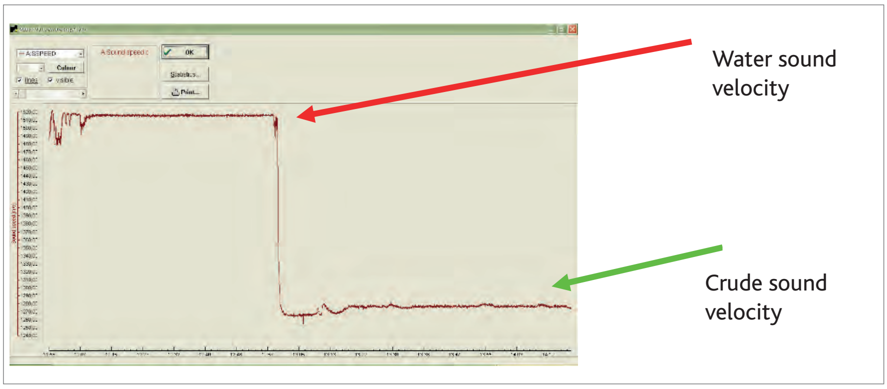

Figure 2 Sound velocity dewatering system – testing on crude

Sound velocity dewatering system

A sound velocity dewatering system utilises a non-intrusive smart sensor, control system, and drain control valve. The non-intrusive sensor has two transducers, which transmit and receive sound waves and recognise the media type based on its unique measured sound velocity (see **Figure 1**).

The sound velocity dewatering system was initially tested on crude tanks since crude has a smaller difference in sound velocity than refined products like diesel and naphtha when compared to water. **Figure 2** shows how a sound velocity sensor can recognise the difference between crude (with sound velocity around 1510 m/s) and water (with sound velocity around 1260 m/s).

There are a number of requirements for the successful set-up of a sound velocity dewatering system. The sound velocity sensor requires correction against the fluid's operating temperature as sound velocity is temperature dependent. The sensor's location on the drain pipe should be correctly selected as the location will always be full of fluid with a certain maximum velocity, to avoid vortices inside the tank and to prevent bubble formation in the drain pipe. If the current piping does not help in achieving that, some minor modifications to the drain pipe will be helpful, such as adding an elbow, a reducer with a smaller pipe size, or adding a manual valve downstream of the sensors which can be partially closed.

The process parameters flow and sound velocity should be displayed remotely at the control system in order to recognise the drained media and calculate its volume, and also to enable the detection of the drain control valve's condition (stuck, passing, or healthy). A sound velocity value should be estimated for the drained water and for the hydrocarbon at operating temperature. This can be found in the literature or calculated by software.

After installation of the system, field testing should be conducted during commissioning to ensure that the sound velocity sensor data is healthy (signal strength, signal/noise ratio, no loss of signals). In addition, testing will enable selection

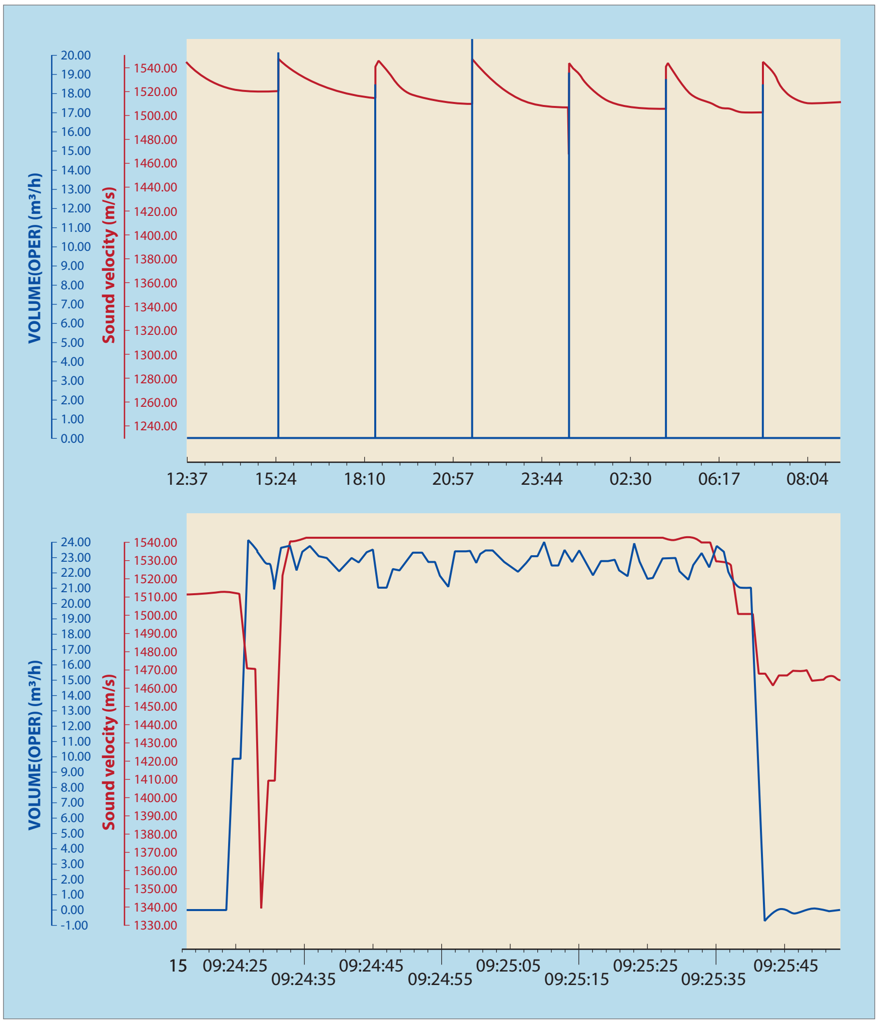

Figure 3 Sound velocity dewatering system – draining cycle operation (blue line is flow measurement, red line is sound velocity measurement)

of the best cut-off point for the valve to start closing at the end of every drainage cycle.

During commissioning, one must cross-check the drained media (water, hydrocarbon, or a mixture/emulsion) by hydrocarbon detection paste throughout the test. This is to confirm that the sound velocity sensor reading matches the media inside the drain pipe.

A sound velocity dewatering system can be operated manually by opening the drain control valve to trigger the drainage cycle, or automatically based on a timer. The time is based on historical data of how much and how often water accumulates inside the hydrocarbon tank. The sequence of operation of a sound velocity dewatering system is:

1. Flush the drain pipe for, say, 30 seconds to ensure that there is no trapped hydrocarbon in the drain pipe.
2. Sound velocity measurement starts as water starts to be drained from the tank.
3. If the sound velocity value drops to a preset value (1400 m/s, for example), the valve will close automatically as the sensor starts to detect traces of hydrocarbon in the drain pipe.
4. In case of failure of the sound velocity sensor, the transmitter, or the signal during the drainage cycle, an alarm is initiated and the drain valve will automatically close.
5. If the dewatering cycle exceeds the expected pre-set duration (20 minutes as an example, determined during commissioning), an alarm is initiated and the drain control valve will automatically close.
6. If the drain control valve is stuck or internally leaking (passing) after receiving a command to close, an alarm is initiated for operations personnel to plan a corrective action.

Figure 3 shows the sound velocity dewatering system in operation.

Figure 4 Sound velocity dewatering system set-up

Figure 4 shows the first sound velocity dewatering system, installed for a crude tank at Saudi Aramco Riyadh refinery.

Internally mounted interface sensors

The sound velocity dewatering system has one limitation whereby at the end of every dewatering cycle some hydrocarbon will be trapped along with water inside the drain pipe. Before the start of the next drainage cycle, this trapped hydrocarbon should be drained before water starts to flow in the drain pipe. To overcome this issue, the addition of an internally mounted sensor was explored.

There are various types of internally mounted interface sensors. The best options include pressure sensors, sound velocity sensors, or guided wave radar (GWR). All of these can be installed inside a hydrocarbon tank and enable direct measurement of the water interface level.

GWR has many advantages as it indicates both the total and interface level, but this technology cannot measure the water interface if the tank height exceeds a certain limit (10m normally) as the GWR signal energy will be lost once it reaches the water level. To overcome this limitation, side-mounting is a solution, but this requires the tank to be empty for it to be installed. A 4in nozzle with a purge mechanism will also be required (see **Figure 5**).

Another promising internally mounted solution is pressure sensors which can be top or side mounted and can measure pressure, differential pressure, water interface level, total hydrocarbon level, and fluid temperature (see **Figure 6**). This solution also has the capability to

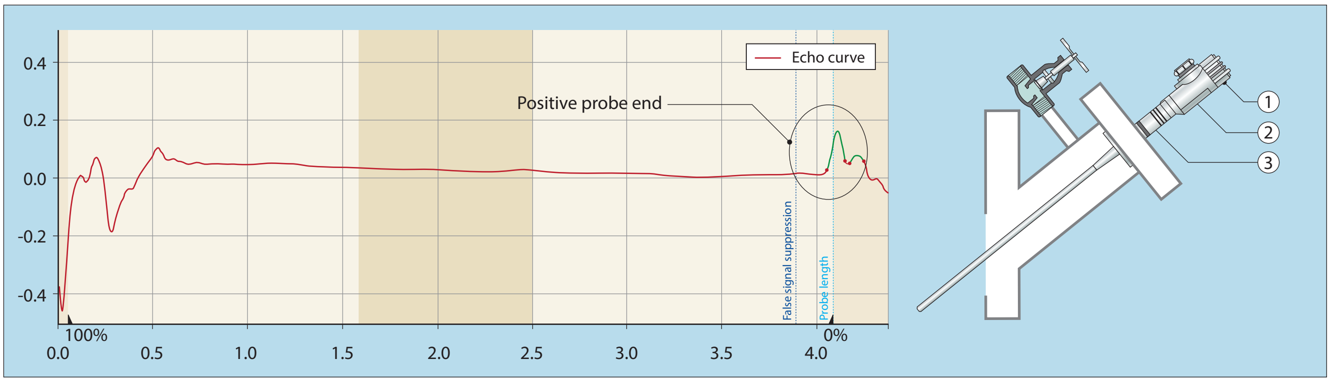

Figure 5 Internally mounted interface GWR sensor side mounted for empty tank echo testing

measure fluid density. The system utilises a pair of smart pressure sensors. Both sensors are of different lengths and are installed from the top. One is immersed so that it is close to the tank bottom where water is present, and the other sensor is inserted in the hydrocarbon (above the maximum expected water level).

The internally mounted pressure sensors system was installed at Saudi Aramco Riyadh refinery for testing. Manual gauging was used to measure the actual water interface level inside the tank and to compare againt the smart sensors' readings. Data was collected during different days and times and revealed matching readings. **Table 1** shows some of the data collected and the difference between the manual gauging and the internally mounted pressure sensor readings. **Figure 7** shows continuous measurement of the water interface level inside the same tank at Saudi Aramco Riyadh refinery.

Internally mounted pressure sensors deliver numerous advantages.

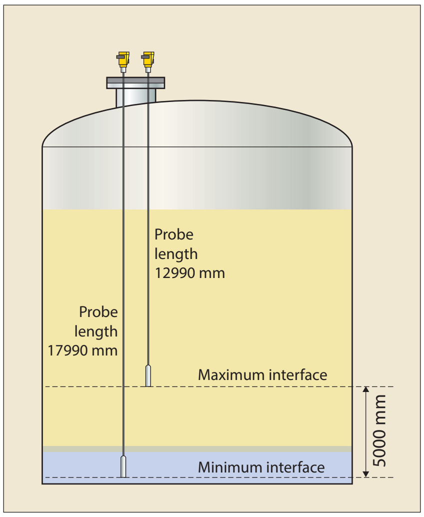

Figure 6 Internally mounted interface (pressure) sensor set-up

Internally mounted interface (pressure) sensors: interface measurement accuracy

Manual dipping, m	DCS reading, m
0.215	0.202
0.215	0.205
0.24	0.221
0.24	0.225
0.24	0.214
0.24	0.225
0.24	0.227
0.24	0.221
0.08	0.11
0.06	0.11
0	0.07
0	0.08
0	0.08

Table 1

One set of smart sensors provides six measurements: pressure, differential pressure, total level, water interface level, temperature measurement, and tank overfill protection. They provide a redundant or alternative level measurement for crude tanks in addition to the existing tank gauging instrument. The sensors can be flush mounted with a self-cleaning diaphragm and are small in size (1in threaded connection). The sensors are easy to install, maintain, and replace while the tank is in operation and provide a cost effective solution for measuring water interface inside hydrocarbon tanks.

Smart dewatering

Smart dewatering is a digital transformation technology which provides a safe, simple, and economical automatic dewatering system by combining a sound velocity dewatering system and internally mounted interface sensors.

The technology has two sets of smart sensors, one measuring the water interface inside the tank and one measuring fluid in the drainpipe, in addition to a controller and a drain control valve. The primary sensor, an internally mounted interface smart sensor, measures the water interface level and starts the dewatering cycle when the water level reaches a set point. The secondary sensor, a sound velocity smart sensor, is mounted on the drain pipe and used as a back-up sensor for stopping the dewatering operation if hydrocarbon is detected in the drain pipe. The secondary sen-

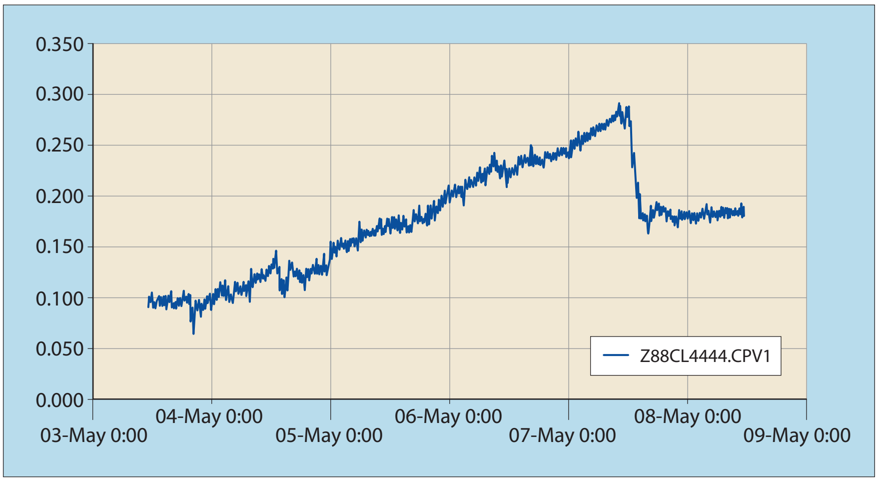

Figure 7 Internally mounted interface (pressure) sensors: water interface in crude tank

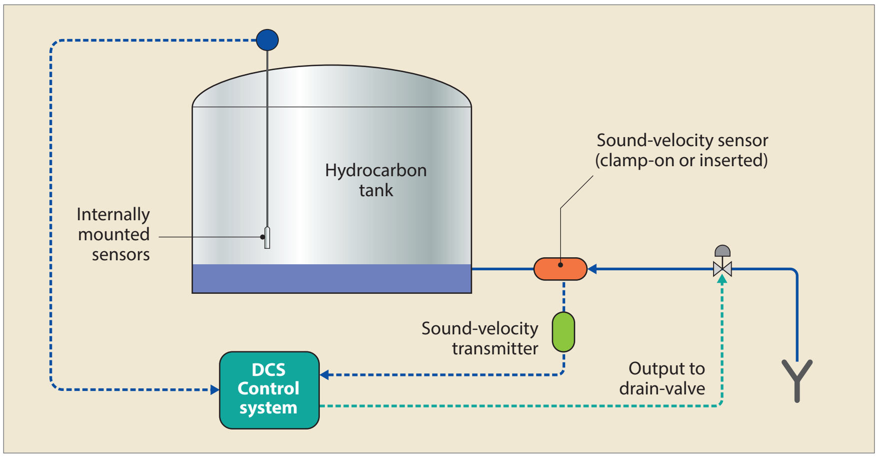

Figure 8 Smart dewatering set-up

sor calculates the volume of drained water in addition to providing analytical information on the drain control valve's condition (stuck, passing, or healthy).

Smart dewatering's advantages include the following:

- Smart dewatering is an IR 4.0 enabler. It has smart sensors providing multiple process parameters and data analytics:
  - Total level
  - Overflow protection
  - Water interface measurement
  - Volume of drained water
  - Temperature of fluid inside the tank and of the drained fluid.
  - Drain control valve analytics (passing, stuck, or healthy)
  - Sound velocity measurement/drained media recognition.
- The technology improves safety by ensuring zero hydrocarbon drainage to the oily water sewer.
- It eliminates exposure to fumes during manual drainage, and eliminates manual verification of the water interface level and of the drained fluid.
- It addresses two important challenges for the oil and gas industry: crude quality and hydrocarbon losses.
- Smart dewatering technology offers multiple dewatering options (sound velocity dewatering system, internally mounted interface sensors, and smart dewatering) for existing and new tanks inside a hydrocarbon facility.
- It eliminates operational upset by preventing water overflowing with the crude to downstream processes inside a refinery.
- It eliminates the time and effort to manually drain water from hydrocarbon tanks by providing a fully automatic solution.
- It eliminates water overflowing to customers during shipment of crude and refined products.

Figure 8 shows the complete smart dewatering set-up with both sets of sensors, control system, and the drain control valve.

Conclusion

Smart dewatering is an example of digital transformation at Saudi Aramco. This in-house developed solution is enabled by smart sensors and data analytics to serve a challenging application in the oil and gas industry. The technology serves crude and refined product tank dewatering processes in refineries, terminals, and bulk plants, and can be implemented while the tank is in operation, without emptying the tank and without waiting for the tank's next scheduled inspection.

Smart dewatering has already been deployed by Saudi Aramco, pending commissioning. The two key elements of the technology – the internally mounted interface sensor and sound velocity dewatering system – have been fully tested and been in operation for some years.

Smart dewatering has the potential for implementation in all hydrocarbon tanks in the oil and gas industry. HSE has been the main driver of this technology as it will ensure zero hydrocarbon drainage to the oily water sewer, and it protects employees from exposure to fumes during manual drainage and while manually measuring the water interface level at the top of the tank.

Acknowledgment

The authors would like to acknowledge inspiration and unprecedented support from Saudi Aramco Riyadh refinery management, primarily the Refinery Manager Abdulrahman Al Fadhel, for supporting the team throughout proof of concept, piloting, filing of two patents, and acknowledging the authors' efforts in this journey which started in 2010. The technology has achieved multiple milestones and received many recognitions, starting with The King Salman Award, then the The Gulf Engineering Union Award and Saudi Aramco company awards (ESARP and BOE).

Further reading

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MAXIMIZE
PROFITABILITY
MINIMIZE RISK

Delivering drop-in renewable fuels

A series of pretreatment, hydrotreating, and distillation steps converts fresh or used lipid based feedstocks to full range, drop-in renewable fuels

CHUCK RED and ED COPPOLA *Applied Research Associates*
ROBERT VALENTE, CHRISTINE CONWAY and LIN ZHOU *Chevron Lummus Global*

Hydrothermal Cleanup

Hydrothermal Cleanup (HCU) is a pretreatment step that uses traditional refinery components to remove inorganic materials from waste fat, oil, and grease feedstocks. During HCU, water is combined with feed oil and then fed to the HCU reactor system at the temperature and pressure necessary to maintain a hydrothermal/liquid-phase environment. Metals that are present in waste fats, oils, and greases (FOG) are mostly in the form of free salts and soaps. Phosphorus is mostly in the form of phospholipids. HCU relies on three primary mechanisms to achieve metals reduction:

1) Removal of soluble, free salts – similar to conventional desalting
2) Rapid acidulation of metal soaps (Na, K, Mg, Ca, Fe, others) using a weak acid
3) Hydrolysis of phospholipids into phosphate salts and phosphate-free lipids. Since oil and water are only partially soluble in each other at operating conditions, flow in the HCU reactor is maintained at a high Reynolds Number to achieve rapid mass transfer between each phase. Rapid mass transfer facilitates metals reduction by the mechanisms identified above.

Biofuels Isoconversion

The Biofuels Isoconversion (BIC) process converts freshly produced or used lipid based feedstocks, such as FOG into renewable fuels including diesel, jet, and naphtha. This process is unique because it produces fuels that are molecularly nearly identical to fuels produced from petroleum. The nearly identical chemistry results in jet and diesel fuels that are true 'drop-in' fuels which do not require blending with petroleum. Therefore, the BIC process can be applied as an insertable unit to existing hydrotreating units which enables co-processing, or built as a stand-alone unit for renewable fuel production.

There are four main steps in the BIC process (see **Figure 1**): a cleanup step (HCU) where contaminants are chemically removed to make suitable feed oil for the next step; the conversion step, called catalytic hydrothermolysis (CH), wherein the feed oil molecules are converted to molecules that are nearly identical to those found in petroleum; a hydrotreating step that is identical to the petroleum hydrotreating processes that removes any remaining heteroatoms (oxygen, sulphur, nitrogen, and metals) down to acceptable levels; and a final distillation step that separates the hydrotreated product into the naphtha, jet, and diesel fuels.

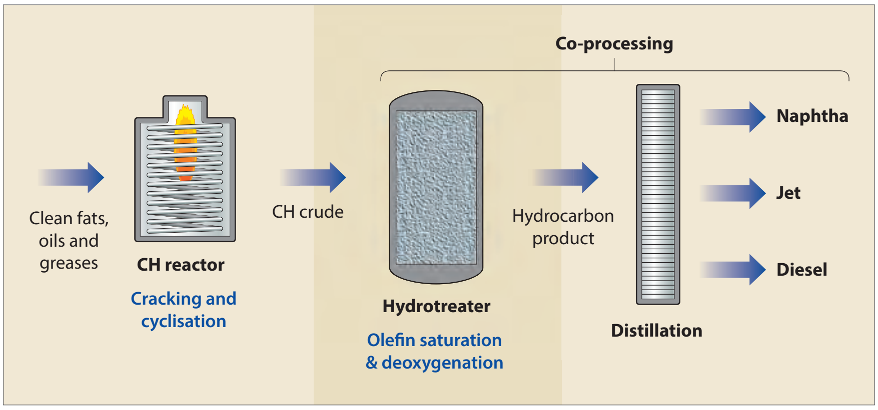

Figure 1 Simplified block flow diagram of the BIC process

Catalytic hydrothermolysis

In the CH process, water is combined with clean FOG products, pressurised, and heated in excess of supercritical water conditions. At these conditions, water and the feed oil become one phase. Water mediates the conversion of free fatty acids into CH crude, containing compounds such as normal and branched paraffins, high-density cycloparaffins, and aromatic molecules ideal for diesel and aviation turbine fuels.

Key reactions that occur during CH conversion include, but are not limited to:

- Hydrolysis of glycerides to produce free fatty acids
- Cracking of fatty acids into lower molecular weight acids and hydrocarbons
- Cyclisation of fatty acids into alkyl cyclohexane compounds
- Cyclisation of fatty acids into alkyl benzene compounds
- Dehydrogenation of naphthenic compounds into aromatic compound
- Decarboxylation of fatty acids
- Skeletal isomerisation of intermediate and product compounds

Typical CH reactions of unsaturated fatty acids, such as oleic acid and linolenic acid, are shown in **Figure 2**. Those reactions that occur in the CH unit eliminate the need for further catalytic reforming, hydroisomerisation, or hydroc-

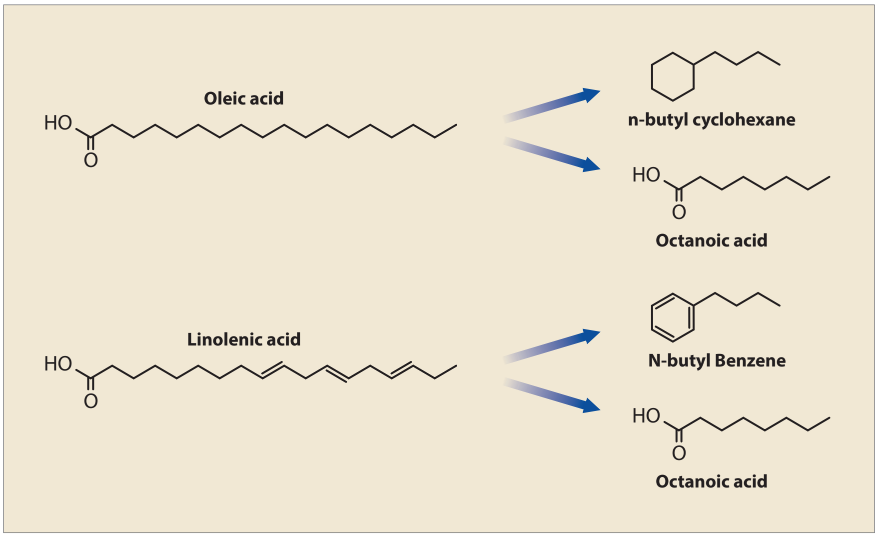

Figure 2 Characteristic CH conversion reactions

racking, and also consume less hydrogen than a route that uses all hydroprocessing.

The process occurs in a single step for less than two minutes of residence time. Product yields and product composition are controlled by adjusting the process variables, which include reaction temperature, reaction pressure, residence time, and water to oil ratio.

Isoconversion

The renewable CH crude contains oxygenated compounds, mainly carboxylic acids. In order to meet the fuel specifications, element oxygen must be removed from those oxygenates to produce pure hydrocarbons, and nearly all of the olefins must be saturated to produce paraffin compounds. For example, the total acid number (TAN, expressed as mg KOH/g) of jet fuel or jet fuel blending component under the CHJ Annex to D7566 must be less than 0.015. Hydrotreating achieves deoxygenation and reduces the TAN to meet the jet fuel specification. This results in jet fuel that has very good thermal and oxidative stability.

The BIC process uses commercial hydrotreating catalyst that results in near-complete oxygen removal (TAN <0.01) without saturating aromatic rings to cycloparaffins, opening cycloparaffin rings to form paraffins, or cracking of jet and diesel range hydrocarbons into naphtha and gaseous hydrocarbons. This results in fuels that contain aromatic and naphthenic isomers similar in concentration and type to petroleum derived fuels. Because cycloparaffin and aromatic compounds are produced and retained in the products, the BIC process uses less hydrogen than hydrotreated esters and fatty acids (HEFA) type processes.

Product distillation

The BIC process produces the entire range of hydrocarbons from naphtha through diesel boiling ranges. To produce jet fuel, the whole hydrotreated product is distilled to meet several specification requirements that include distillation, distillation slope (T90-T50 and T90-T10), flash point, and freezing point.

BIC technology has features that overcome deficiencies with technologies that practise direct catalytic hydrogenation of triacylglycerides-rich feedstocks using fixed bed hydroprocessing catalysts. They include the following.

Unlike direct catalytic hydrogenation, which essentially converts triacylglycerides to their corresponding straight-chain n-alkanes (primarily high concentrations of n-hexadecane and n-octadecane), the BIC process incorporates cyclisation and aromatisation reaction chemistry to produce renewable jet and diesel fuels containing n-alkanes, isoalkanes, naphthenes, and aromatics, much more analogous to those in petroleum derived distillate fuels.

The catalytic hydrothermolysis reactor acts as a guard device to remove/transfer any inorganics and potential hydroprocessing catalyst foulants into the aqueous phase product such that the downstream Isoconversion catalysts will sustain relatively longer catalyst lives.

Unlike direct catalytic hydrogenation, which converts the glyceryl backbone of the triacylglycerides to propane, and thereby results in consuming additional hydrogen, the BIC process converts the glyceryl backbone non-hydrogenatively into fuel gas for captive use in the CH reaction system.

Chemical hydrogen consumption in the BIC process is significantly lower than that in direct hydrogenation processes due to the supercritical water reforming of olefinic bonds in the unsaturated triglycerides via cyclisation and aromatisation reactions that produce lower hydrogen content naphthenes and aromatic hydrocarbons. By way of example, for a feedstock having a 13/1 unsaturates/saturates ratio, such as that in conventional rapeseed oil, the chemical hydrogen consumption for the direct hydrogenation route can be as high as 148% that of the BIC process.

In the production of jet fuels, aromatic content (ASTM D6379) is required to be 8-20 vol%. BIC technology produces aromatic rings, which enable drop-in jet fuel production independent of feedstock compositions.

A testing program carried out at Chevron Energy Technology Center in Richmond, California, has shown that the ReadiNaphtha can be catalytically reformed to produce reformate having a 98.8 RON and 87.3 MON (93 Anti-Knock Index) at a C_5+ reforming yield of about 70 vol%.

ASTM certification

ASTM D7566 Annex A6 has been approved to add a new standard for jet fuel (CHJ) produced by the Biofuels Isoconversion process. ASTM D7566 was developed by ASTM International (formerly the American Society for Testing and Materials) as an international standard for renewable jet fuel. Renewable jet fuel produced in compliance with the ASTM D7566 standard is deemed to meet the same require-

ments as those for conventional petroleum derived fuel, and thereby only renewable jet fuel produced and quality-controlled in compliance with this standard can be carried in commercial aircraft. The new annex allows the blending of up to 50% of ARA and CLG's ReadiJet with petroleum derived jet fuel.

Details of the new ASTM D7566 certification include:

- Date of issue: January 30, 2020
- Standards developing organisation: ASTM International
- Technology developing company: Applied Research Associates & Chevron Lummus Global
- Standard Number: ASTM D7566 – 19b (Annex A6 catalytic hydrothermolysis jet (CHJ))

Renewable oils co-feedstock component

Many feedstocks have been tested successfully in the CH conversion process since bench and pilot operations began in 2006. The CH process is tolerant of a wide range of renewable feedstock chemistries. Feedstocks may be highly saturated, such as tallow, or highly unsaturated, such as tung oil; they may contain esters with short chains, such as coconut oil (C_{12}), or long chains, such as rapeseed and carinata oil (C_{22}); they may be clean triglycerides or clean fatty acids. Feedstocks that have been successfully tested include waste oils, such as used cooking oil, tallow, and distillers corn oil, as well as virgin plant oils such as algae, camelina, canola, carinata, castor, coconut, corn (from distiller's grain), peanut, pongamia, soybean, and tung oil. More recently, work has been done that allows highly contaminated FOGs such as brown grease to be processed by pretreating with HCU. While feedstock chemistry affects conversion rates and product chemistry to a degree, the breadth of testing data enables CLG/ARA to provide sufficient process control to enable the production of jet and diesel fuels with consistent chemistry and quality.

Hydrotreaters

Renewable oils such as those from vegetable derived seed oils, non-edible plant oils, and animal fats are characterised as hydrocarbonaceous oils containing:

- Three long-chain fatty acid molecules in the 12-24 carbon number range each connected to a glyceryl backbone
- Some unsaturated double bonds as non-aromatic olefins
- Some trace amounts of organic sulphur and organic nitrogen
- Some trace levels of metals such as Na, K, Ca, P, Fe, Mg

In the conventional direct hydrotreating process, these feedstocks are converted into a saturated and hydrodeoxygenated, mostly diesel range hydrocarbon mixture having essentially all straight-chain paraffins. Many literature references are showing that direct hydrotreating of renewable oils fails to meet diesel cold flow properties unless an expensive downstream selective isomerisation unit is installed. Therefore, the direct hydrotreated mixtures need further downstream catalytic hydrotreatment to significantly increase the isomer/normal paraffin to meet diesel fuel cold flow properties.

The CH step of the BIC process performs specific chemical reactions that generate not only iso olefins and iso-paraffins but also naphthenic and aromatic compounds in the CH crude oil derived co-feedstock component. This renders it much more like petroleum distillates than those of direct hydrogenated n-paraffinic rich renewable oils.

Some of the features of co-hydroprocessing renewable oils derived from the BIC pretreatment process with petroleum distillates include:

- HCU and CH reduce total metals content to less than 5 ppm, even for feedstocks with metals content starting at over 1000 ppm. This will allow co-processing of CH crude from renewable waste feedstocks without fouling the hydrotreating catalyst.
- Typical mid-distillate hydrotreating reactors can operate at a severity to simultaneously reduce the oxygen content of the renewable CH crude oil to less than about 10 ppm and the sulphur content of the petroleum compounds to less than 5 ppm.
- CH crude oil co-feedstock has a very attractive mix of hydrocarbon types in the diesel precursor fraction that eliminates the requirement for expensive downstream selective isomerisation.
- Since most renewable oils are not available at volumes nearing nameplate capacities comparable to current petroleum hydroprocessing units, the co-hydroprocessing of blended petroleum/BIC partially treated crudes results in an advantageous economy of scale.
- Since hydrodeoxygenation of the BIC partially treated crudes produces water along with the hydrocarbon products, a water phase will be present in the recovery section to dissolve any ammonium sulphide produced from the hydrotreatment of the petroleum hetero-compounds to avoid potential solids deposition problems and without having to inject water externally.

Ebullated bed residue hydrocrackers

Recently, there has been interest in co-processing renewable oils and waste oils in an ebullated bed residue hydrocracker such as CLG's LC-Fining process. This co-processing option is generating much interest among refiners in Europe. As indicated above, the HCU process would be an excellent pretreatment step to remove impurities such as phosphorous and chlorides to a level that is acceptable to the catalyst and metallurgy of the unit. For this process, the CH step would be by-passed since the HCU oil will go directly into a hydrocracking environment.

Recently, the Environmental Protection Agency (EPA) enacted 40 CFR 80.1126, which allows for renewable oils to be co-processed with fossil derived oils in a petroleum refinery, with the renewable oil component qualifying for the Renewable Identification Number (RIN) programme.

Commercial development of the BIC process

ARA and CLG have advanced the commercialisation of BIC at a steady pace since its invention in 2006. ARA developed continuous flow bench and pilot systems in 2008 and 2010 and built a 100 b/d CH demonstration system in

2016, which was used to make over 160 000 gallons of 100% drop-in renewable jet and diesel fuels for US Navy MILSPEC certification testing in the F/A-18 Hornet and Spruance Class Destroyer.

The following are ongoing commercial activities for the BIC process:

- Euglena: a Japanese licensee recently completed the construction and start-up of an integrated demonstration system in Tokyo. The feedstock is a 30% algae (euglena) lipids/waste 70% palm oil mixture. The 5 b/d demonstration plant successfully produced ReadiJet and ReadiDiesel in early 2020.
- Confidential Europe: a commercial engineering study was completed to process 3900 b/d of rapeseed oil/animal tallow/used cooking oil.
- ReadiFuels-Iowa (RFI): a 2650 b/d commercial unit is currently in the final phases of basic engineering completion. Feedstock is 50% distiller's corn oil/50% used cooking oil.
- Confidential USA 1: a 5300 b/d commercial unit is scheduled to resume basic engineering activities soon. Feedstock is 50% yellow grease/50% brown grease.
- Confidential USA 2: a 5000 b/d commercial unit's basic engineering activities are currently on hold. Feedstock is 60% yellow grease/40% brown grease.
- Confidential USA 3: a 3130 b/d commercial unit is currently in basic engineering. Feedstock is 50% distiller's corn oil/50% used cooking oil.

Biofuels ISOCONVERSION, ReadiNaphtha, ReadiDiesel and ReadiJet are marks of Applied Research Associates and Chevron Lummus Global. LC-FINING is a mark of Chevron Lummus Global.

Chuck Red is a Vice President with Applied Research Associates (ARA) and has led ARA's fuels programme since 2009. He has led the development and commercialisation of hydrothermal clean-up and catalytic hydrothermolysis technologies that produce 100% drop-in renewable jet and diesel fuel from waste fats, oils, and greases. He is a United States Naval Academy graduate with a BS in electrical engineering and holds MS in Business Management from Troy University.

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Christine Conway is a Senior Principal Technology Specialist with CLG. With 20 years' experience working with refining and petrochemical technology licensing companies, she leads the development and design of the BIC technology. She holds a bachelor's degree in chemical engineering from the University of Minnesota.

Lin Zhou is a Process Engineer with Lummus Technology in Bloomfield, New Jersey, where she is responsible for the process design of CLG's BIC technology. With over 10 years of process engineering and R&D experience in biofuel production from bio-feedstocks, her research focuses on process intensification and catalyst formulation. She holds a PhD in chemical engineering from Stevens Institute of Technology, Hoboken, New Jersey.

Protecting your hydroprocessing reactor

Owners and operators respect a hydroprocessing reactor's minimum pressurisation temperature but can fail to understand factors other than the temperature

ERIC LIN and RICHARD TODD
Norton Engineering Consultants

When an owner or operator in charge of a hydroprocessing unit is asked what a reactor minimum pressurisation temperature (MPT) is, they may correctly respond that it is the lowest temperature at which a reactor can start pressurising above a predetermined limiting value after it has already seen hydrogen service. Some may even understand that the purpose of respecting the MPT is to protect the reactor against brittle fracture caused by diffused hydrogen. However, far fewer understand MPT implications beyond those two critical points.

Most hydroprocessing reactors are susceptible to failure mechanisms caused by temper embrittlement as well as hydrogen embrittlement. Whether it be concluding turnaround activities or overcoming an upset condition, respecting the MPT is important to ensure reliable and safe operation of the reactor vessel. This article provides insights and understanding around MPT that can impact hydroprocessing reactor integrity along with other equipment in the high pressure loop that is exposed to hydrogen.

Many papers and industry standards have been published that address concerns surrounding MPT. A recent series of articles by Pillot *et al.* focused on the effect of temper embrittlement and hydrogen embrittlement on a material's mechanical properties,[1] along with a methodology to determine MPT for reactors that are already in service.[2] These two articles provide a framework to further examine MPT for a hydroprocessing unit.

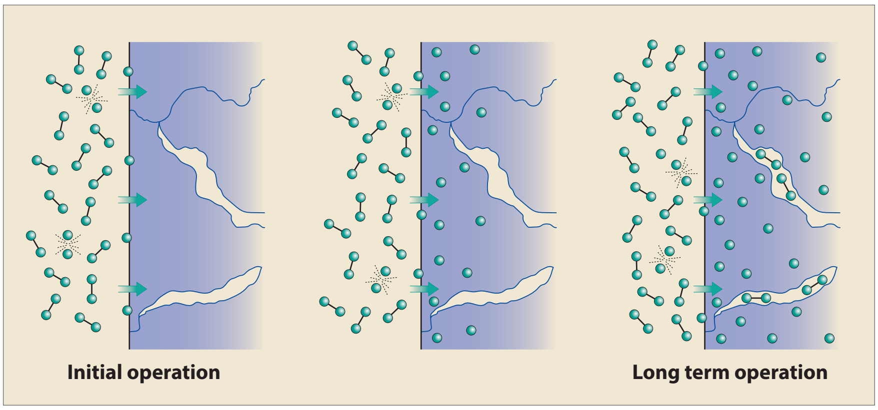

Figure 1 Hydrogen embrittlement

Temper embrittlement

API RP 571 describes temper embrittlement as "the reduction in toughness due to a metallurgical change that can occur in some low-alloy steels as a result of long-term exposure in the temperature range of about 650°F to 1070°F (343°C to 577°C). This change causes an upward shift in the ductile-to-brittle transition temperature as measured by Charpy impact testing. Although the loss of toughness is not evident at operating temperature, equipment that is temper embrittled may be susceptible to brittle fracture during start-up and shutdown."[3]

API 571 best practice recommends limiting the amount of tramp elements such as manganese, silicon, phosphorus, tin, antimony, and arsenic in the base metal and welding consumables to avoid the effects of temper embrittlement. When the steel contains vanadium in the base material, it is less sensitive to temper embrittlement than when the steel does not contain vanadium.[1] It has become standard practice in recent years to use a low alloy steel that contains vanadium with tight control on the tramp elements to fabricate the steel walls of hydroprocessing reactors.

Hydrogen embrittlement

The National Association of Corrosion Engineers (NACE) describes hydrogen embrittlement as "the ingress of hydrogen into a component, an event that can seriously reduce the ductility and load-bearing capacity, cause cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials."[4]

At elevated temperature and pressure, molecular hydrogen partially dissociates to form atomic hydrogen, $H_2 \leftrightarrow 2\ H$, which is a reversible, equilibrium-limited reaction. Atomic hydrogen is soluble in steel and will enter the lattice structure of the walls. The inner surface of the steel becomes saturated and atomic hydrogen starts diffusing towards the outer surface. If a discontinuity or defect is present, then atomic hydrogen that is diffusing through the steel can reversibly form molecular hydrogen in the void, which becomes trapped and starts to accumulate. These trapped pockets of hydrogen create fissures that lead to intergranular cracking. **Figure 1** depicts atomic hydrogen entering the wall and accumulating in the grain boundaries, weakening

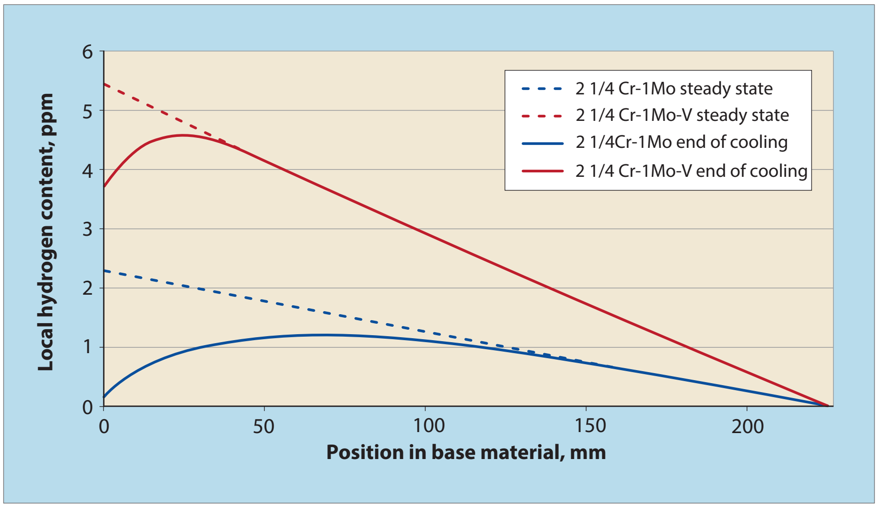

Figure 2 Profiles of H_2 content before and after cooling[1]

the material and leading to a loss of ductility and strength. A reactor wall that has become compromised is not immediately obvious without the assistance of tests and scans. Eventually, microfractures become large cracks that can lead to complete loss of integrity and failure.

As stated previously, MPT is a minimum temperature that must be obtained during start-up before a reactor can be pressurised beyond 25% of its design pressure. Per API RP 571, this 25% point is critical to prevent brittle fracture. The MPT tries to re-establish the equilibrium profile for atomic hydrogen through the steel to minimise the potential for molecular hydrogen being present at the grain boundaries that could result in rapid brittle failure. During unit start-up, this is normally accomplished by heating up a recycle gas stream that passes through the heat transfer coil of a heater before entering the reactor. Once the minimum temperature has been achieved, it is safe to start increasing pressure in the system up to the normal operating point.

Factors such as climate, heater, and compressor size in the hydroprocessing unit will also play an important role in determining the time required to heat up the reactor. It is far quicker to heat up the steel walls of a reactor in a warm climate during the summer months than it is to achieve the same MPT in a cold climate during the winter months.

Determining MPT

With an understanding of the mechanisms that lead to brittle failure in a hydroprocessing reactor, how is MPT determined? MPT is a function of fracture mechanics and/or Charpy V-Notch (CVN) toughness calculations. It will not be surprising then that the MPT is normally calculated by the reactor fabricator based on the base material selected for the reactor wall. Common base materials for hydroprocessing reactors include 2¼ Cr–1 Mo and 2¼ Cr–1 Mo–V. The addition of vanadium allows a reactor of the same size to be lighter in weight. Another advantage with the addition of vanadium to the base metal is the difference in atomic hydrogen content between the cold start-up condition and the hot, steady state condition during normal operation. **Figure 2** shows an example profile of the hydrogen content through the steel wall between the hot and cold condition. Although hydrogen content is higher in vanadium-enhanced steel, the more important feature is that the difference between the hot and cold condition is small, making this a desirable material of construction to use. (There is much less hydrogen diffusing in and out of the wall during a cooldown and heat-up cycle when vanadium is present in the steel.)

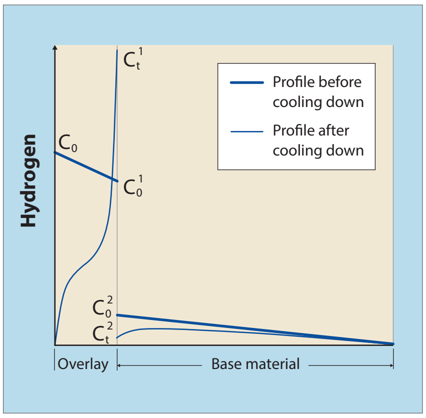

Figure 3 Profiles of hydrogen concentration in material and overlay before and after cooling down of a reactor in a refining plant[1]

Additionally, the base material is usually followed by a stainless steel weld overlay such as 347, which protects the low alloy steel from corrosion and degradation. The addition of this overlay, though necessary, increases the potential for premature failure of the reactor due to a phenomenon known as hydrogen induced disbonding (HID), which is characterised by a crack propagating at the interface between the base material and the austenitic stainless steel weld overlay/cladding.[5] The difference in hydrogen solubility between the base material and the austenitic stainless steel overlay creates a region where hydrogen content goes through a step change (see **Figure 3**). During reactor cooldown, the interface becomes a point where hydrogen content increases, which will accumulate if a defect is present. Coudreuse *et al*. provide more guidance that identifies how parameters such as operating temperature, hydrogen partial pressure, cooldown rate, material thickness, hydrogen diffusion coefficient and time can influence hydrogen content at the interface.[5] Anecdotal evidence from an API survey suggests that nearly 30% of reactors suffered from HID. ASTM G146 - 01(2018) is the latest industry standard that evaluates disbonding in high temperature, high pressure hydrogen service.

Fabricators can either roll and weld plates or combine forged rings to create reactor shells. Due to the variability in quality and method of supplied base material, it is recommended to work with a list of approved reactor vendors if one is available. These vendors work with experienced suppliers that are more likely to have uniform quality in the base material and thus are less susceptible to embrittlement. They will also have competency and experience in welding and post-weld heat treatment (PWHT) techniques.

To save time, fabricators may be tempted to re-use exact reactor specifications for a 'copy job', especially if one reactor is already in service and has experienced no issues to date. Reputable fabricators will always confirm the base and filler materials received are specific to a particular project.

Calculating the MPT

The following example will outline the steps required to analyse a reactor to determine the appropriate MPT. A hydroprocessing reactor with a 300 mm thick wall (base material) that is made of 2¼ Cr–1 Mo with a normal operating temperature of 400°C and pressure of 150 kg/cm²g will be examined.

The first calculation step is to determine the susceptibility of the base metal and weld metal to temper embrittlement through calculation of the fracture appearance transition temperature (FATT). The FATT at a 99% confidence level is given by:[1]

$$FATT_{99\%} = -15.416 + 0.72670\, J_{TE} - 8.0043\times10^{-4}\, J_{TE}^{2}$$

J_{TE} (Watanabe factor) is a parameter representative of the base metal composition and the maximum recommended value is 100 for 2¼ Cr-1 Mo (per API RP 571). As established earlier, temper embrittlement is a function of the tramp elements in the base metal so it is not surprising that J_{TE} is a function of the manganese (Mn), phosphorus (P), silicon (Si), and tin (Sn) compositions in the base metal, expressed in wt%.

$$J_{TE} = (Si + Mn) \times (P + Sn) \times 10^{4}$$

Assuming a J_{TE} of 100 and solving for $FATT_{99\%}$ gives a value of 49.2°C. Rounding to the next largest integer, we get a value of 50°C.

The Bruscato factor, denoted X, is a parameter that represents the weld material and the accepted upper limit for 2¼ Cr-1 Mo is 15 (API RP 571). Similar to J_{TE}, X is a function of phosphorus, antimony, tin, and arsenic content in the weld metal expressed in ppm.

$$X = (10P + 5Sb + 4Sn + As)/100$$

Both J_{TE} and X are parameters that are controlled by the reactor fabricator during manufacture of the reactor.

Upon shutdown of the reactor, residual hydrogen is present and will therefore impact the integrity of the reactor wall. This requires a correction to be added to the $FATT_{99\%}$ to account for hydrogen embrittlement. Correlations have been developed to estimate the expected residual hydrogen content in ppm based on operating conditions.[6] The corresponding residual hydrogen content at 400°C and 150 kg/cm²g for a 300 mm thick wall is 2.1 ppm. **Figure 4** shows different values for the shift in FATT due to the presence of hydrogen in units of °C per ppm of hydrogen content in the steel wall.

The industry accepted temperature shift for 2¼ Cr-1 Mo is 10°C per ppm of hydrogen content in the steel. Based on this value, the overall temperature shift is calculated as:

$$\Delta T = (\text{residual } H_2 \text{ content, ppm}) \times (FATT_{99\%} \text{ shift, °C / ppm})$$

For the current example, ΔT = 2.1 ppm x 10°C / ppm = 21°C. The final calculation for MPT is the sum-

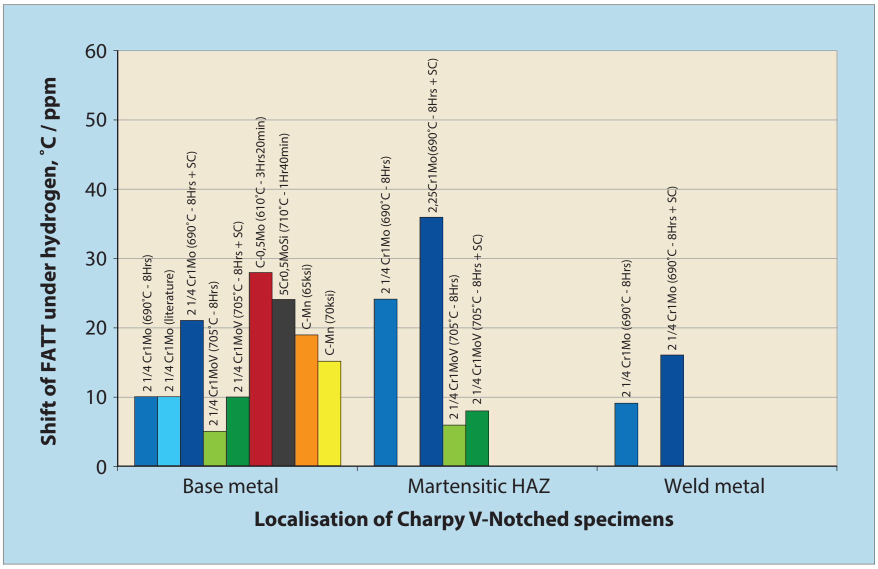

Figure 4 CVN transition curve shift as a function of H content (wtppm) in Cr-Mo(-V) and C-Mn steels[1]

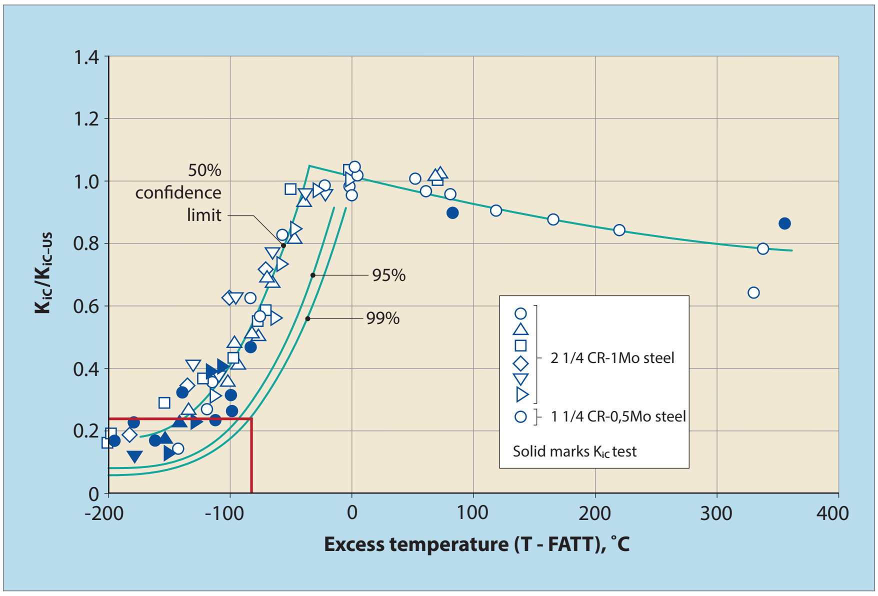

Figure 5 Relationship between $K_{ic}/K_{ic\text{-}US}$ and excess temperature for ferritic steels[7]

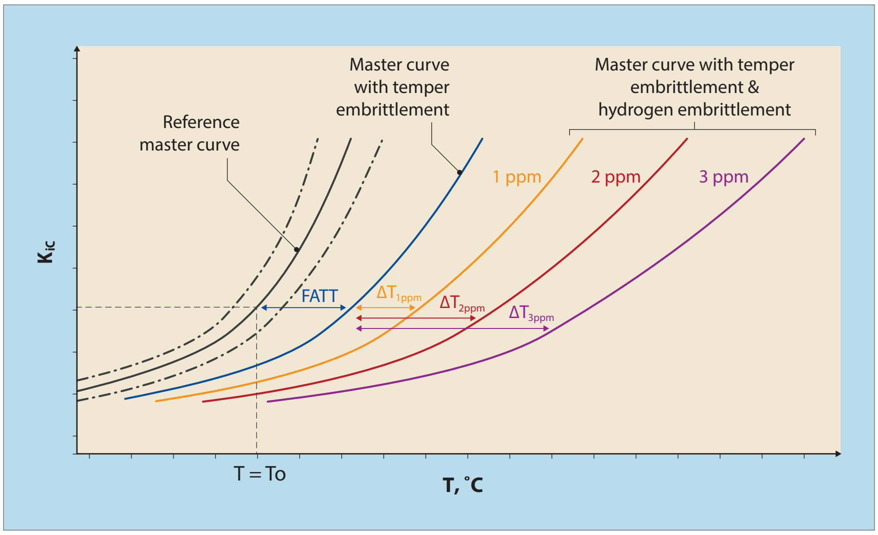

Figure 6 Cumulative effect of ageing and hydrogen embrittlement on quasistatic fracture toughness

mation of $FATT_{99\%}$ and ΔT which is 71°C.

Calculating the 25% pressurisation temperature

In the next calculation, the minimum temperature necessary to safely pressure up the reactor to 25% of design pressure will be determined. This sets the lower boundary for reactor start-up, even before 25% of design pressure is achieved. K_{IC} is a measure of the plane strain fracture toughness of a given material. 'Master Curves' of these K_{IC} values can easily be found in the literature for base materials such as 2¼ Cr-1 Mo. **Figure 5** plots the $K_{IC}/K_{IC\text{-}US}$ ('upper shelf') ratio against an excess temperature, which is defined as the temperature under consideration minus the FATT.[5]

In the current example, the FATT in consideration includes the hydrogen shift (that is, MPT). 25% of the design pressure is to be evaluated so the y-axis value of 0.25 for $K_{IC}/K_{IC\text{-}US}$ becomes the starting point. Moving across to the right until the 99% confidence limit is reached and then reading down in **Figure 5** yields an excess temperature of -80°C. Subtracting 80°C from the MPT yields a minimum 25% pressurisation temperature of -9°C. Some fabricators have been known to conservatively round this temperature to 0°C.

Climate was identified earlier as an important factor when considering start-up time and MPT. For the current example, a fair weather locale in the middle of summer (southern USA for instance) would have no trouble reaching 0°C for the 25% pressurisation temperature, but it could prove difficult to achieve this temperature in a frigid climate during the middle of winter (say in northern Canada or Russia).

Older reactors and ageing

Pillot *et al.* correctly point out that the age of a reactor can have a large impact on effective MPT.[2] As a reactor experiences multiple start-ups and shutdowns, the MPT will start to increase, possibly requiring longer start-up times. Oftentimes, a refiner will apply a healthy margin above the MPT so that every start-up will have a consistent temperature to overcome in order to compensate for such ageing. Unfortunately, many older reactors made of CS may also be dealing with the effects of high temperature hydrogen attack (HTHA) as their curves fall well below those for low alloy on the Nelson Curves (API RP 941). **Figure 6** depicts the toughness curves and shifting MPT of an ageing reactor where the black master curve represents a virgin reactor wall and the curves to the right represent the effects of temper embrittlement and increasing residual hydrogen.

If initial MPT is not known, it is possible to remove a test coupon from the reactor (if installed) and subject it to de-embrittlement heat treatment. Pillot *et al.* noted that reactors built before 1975 with electro-slag welds (ESW) have FATT values as high as 170°C.[2]

Start-up challenges

A Russian refiner started up its unit during a time when the ambient temperature was -10°C. It took some time for the unit to reach 0°C let alone the MPT. After a couple of days, the reactor finally reached MPT but there was a problem. Downstream of the reactor was a hot high pressure separator (HHPS) made of the same material as the reactor, which is typical in some hydroprocessing units. This HHPS will have its own MPT but was having trouble warming up. An inspection of the unit determined that a drain from the HHPS liquid line had been removed during 'value engineering'. The original purpose of this drain was to allow warm start-up gas to circulate throughout the HHPS and then exit through the liquid outlet line. Without the drain, warm start-up gas simply entered the HHPS and exited through the vapour outlet, completely bypassing the lower half of the vessel. The client ended up using an electric jacket to assist in the HHPS warm-up but this could have easily been avoided had the drain been present.

Ask an operator what the reactor MPT is and you may get a prompt response. Ask them what their HHPS MPT is and they will need to search their records for the information. The operating conditions in the HHPS are similar to the conditions in the reactor and as a result the base material of the HHPS is usually the same as the reactor. The HHPS vessel also falls under ASME Sec. VIII Div. 2 of the pressure vessel code. Since it is located in the same high pressure loop, the HHPS is exposed to hydrogen partial pressures that are similar to the reactor. With the same material and comparable residual hydrogen content, one can conclude the HHPS vessel is also susceptible to the effects of temper embrittlement and hydrogen embrittlement like the reactor. During start-up, the HHPS typically lags the temperature wave increase that is measured in the reactor. It can be expected that once the reactor reaches MPT, the HHPS most likely has not. For cold climates, it would be extremely tempting to start pressuring up beyond 25% of design pressure once the reactor has reached MPT without waiting for the HHPS MPT. It is better to monitor HHPS skin temperatures as well to ensure integrity of the base material for the entire high pressure circuit.

Another refiner had a naphtha hydrotreater that was undergoing start-up. The feed to a naphtha hydrotreater does not require a large amount of heat input to reach reactor operating temperature so instead of using a fired heater, a steam heater was installed. Temperatures were ramped up at a steady rate and the reactor eventually reached MPT. After a few minutes of pressuring up beyond 25% of design pressure, reactor skin temperatures started to drop. When the question was asked about why skin temperatures were dropping, the refiner mentioned they were experiencing some hammering in the utility line and the steam supply to the heater had to be isolated. Understanding the relationship between MPT and pressurisation temperature, the refiner was warned that unless they started depressurising, temperatures would drop below MPT which could lead to serious reactor damage. Once the refiner's engineers heard "MPT" they understood the danger and immediately initiated a depressurisation of the unit. This naphtha hydrotreater was an older unit located in a cold region and its MPT was well above 75°C. In comparison, modern reactors will have MPTs that fall in the range 40-70°C, especially those that conform to API RP 934-A. This example showcases how important MPT is not only with increasing temperature but also when temperatures start dropping and the reactor is already above 25% of design pressure.

MPT as a design consideration

A unit that desires a quick start-up, especially in a cold locale, does not need to be at the mercy of the MPT. A typical dewaxing unit may have sized the reactor fired heater and recycle gas compressor appropriately for the process but could make start-up of the unit challenging. Adequate over-design in the fired heater should be available not just for the process but also for start-up considerations. Promoting more heat circulation by running a recycle gas compressor and its standby is a strategy that is commonly used. If the compressor does not have an installed standby, it is possible to use a temporary boost compressor solely for start-up purposes. As illustrated by the example above, adding a drain valve to the HHPS liquid line should also promote even heating of the vessel and ensure the MPT is met here also.

The process engineer/operator should always consider MPT not only when starting up but also when temperatures start to fall, whether it is on purpose as in a shutdown or otherwise

Conclusion

The process engineer/operator should always consider MPT not only when starting up but also when temperatures start to fall, whether it is on purpose as in a shutdown or otherwise. There may be another vessel in the high pressure loop similar to the reactor that also has its own MPT value and that must be considered before any pressurisation above 25% of design pressure is initiated. Not knowing the MPT can result in a catastrophic failure so consult original records or have a coupon from the reactor tested (if available) to determine an appropriate MPT. The attainment of MPT can be challenging in some locations but there are solutions that can be implemented either during the design phase or even after the unit has been built, to achieve a fast, safe, and reliable start-up of the hydroprocessing unit.

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Amine anomaly in a mild hydrocracker

Simulation and operational changes help to crack the riddle of frequent amine carry-over from a high pressure amine absorber

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A vacuum gasoil mild hydrocracker (VGO MHC) unit in a refinery treats VGO from the vacuum distillation tower of the crude distillation unit. Treated VGO serves as a feedstock for the FCC unit for (Bharat Stage) BS-IV/VI grade gasoline production. The VGO MHC unit at BPCL Kochi refinery (1.7 million t/y throughput) is operated to produce low sulphur feedstock for the FCC unit, together with conversion of excess VGO to low sulphur diesel. The design maximum feed sulphur in VGO is 1.6 wt%.

The feed is charged to the reactor using charge pumps and is preheated in the reactor effluent feed heat exchangers and the charge heater. The reactor needs hydrogen supplied by the recycle gas compressor (RGC) for hydrocracking and hydrotreating reactions. The effluents from the reactor consist of cracked products, desulphurised VGO, hydrogen sulphide, ammonia, and excess hydrogen which are separated in separators/flash drums into liquid and gas streams. The liquid streams then find their way to the fractionation section, whereas the gas streams are further purified in separators to remove heavier ends and in the high pressure amine absorber to remove H_2S. The purified recycle gas leaving the HP amine absorber is then fed to a recycle gas compressor knockout drum (RGC KOD) to remove any amine droplets before being routed to the suction of the RGC. The system pressure of the VGO MHC is 105 kg/cm^2 (g) and cracking and treating reactions are adjusted by varying the temperature between 340-400°C. The hydrogen consumed in reactions is replenished by make-up gas compressors. The unit process flow diagram is shown in **Figure 1**.

The HP amine absorber has a total of nine single-pass fixed valve trays. Recycle gas is scrubbed of H_2S using 35 wt% methanol diethanol amine (MDEA).

Cracks and blisters in the amine absorber

During unit turnaround in late 2017, a number of internal cracks and hydrogen blisters were identified in the HP amine absorber when the vessel was offered for inspection. Phased array ultrasonic testing (PAUT) and wet florescent magnetic particle inspection (WFMPI) were carried out to analyse the depth of the internal cracks. Major cracks were observed on the shell internal surface below the trays. Some cracks were observed on the welds of ladder rungs on the shell. Hydrogen blisters were observed on the skim baffles, LT nozzles, and on the longitudinal seam of the absorber column. Multiple major and minor hairline cracks were also found at multiple circumferential seam regions of the absorber column (see **Figure 2**). Hydrogen blisters with cracks were also observed near the 12in recycle gas inlet nozzle, extending out towards the column shell and on the impingement

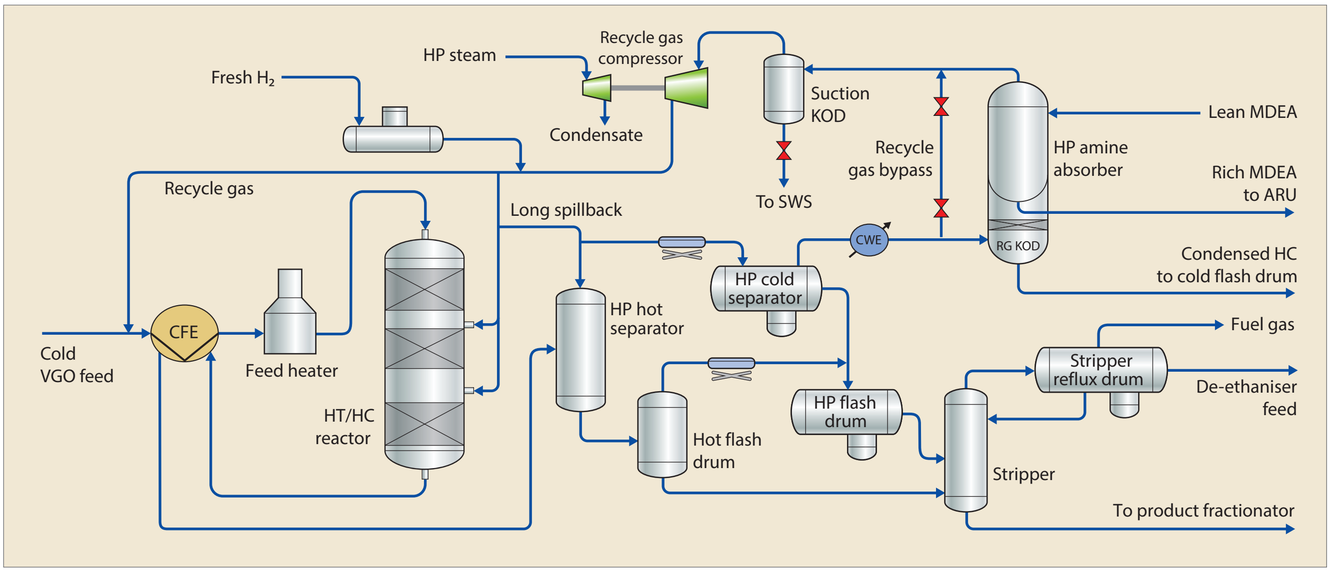

Figure 1 Process flow of VGO MHC at BPCL Kochi refinery

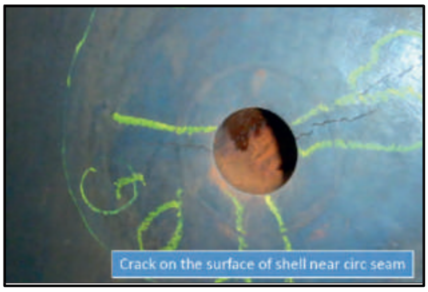

Figure 2 Crack on the shell surface near the circumferential seam

Figure 3 Hydrogen blistering on the impingement plate

Comparison of old and new tray designs

Parameters	Old trays	New HC trays
Tray type	Fixed valve	Fixed valve
Number of passes	1	1
Inner diameter, mm	2000	2000
Tray spacing, mm	600	600
Tray thickness, mm	2	2
Tower area, m^2	3.14	3.14
Active area, m^2	2.43	2.47
Active area, %	78.6	78.6
Open area, m^2	0.271	0.271
Open area, %	11	11
Downcomer data & type	Standard straight	Standard sloped
Top width, mm	340	400
Bottom width, mm	340	250
Clearance height, mm	40	65
Outlet weir height, mm	50	65
Outlet weir length, mm	1503	1600
Downcomer top area, m^2	0.354	0.447
Downcomer bottom area, m^2	0.354	0.227
DC area, %	11.27	14.24

Table 1

plate (see **Figure 3**). Hardness tests were carried out near the cracks and blisters; the result less than 180 BHN (Brinell hardness number). Cracks were eliminated by grinding the blistered surfaces and weld filling the internal cracks followed by post-weld heat treatment. Later, in 2019, an unplanned shutdown was carried out for partial replacement of the bottom portion shell of the amine absorber due to aggravation of cracks that developed on the internal surface of the column shell.

Impact on unit operation

The major reason identified for hydrogen induced cracking and hydrogen blisters was high rich amine H_2S loading of more than 0.50 mol/mol of MDEA, against the maximum acceptable industry limit of 0.40 mol/mol of MDEA. This necessitated an increase in lean amine flow to the HP amine absorber. But increased flow led to amine carry-over issues which were as frequent as 10-12 instances during a shift. Amine carry-over from the absorber led to loss of amine and required frequent replenishment in the amine regenerating unit. To reduce the carry-over events, the charge of the unit was reduced to maintain amine loading at 0.4 mol/mol of MDEA. Management finally decided to replace the existing trays of the absorber with high capacity trays, in the hope of a solution to the problem. But the issue became murkier with the change to high capacity trays.

Change to high capacity trays

Because the company's purchase plans involved purchasing more high sulphur crude, a level higher than the design flow rate of amine would have to be pumped into the column to maintain amine loading at less than 0.4 mole H_2S/mole of MDEA. The original trays were designed for a 105% amine flow rate (115 t/h), but with processing of high sulphur VGO in mind along with the existing problem of amine carry-over it was decided to consult with the tray manufacturer for trays with liquid flow rates at 130% turn-up (150 t/h). The manufacturer hinted at downcomer velocity limitations at 130% turn-up for the existing trays and hence proposed mechanical modifications to the column relating to downcomer design along with new trays with Type-I and Type-II fixed valves. The downcomer design was changed from the earlier segmental type to a sloped type. The downcomer top width from the column shell was increased to overcome the limitation in downcomer velocity indicated in preliminary tray rating simulations. The high capacity tray dimensions are shown in **Figure 4**. A comparison of old and new trays design details is provided in **Table 1**. But ironically, after the change to high capacity trays, amine carry-over issues and an increase in ΔP across the HP amine absorber were observed at both higher (80-100 t/h) and lower (40-50 t/h) amine flow rates. This aroused the curiosity of the operators who were unable to comprehend the phenomenon.

Amine carry-over at higher flow rates

After the trays in the original column were replaced with high capacity trays, the operators maintained a H_2S/amine ratio of 0.4 mole/mole of MDEA during normal operation. But when processing high sulphur VGO, the amine requirement would increase in order to maintain the same mole ratio. This necessitated an increase in MDEA flow. However, beyond an amine flow rate of 80 t/h, the operators observed liquid carry-over from high pressure amine absorber to the knockout drum

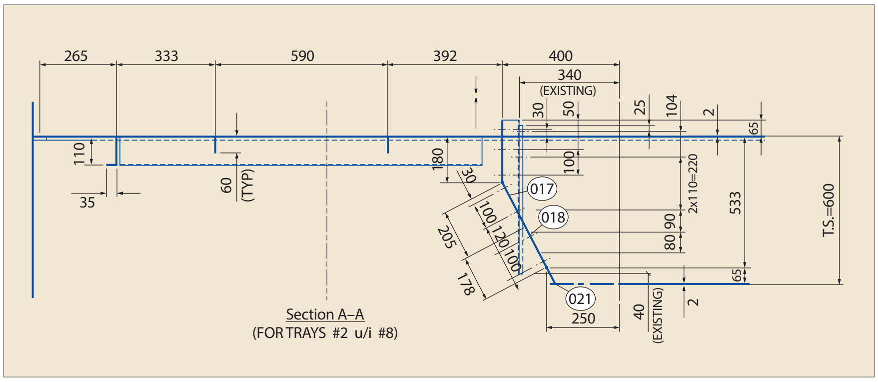

Figure 4 Existing trays converted to high capacity trays

downstream. Because the amine flow rate could not be increased beyond 80 t/h, the hydrocracker charge had to be reduced to maintain the safe H_2S loading limit of 0.4 moles H_2S/mole MDEA for increased feed sulphur.

The problem was acute with high sulphur VGO: the charge had to be reduced to even turndown values for longer periods of time. At times, VGO was diluted with diesel to meet the mole ratio. This resulted in inventory build-up of high sulphur VGO, requiring export to sustain refinery operations. Whenever liquid carry-over occurred in the amine absorber, the following changes in the process parameters were observed:

- Increased differential pressure across the amine column from a value of 0.07 kg/cm^2 (g) to 0.14 kg/cm^2 (g) for nine trays
- Loss of liquid level in the absorber whenever the liquid carry-over problem was about to surface
- A shift in temperature isotherm, with the top vapour outlet temperature from the amine absorber increasing rapidly from 45°C to 55°C

A literature survey was undertaken to find out the root cause of liquid carry-over. An article pinpointed the same effects of foaming that our unit was experiencing which included an increase in ΔP across the column, loss of liquid level, and shift of temperature isotherm.[1] Another article revealed some symptoms of foaming which matched closely our unit's experiences.[2] In the process of analysing the root cause of the problem, a lot of measures were taken to mitigate possible hydrocarbon condensation, to improve amine quality, and reduce gas load in the amine absorber:

1. Reducing cold separator temperature[3] to 45°C
2. Reduction of cooling water flow to the recycle gas cooler upstream of the HP amine absorber
3. Increasing the lean MDEA (LMDEA) temperature to 52°C to maintain a temperature differential of 10°C between LMDEA and recycle gas
4. Reducing the cold separator hydrocarbon level

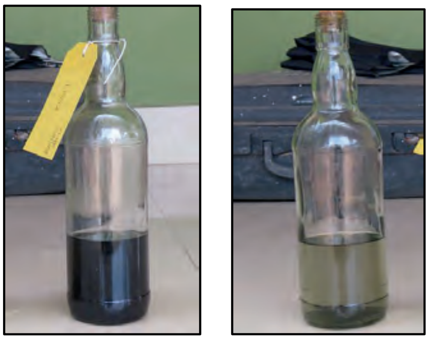

Figure 5 RMDEA at battery limit after (left) and before (right) amine washing

5. Increasing system pressure from 105 kg/cm^2(g) to 106 kg/cm^2(g)
6. Reducing the hot separator temperature to 235°C from 270°C
7. Reducing conversion from 45% to 20%

None of these steps helped to resolve the issue.

Improving amine quality

Before going into the details of steps taken to improve amine quality, it is imperative to know that during a refinery expansion, which included commissioning of a delayed coker in 2016, a few changes were made in the amine system. A common amine sharing network was established across the refinery. It was later noticed that the quality of amine degraded and the presence of particles in the amine was observed as amine suspended solids increased to 300 ppm. It was this amine that was in circulation through the VGO MHC. Also important to note is that the amine in the refinery was changed from DEA to MDEA because of its better amine properties and lower steam requirement for regeneration. To improve the amine conditions as part of the troubleshooting, the following actions were taken:

1. Starting antifoam injection to the amine pump suction
2. Amine sharing with other units halted to reduce total suspended solids
3. Cartridge filter installation reduced visible particulate content
4. MDEA strength was increased to 40%. The results were encouraging at the early stages as lesser amine flow was needed, but this could cause more corrosion problems in the long run. As per the literature, increasing strength of amine may lead to more foaming/liquid carry-over[4]
5. Replacement of charcoal in the charcoal filter with material with a high iodine number:[9] this activity also helped in reducing the frequency of amine carry-over to the recycle gas knockout drum
6. Amine washing of the amine absorber: each time amine washing was done, the amine sample from the RMDEA line was black in colour (see **Figure 5**), indicating that the trays probably had some sludge on them

Norman P Lieberman[5] specifically indicates the presence of erosion corrosion products in the amine if the colour of the amine is black, and our amine sample was black after amine washing.

This probably implied that the corrosion particles were stuck to trays and, because of vigorous washing, became detached from the trays and moved out of the column. A technical paper[2] mentions that high concentrations of suspended solids in the amine solvent, high soluble iron in the lean amine, and excess antifoam injection can be causative agents of foaming.

Amine samples taken at the VGO MHC and amine regeneration unit were surprisingly devoid of hydrocarbons. The main reason, which was understood later, was that the hydrocarbons which became mixed with amine in the high pressure absorber operating at 105 kg/cm^2(g) might have flashed in the flash drum of the amine regeneration unit.

Reducing gas flow to the amine absorber

The gas/oil ratio was reduced from 1288 Nm^3/m^3 to 700 Nm^3/m^3 after clearance from the licensor. The mild hydrocracker was run on full diesel mode which resulted in reduced amine carry-over as the amine requirement reduced. The gas bypass of the amine absorber was opened partially, allowing 30-40% of the gas flow to pass through the bypass and the rest to pass through the amine absorber.

These procedures brought about huge relief in the plant as the amine

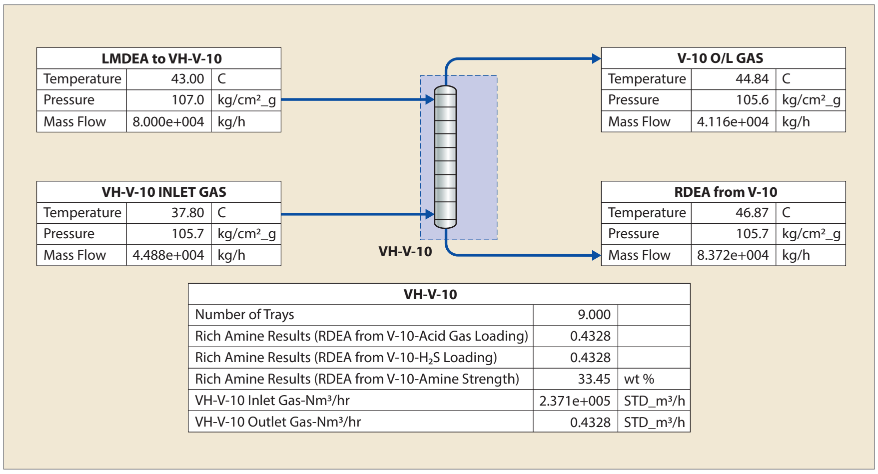

Figure 6 Snapshot of simulation of amine absorber

carry-over issue subsided completely. However, this led to higher H_2S in the recycle gas, which necessitated opening of the purity vent to purge impure recycle gas from the high pressure system to the medium pressure system where the gas was amine treated and sent to fuel gas. Licensor confirmation on metallurgy compatibility was taken wherever high H_2S concentration was expected. A downside of this measure was loss of H_2 through the purity vent.

As a result of all these positive changes, the charge of the plant was increased from 140 t/h to 245 t/h with feed sulphur at 2.2 wt%. Amine flow was increased to 125 t/h, keeping a H_2S loading of 0.4 moles/mole of MDEA with an amine strength of 40%. The continuous filtration of amine also helped operators to slowly close the bypass over a period of time without any instance of amine carry-over. Purging high H_2S from the recycle gas through the purity vent and occasionally changing over to low sulphur VGO feed also helped to increase the hydrogen purity of the recycle gas.

Although the gas bypass provided relief to the operators and helped to increase the charge, the riddle of amine carry-over was not completely solved. The presence of particulate matter in RDEA after amine washing did provide a clue, but the possibility of abnormality in other parameters was not ruled out. In the quest to find out the other reasons and to revalidate some of our field experiments outlined earlier, a steady state simulation of the plant was done.

Steady state simulation of VGO MHC

Based on field observations, a steady state model was developed using Aspen Hysys to understand the operation of the amine absorber. Various parameters including hydrocarbon dew point, amine absorber temperature profile, and the impact of varying feed sulphur content was studied by simulation.

Another goal of the simulation was to vary gas and liquid flows in the column and to mimic the effect of fouling of trays. The Peng-Robinson property package was chosen as the thermodynamic property package for simulating the hydrocarbon section, whereas the amine section (HP amine absorber) of the simulation was modelled using the Acid Gas property package. A snapshot of simulation in Hysys is shown in **Figure 6**. The fidelity of the developed model was confirmed with plant data and was found to be satisfactory. Rich amine H_2S loading calculated normally by operators (using the following calculation) and using empirical formulae matched the rich amine H_2S loading output generated by the simulation run:

Rich amine H_2S loading (mol/mol of MDEA)

$$= \frac{(F*S*0.00025)}{(A*w*8.4*10^{-5})}$$

F – Unit throughput, kg/hr
S – Feed sulphur, wt%
A – LMDEA flow rate to absorber, kg/hr
w- Amine strength, wt%

Sensitivity analysis

A sensitivity analysis was carried out to capture the variation in recycle gas scrubber gas outlet temperature with the following parameters:

1. HP cold separator inlet temperature (hydrocarbon dewpoint)
2. Conversion at the outlet of the reactor
3. Varying feed sulphur from 1.7-3.3 wt%

Simulation showed that the hydrocarbon dewpoint varied linearly with cold separator inlet temperature, but as a temperature difference of 10°C between LMDEA and the cold separator was always maintained, there was little chance of carry-over. It was also noted from the simulation that the outlet gas temperature being higher than the LMDEA inlet temperature in the amine absorber was not due to increased conversion. Simulation predicted a maximum temperature of 74°C near the fourth and fifth trays inside the absorber on increasing the feed sulphur from 1.7% to 3.2%, while during amine carry-over incidents the top temperature was observed to increase to 52°C (see **Figures 10** and **11**). A shift in temperature bulge upwards was also observed when the feed sulphur was increased.

Plugged recycle gas knockout drum

A recycle gas knockout drum is placed upstream of the HP amine absorber to prevent carry-over of any condensed liquid hydrocarbon to the amine absorber. It was observed during the operation that the control valve of the recycle gas knockout drum drain was open 100% throughout the operation. There was no gas blow-by to the cold flash drum from the recycle gas knockout drum. This indicated that the knockout drum bottoms was plugged. Deplugging during plant operation was risky at a pressure of 105.0 Kg/cm²g (see **Figure 8**). When the unit was shut down, the recycle gas knockout drum bottoms

Figure 7 Inspection after shutdown showed that the outlet piping of the knockout drum was plugged

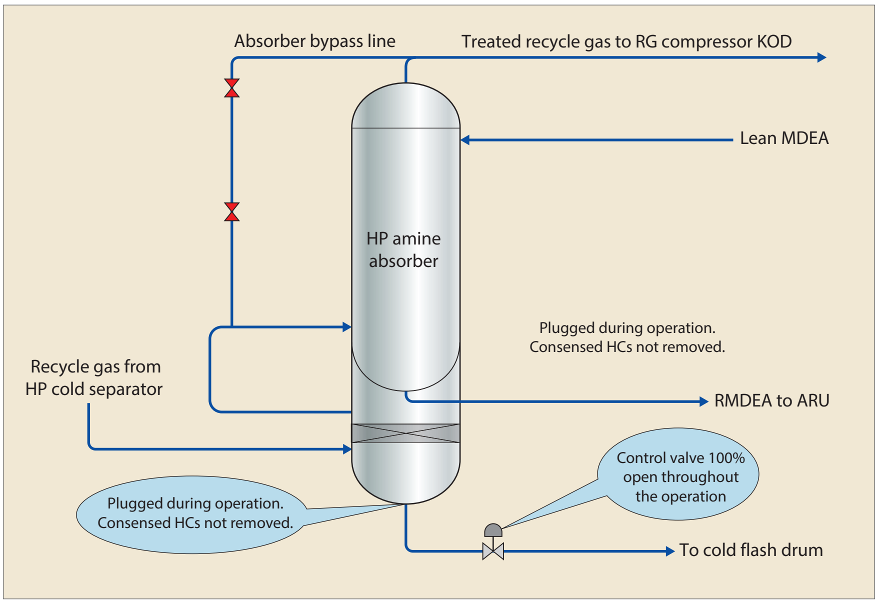

Figure 8 HP amine absorber bypass and recycle gas knockout drum

was found to be heavily plugged (see **Figure 7**) which confirmed our suspicion. Liquid collected in the recycle gas knockout drum would then have to move out along with the gas since the drain line was plugged and this could be the cause of hydrocarbon carry-over and associated foaming issues in the HP amine absorber.

Symptoms of plugging

LMDEA entering the HP amine absorber carried particulate contamination, as amine washing demonstrated. This was also partially responsible for the plugging of valves in the topmost trays of the HP amine absorber. It was suspected that particulate contamination had occurred over a period of time when amine sharing with other units was in practice and had settled on the top trays and was washed off only during amine washing. On inspection of the trays during shutdown, at a later point of time, it was observed that the trays were relatively clean as they were amine washed before shutdown. But the stagnant areas of the trays showed deposits which were rich in iron and could have been a contributor of foaming. Dry sludge deposits formed in the seal pan area and inside the downcomer of one of the trays of the HP amine absorber. The above mentioned theory prompted us to use a proprietary tray design/rating tool to check the hydraulics of the installed high capacity trays for partial plugging and hydrocarbon condensation scenarios.

Hydraulic evaluation of trays

The thermophysical properties of liquid and gas entering the HP amine absorber were obtained by Aspen Hysys simulation which served as input to the proprietary tray design/rating tool. A proprietary tray design/rating tool with built-in capability to rate such trays was used to rate the existing design of the high capacity trays and to check various tray hydraulic parameters on different liquid-vapour flow conditions which would indicate the possibilities of liquid carry-over from the tray.

To evaluate the hydraulic robustness of the trays, it was essential to find out the quantity of recycle gas bypassing the HP amine absorber. This was calculated using material balance equations. The recycle gas H_2S composition at the exit of the HP amine absorber had increased to 0.6 vol% and the inlet composition was close to 1 vol%. The amount of gas bypass was found to vary between 17 t/h and 25 t/h out of a total 40-45 t/h of recycle gas. A hydraulic study of the HP amine absorber trays was performed for recycle gas flow with and without bypass. The results suggested that in the case of hydrocarbon+amine (depicted by a foaming factor of 0.6) and without gas bypass (gas flow 45 t/h and amine flow 100 t/h), the froth height on a tray increased to 76% of tray spacing, suggesting the initial stages of foaming in the column. If gas bypass was practised (gas flow 25 t/h, amine flow 100 t/h), the froth height fell to 48.3% of tray spacing, indicating why the foaming issues subsided with bypass. Thus the issue of foaming at higher amine flow rates could be answered and gas bypass helped solve the problem. But operators faced a problem of amine carry-over at lower flow rates too. The next section tells us the reason behind it.

Carry-over at lower flow rates

Even after changing over to higher capacity trays, the problem of amine carry-over persisted. Amine carry-over was also observed at times as amine flow rate was reduced to contain amine carry-over to the recycle gas knockout drum. This was puzzling as amine carry-over was expected only at higher flow rates of amine. This anomaly of amine carry-over at both lower and higher amine flow rates brought the unit to its knees. To ascertain the cause of this anomaly, tray details were studied and simulations performed. An interesting observation in the new tray installation was the presence of only dynamic seal. In other words, the downcomer clearance and exit weir height were the same. Although most high capacity trays have only dynamic seal to reduce the exit velocity losses,[10] it is a cause of potential downcomer unsealing at lower flow rates where the liquid enters spray regime. Spray regime occurs at low liquid flow rates, at weir loadings of < 2.5-3.3 g/m/in (20-30 m^3/hr-m)[7] when the crest height is less and at high

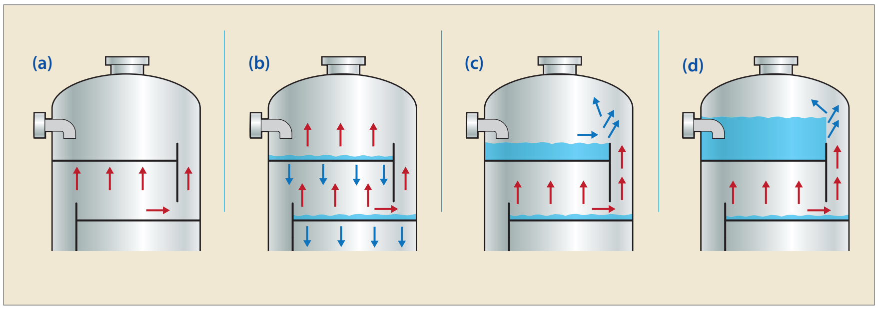

Figure 9 How downcomer unsealing bottlenecks a tower in the spray regime
Reproduced with permission[8,9]

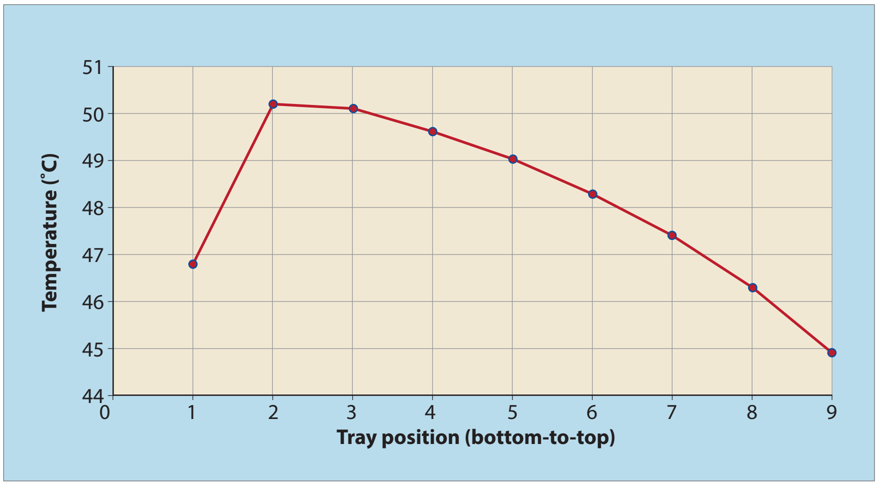

Figure 10 Stage-wise (bottom-to-top) temperature profile (conversion = 30 %, feed S = 1.7%, amine flow = 80 t/h)

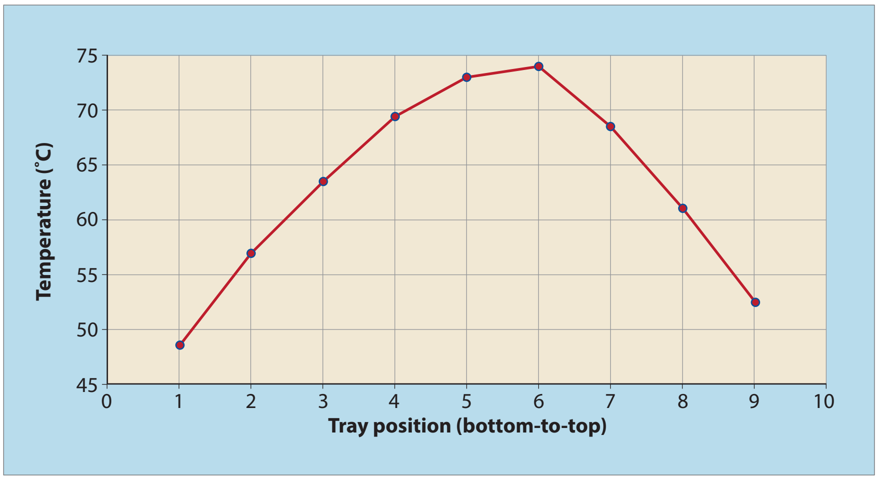

Figure 11 Stage-wise (bottom-to-top) temperature profile (conversion=30 %, feed S = 3.2%, amine flow = 100 t/h)

gas velocities. The gas atomises the tray liquid, forming a dispersion. There is no frothy pool, and the liquid resides as atomised drops in the space between the trays. The continuous gas phase reaches the downcomer outlet. There is no static seal to prevent gas from rising into the downcomer. Spray regime is evident in simulations by low downcomer exit loss and low height of clear liquid below the froth zone on trays. An article by H Z Kister[6] provided more evidence of potential downcomer unsealing problems at low liquid flow rates.

The concept of downcomer unsealing is encapsulated in this article and reproduced with kind permission in **Figure 9**. Simulation was done on the high pressure section to ascertain the downcomer exit loss. A lower exit loss indicates lower liquid flow rates and unsealing of downcomers. Simulation in a proprietary tray design tool provided an exit loss of 2.3 mm at an amine flow rate of 40 m^3/h.

The weir loading was also on the lower side with a value of 24 m^3/h m. **Table 2** summarises the results of simulation. This suggests that the trays may have been operating in spray regime as the recycle gas flow rate was high for the low flow rate of amine. Downcomer unsealing flood could have occurred. Unfortunately, the supplier's software was unable to evaluate whether the trays operated in the spray regime and whether downcomer unsealing flood actually occurred. If it indeed occurred, the amine was sprayed over to the recycle gas compressor suction knockout drum. Hence, operating at lower than turndown flow was stopped.

The hydraulic analysis was unable to provide complete answers. At higher gas and amine flow rates, a foaming factor of 0.6 had to be used, which is lower than the 0.7-0.75 usually used for these systems. But even with a foaming factor of 0.6, froth height of only 76% of tray spacing was achieved, which is still a low number to explain flooding. For the low liquid flow rates, the hydraulic analysis established the likelihood of downcomer unsealing, but was unable to determine whether the unsealing would lead to flood. This remained unexplained in the supplier's proprietary tray rating software. To gain better understanding, a rigorous hydraulic analysis was needed.

Replacement of amine absorber

The hydraulic calculations were done later. But replacement of the amine absorber and its upstream recycle gas knockout drum (whose drain line was plugged) was carried out to solve the problem prior to the hydraulic calculations. The amine absorber was changed over from a tray column to a packed column. Charcoal filters in the amine regeneration unit were replaced and the unit was taken back online. The issue of amine foaming subsided and the unit has been running on full throughput ever since. A conservative estimate of the savings due to charge increment for just three months is shown in **Table 3** as Rs 58 crore. It includes the savings accrued due to stoppage of export of VGO at a discount of $9/bbl when compared with crude and stoppage of amine losses as part of continuous draining during periods of continuous carry-over.

Conclusion

Amine columns in high pressure systems have a higher foaming tendency. Foaming most likely happens because of a combination of factors. Corrosion particles including iron sulphide[9] carried by amine can stick to the trays of the column and contribute partially to foaming. Inadequate draining of condensed hydrocarbon from the knockout drum placed upstream of the amine absorber may result in carry-over and can aggravate foaming. Too much antifoam increases foam stability rather than reducing it.[8] Foam tests of amines obtained from high pressure amine absorbers need not indicate the presence of hydrocarbons. This is because most of the hydrocarbons may flash off by the time the amine reaches the amine regeneration unit from where amine samples are taken for the foam test and hydrocarbon analysis. Amine quality needs to be monitored regularly to ascertain efficient and stable amine operation. High capacity trays, if run at very low liquid flow rates, could move from the froth regime to the spray regime and could be a potential cause of amine carry-over. Many high capacity trays rely only on dynamic seal and do not have positive sealing. Positive sealing in trays is where the downcomer clearance is less than the outlet weir height. It is suspected that the absence of dynamic seal, especially at low flow rates, can aggravate the liquid carry-over problem and could be a potential cause of amine carry-over. Randomly packed columns are better in the case of high pressure amine absorbers because of their inherent low pressure difference across the packing and their chances of foaming being less. High iodine number in charcoal can help in the removal of compounds which promote and stabilise foam.[9] In the case of an upset in the HP amine absorber purging high H_2S gas through the purity vent and treating this gas in a medium pressure absorber is also possible as the lines are generally capable of handling H_2S rich gas.

Tray parameters at different liquid loads

Description	Design	No bypass		Gas bypass
Gas flow rates, t/h	60	45	45	25
Amine flow rates, t/h	149	100	40	100
Downcomer loading (top), $m^3/hr\text{-}m^2$	324.8	218	87	218
Downcomer loading (bottom, $m^3/hr\text{-}m^2$	641.0	431	172	431
Weir loading, $m^3/hr\text{-}m$	90.7	60	24	60
Downcomer exit loss, mm liquid	31.38	14	2.3	14.05

Table 2

Savings due to charge increase in VGO MHC

Average VGO MHC charge from Apr-Dec'19	175, t/h
Average VGO MHC charge from Jan-Mar'20	225, t/h
Charge increment	50 , t/h
HS VGO build-up @ VGO charge of 175 t/h	110.4, TMT
Discount for VGO parcel export (w.r.t Dubai crude oil)	9 ,$/bbl
Barrelage factor	7.5, bbl/t
Exchange rate	75, Rs/$
Savings by preventing VGO export	55.8, Rs Cr
Reduction in amine make in SRU	50, t/month
Cost of amine	150, Rs/kg
Savings due to lower amine consumption	2.25, Rs Cr
Total savings	**58.1, Rs Cr**

Table 3

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Dividing wall revamp boosts octane and throughput

Dividing wall column technology reduces energy and capex, but increasingly contributes to higher revenues from better products, as in this application to light naphtha isomerisation

MANISH BHARGAVA and ANJU PATIL
DWC Innovations

Economic growth and environmental awareness require refineries to produce clean, high-octane gasoline products. The octane number or RON is primarily the knock resistance measure of gasoline. It has a numerical value from 0 to 100 and primarily describes the behaviour of the fuel in the engine during combustion at lower temperatures and speeds. To take RON values to higher levels, the reforming and light naphtha isomerisation process became an integral part of refineries. Light naphtha isomerisation not only produces high octane isomerate products but it also takes care of the latest stringent gasoline specifications. Isomerisation units can handle the benzene content of the gasoline pool and most benzene and its precursors are diverted to the light naphtha fraction as the feed to this unit. The isomerisation unit saturates benzene to cyclohexane. The configuration of an isomerisation unit depends on the required RON value of the gasoline pool.

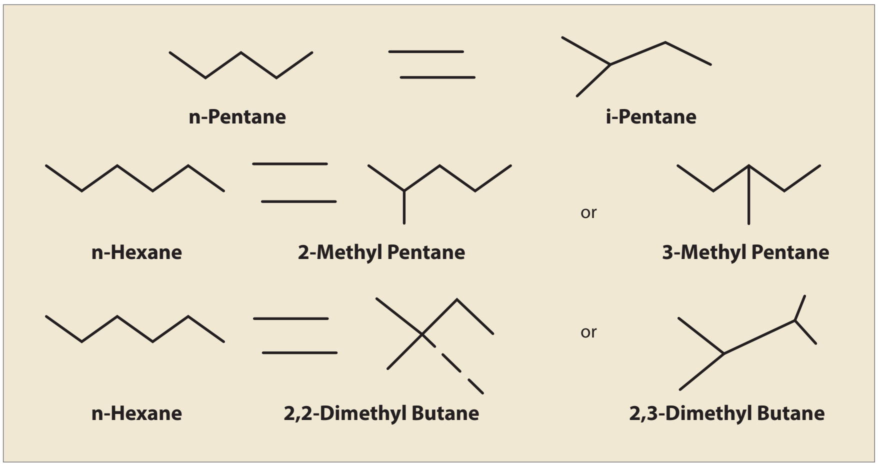

Figure 1 Primary reactions in a light naphtha isomerisation unit

RON values of individual components in a light naphtha isomerisation unit

Component	Boiling point, °C	RON
i-Pentane	27.8	93.5
n-Pentane	36.1	61.7
2,2-Dimethylbutane	48.7	93
Cyclopentane	49.3	101.3
2,3-Dimethylbutane	58	104
2-Methylpentane	60.3	73.4
3-Methylpentane	63.3	74.5
n-Hexane	68.7	30
Methylcyclopentane	71.8	95
Benzene	80	>100
Cyclohexane	80.7	83

Table 1

Overview of a light naphtha isomerisation unit

Isomerisation and reforming are processes which help to improve the octane barrel of the end product by either converting straight chain paraffins to their branched isomers or by changing linear hydrocarbons into branched alkanes and cyclic naphthenes which are then partially dehydrogenated to produce high-octane aromatic hydrocarbons.

Isomerisation reactions are reversible and mildly exothermic. Conversion to iso-paraffins does not reach completion since the reaction is equilibrium governed. The presence of other components in the feed such as benzene and naphthenes tends to raise the reaction temperature as benzene saturation and naphthene ring opening are highly exothermic, while low temperatures favour the conversion of n-paraffins to iso-paraffins. However, operating at low temperatures will decrease the reaction rate, so to overcome this a very active catalyst is usually employed.

Light naphtha isomerisation is evaluated on the basis of the product yields and the RON of the isomerate product. The liquid product yield is determined principally by the extent of hydrocracking which takes in the isomerisation unit. Hydrocracking is an undesirable side reaction which converts light naphtha into light hydrocarbon gas molecules which are low RON components. There is an inbuilt tendency in molecules with higher molecular number such as the heptanes and above to crack and produce undesirable components. C_7+ molecules are diverted to the CCR unit instead of the isomerisation unit, and benzene and benzene precursors help to manage this well. **Figure 1** shows the primary light naphtha isomerisation reactions.

The isomerisation reaction enhances the octane values of straight chain alkanes by isomerising the n-pentane (nC_5, RON value 62) to iso-pentane (iC_5, RON 93.5). Other low RON components like nC_6 (RON 31) are isomerised to 2-methylpentane (2MP, RON

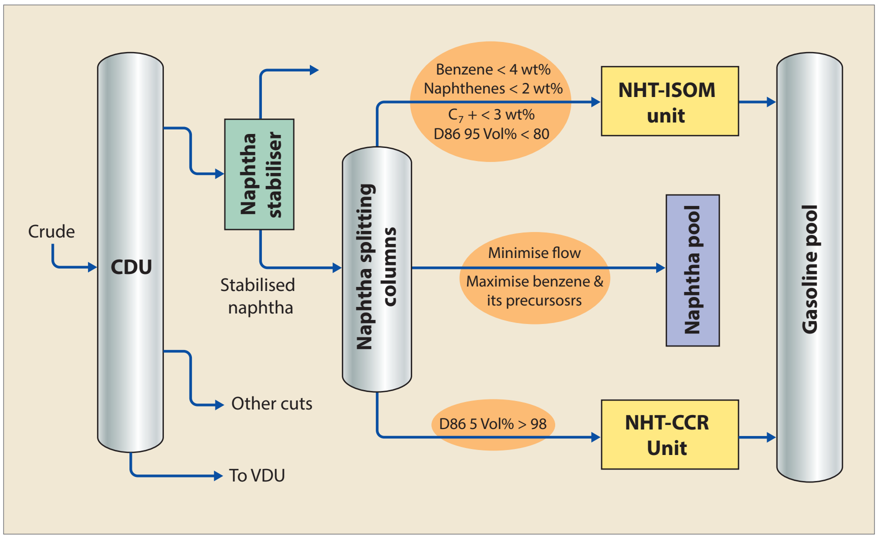

Figure 2 Typical location of a light naphtha isomerisation unit in a refinery

74) and 3-methylpentane (3MP, RON 76). These 2MP and 3MP molecules are then isomerised to 2,2-dimethylbutane (22DMB) with a RON of 94 and 2,3-dimethylbutane (23DMB) with a RON of 104. **Table 1** shows the comparative RON values of individual components in an isomerisation unit.

Unit configurations to meet RON requirements

As isomerisation reactions are in equilibrium, various methods are used to push the reactions in the forward direction. The target RON desired for the combined isomerate product depends on two criteria, the first being removal of products from the isomerate stream and the other recycling low octane molecules from the product back to the isomerisation reactors. For this purpose, the depentaniser and deisopentaniser are installed. It can be concluded that, since the isomerisation reactions are in equilibrium, the product octane number is defined by the number of separation units in the process. The sequence of columns used for separation of isopentanes or isohexanes clubbed with the isomerisation unit with recycle give benefits on account of managing the equilibrium of the reactions taking place in the isomerisation unit to maximise RON. As the benchmark for RON is increased, there is an increase in reboiler duties which can be attributed to the following factors:

- Increase in RON requires a sharp separation between low and high-octane molecules due to which the reboiler load of the column increases.
- RON can also be increased by recycling low RON components back to the reactor, which increases the reboiler duties of the downstream columns.

Apart from increased opex, the capex involved in deploying various columns in the process of boosting octane makes the technocrats in the facility rethink other options. Also, with facilities that have already invested in these columns, further enhancement of RON is always on the table. In this article, we will be discussing the various configurations of an isomerisation unit. **Figure 2** shows the typical location of an isomerisation unit in a refinery. The top product from the naphtha splitter with C_7 less than 3% is sent to the isomerisation unit.

Typical configurations of isomerisation units in a refinery

Once-through vs hexane recycle

The simplest isomerisation units are once-through units. Fresh feed is sent to a feed pretreatment section and then passes through a series of isomerisation reactors after mixing with hydrogen gas where it comes into contact with the catalyst. The reactor effluent is sent to a stabiliser column where hydrogen and light hydrocarbons produced due to hydrocracking are removed from the top as off-gas and the isomerate is removed from the stabiliser bottoms. The RON achievable through these once-through processes is about 85.

Refineries that want to achieve RON beyond a value of 85 deploy ways to recycle low octane molecules back to the isomerisation reactor. Facilities which have an isomerisation reactor followed by a deisohexaniser (DIH) column can achieve a product RON of up to 88 by recycling a high percentage of the n-hexane, 2-methylpentane, and 3-methylpentane, which are low in RON, back to the reactor.

This is achieved by drawing the mid-cut from the DIH column. The DIH produces a light isomerate distillate product consisting of C_5 and branched C_6 molecules (rich in DMBs), a C_6 recycle side draw, and a C_7+ bottoms product. For a recycle stream at 60% of the fresh feed, an octane increase of several points is achieved compared to the once-through operation. Typically, one can expect a RON increase from 83-84 to 87-88 with DIH column hexane recycle to the isom-

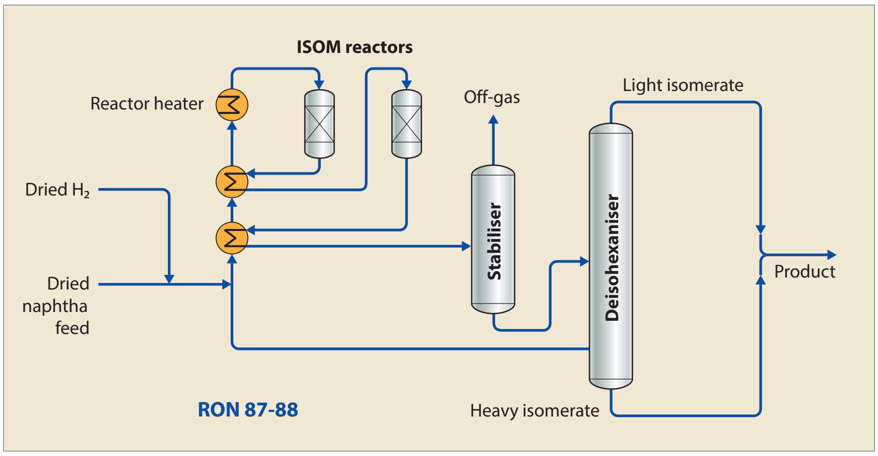

Figure 3 Typical configuration of a light naphtha isomerisation unit with hexane recycle

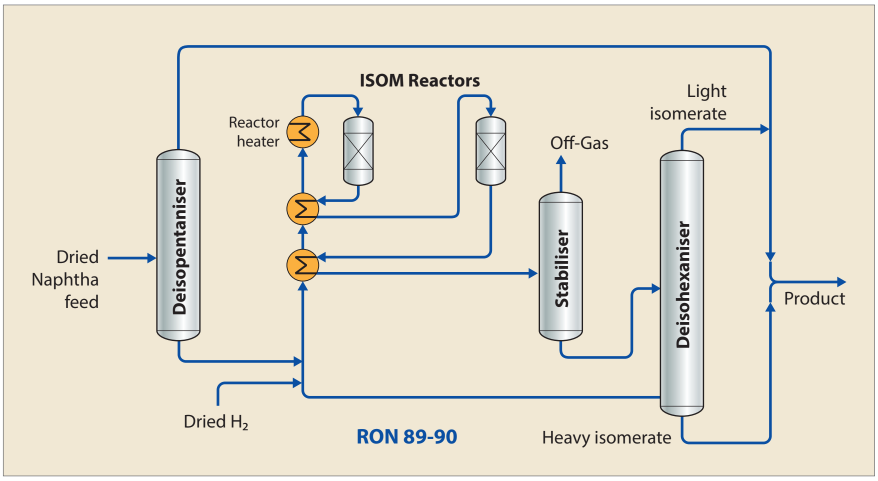

Figure 4 Typical light naphtha isomerisation unit with hexane recycle and deisopentanised feed

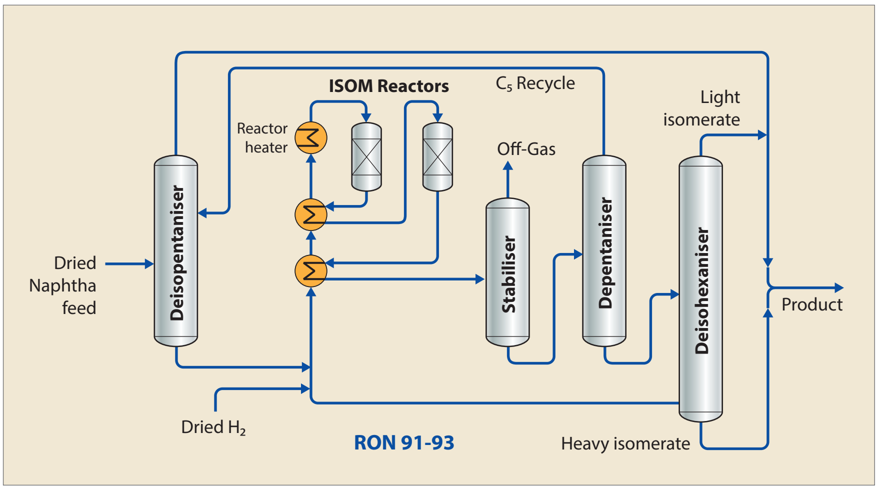

Figure 5 Isomerisation unit with hexane recycle, deisopentanised feed, and C_5 recycle

erisation reactor. **Figure 3** shows a typical configuration of a light naphtha isomerisation unit with hexane recycle.

Isomerisation unit with hexane recycle and deisopentanised feed

Some facilities, in addition to a DIH column with recycle, have a deisopentaniser (DIP) column installed before the isomerisation reactor. This helps in achieving an isomerate product of RON up to 90. As the DIP is placed in a feed fractionation section, it removes iC_5 from the feed as overhead distillate product, which pushes the reaction in the forward direction. The balance of the feed is sent to isomerisation reactors and the reactor effluent is sent to a DIH column to separate high octane C_5/C_6 isomerate product from low octane C_6 molecules which are recycled to the isomerisation reactor. Thus the addition of a DIP increases the RON over that of a 'DIH only' configuration (see **Figure 4**).

Typical RON for various isomerisation unit configurations		
Isomerisation unit process configuration	**No of column**	**RON of isomerate product**
Once-through	Stabiliser	81-84
Hexane recycle	Stabiliser + deisohexaniser	87-88
Deisopentanised feed and hexane recycle	Deisopentaniser + stabiliser + deisohexaniser	89-90
Pentane and hexane recycle	Deisopentaniser + stabiliser + Depentaniser + deisohexaniser	91-93

Table 2

Isomerisation unit with hexane recycle, deisopentanised feed, and C_5 recycle

Unconverted n-pentanes with RON values as low as 61 are sent to the DIH distillate and thus become a part of the final isomerate product. For full conversion of all normal paraffins, recycling is required via a depentaniser (DP) installed before the DIH column. This helps to make a sharper separation between the DMB-rich C_6 isomerate product and the iC_5/nC_5 recycle stream. The DP column removes iC_5/nC_5 as an overhead distillate product upstream of the DIH and recycles it back to the deisopentaniser column, which in turn separates iC_5 as the high RON top product, and nC_5 is recycled back to the reactor via bottoms product. This again helps in pushing the equilibrium reactions in the forward direction. The configuration (see **Figure 5**) improves RON up to 93.

Table 2 shows how the introduction of DP/DIP/DIH columns in the isomerisation loop in various combinations, clubbed with the type of process employed, impacts the achievable RON.

Developments in dividing wall column technology applied to isomerisation

Advances in distillation play a key role in minimising the costs of new and revamped projects in a refinery. Dividing wall column (DWC) technology had limited acceptance 20 years ago but is now reshaping our distillation processes. DWC technology is increasingly used to modernise conventional distillation sequences, especially in revamps of existing units. Besides energy and throughput improvements, a DWC revamp significantly improves the performance of downstream units.

The alignment of the dividing wall inside the column plays a dominant role in the selection of DWC for a particular separation. The middle DWC is an ideal alternative for side cut columns, which helps to increase throughput and gives better product specifications. The top DWC provides an additional source of heat integration

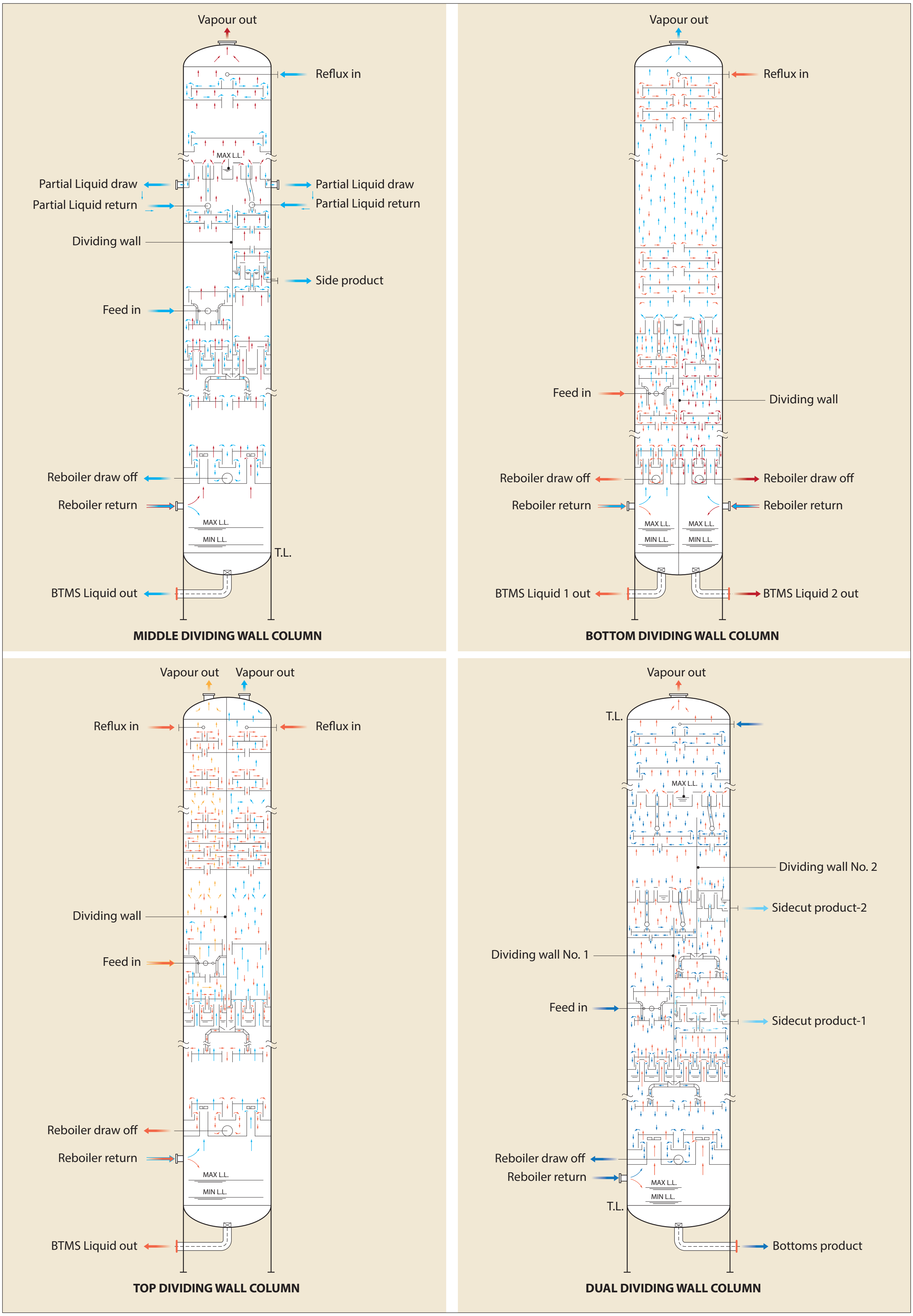

Figure 6 Elevation of commonly used dividing wall columns Source: DWC Innovations

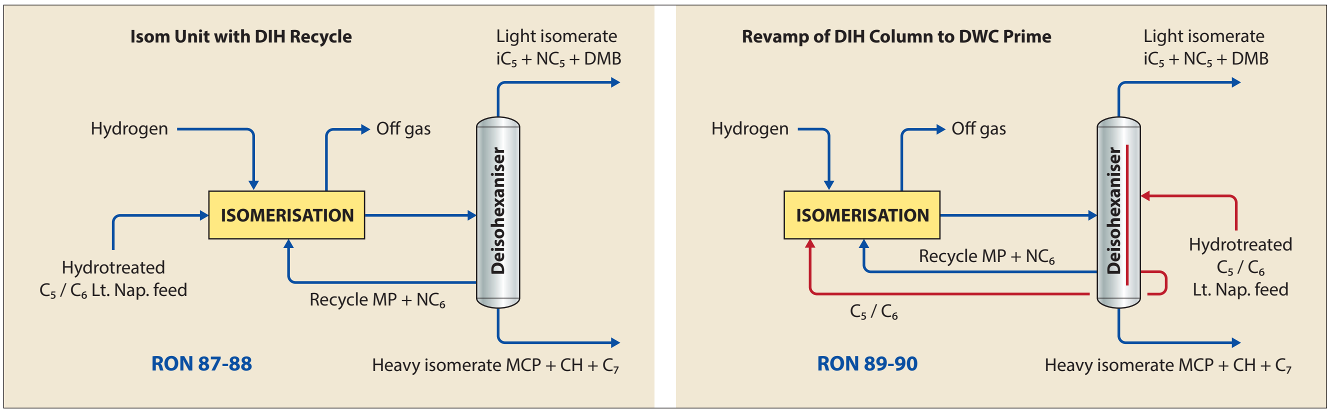

Figure 7 Revamp of a DIH column to DWC in an isomerisation unit with hexane recyle

with other process streams. On the other hand, the bottom DWC has the advantage of replacing a two-column arrangement in an indirect sequence.

The latest advance in DWC technology is dual wall dividing columns which are known to have a higher thermodynamic efficiency than their counterparts. From the outside, it is no different from a simple DWC but has the capability to deliver four or more high purity products from a single column. As dual wall columns are robust, flexible, and easy to operate, this technology has become viable. **Figure 6** shows the elevations of commonly used DWCs.

Revamp of a deisohexaniser column using DWC technology

DWC technology plays a key role in enhancing the performance of isomerisation units. Facilities that want to improve the RON of the final isomerate find divided wall column technology lucrative as this involves only the deisohexaniser (DIH) column being revamped, so as to include the additional functionality of DIP or DP columns as the case may be. Besides enhancing separation, DWC revamps provide considerable energy savings when compared to conventional distillation column flow schemes. The use of DWC technology in an isomerisation unit not only targets improvement in RON but brings the added advantage of increased throughput which would otherwise require installation of new columns. The remaining part of this article focuses on the applications and outcomes of revamping the DIH column in various configurations.

Application of DWC in isomerisation units with hexane recycle

The DIH column recirculates unbranched molecules, mainly n-hexanes and methylpentanes, after removal of branched, high-RON molecules back to the isomerisation reactor. The top product, the light isomerate, contains mainly isopentanes, dimethylbutanes, and methylpentanes. The less the amount of methylpentanes going to the top product, the better the RON value of the final isomerate. Although this configuration definitely gives a higher RON than a once-through process, the RON can be further increased by recirculating methylpentanes back to the reactor. Also, separation of isopentanes present in the fresh feed going to the isomerisation reactor contribute to higher RON values. The isopentanes present in the fresh feed take a free ride in the isomerisation reaction process and restrict the forward reaction to produce more branched chain components. The conventional method for removing isopentanes from fresh feed is to install a DIP column upstream of the isomerisation reactor.

The revamp of an existing DIH column to a DWC enables it to have the dual functionality of a deisopentaniser. Hydrotreated naphtha is first sent to the revamped DIH column which now produces four sharp cuts. As **Figure 7** shows, the light/heavy isomerate and the recycle are managed in a way similar to that before the revamp, while the fourth cut is the fresh feed to the isomerisation reactor without iso-

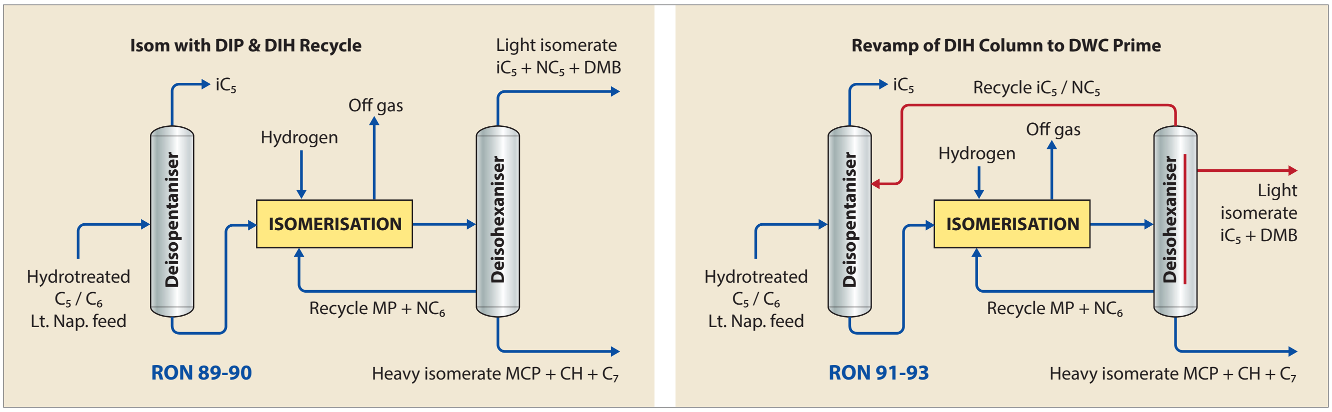

Figure 8 Revamp of a DIH column to DWC in an isomerisation unit with hexane recycle and deisopentanised feed

Performance of an isomerisation unit after revamp of a DIH column to DWC

No of columns in isomerisation unit configuration	RON of existing isomerisation unit	Performance of isomerisation unit after revamp of deisohexaniser column to dividing wall column		
		RON	Increase in throughput	Remarks
Stabiliser + deisohexaniser (DIH)	87-88	89-90	10-20%	Existing DIH column performs dual functionality of hexane recycle & deisopentaniser after the revamp to DWC
Deisopentaniser (DIP) + stabiliser + deisohexaniser (DIH)	89-90	91-93	5-10%	Existing DIH column performs dual functionality of hexane recycle & depentaniser after the revamp to DWC

Table 3

pentanes. This is an attractive and lucrative scheme as a DWC revamp of a DIH saves the installation of a DIP column, though offering the same benefits.

The advantage of this revamp is a boost in RON to 90, from 87 previously, along with a fresh feed increase of 10-20%. **Figure 7** compares a conventional DIH to a post-revamp version converted to a DWC configuration unit with hexane recycle.

A conventional configuration of an isomerisation unit with hexane recycle and a DIP column can attain a RON close to 90 as the presence of the DIP column helps remove most iC_5 before the reactor which in turn affects the reaction equilibrium in the forward direction. But to achieve RON values beyond this number, unreacted nC_5 needs to be recirculated back to the reactor. The DIH column in the conventional configuration is not able to restrict nC_5 going to the light isomerate, hence maximum conversion of nC_5 to its high-octane isomer is not achieved. Also, because some portion of nC_5 becomes a part of the light isomerate this affects the RON adversely. By revamping the conventional DIH column to dividing wall, more of the sharper cuts can be obtained and the RON of the isomerate can be improved further.

Figure 8 shows that, to improve the RON of the final product further, the DIH column is revamped to a DWC so as to draw four cuts from the column. The light and the heavy isomerate are combined and sent to the gasoline pool, while the third cut is recycled to the reactor in a manner similar to the conventional scheme. The fourth cut drawn from the DIH column primarily consists of iC_5 along with unreacted nC_5 which is recycled back to the DIP column. The deisopentaniser column removes isopentanes from the fresh feed along with the recycle stream from the revamped DIH column. The bottoms of the DIP column are rich in straight chain components and are routed to the isomerisation reactor. The revamp of a DIH column in this configuration provides the dual functionality of a DP column and helps in achieving a RON of 91-93 in the final isomerate product.

Table 3 summarises the benefits of DWC technology for various isomerisation configurations.

Conclusion

The benefits of DWC technology have grown beyond reduction in energy consumption or capex. Refineries are using DWC technology for maximising revenue from newer or better products. It is increasingly used in debottlenecking existing units in the refinery. Light naphtha isomerisation is one such example, in which the simple revamp of a DIH column improves the unit's performance by improving RON along with an increase in throughput.

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Taking a holistic approach to a revamp

If all aspects of a system are carefully examined, even minor changes can lead to large gains in unit performance and profitability

JOE MUSUMECI and JOHN ESTILL *Ascent Engineering*
GREGORY MITCHELL *Shell Norco*

Engineers frequently focus on one piece of the puzzle as a cause for poor performance. Blinkers on, fixing that one problem becomes the project goal. A tray specialist will focus on the tray design, a hydraulic engineer will focus on hydraulics, and so on. While some improvement is obtained, many opportunities to yield major benefits can be missed. Instead, a holistic review of the entire plant operation by engineers familiar with all disciplines best identifies and captures the processing opportunities.

A recent review of a butane splitter illustrates how analysing the entire system – trays, reboiler, condenser, controls, and operation – uncovered multiple changes and modifications that, if implemented individually, would each improve isobutane recovery to varying degrees.

Taken together, however, finding and implementing all these changes resulted in a predicted 50% increase in isobutane recovered at design charge rates. A review of post-revamp operation has shown that the modified tower has improved the refinery's bottom line by at least \$2.6 million/y through a combination of improved operating guidelines and capital fixes to existing design issues.

Background

The butane splitter column presented here recovers isobutane from a mixed C_4 stream originating in the crude unit saturates gas plant (SGP). The isobutane is used as make-up to the alkylation unit.

The tower was originally built in 1965 for a different service and was converted to butane splitter service later. Diameter limited, the column had been revamped in 1999 with high capacity trays and some additional condensing capacity. The tower had under-performed since that revamp, leaving excess isobutane in the bottom product. This required the refinery to purchase additional isobutane for the alkylation unit and limited the amount of butane that could be blended into gasoline, both of which resulted in a considerable economic penalty.

A study was commissioned a few years after the 1999 revamp to determine the causes of poor separation. Since the trays were changed from conventional valve trays to high capacity trays during the revamp, it was felt that the trays were at fault, and the study focused on the tray design and efficiency. The study presented several recommendations regarding tray design details and proposed the tower be retrayed again. No action was taken at that time.

Several years later, a short column outage was planned that would allow potential modifications to improve tower performance. Ascent Engineering was asked to review the previous study and other, more recent troubleshooting efforts and propose modifications that would improve the tower performance. Based on the previous study, new trays were an expected recommendation. Reboiler performance was a known issue. The upcoming shutdown was expected to be short, and the time allotted would not allow for the installation of new major equipment such as a new reboiler. Tie-ins for new equipment could be made if necessary. Because the shutdown had already been scheduled prior to the project kick-off, the new study was fast tracked in order to meet the already planned shutdown window.

The project methodology Ascent used was not only to focus on the tower trays, as was previously done, but to take a holistic approach to look at the entire system. This was particularly important since the tower had been designed for a different service, and some aspects of the equipment layout may not have been ideally suited for butane splitter service. Ascent started with a very detailed plant match simulation and evaluation of all major system components to identify deficiencies and opportunities. Verifying the reboiler, the condenser, the controls, the operating philosophy, and the other tower internals in addition to the trays was required if the project was to be a success.

Butane splitter operation

As **Figure 1** shows, a mixed C_4 stream from the SGP is preheated by a set of feed/bottoms exchangers before entering the butane splitter between trays 35 and 34. The tower overhead vapour is condensed to bubble point in a bank of air coolers. There are eight parallel air cooler bays in this bank.

The bottom tray is a chimney tray which collects liquid and gravity-feeds an elevated kettle reboiler. The reboiler vapour return is distributed by a Schoepentoeter, located just above the chimney tray. Schoepentoeter is a proprietary Shell vane type inlet device that is used to introduce gas/liquid mixtures into a vessel or column. The liquid from the reboiler gravity flows to the tower sump.

The butane splitter feed is fractionated into two products:

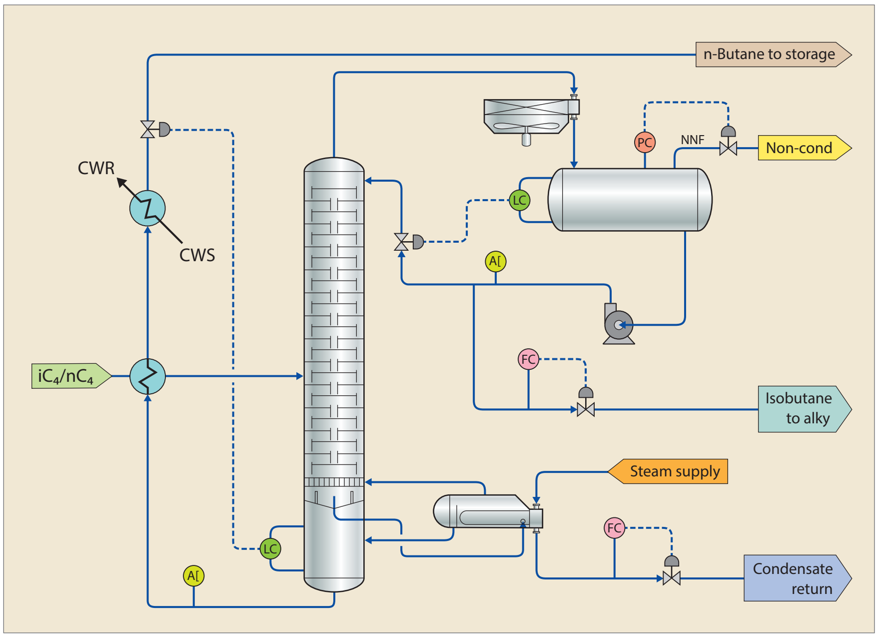

Figure 1 Butane splitter flow scheme

- An isobutane distillate which provides part of the alkylation unit's isobutane make-up requirements.
- Normal butane and heavier material from the column bottom which is pressurised out to a storage sphere and eventually blended to gasoline.

Column operation was reported to be steady. Previous tower scans showed no evidence of flooding. The tower appeared to be reboiler limited since increasing steam flow beyond a certain point resulted in condensate flow meter instability and control valve swings. The amount of isobutane in the bottoms was significantly more than the 1999 design prediction, even at charge rates well below design. Because the tower pressure had to be set high enough to allow the bottom product to be pressured out to storage (approximately 100 psig), the tower seemed to have excess condensing capacity.

Ascent collected data sheets and mechanical details for all equipment in the system. The client provided operating data from the DCS system and product analyses from the laboratory.

Initial calculations and test run

With this information in hand, we proceeded to evaluate all aspects of the system. Tower operation was simulated and rigorously verified against the operating data. Tray and tower drawings were closely reviewed, and flooding calculations were performed for the trays. The tower control system and logic was reviewed. The reboiler and condensers were rigorously rated. A nozzle elevation review revealed that there was little static head driving the reboiler flow, so detailed hydraulic calculations for the reboiler circuit were performed.

The initial simulation results and equipment calculations showed that the tower's performance with existing equipment was much worse than calculated. The primary issues identified were hydraulic limitations with the reboiler piping and issues with the control scheme and operating philosophy. Tray flooding was found to be unlikely, though low tray efficiency (which had been previously identified by the client) was confirmed to be a problem.

A plant test was scheduled to determine whether changes in operation could improve tower performance immediately. Gamma scans of the tower were also scheduled to see if the trays were prematurely flooding and to help confirm the conclusions made regarding the reboiler piping having insufficient head. The results of these tests were used to develop the final scope of modifications recommended to improve tower performance, maximise isobutane recovery, and maximise refinery profit.

Operating strategy and controls

The tower control scheme is included in **Figure 1**. The distillate product is on regulatory flow control, as is the reboiler steam flow. On-line analysers allow the console operator to monitor purity of both products.

The operating strategy for the tower was reviewed. It was learned that the console operator's first priority was to adjust manually the distillate rate to maintain approximately 5% nC_4 in the isobutane distillate. Secondly, the reboiler steam condensate rate was set at a conservative value that was stable and kept the tower overhead fully condensed. The console operator tended to vary the reboiler condensate rate set point with tower charge rate, and at lower charge rates the reboiler steam flow was significantly lower than the observed limit. Finally, the tower pressure was set as low as possible. Note that this is a 'non-material balance' type of control scheme, which does result in stable operation, but is not recommended unless other control schemes have been proven to be unsuitable.[1] This control scheme may have been a holdover from the previous service, before the tower was converted into a butane splitter.

With the distillate product rate fixed, the tower suffered from poor product purity control. To illustrate the problem, consider a tower feed that is 5000 b/d of isobutane and 5000 b/d of normal butane. If the operator sets the distillate rate at 4900 b/d, then the distillate will be nearly pure isobutane if there is adequate reflux, and the 5100 b/d tower bottom product will have some small percentage of isobutane. If the tower feed rate drops to 4000 b/d of each component, and the operator does not change the distillate rate set point, the 4900 b/d distillate will become contaminated with 900 b/d of normal butane. Similarly, if the tower feed jumps to 6000 b/d of each component, 1100 b/d of isobutane must leave with the bottom product unless the distillate rate set point is changed by the panel operator. Similar results occur if the feed composition changes instead of the feed rate.

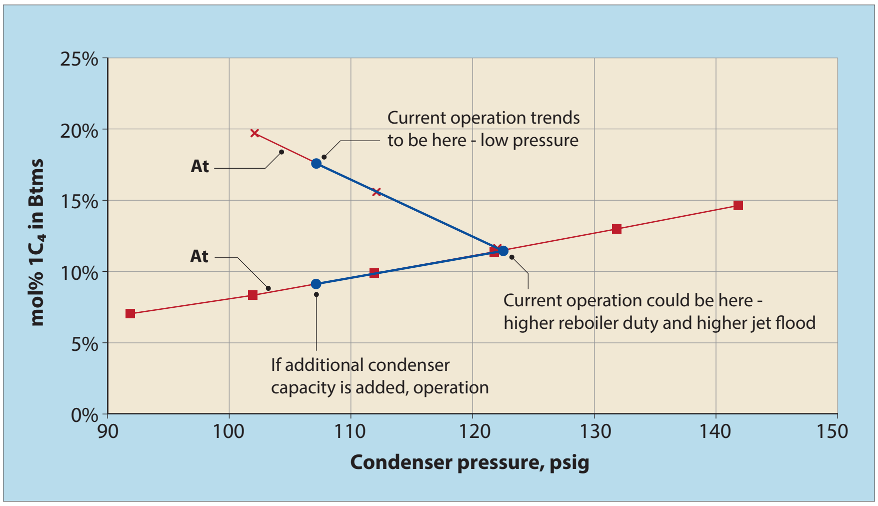

Figure 2 iC_4 in Btms vs pressure and jet flood at constant charge

This mode of operation can be seen in **Figure 3**, which shows considerable variation in bottom product isobutane concentration at any given tower charge rate. The console operator had to make manual adjustments to the reboiler duty and distillate flow rate in response to changes in feed rate and composition resulting from changes in crude slate or SGP operation.

It should be noted that this type of scheme can work with continuous operator intervention. However, this column was only one part of a larger operating unit, and so the butane splitter received reduced attention. As would be expected, this resulted in frequent operation at less than optimum conditions since the 'non-material balance' type of control scheme required frequent operator intervention.

Maximum separation occurs when the reboiler and condenser duties are maximised bringing the vapour and liquid flows up to the limits of the column diameter, no matter what the tower charge rate is. This duty-maximising mode of operation is illustrated in **Figure 2** which shows how separation could be improved by increasing reboiler duty and column traffic at a higher pressure.

This concept was applied during the test run, and the results showed that current operation could be markedly improved. During the test run, the reboiler steam flow was set near the observed limit and was not adjusted for changes in tower charge rate. The tower pressure was allowed to increase as required to maintain total condensation of the overhead vapour. The distillate composition was continually monitored and the distillate rate adjusted as needed. As **Figure 3** shows, the isobutane recovery was improved, particularly at lower charge rates. Whereas previous operation at a low charge rate might have seen 12-17% isobutane in the tower bottoms, the changes in operating strategy resulted in 5-10% isobutane in the tower bottoms. With no capital investment, isobutane recovery was markedly improved. At higher charge rates, the data shows that the test run results were similar to typical operation. Thus the column was shown to be ultimately limited by its hardware rather than by its control scheme.

Looking for a permanent solution, it was desired to convert the control system into a 'material balance' type scheme which would allow the control system to automatically maintain product purities by adjusting the tower material balance in response to feed rate or composition changes. The chosen control scheme[2] is very close to the existing control scheme, only needing a new control variable to use as the basis for adjusting the distillate flow. A typical overhead temperature control system was reviewed and rejected, with the tower overhead temperature too insensitive a variable for good control, particularly in light of the operating pressure variations expected from day to night and summer to winter. The existing on-line distillate analyser was deemed accurate and reliable enough to cascade to the distillate flow controller, and this was recommended to provide the desired material balance and composition control.

An advanced process control (APC) system for the butane splitter existed, but its use had been discontinued. Ascent recommended the APC system be put back into service. The APC could be used to implement the strategy of maximising the reboiler duty up to a tray flooding limit at all times and minimising tower pressure only after the reboiler and tray limits had been reached.

Trays

The tower was simulated to match

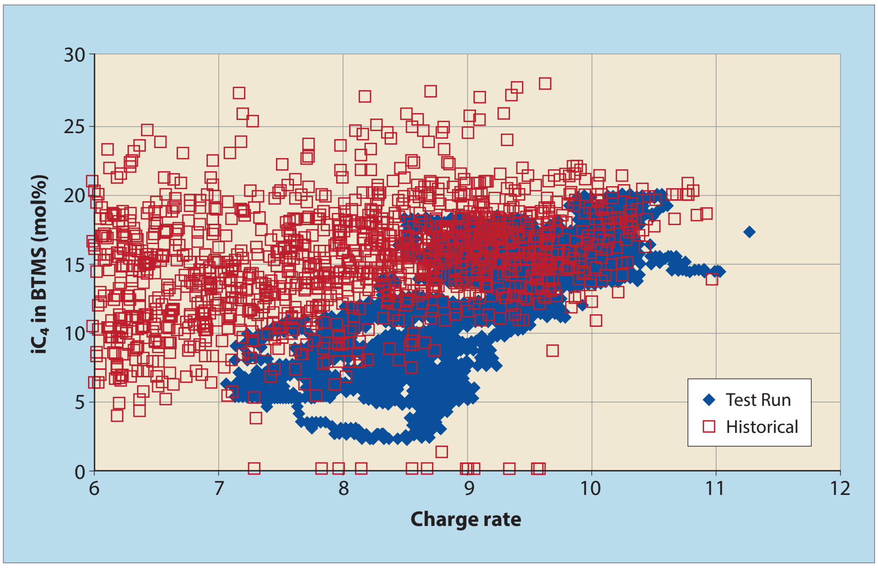

Figure 3 Charge rate vs iC_4 in bottom nC_4 product

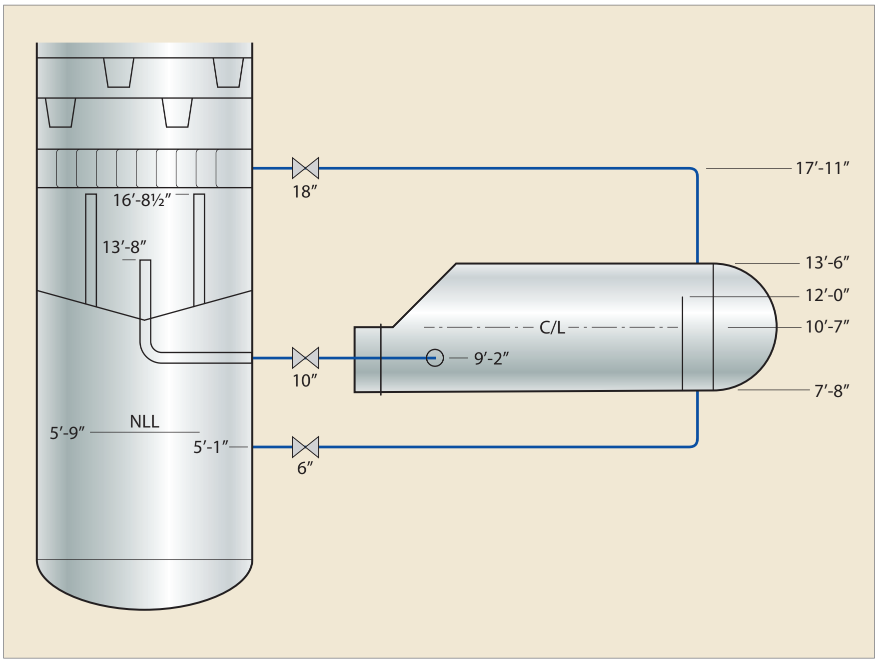

Figure 4 Kettle reboiler piping and elevations

the observed flows, temperatures, and purities. The number of theoretical stages in the tower was adjusted to match the observed product purities and reflux rate. The existing high capacity trays were rated using the simulation results and found to be lightly loaded at approximately 57% of flood. This result was confirmed by several gamma scans made while the tower was at lower feed rates, which showed no signs of flooding.

Despite the lack of flooding, the efficiency of the existing trays was a concern. The efficiency was estimated to be approximately 73%. This was roughly in agreement with a previous 2001 estimate of 68% efficiency, and a vendor estimate of 70-75% efficiency for this type of tray. The observed tray efficiency is lower than typically expected for a iC_4/nC_4 system, which could reach 100% or more with conventional trays. Tray efficiency is crucial in this system and similar systems with relatively close boiling points and low relative volatility difference. This is particularly true for this tower, since the number of trays is on the low side for a typical butane splitter.

It was determined via simulation that new, higher efficiency trays would increase the isobutane recovery with no other changes to the tower. An increase in tray efficiency from 73% to 85% would reduce the isobutane in the bottom product at design conditions from 24.5% to 22.6%. This would result in an estimated $1 million annual benefit to the refinery, which justified a complete retray. A different type of high capacity tray, expected to have a higher efficiency, was recommended even though the capacity increase over the existing high capacity trays was marginal.

It was determined via simulation that new, higher efficiency trays would increase the isobutane recovery with no other changes to the tower

Reboiler review

The butane splitter utilises a kettle type reboiler that is intended to take the total liquid coming from the chimney tray as its feed. Steam that is let down from 175 psig to approximately 55 psig is used on the tube side to heat the process liquid. Concerns about the reboiler were expressed at the project kick-off meeting, and it was noted that the reboiler was considered to be a column limit. Several aspects of the reboiler system needed verification to ensure the performance required.

As previously mentioned, the maximum reboiler steam rate was limited. Beyond this limit, the condensate flow became erratic and the steam control valve would swing. During the test run, the steam let-down valve was swinging between 55% and 65% open, with the reboiler supply pressure then varying from 52 psig to 60 psig. The condensate valve varied from 32% to 38% open during this time. It appeared the reboiler could not condense any more steam past the observed maximum rate, at which point steam would blow through and the condensate flow became two-phase. Trying to measure two-phase flow with an orifice plate resulted in erratic condensate flow meter output and unstable operation. Also, with steam blowing through the exchanger and the condensate level control valve no longer maintaining back pressure, the steam chest pressure in the reboiler dropped, reducing the LMTD available and therefore limiting heat transfer.

Initial thoughts were that the reboiler was under-surfaced. Lack of surface area could have been the cause for the inability to condense more steam and provide more reboiling duty to the tower. From the symptoms observed, concluding the reboiler was fouled instead of under-surfaced (or under-surfaced because of excessive fouling) is also perfectly reasonable. However, other possibilities needed evaluation as well. A poorly designed condensate system, improper condensate flow meter installation, and reboiler hydraulics were all possibilities to be considered.

The reboiler was thermally rated and was found to be approximately 67% over-surfaced at project design conditions, even with a conservative fouling factor. The over-surface was much higher at the observed operating conditions, which had a lower charge rate and lower reboiler duty. The conclusion drawn from this review was that the reboiler size was adequate, fouling was unlikely to be limiting the reboiler, and the cause of the reboiler issues lay elsewhere. A recommendation was made to pull the bundle for cleaning during the turnaround, in case it was severely fouled.

A hydraulic review of the process side of the reboiler system was performed. The existing reboiler had a 10” liquid feed line, an 18” vapour return line, and a 6” liquid product line. As **Figure 4** shows, a chimney tray collects the bottom tray liquid and feeds it to the reboiler via a standpipe. The relative elevations of the tower and reboiler provided only 4’-8½” of liquid static head to drive the liquid flow to the reboiler and the vapour return flow back into the tower. The bottom tray liquid, primarily normal butane, is very light, and the static head available equated to approximately 1 psi of driving force. The low driving force immediately made this circuit suspect; a hydraulic limitation had a high probability of being a major cause for the reboiler limitation.

Detailed hydraulic calculations of the reboiler feed and return piping indicated that the liquid head available on the chimney tray to overcome the piping frictional losses was marginal for the observed operation, and definitely insufficient for design conditions. The reboiler circuit capacity was estimated to be 950-1100 g/m.

Based on detailed hydraulic calculations, it was hypothesised that a significant amount of liquid was overflowing the chimneys and bypassing the reboiler. A restricted reboiler feed rate would explain the following observed issues around the reboiler:

- As steam to the reboiler was increased, liquid vaporisation in the reboiler reached 100%. Past that point, more steam was being brought in than could be condensed. This excess steam left with the condensate, and the two-phase condensate flow gave an unstable flow measurement which resulted in both the condensate flow control valve and 175# steam let-down valve opening and closing rapidly.
- The reboiler duty could not be increased enough to get the tower vapour load up to the tray flooding limit. The available tower diameter was not being effectively used to separate iso- and normal butane.
- Liquid from the bottom tray, which is richer in isobutane, bypassed the reboiler completely, further increasing the isobutane lost to the bottom product. Once the reboiler reached 100% vaporisation all of the tower bottom product came from liquid that spilled over the chimneys and bypassed the reboiler.

Including a reboiler bypass in the simulation, such that the 175 g/m tower bottom product was composed entirely of bypassed bottom tray liquid while the reboiler vaporised 100% of the 950 g/m fed to it, improved the simulation match to plant data.

Ascent recommended the tower be gamma scanned to verify that insufficient hydraulic head existed to force flow through the reboiler rather than overflowing the chimneys. A liquid level at the top of the chimneys would prove the reboiler hydraulic limitation hypothesis that bottom tray liquid was spilling over the chimneys and bypassing the reboiler. A gamma scan would also check for unexpected tray flooding, help determine if there was equipment damage, and look for any unexpected issues inside the tower.

As expected, the gamma scans showed the chimney tray to be liquid full up to the level of the chimneys at nearly all charge rates. It was confirmed that this was the biggest bottleneck in the tower – bottom tray liquid was bypassing the reboiler because of insufficient hydraulic head, limiting the reboiler duty and allowing excess isobutane to escape into the bottom normal butane product.

The detailed plant match data, simulation, and calculations were thus validated with gamma scans, resulting in complete confidence that a cause had been found and could be fixed with appropriate modifications.

To achieve the required reboiler duty at the new design conditions, which would increase the vapour/liquid traffic in the tower up to the flood point, a reboiler feed rate of 1600 g/m was needed. To achieve the desired 1600 g/m of flow while maintaining the liquid level on the chimney tray at approximately 50% of the chimney height, the following modifications were required:

- The existing 10” reboiler feed line was replaced with new 16” piping, including new 16” nozzles on the butane splitter and on the reboiler shell. The tower’s internal reboiler draw piping was also replaced with 16”.
- The standpipe on the chimney tray was removed. This eliminated the stagnant volume present below the top of the standpipe and helped reduce the pressure drop. The new 16” reboiler draw was installed flush with the tray deck and a vortex breaker was placed over the new opening.
- The existing 18” vapour return line, reboiler and tower nozzles, and Schoepentoeter were replaced with 24”.
- An impingement plate mounted inside the reboiler shell at the existing feed nozzle was removed as part of the nozzle replacement. A new impingement plate was attached to the tube bundle instead. This increased the open area at the reboiler feed nozzle, resulting in a lower pressure drop through the nozzle.
- Two non-condensable vents were added to the reboiler channel, one at the top of the channel and one underneath the partition plate. The lower vent is typically left cracked open during operation. Venting non-condensable gases such as air and CO_2 reduces the risk of corrosion and also improves heat transfer efficiency. The vents also help purge air from the reboiler during start-up.
- In order to improve reboiler control stability, the steam flow control point was moved from the flow meter on the condensate to a flow meter on the steam supply line. Measuring marginally sub-cooled condensate with a flow meter invites flashing and inaccurate measurements as compared to more accurately measuring the single phase steam flow.

Fixing the reboiler feed limitation, with no other changes, was expected to reduce isobutane in the bottom product from 24.5% to 17%

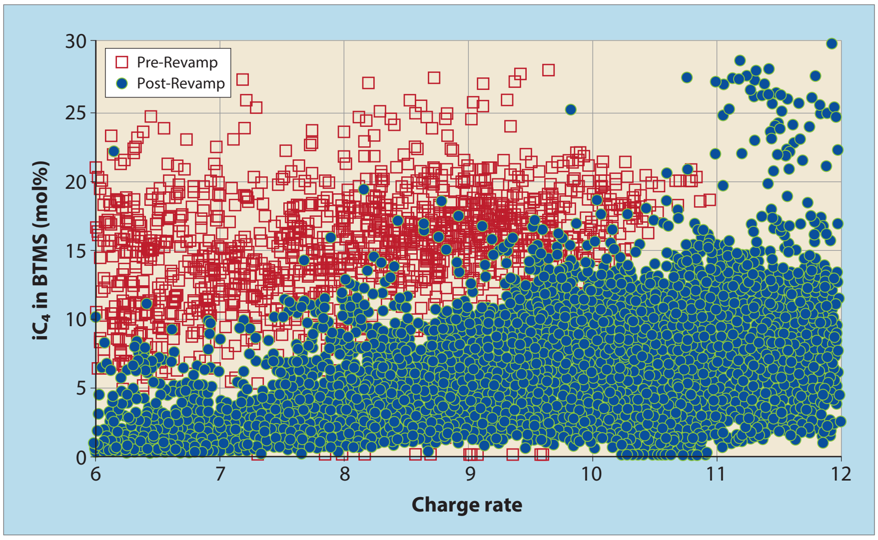

Figure 5 Charge rate vs iC_4 in bottom nC_4 product, post-revamp

at design conditions. When combining the reboiler modifications with new, higher efficiency trays, isobutane in the bottom product was expected to be reduced even further to 13.2%.

Condenser review

Eight parallel air cooler bays are used to condense overhead vapour from the butane splitter. As discussed previously, isobutane recovery is maximised when the tower is operated at its tray flooding limit at the lowest pressure the condensers can achieve as limited by rundown hydraulics.

The existing air coolers were rigorously rated. Due to improved isobutane recovery, there is an incentive to maintain the tower pressure close to 100 psig during hot weather. This incentive is shown in **Figure 2**. The rigorous condenser rating showed that an inlet air temperature of approximately 80°F (27°C) was required for the existing condensers to maintain a tower pressure of 100-105 psig when the tower is operating at or near the flood point. At the design air inlet temperature of 95°F (35°C), the existing condensers would maintain the column pressure at approximately 125 psig when operating the tower close to its flood point.

At project kick-off, the condensers were believed to have excess capacity, but current operation was deceiving because of the reboiler limitations. An incentive actually existed to increase the condensing capacity for operation during warm weather.

The following modifications were recommended to increase the condensing capacity during the summer months.

The tubes of all the condenser bays were scheduled to be replaced in kind during the turnaround due to their poor condition. Four of the tube bundles had fin counts of six fins per inch, while the other four bundles used tubes with 10 fins per inch. To maximise heat transfer area within the existing bundle design, Ascent recommended that all replacement tubes be 10 fins per inch.

Rigorous analysis of the exchangers showed that increased air flow was a relatively inexpensive method to increase the condensing duty. Ascent recommended new fans and higher powered motors. Five of the motors included variable frequency drives with automatic controls to improve controllability.

Increasing the condenser capacity, when combined with the other recommended changes, was expected to reduce isobutane in the bottom product from 13.2% to 10.1% at design conditions.

Project execution

The design portion of the project was fast-tracked, taking just seven months from kick-off meeting to column shutdown. Fast-tracking a capital project within a large organisation can be a project of its own. Clear justification for each piece of the scope to be executed was key in convincing the site to execute the project on such a compressed schedule. A partnership with Ascent and the tray technologists was another key enabler, as the tray rating and data sheets could be developed in parallel to the overhead condensing and reboiler development work. The tower revamp work was to be performed in a running unit, which added safety and constructibility concerns.

Once project execution was initiated, installation of the new trays proved to be difficult and time consuming. Upon entry, the column was found to be out-of-round and the new trays were found to have some fabrication deficiencies. The tray fabrication issues were addressed in a temporary construction shelter at the site, and installation required constant fit-up corrections with the tray panels themselves.

Fitting up the tray panels and getting buy-off from process engineering inspection initially seemed as though it would bust the schedule. However, process engineering ensured quick responses and the tray installers improved fit-up timing efficiency. As new trays were being flown up the tower by crane, the next trays were being modified using a new weld plan and corrected drawings within the temporary construction shelter. This effort allowed the project to meet the original schedule.

Installation of the new, larger reboiler supply and return nozzles in the 50-year-old tower shell also proved to be a challenge. In the end, the reboiler related work required 57% of the total project investment, 25% went to the trays, and 18% went to the condensers.

Revised operation

Most of Ascent's recommendations were implemented during the shutdown. The reboiler and condenser modifications described previously were all completed. New high capacity trays of the same type but with efficiency enhancements were installed.

Performance of the tower, as measured by isobutane in the bottom product, improved markedly upon start-up. One set of data taken shortly after start-up showed 14.5% isobutane in the column bottom product at 113% of the design charge rate. This was a considerable improvement on previous tower performance, particularly considering a temporary limitation on reboiler steam supply in place at the time. A review of the refinery isobutane purchases a month after start-up showed annualised savings of $2.6 million. This isobutane recovery benefit did not include the economic impact of being able to blend more butane into gasoline. Longer term post-revamp operation is plotted against pre-revamp operation in **Figure 5**.

There is still room for additional improvements. The APC was configured and placed into service well after the modified tower had been returned to operation. Some enhancements were made as operating experience was gained, such as increasing the maximum allowable tower pressure drop. When in service, the APC can minimise the isobutane losses, although at times the isobutane losses are not minimised in favour of meeting other objectives. Operations does not consistently use the APC, however, and the reasons for this should be explored.

Conclusion

These results demonstrate the success that can be achieved when all aspects of the system are carefully examined. A detailed plant match simulation and detailed equipment calculations are crucial to identifying the opportunities and solutions. Studies such as this isobutane recovery effort often reveal opportunities for higher throughput, improved operation, and increased profits that were not previously known or considered. In many cases, relatively minor changes often lead to large increases in unit performance and profitability.

References

1 Kister H Z, *Distillation Operation,* McGraw Hill Inc, p492.

2 Kister H Z, *Distillation Operation*, McGraw Hill Inc, p498.

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Selecting catalysts for marine fuels production

Accelerated activity and stability testing of hydrotreating catalysts

ABRAR HAKEEM *Q8 Research*
ED OUWERKERK *Catalyst Intelligence*

Catalyst activity and stability are important factors in boosting the refining margin of units like reformers, hydrocrackers, and hydrotreating units. A refinery has little influence on feedstock and product prices, but can increase its margin by selecting the best catalyst for the unit configuration and by wisely planning its activity over the cycle.

A western European refiner wanted to select a catalyst best suited to its 100 m^3 single bed hydrodesulphurisation (HDS) reactor operating at medium pressure with the aim of producing marine fuels. The aim is to produce fuels in three separate modes using three different Urals feed cuts. The main product components using three different feed cuts are: 50 ppm sulphur industrial gasoil (IGO), 800 ppm sulphur marine gasoil (MGO), and 4500 ppm sulphur low sulphur fuel oil (LSFO). In view of the size and duration of the catalyst supply contract, the refinery decided to perform catalyst testing and not base its catalyst selection on vendor claims alone. Q8 Research together with Catalyst Intelligence designed an experimental protocol for catalyst testing which guided the selection of the best performing catalyst. The catalyst testing was performed at Q8 Research under actual process conditions with actual feedstock used in the refinery.

A maximum cycle length for the catalyst is highly desirable. Moreover, it is beneficial for the refinery to have lower hydrogen consumption and at the same time meet all product specifications. The catalysts used for hydrotreating have a lifetime ranging from one to six years, depending on the composition of the feed (gasoil, vacuum gasoil, atmospheric resid, and so on) and process conditions (pressure, hydrogen/oil ratio, temperature, LHSV, hydrogen purity) used in the reactor. Deactivation of hydrotreating catalysts occurs typically due to coke formation, metals deposition, and sintering of active sites.[1] In the case of processing middle distillates (kerosene or gasoil), the metal content of the feed is low and catalyst deactivation occurs most likely due to coke deposition over its lifetime.[2,3] In the case of heavier feedstocks (atmospheric residue, vacuum resid), catalyst deactivation occurs most likely by both metal deposition on catalysts and coke formation. Moreover, hydroprocessing catalyst deactivation is possible for all feeds due to the sintering of active sites over its lifetime. Sintering of active sites is directly related to temperature and can be enhanced when the reactors are operated at higher temperatures near to the end of life of the catalyst, or at high temperatures during operations, caused by upsets in the commercial reactor.

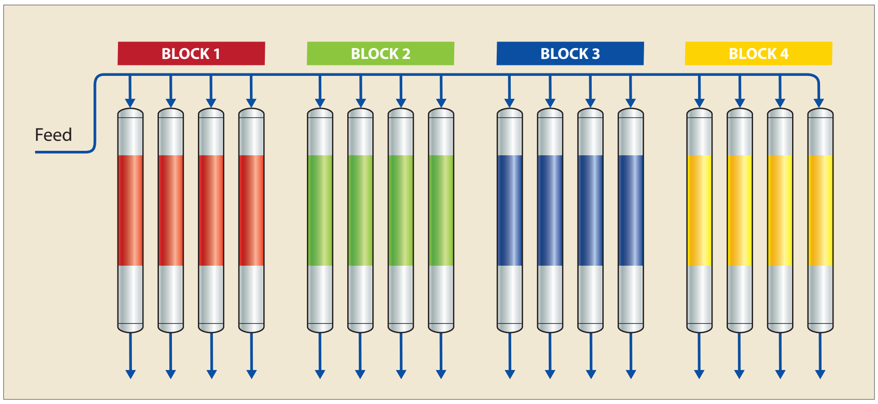

Figure 1 Layout of reactors in different heating blocks (1-4) in the catalyst testing unit

To evaluate hydroprocessing catalysts' stability, it is essential to perform an accelerated aging test, as it is not practically feasible to run a test for the exact lifetime of the catalyst. However, the parameters used to design the accelerated test must be within the operating window of the actual process conditions used in the refinery.

The term accelerated deactivation has no strict definition for a catalyst and can apply to different sets of process conditions used in a pilot unit, depending on the type of test. Many times, accelerated tests are designed with process variables which are never experienced in a real process and can result in different deactivation mechanisms that may not be relevant for actual stability comparison between the catalysts.[4] The term completely loses its purpose when it is referred to without indicating the actual process conditions (pressure, temperature, hydrogen/oil, LHSV) at which the respective catalysts were operated.[1,5] The experimental set-up in our case is designed in such a way that performance feedback at start of run (SOR) conditions is obtained from separate parallel reactors, and accelerated deactivation feedback is obtained from another set of parallel reactors. The conditions selected for accelerated deactivation are within the operating range of a commercial hydrotreatment reactor. Moreover, the design of the experiment allows a comparison of differently operated reactors under

Refinery feed streams used to perform catalyst testing			
Analysis	**Straight run gasoil (SRGO)**	**Light vacuum gasoil (LVGO)**	**Heavy vacuum gasoil (HVGO)**
Density 15°C, kg/l	0.8445	0.8902	0.9242
Sulphur, wt%	0.83	1.42	1.88
Total aromatics, wt%	30.2	34.9	51.8
Simulated distillation			
IBP, wt%	134	174	324
10, wt%	216	286	392
20, wt%	239	318	415
40, wt%	273	358	445
60, wt%	306	387	472
80, wt%	345	415	503
95, wt%	388	444	541
FBP, wt%	422	478	594
Contaminants			
Ni/V, wtppm	<1	<1	<2
As, wtppm	<0.05	<0.05	<0.1

Table 1

uniform hydrotreatment conditions at the end of the test.

Experimental

A 16-flow parallel reactor unit was used to perform catalyst testing. It has four different heating blocks (see **Figure 1**). Each heating block contains four reactors which can be set at different temperature to allow testing of multiple process conditions simultaneously. All of the experiments were performed at the same pressure, hydrogen purity, liquid hourly space velocity (LHSV), and hydrogen/oil ratio as is used in an actual reactor in the refinery.

In order to have equal internal mass transfer influence on catalyst performance from different vendors, the catalyst extrudates as received were sorted in a length range of 2-4 mm. A customised robot is used at Q8 Research to perform catalyst sorting and size distribution analysis. This is an important step, as smaller catalyst particles allow more surface area and hence higher activity. Uniform size distribution is critical to provide precise comparison of catalyst activity, especially when using small scale reactors (<20 ml) for testing commercial catalysts from different vendors. Higher amounts of poisons (metals) and other foulants were absent from the feedstocks (see **Table 1**), so no hydrodemetallisation catalyst beds were loaded into the reactors.

Hydrotreatment catalysts from two different vendors (CatY and CatZ) were compared to evaluate their performance. The catalysts were loaded in 8 mm ID reactors and packed with inert silicon carbide to ensure that plug flow criteria are maintained (no bypassing and limited axial dispersion). Three different feeds (see **Table 1**) were used to compare the performance of the catalysts under typical refinery process conditions. A common wetting and activation/sulphiding procedure was implemented and agreed with all the catalyst vendors. Dimethyl disulphide (DMDS) was added (3 wt%) to straight run gasoil for catalyst sulphidation/activation. Catalyst activation was followed by a SOR temperature of 360°C using straight run gasoil (SRGO) feed.

Design of experiment

The experiment was designed in such a way that the activity as well as the stability of the catalysts could be compared within a relatively short period (30 days). For comparison of activity, heating blocks 1 and 2 were run close to the SOR temperature for different feeds. For insight into catalyst deactivation, conditions were repeated using LVGO feed (see **Table 2**). During commercial operation, catalyst deactivation is measured by an increase in the required weighted average bed temperature (WABT) to meet the required sulphur specification. Typical deactivation rates in middle distillate hydrotreatment is around a 0.5-2°C increase in WABT per month. To measure this deactivation with some accuracy, a normal test programme would typically require three months or longer. In parallel, heating blocks 3 and 4 were run close to EOR temperatures (395-405°C) to accelerate deactivation. The hydrogen to oil ratio, hydrogen purity and total operating pressure remained the same for all test conditions. In addition, as was the case with heating blocks 1 and 2, catalysts were finally tested by a repeat condition using LVGO feed to evaluate deactivation (see **Table 2**). In this repeat condition, the catalyst from each vendor can now be assessed at both normal as well as accelerated deactivation conditions.

Results and discussion

Catalyst testing (blocks 1 and 2) was carried out around the target effluent sulphur concentration for different types of feed (see **Table 2**) by adjusting the temperature. A pseudo first order kinetic plug flow reactor model was used to model the hydrodesulphurisation reaction rate obtained at different temperatures

Experimental design using four different heating blocks for simultaneous comparison of catalyst activity and stability at different conditions					
Duration (days)	**Feed**	**Sulphur (ppmw)**	**Heating blocks 1 & 2 (LSHV = 2 h^{-1}) Purpose / T (°C)**	**Heating block 3 (LSHV = 2 h^{-1}) Purpose / T (°C)**	**Heating block 4 (LSHV = 4 h^{-1}) Purpose / T (°C)**
5	Straight run gasoil (SRGO)	50	SOR activity (360-364)	SOR activity (360-364)	SOR activity (360-364)
9	Light vacuum gasoil (LVGO)	800	SOR activity (360-364-368)	EOR deactivation (395)	EOR deactivation (395)
12	Heavy vacuum gasoil (HVGO)	4500	SOR activity (352-360-364)	EOR deactivation (405)	EOR deactivation (405)
3	Light vacuum gasoil (LVGO)	800	SOR deactivation (360-368)	EOR deactivation (360-368)	EOR deactivation (360-368)

Table 2

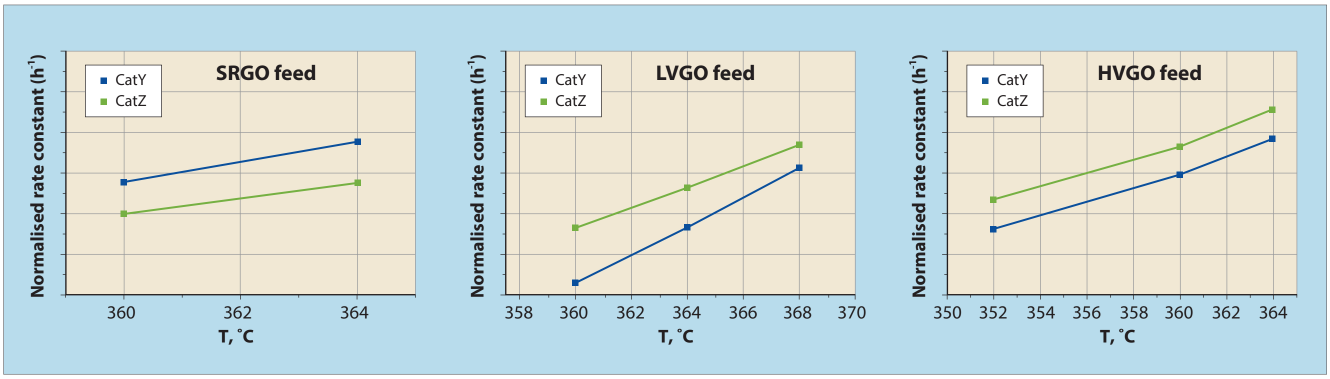

Figure 2 Start of run activity comparison at different temperatures for two commercial hydrotreating catalysts

and using different feeds. The apparent first order rate constant for the catalysts at different temperatures was calculated as follows and compared for each feed (see **Figure 2**):

$$k\,(T) = LHSV\left[\ln\left(\frac{C_{feed}}{C^{(T)}_{effluent}}\right)\right]$$

where k(T) is the apparent first order reaction rate constant, C_{feed} is the sulphur concentration in the feed, LHSV is the liquid hourly space velocity, and $C^{T}_{effluent}$ is the concentration of sulphur in the effluent at T temperature.

For LVGO and HVGO feeds, CatZ showed better activity compared to CatY (see **Figure 2**). However, in the case of SRGO feed, CatY showed higher activity compared to CatZ at similar process conditions (see **Figure 2**). It seems that CatY is better designed for middle distillates with lower density feed but lower functionality towards removal of the refractory types of sulphur species present in heavier hydrocarbons, or other properties related to catalyst design, both of which were outside the scope of this study.

It is interesting to see how performance evaluation can change based on the type of feedstock with the same catalysts. This underlines the value of catalyst testing and using actual feed and process conditions for an accurate comparison of catalysts. By analysis of concentration of aromatics in the liquid effluent, no significant difference in hydrogen consumption was observed between the two catalysts (CatY and CatZ).

To evaluate catalyst deactivation, LVGO feed was used during the first and the last stage of catalyst testing under the same conditions. At SOR conditions (blocks 1 and 2), CatY and CatZ experienced different feeds and temperature in the range 352-368°C (see **Table 2**). The sulphur concentration in the effluent at the end of catalyst testing (TOS = 30 days) compared to the sulphur concentration at the start (TOS = 4 days) for each catalyst were at similar levels (see **Figure 3a**). This indicates that, after 30 days of operation at SOR temperatures, it is difficult to measure catalyst deactivation for diesel hydrodesulphurisation catalyst. This was expected with typical deactivation rates of around 0.5-2°C of WABT per month.

In parallel reactors containing CatY and CatZ catalysts (blocks 3 and 4), catalysts were tested at a higher temperature (EOR). With different feeds and actual EOR conditions (395-405°C), both catalysts deactivated significantly during the test period. Sulphur concentration in the effluents of CatY and CatZ at the start (time on stream [TOS] = 4 days) was significantly lower than during the last stage (TOS = 30 days). CatZ is better in terms of stability compared to CatY, as effluent sulphur in the case of CatZ is much lower than for CatY at TOS = 30 days (see **Figure 3b**).

Testing at EOR temperatures, which are within the actual temperature range of commercial operation, is a good choice to evaluate deactivation rates in a short period of time. As the commercial reactor operates in an adiabatic mode, the temperature increases along the length of the bed. This means that, even at the SOR conditions of a commercial reactor, the lower catalyst bed in the reactor will also experience higher temperatures (depending on the temperature rise in the

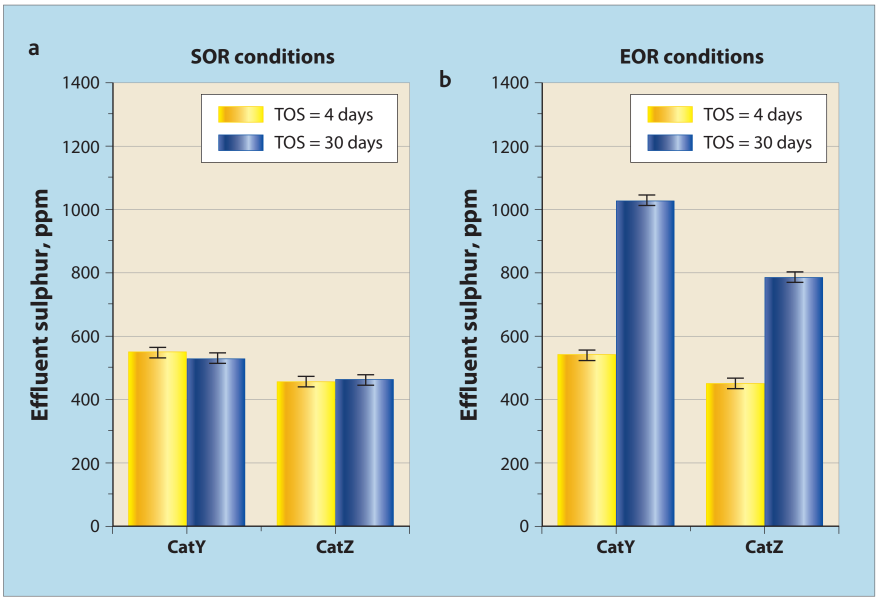

Figure 3 Catalyst deactivation by comparing sulphur concentration during repeat conditions at start and end of run using LVGO feed: (a) start of run conditions experienced by the catalysts; (b) End of run conditions experienced by the catalysts

reactor). This section of the bed can be used to compare the deactivation experienced at lab scale.

As discussed above, the most likely cause of deactivation in processing middle distillates and feeds with low metal content is coke formation. Over its lifetime, a catalyst may experience some sintering of active sites. This is one of the reasons why the activity of a regenerated catalyst is significantly restored after coke removal.[6] Around 80-90% of the hydrodesulphurisation and hydrodenitrification activity is typically restored with a simple coke burn-off, depending on how the commercial middle distillate (without Ni/V in feed) hydrotreating reactor was operated during its lifetime.[2] High temperature conditions thermodynamically favour formation of polyaromatic species and less adsorption of hydrogen on the catalyst surface, which leads to coke formation on the catalyst. In a 30-day period with EOR temperature conditions, significant (12-15°C) deactivation was observed in both catalysts (CatY and CatZ). However, CatZ clearly performs better in terms of stability.

Conclusion

A 30-day time-on-stream operation allows a clear comparison of activity and stability of commercial hydrotreating catalysts by applying an effective experimental design in a parallel reactor unit. CatZ is better in terms of stability and activity for LVGO and HVGO desulphurisation. A change of feed type and composition can change the ranking of catalyst in terms of activity. The catalyst ages around 4-5 times faster than in normal operation when operated at EOR conditions. This allows ranking of catalysts on their stability, which is not possible in a SOR activity test run for a period of one month.

To further evaluate deactivation, it is important to compare the coke profile in the accelerated (within normal operating temperature range) aged catalyst with spent catalyst from a commercial reactor taken at the appropriate position. This can further validate accelerated ageing of hydrotreating catalysts.

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FCC SOx additives and security of supply

Rare earth prices could accelerate again as a result of trade tensions

TOM VENTHAM, CJ FARLEY and NATALIE HERRING
UNICAT B. V. and G. W. Aru, LLC

Although it happened nearly a decade ago, refiners and suppliers still bear scars from the last spike in rare earth prices that occurred in 2010-2012 and the severe impact this had on refinery bottom lines. Export restrictions on rare earth raw materials imposed by China, which accounts for 94% of global production, caused a 30-fold increase in market price of some of these commodities.[1] This hurt the refining industry in two areas due to a reliance on particular rare earths: lanthanum oxide, which is a key component of FCC fresh catalyst,[2] and cerium oxide, which is a crucial component of FCC SOx reduction additives.[3]

The use of a catalyst additive is a known straightforward and flexible way to meet FCC SOx emission limits and has become accepted technology for many refiners. Alternatives for rare earth components in FCC catalyst and SOx additive formulations were studied, and although thrifting and optimisation helped minimise short-term pain, effective alternatives were not successfully implemented before the rare earth bubble burst in 2012.[9] Therefore the refining industry remains in a precarious position and at the mercy of future price spikes, with China remaining the major producer of rare earths.[4] Reports suggest a likelihood that, in the case of faltering trade talks with the US, China could implement new trade sanctions on rare earth minerals.[4] A harbinger of this possibility was seen in May 2019 when prices of rare earth materials spiked almost 50% merely on rumours of another embargo.[5] It is expected that future sanctions would apply to raw materials rather than finished goods containing rare earth, thus only impacting importers of rare earth components and raw materials, not those exporting final catalysts or additives.

Here, our focus is on cerium oxide as a component of FCC SOx reduction additives, and how alternative additive supply options offer a solution to manage risk. Utilising a broad approach to sourcing SOx reduction additives, Unicat and G. W. Aru, LLC offer security of supply and high performance.

SOx reduction chemistry

SOx reduction additives typically comprise of three key components, each having a different function within the FCC operation. The largest proportion of a SOx additive by mass is magnesia-alumina mixed metal oxide sorbent, which is effective for absorbing sulphur trioxide (SO_3) in the regenerator as magnesium sulphate. The magnesia to alumina ratio determines whether the additive is referred to as a spinel or hydrotalcite-type with low or high magnesia content respectively. SOx is a combination of SO_3 and SO_2 where these species exist in equilibrium, which favours SO_2 in the approximate proportions 95% SO_2 to 5% SO_3.[6] Since the sorbent can only absorb SO_3, the efficiency of SOx removal would be severely limited if SO_2:SO_3 equilibrium was not quickly restored local to the SOx additive absorption site.[6] Cerium oxide is included in the additive formulation to assist oxidation of SO_2 to SO_3 and improve effectiveness. It has been found that SOx additives lacking cerium oxide result in low overall SOx absorption, measured commercially as low pick-up efficiency.[7] The final step is SOx additive regeneration in the FCC riser/reactor. Here, a non-mobile vanadium component is used to promote reduction of absorbed sulphate to hydrogen sulphide. H_2S is removed from the process in the FCC dry gas stream. Once the H_2S is released, magnesium sulphate returns to magnesium oxide and is available for further SOx pick-up in the regenerator.[6] This circular process continues until activity is lost through sintering of cerium oxide and densification of the magnesia-alumina phase.

The most effective way to determine which SOx additive is best for your FCC operation is by performing a series of industrial trials

Although use of rare earths has been a sensitive issue for refiners due to past experiences of price spikes, high performance SOx additives need to correctly balance each component of the tri-functional system to function efficiently. FCC unit configuration and operation will dictate the relative importance of each component where formulations may be optimised for full burn, partial burn, or low reactor temperature operation. For example, in typical full burn units the limiting factor for SOx pick-up is believed to be absorption site availability. Conversely, in partial burn operations oxidation of reduced sulphur species to SO_3 is critical. For low riser temperature operation, otherwise called diesel or distillate

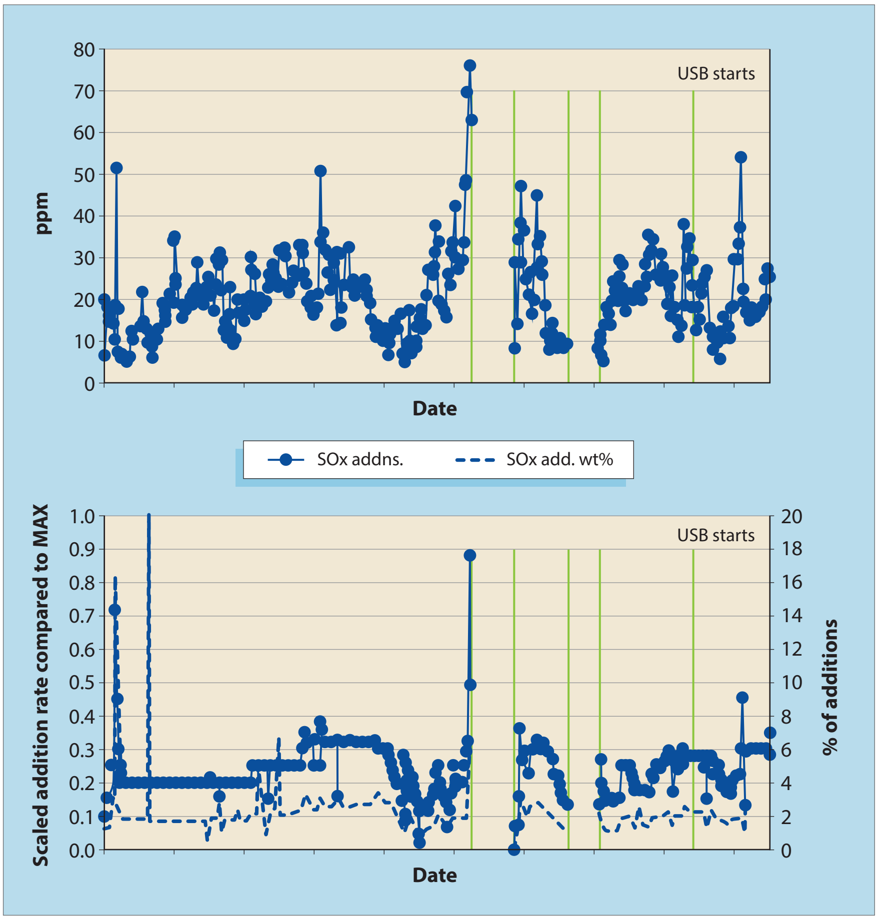

Figure 1 (a) Time plot of Refinery A flue gas SOx emissions **(b)** Time plot of Refinery A SOx additive additions. Vertical lines indicate shutdowns and the start of USB-M60 trial

mode, good SOx additive regeneration is essential for release of sulphate, which is less favourable at lower temperatures. Many refiners find that they switch between such modes frequently. In these cases, it is best practice to select the optimum SOx additive for the current operational strategy as it is also found that some SOx additive types are incompatible with certain modes of operation. In all cases, a SOx additive with the appropriate magnesium to aluminium ratio and with good dispersion within the particle should be selected. In summary, a superior SOx reduction additive should excel in all three of these areas, and refiners should work with a competent additive supplier to ensure the correct SOx additive is chosen for their operation.

SOx reduction additive trial

The most effective way to determine which SOx additive is best for your FCC operation is by performing a series of industrial trials. Daily pick-up factor (PUF), as defined in the following equation, is a calculation typically used to quantify SOx additive effectiveness:

Daily PUF = (mass of SOx removed per day) / (mass of SOx additive added per day)

Daily PUF may initially be estimated through simulation models or from experience of similar FCC unit responses. However, an accurate daily PUF should be validated by industrial test as local fluctuations in the regenerator (such as spent catalyst mixing or maldistribution) or riser (regeneration efficiency) operation can greatly affect true SOx additive response in any FCC unit. Daily PUF from an industrial test for one FCC unit cannot be assumed to be a direct facsimile of daily PUF expected for another FCC unit, no matter how similar the operation. The same can be said regarding SOx additive performance straddling a major turnaround, particularly if known mechanical issues were repaired or design enhancements were introduced during the turnaround. This is also true for emergent operational issues following unit shutdown or start-up compared to stable operation. In all cases, it is appropriate to re-evaluate SOx additive performance to ensure the best performing additive is selected for the operation.

Ultra SOxBuster additives

Ultra SOxBuster (USB) additives are offered by G. W. Aru, LLC to refiners in North America, and under the Unicat brand in Europe and around the world. These additives are produced by manufacturing partners in China and other locations worldwide. Chinese manufacturers have been producing high quality additives for domestic markets for many years. SOx additives conforming to standards of western catalyst and additive manufacturers, for example in the US and Europe, have been developed in China for use in Chinese refineries. The quality of these additives is consistent with those produced in western markets but cost structure differs significantly. Access to these FCC additives is now made available to refiners outside of China with local technical support close to the end user. Moreover, the sourcing approach taken by G. W. Aru, LLC and Unicat means refiners are offered a wide selection of SOx additive types to ensure the best SOx additive is selected for the operation. Included in the Ultra SOxBuster range are USB-M30 and USB-M60, which contain approximately 35 wt% and 60 wt% MgO respectively. These additives have similar physical properties and ceria and vanadium content as SOx additives currently used by refiners today.

Trial at a US refinery (Refinery A)

Ultra SOxBuster-M60 was evaluated at Refinery A, which is a site in the US belonging to a major international oil refining company. Results were compared against a top selling competitive SOx additive that had been in use at this site for many years on a continuous basis. As both additives are hydrotalcite based with similar physical properties, performance on a per mass basis was expected to be similar. Like-for-like performance would give the refiner access to an alternative, lower cost SOx reduction additive to achieve their compliance requirements. Proving the performance of USB-M60 also gives this refiner confidence that SOx control costs would be manageable should cerium oxide prices again escalate following trade disputes. Unicat and G. W. Aru, LLC uses their knowledge of FCC operations and experience of SOx additive performance to analyse the trial results and determined that USB-M60's performance exceeded that of the competitive SOx additive.

Upon commencing the trial, the first indication of a positive response with USB-M60 was that flue gas SOx emissions were maintained at the required low level (see **Figure 1a**). Additive consumption is also maintained within normal range to achieve this low SOx emissions level (see **Figure 1b**). Although these first views are positive, deeper analysis is required. This starts with comprehensive unit monitoring analysis using time plots to ensure

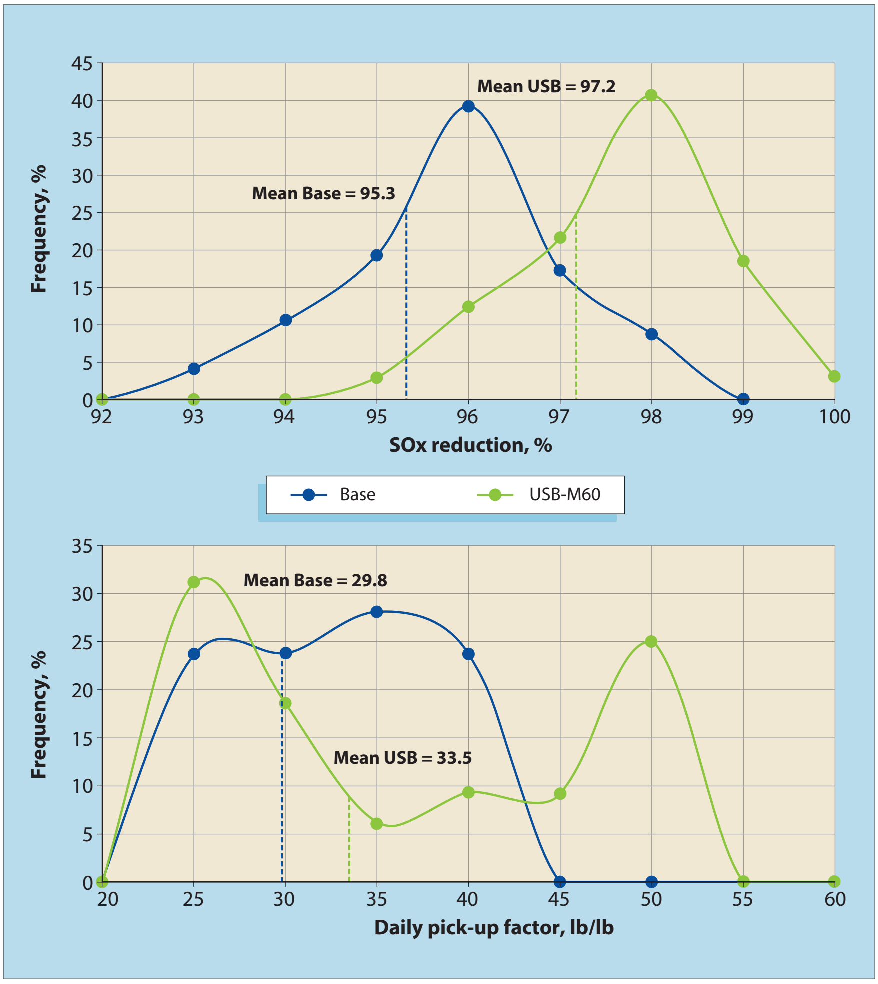

Figure 2 (a) Histogram of Refinery A SOx reduction **(b)** Histogram of Refinery A daily pick-up factor

An industry recognised technique to differentiate performance in FCC operations is cross-plotting

absence of, or to account for, fundamental changes in FCC feed properties, operation, or catalyst properties throughout the trial period that may corrupt test data or challenge trial validity. Once representative test periods are identified, average results are compared to determine superficial quantitative differences between test periods (see **Table 1**).

Although average data offers a convenient overview of trial results, it gives little information on repeatability, consistency, presence of outliers, or the ability to achieve certain target results (such as frequency and reliability of exceeding 95% SOx reduction or number of days under 20 ppm SOx emissions, for example). Histograms are used to further contextualise the results observed (see **Figure 2**). Using these methods of analysis confirms that the performance of USB-M60 exceeded that of the previous additive.

However, viewing bulk average data does not account for unit shifts and fluctuations which are unavoidable in the majority of FCC operations. Also not accounted for are certain dynamic variations and sensitivities that are important in SOx additive trials, such as changes in SOx additive addition rate or addition strategy. An industry recognised technique to

Refinery A mean average FCC data during SOx additive trials

Period	Baseline	USB trial
Feed S, wt%	0.21	0.22
Feed CCR, wt%	0.94	1.14
Rgn. dense T, °F	1324	1320
Cat. circ., tpm	Base	Base x 0.98
Air:coke, wt/wt	=	=
Excess O_2, vol%	2.0	2.3
Slurry S: Feed S, wt/wt	2.9	3.0
Slurry S, wt%	0.6	0.7
SOx additive addns., lb/day	Base	Base x 1.09
SOx reduction, %	95	97
Daily pick-up factor, lb/lb	30	34
SOx emissions, ppm	24	19

Table 1

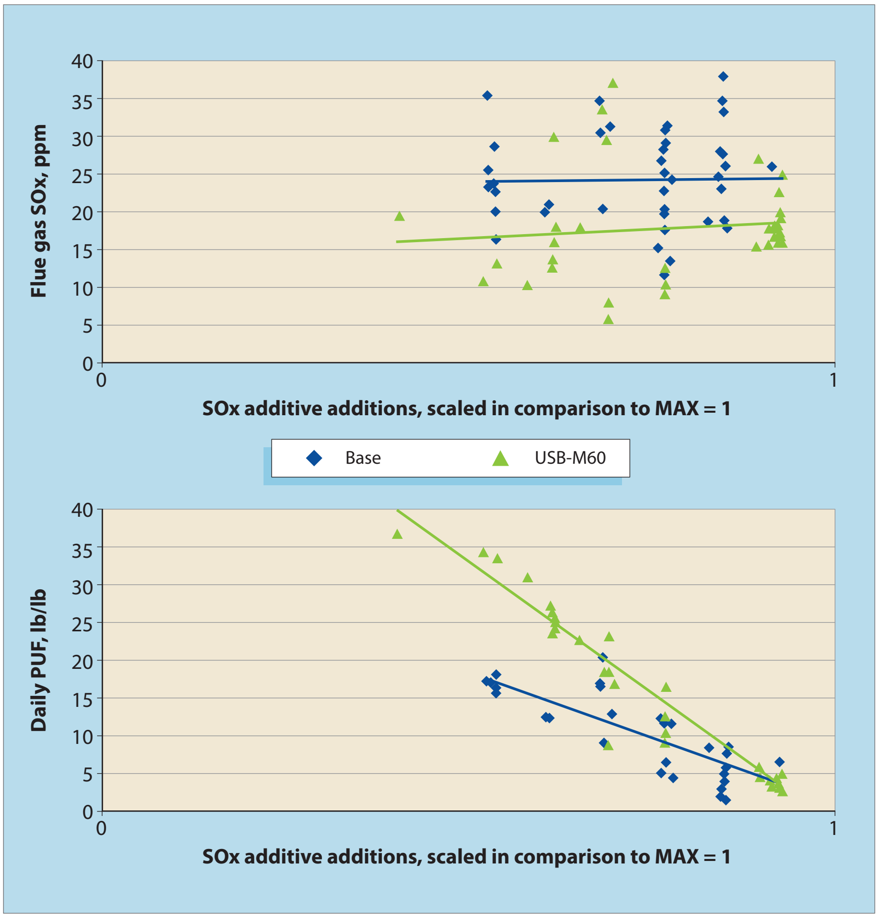

Figure 3 (a) Refinery A SOx emissions plotted as a function of SOx additive additions, and **(b)** Refinery A daily PUF plotted as a function of SOx additive additions

differentiate performance in FCC operations is cross-plotting. This method is used to observe changes in key dependent variables at a fixed single independent variable. Cross-plots show that at constant SOx additive addition, SOx emissions are 25% lower with USB-M60 than with the previous additive (see **Figure 3a**). As expected, daily PUF for USB-M60 is higher compared to the competitive additive (see **Figure 3b**). This is taken as the clearest conclusion of relative additive performance: USB-M60 is 20-25% more efficient than the previously used additive.

Following complete, multi-faceted, and precise analysis by FCC technical service engineers, conclusions can be drawn that USB-M60 outperformed the previous SOx reduction additive at Refinery A (see **Table 1**). This increased performance directly translates into cost savings for the refiner as well as an ability to improve FCC SOx control through use of a more active and therefore more responsive additive.

Conclusion

Introduction of Ultra SOxBuster additives offers refiners the opportunity to increase cost savings and future-proof themselves against potential rare earth price spikes. Industrial trials have been conducted that prove superior performance versus incumbent SOx reduction additives. Results from one such trial have been discussed here.

UNICAT and G. W. Aru, LLC help refiners to reduce environmental control costs through use of FCC additives and support from an experienced team. G. W. Aru LLC, Unicat Catalyst Technologies, Inc. and Magma Catalysts are partners to bring cost-effective and innovative catalyst solutions including the Magma steam methane reforming catalyst to refiners worldwide. This alliance utilises Unicat's existing support infrastructure and management of regulatory requirements such as REACH in the European Union. This collaboration has brought multiple benefits and gives refiners access to new technology.

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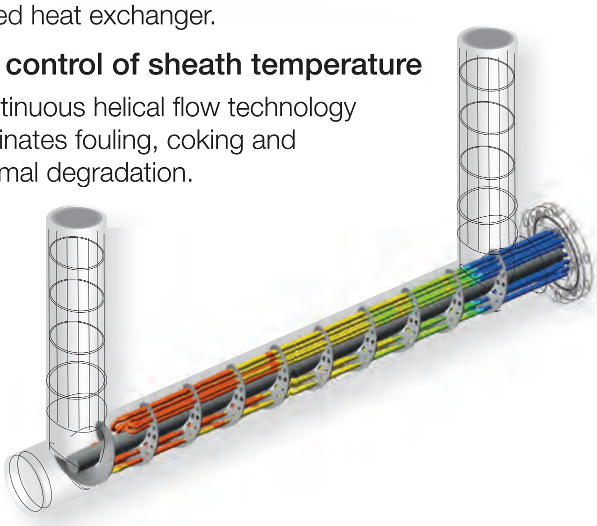

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Designing steam heat exchangers and tracing systems

Fundamentals must be considered when designing an industrial steam system to avoid premature failure or under-performance

ALEX CHU
Swagelok

When designing a steam heat exchanger or steam heat tracing system, a full understanding of the overall process and how the system will operate is essential. Inadequate performance can often be attributed to a design engineer's failure to consider all characteristics of a steam system. Before engaging in the design process, a thorough review of the steam system's operating parameters and documentation must be conducted to understand the context of the application (see **Figure 1**). Failure to do so will result in inappropriate control or selection of system components.

Engineers must understand the basic fundamentals of industrial steam systems to prevent premature failure or under-performance. After a comprehensive review of industrial heat transfer applications across different locations and industries, the most common issues can be categorised into incorrect component selection or poor installation practices. The most common issues that are observed include:

- Unacceptable quality of end products
- Premature failure of components
- Poor temperature control
- Inadequate heat transfer
- Water hammer
- Fouling of the heat transfer equipment
- Code and standard violations

Best practices for steam system design

Designing a proper industrial steam system does not have to be complicated if engineers adhere to some simple guidelines and proven field techniques. The following recommendations should be reviewed and implemented into your facility's steam system design, maintenance, and specification program before determining the equipment for your next steam heat exchanger and tracing system.

Figure 1 A thorough review of a steam heat exchanger system's operating parameters and documentation is required to design a proper system

Eliminate steam supply condensate build-up and carry-over

Control valves are required to control process steam flow between 0% and 100%. When there is either low or no steam flow in the system, condensate can build up before the inlet of the control valve and cause water hammer. In addition, if condensate flows through a steam control valve at high velocities, it can cause premature wear to the valve internals and subsequent failure to control or seal.

There are several methods to keep condensate from accumulating. For example, installing a drip leg prior to the valve, adding insulation improvements, correctly grading the steam line, or installing a steam separator prior to the control valve. Each method on its own, or a combination of different methods, will prevent condensation from forming or ensure that if it does form it is diverted away from the control valve to a steam trap where it can be evacuated from the system.

Follow turndown ratio guidelines for control valves

To control process temperatures effectively, correctly sized control valves must be specified. The most important consideration when choosing a control valve is the turndown capability, rangeability, or working range of the valve.

Due to physical valve design constraints, all valves will exhibit some uncontrollable flow because of sealing tolerances and the linearity of flow, especially at the extreme ranges of the valve stroke.

Here are some guidelines for the turndown ratios of control valves:

- Cage control: 40:1 turndown ratio provides the highest degree of controllability
- Globe control valve: 30:1 turndown ratio
- Regulating valve: 20:1 turndown ratio

Figure 2 Installing a pressure gauge before and after a control valve and on a condensate return leg after the steam trap helps to provide accurate data for monitoring a steam system

For steam applications, in addition to the turndown ratio, it is recommended to avoid using the lower and upper 20% of the valve stroke – the lower 20% to avoid excessive velocities across the valve seat and the upper 20% for controllability.

If control valves are not sized properly, the results can be poor process temperature control, premature wear of the valve seats, and excessive noise.

Install pressure gauges before and after the control valve

Pressure gauges (see **Figure 2**) will provide the basic information necessary to understand the conditions at each part of the system. This will aid performance verification and troubleshooting. It is good practice to install a pressure gauge before and after a control valve and on the condensate return leg after the steam trap. This provides accurate data to assist in understanding the pressure characteristics of the steam passing through the steam heat exchanger. In addition, all pressure gauges should be installed with a coil siphon (pigtail) to prevent high temperature damage and double block isolation valves to allow maintenance.

Install vacuum breakers

Vacuum breakers are essential equipment when steam systems are isolated from the steam supply and are not open to atmosphere. Equipment that requires vacuum breakers includes steam lines, kettles, plate or shell and tube heat exchangers, and any other equipment not rated for vacuum use.

The reason they are necessary is that when steam cools down inside a closed volume, it will condense. Since condensate can occupy only up to 1/1700th of the total volume of its mass compared to when it is in gas phase, a vacuum will be formed.

When steam systems are isolated, vacuum breakers prevent system collapse from external pressures. As a result, most steam equipment requiring air vents and vacuum breakers will have designated installation points specified by the equipment manufacturer. These should not be ignored.

Install automatic air vents

When a steam system is shut down or being maintained, air will leak into the system. This air must be purged before the system can be returned back to service. If air is not purged properly from the system, it will result in slow start-ups and could form thin boundary layers on heat transfer surfaces, creating an insulating effect that will inhibit efficient heat transfer. A boundary layer of air only one thousandth of an inch thick has the same efficiency of heat transfer as 13in of copper or 3in of cast iron.

Steam traps should not be relied on to vent air as they are usually located at the lowest part of the system and therefore cannot be relied on to do it properly since hot air tends to rise and be trapped at the highest point. An air vent fitted on the end of a steam main, or at the highest point on a piece of equipment in conjunction with a vacuum breaker, will open when air is present. This occurs due to the differential temperature between the air and the steam.

Avoid back pressure within heat transfer equipment

Condensate drainage is a critical consideration when design engineers create heat transfer equipment for steam systems. Condensate drainage is accomplished by either gravity or a pressure differential. If possible, heat transfer equipment should be installed to promote gravitational drainage with no vertical lift before or after steam traps. This is crucial in any application that has a modulating steam control valve.

Certain applications do not allow for gravitational drainage, and when that happens it is critical that condensate devices, like steam traps or control valves, are not subjected to back pressure. Unanticipated back pressure, which results in condensation collecting in the equipment, leads to premature failures and performance problems and can create water hammer, inadequate temperature control, reduced efficiency, and corrosion issues.

Prevent superheated steam

In most cases, steam heating applications demand 100% quality saturated steam supply; this level of quality refers to steam containing no entrained droplets of condensate or vapour. Superheated steam, or steam at a higher temperature than its saturation point, should be prevented from entering the heat transfer process. Superheated steam will degrade performance because it has less energy per unit volume than saturated steam unless it is accounted for within the original design. Superheated steam supply can be conditioned by installing a desuperheater.

Lockout ball valves

Ball valves are a common, safe, reliable, and cost-effective option that allows for leak-tight isolation and quick identification of isolation states in a steam system because of the handle orientation. Ball valves 2in or smaller can be purchased with locking handles, which is a safety best practice for a lockout or tagout. Before installation, contact safety and inspection departments to be sure the installations comply with any site or local regulations dealing with lockout or tagout procedures for steam systems.

Correct steam trap sizing

There are many designs of steam traps. Different designs cater to different applications and some designs are more reliable than others in certain cases. In a steam heat exchanger application, for example, mechanical-type steam traps will be best suited to a modulating flow and pressure environment. Steam heat tracing applications, on the other hand, allow for a much wider variety of steam trap designs, but are still application specific.

The sizing of the steam trap depends on maximum and minimum flows through the system. Designers must also think about the requirements for priming, air venting, functional testing, and mounting options. Generally, universal mounts are best for smaller steam traps because they are easier to maintain and replace if necessary.

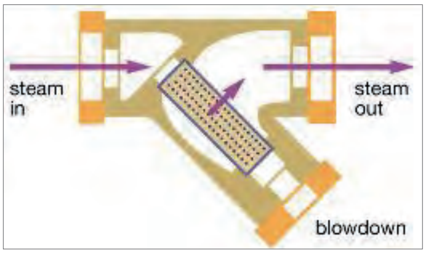

Figure 3 A Y-strainer serves as a filter to remove contaminants from steam lines to prevent premature failure or fouling of downstream components and the steam system itself

Install a strainer to prevent foreign contamination

Steam lines can contain corrosion and maintenance debris, putting control valve trims, isolation valve seats, and steam trap seats at risk of failure or fouling. Installing a strainer, which will act like a filter, will keep foreign objects out of the critical parts of the steam system (see **Figure 3**).

When installing a strainer, always install a blowdown valve with a lockout facility. This will improve strainer maintenance. Ensure that when blowing down the strainer, the discharge is vented to a safe location. Strainers should be installed in the horizontal position, so that condensate does not collect in the strainer body.

Education is key

Training courses are available to teach engineers about how to enhance your facility's steam systems and are designed to educate you about specific industries and needs. Inquire with your manufacturer's representatives about training at your facility.

Alex Chu is Engineering Manager with Swagelok Bristol and an Industrial Steam System SME for the Swagelok Company Field Engineering Group, providing training and engineering evaluation services. He is experienced in analytical Instrumentation, furnace combustion, and steam systems to solve fluid system challenges. He holds a degree in electrical and electronic engineering.

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Neutralising amine selection for crude units

Making a proper selection of neutralising amine chemistry is a challenging task

ERIC VETTERS
ProCorr Consulting Services

Even though crude units have been around for a long time, maintaining long term reliable operation continues to be a challenge. The unit design, operating conditions, feedstocks, and corrosion control programme must all work together to achieve reliable operation (see **Figure 1**). If any part of the system is out of sync, the whole unit will suffer. With constantly changing feedstocks and operating conditions, as well as some unique challenges posed by many opportunity crudes, it can be a challenge to keep everything running properly.

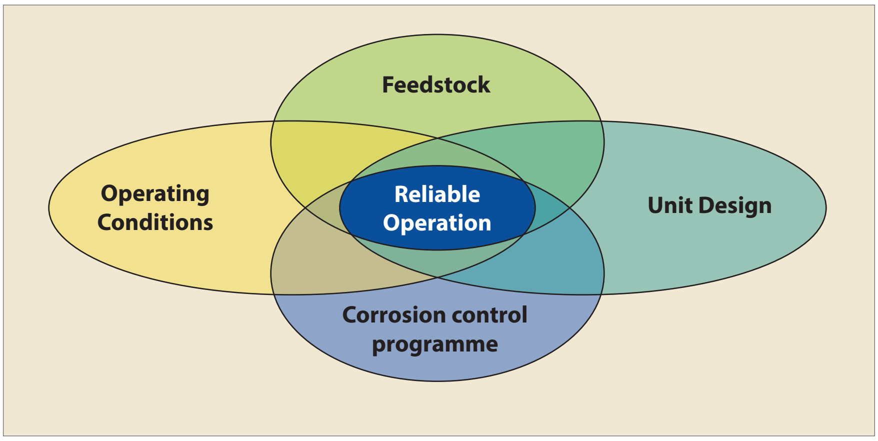

Figure 1 Factors influencing crude unit overhead corrosion and their interaction

The neutraliser system is a critical part of the corrosion control programme on crude tower overhead systems. This article will focus on understanding and applying some basic concepts to the design of neutraliser systems and on some more subtle aspects of neutraliser selection that are often overlooked.

Corrosion control basics

Some of the residual salts remaining in desalted crude hydrolyse to form HCl in the crude furnace. The HCl then ends up in the overhead system of the atmospheric tower. There can also be light organic acids in the crude oil as well as light organic acids formed from the thermal degradation of naphthenic acids in high TAN crudes, which also put additional acids into the overhead system. Neutraliser demand can easily increase by 50-100% when switching to a high TAN crude slate. Opportunity crudes often are difficult to desalt, which increases the amount of HCl formed. They may also contain tramp amine byproducts of H_2S scavengers.

If nothing is done to neutralise these acids, the condensation of steam in the overhead system will produce a highly corrosive, very low pH steam condensate stream. To control pH and reduce corrosion, bases such as ammonia or amines (referred to commonly as neutraliser or neutralising amine) are injected into the overhead system. If these neutralising compounds are improperly employed, they can also lead to fouling and/or corrosion through the formation of ammonium chloride or amine hydrochloride salts.

To prevent formation of salts and to quickly dilute any acids present, a water wash stream is often injected into the overhead system. The water wash, which is typically water recycled from the overhead accumulator, can be injected into the overhead line or into the inlets of heat exchangers. The net water from the overhead accumulator contains a mixture of organic and inorganic acids and bases. This water is commonly used as wash water in the desalter, which provides a potential route for these acids and bases to get back to the crude tower. This recycling of amines will be discussed in more detail in the desalter section.

Neutraliser selection primer

Neutralising amine selection is typically based on a few key parameters. Basically, the neutralising amine must be a strong enough base to raise the pH at the water dew point enough to control corrosion at acceptable levels. It also must not form salts ahead of the initial point where free water is present, either from condensation or injection of water wash. It should be readily available at a reasonable price. Petersen, Lordo, and McAteer[1] go into more depth on this subject.

The nature of any neutraliser salts that might form is an important consideration in neutraliser selection. Some amines, such as ethylene diamine (EDA), will form a solid salt which is a fouling and under deposit corrosion concern. Other amines, such as monoethanol amine (MEA), form liquid salts at typical process conditions. The liquid salts tend to corrode more aggressively than solid salts. Liquid salts tend to be more of a corrosion concern with some fouling potential from the corrosion products that form, whereas solid salts tend to be more of a fouling concern with some level of under deposit corrosion also occurring.

The salt point, that is the temperature where the chloride salt of the amine begins to form as a free phase, is another important consideration in neutraliser selection. The goal is to select an amine neutraliser that does not begin to form a salt ahead of the water dew point. After the bulk water dew point is reached, the water solubility of the salts precludes formation of a separate salt phase. This approach to neutraliser selection provides the pH control desired without the formation of corrosion and fouling inducing salts. In the absence of a water wash it can be challenging to find an amine that will actually accomplish its mission without forming salts.

Because the amines tend to behave independently of each other in forming salts, amine blends are sometimes used to reduce the salt formation temperature. For instance, a 50/50 molar blend of two different amines would cut the amine partial pressure in half compared to the use of 100% of either amine. Some suppliers may use five or more amines blended into a neutraliser product.

For any given amine, the salt point or sublimation point is defined by this equation:

$$K_p = P_{amine} * P_{HCl} \qquad [1]$$

K_p is the dissociation constant for the salt, which is a strong function of temperature. P_{amine} and P_{HCl} are the partial pressures of the amine and HCl respectively. The value of K_p defines the maximum amount of amine and HCl that can exist in the vapour phase at that temperature. If the product of the partial pressures of the amine and chloride present is greater than the dissociation constant K_p then salts will form. If the temperature where the salts form is ahead of the bulk water dew point then a corrosive salt phase will form. Ironically, the product used to control corrosion can help cause corrosion if misapplied.

The following discussion covers a number of different crude tower design and operating parameters that can impact neutraliser selection:

- Overhead water wash vs no water wash
- Tramp amines
- Overhead temperature
- Desalting

Water wash vs no water wash

The use of an overhead water wash typically increases the flexibility the refinery has when it comes to selecting a neutraliser. The water wash forces an immediate water dew point, which greatly reduces the risk of salt formation that could otherwise occur during the more gradual cooling that happens in overhead condensers. With no perceived risk of salt formation, refiners and chemical suppliers are typically happy to use a stronger base with higher salt forming tendencies because these neutralisers are cheap and effective for the intended purpose of neutralising HCl. Water wash also reduces the risks associated with changing process conditions such as temperature and chloride concentrations, assuming that the water wash rate is adjusted to account for upward shifts in overhead temperature. When water wash is injected close to the neutraliser injection point, there is practically speaking no amount of neutraliser that could be added which would lead directly to salt formation in the overhead system.

There is a risk, however, that is often overlooked. This is the risk of salt formation in the atmospheric tower when overhead water is recycled back to the desalter. Amines are organic bases, and as such they have at least some affinity for the hydrocarbon phase. How much of the amine partitions into the crude oil rather than the water is primarily a function of the distribution coefficient and the relative rates of crude oil and wash water. Water entrainment from the desalter also increases the effective amount of partitioning to the desalted crude.

The distribution coefficient, D, is the ratio of the solute concentration in octanol to the solute concentration in water:[1]

$$\log D_{\mathrm{oct/wat}} = \log \left(\frac{[\mathrm{solute}]_{\mathrm{octanol}}}{[\mathrm{solute}]^{\mathrm{ionized}}_{\mathrm{water}} + [\mathrm{solute}]^{\mathrm{neutral}}_{\mathrm{water}}} \right) \qquad [2]$$

The distribution coefficient is sometimes also called the partitioning coefficient, although strictly speaking the two are not the same. The partitioning coefficient calculation is the same as the distribution coefficient except that it does not include ionised forms of the solute in the calculation.

If enough amine partitions to the desalted crude, then it is possible to form an amine chloride salt in the atmospheric tower. Amines which have a high partitioning coefficient, and/or those with higher natural salt points, increase the probability of having salt formation via this recycle route. The effect of desalter operation on amine distribution is discussed later.

The different risk related to water wash is the effect of water carryover from the overhead accumulator back to the atmospheric tower via the reflux. This risk is especially a concern when water wash is started for the first time or the rate is substantially increased in an existing unit. A trend in recent years at many US refineries has been to process increasing volumes of very light shale crudes and condensates. Increased overhead and wash water rates that result from these feedstock changes will increase the load on the overhead accumulator, which can lead to increased water carry-over.

Entrained water from the accumulator carries dissolved salts with it. When the salts are carried back to the tower with wet reflux, they tend to deposit on the trays as the water boils off. Neutraliser selection can impact how the resulting problems manifest themselves (corrosion or fouling). Changing neutraliser will not typically undo any fouling that has occurred prior to the change, although it can stop it from getting worse.

For units with no water wash the risks are a bit different. The primary risk of salt formation is in the overhead system itself. Without a water wash to force the dew point, the salt forming characteristics in the overhead system are closely linked to the type and amount of neutraliser used as well as the amount of chlorides present. As these values go up and down, the corrosion risk is constantly changing as well.

From a practical standpoint, there should never be more neutraliser recycling back to the crude tower than is present in the overhead system, so the highest risk for salt formation is in the overhead system and not the tower when no water wash is employed. When trying to use an ionic model to estimate the salt point, great care must be taken to use the correct quantity of amine.

One approach is to measure the actual amine concentration in the overhead accumulator boot water, but most refineries do not have the capability of doing that analysis. If significant salt is forming in the overhead system, the overhead water, however, will not reflect the total amine present because some of it is depositing as salts in the condensers. A second approach is to use the measured chlorides and the actual neutraliser injection rate. This approach, however, does not take into account the recycle of neutraliser back to the crude tower via the desalter or reflux (either via entrained water or neutraliser solubility in hydrocarbon). For units that use an alkanol amine (such as MEA) and have desalters that operate with an acidic pH, this second approach may be reasonable. For units that have desalters operating at high pH and/or that use alkyl amines in their neutraliser, this approach can lead to under-prediction of the salt point and the resulting overhead corrosion risk. In this case, a third approach is to use the actual neutraliser injection rate plus an estimate for the amount of amine recycle based on desalter operating conditions and/or estimated recycle via reflux. The best (most conservative) overall approach is to use the larger overhead amine rate as estimated from both the actual injection plus estimated recycle and amine rate estimated from the boot water concentration plus estimated recycle.

This latter approach should provide the most realistic estimate of the real salt formation potential of a given neutraliser. Any neutralising amine recycle reduces the amount of neutraliser needed, so in the case where neutraliser demand is being estimated based on the amount of acids present, such as in a chemical bid process, the amine recycle usually does not need to be accounted for except to the extent that hydrocarbon solubility renders the amine unavailable to neutralise acids in the water phase.

Tramp amines

Tramp amines can make it into the crude unit from four primary sources – slop, make-up water to the desalter, neutralisers in the steam supply, and H_2S scavenger treated crude. Slop systems are most likely to pick up the amines used in the refinery treating systems – typically MEA, DEA or MDEA. Similar to slop, treating amines can end up in the sour water system and make it to the crude unit when stripped sour water is used as desalter wash water. Neutralisers are amines added to steam to prevent acidic condensate formation. For best control and troubleshooting, different amines should be used in the steam and crude overhead neutralisers.

Crude oil that has been treated with triazine will contain either MEA or methyl amine depending on which amine was used to manufacture the product. MEA is by far the most common amine found in H_2S scavenger treated crude oil today. Triazine is also sometimes used to reduce the H_2S load to the flare stack. Great care should be taken to ensure that the MEA byproduct of flare system scavenging cannot end up back in the crude unit.

Amines mostly behave independently of each other when calculating salt points, so with regards to neutraliser selection the primary concern is when the tramp amine is the same as one of the amines in the neutraliser. In that situation, the amine sources can become additive in nature, thus increasing the salt formation risk. For instance, in a crude unit that uses a neutraliser containing MEA, the MEA partial pressure is calculated based on the MEA in the neutraliser plus the MEA entering the crude tower via tramp sources.

MEA is the primary amine that is common as both a tramp amine and a neutralising amine. Refineries that use MEA in their amine treating system or which have problems with H_2S scavengers in their crude supply, should avoid the use of a neutraliser product containing MEA. In addition to the salt formation risks mentioned previously, having multiple sources of MEA can make the challenge of troubleshooting MEA related contamination problems difficult.

Overhead temperature

Overhead temperature plays a dual role in impacting amine behaviour in a crude column. Firstly, the amount of amine that can be present in the overhead system before salts form is a strong function of temperature. Secondly, the temperature can have a significant impact on the amount of hydrocarbon leaving the top of the column.

K_p is a function of temperature for ammonia.[2] Over the temperature range from 200 to 300°F where most crude tower overheads typically operate, the value for K_p increases by roughly an order of magnitude for every 30°F increase in temperature. For constant pressure, vapour rate, and chloride content, this change in K_p with temperature means that every 30°F increase in overhead temperature would allow a 10x increase in ammonia before solid ammonium chloride would start to form. While the absolute values of K_p will be different for amines, K_p would still be expected to undergo similar relative changes with increasing temperature. Ionic modelling can be used to quantify this effect.

As the crude tower overhead temperature increases, the total volume of hydrocarbon going overhead would be expected to increase at a constant crude charge rate and composition. The increase in overhead hydrocarbon decreases the partial pressure of any amines and HCl present, which has the effect of decreasing the potential for salt formation. The effect on salt formation potential of increased hydrocarbon decreasing contaminant partial pressures is normally much

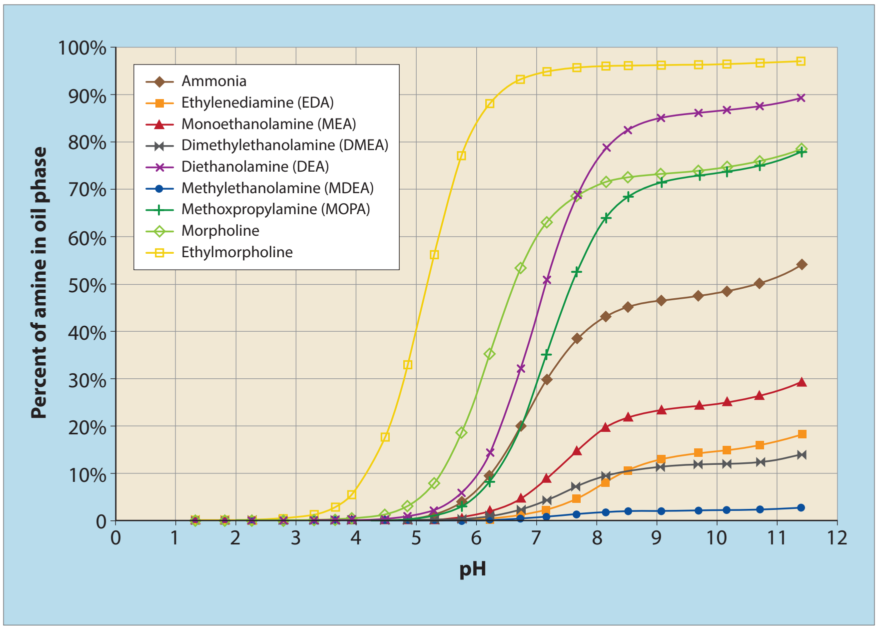

Figure 2 Desalter partitioning characteristics of some common amines
Taken from An In-Depth Look at Amine Behavior in Crude Units Using Electrolyte-Based Simulation, NACE Paper No. 05570.3

smaller than the impact of increasing temperature on K_p. The inverse, however, is also true. Decreasing the overhead temperature decreases the hydrocarbon partial pressure (increases P_{HCl} and P_{amine}) and at the same time decreases the value of K_p (decreases the amount of allowable HCl and amine before salts start to form).

In terms of neutraliser selection, the lower the overhead temperature is, the less flexibility there is in choosing a neutralising amine. For a low crude tower overhead temperature, a neutraliser with a strong affinity for the aqueous phase in the desalter and a low salt formation potential (high value of K_p) is required. Often times in such systems these dual objectives cannot be met with a single amine so the chemical supplier is forced to use a blend of amines to minimise salt formation risk in the crude column. Blended amine products are typically significantly more expensive than single amine products, but the costs are normally easy to justify based on the improved operating flexibility. Blended amine neutralisers are especially valuable to the refiner trying to maximise diesel production, which normally involves operating the crude tower overhead temperature as low as possible to minimise naphtha yield. Some refineries will use a lower cost neutralising amine when the refinery is operating in a maximum gasoline mode and an amine blend when in a maximum diesel mode to lower neutraliser cost without substantially increasing corrosion risk.

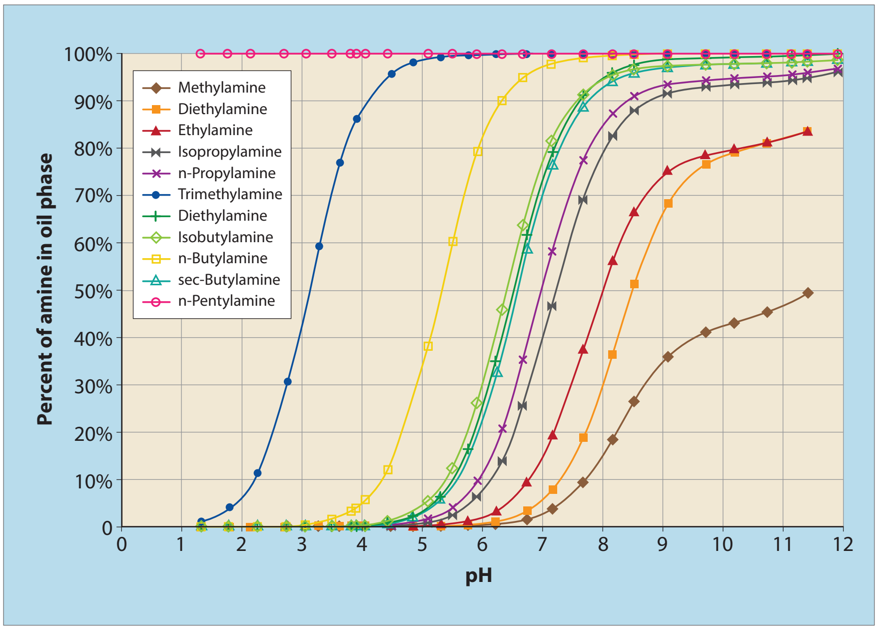

Figure 3 Desalter partitioning characteristics of common alkyl amines
Taken from An In-Depth Look at Amine Behavior in Crude Units Using Electrolyte-Based Simulation, NACE Paper No. 05570.3

Desalting

As mentioned previously, when atmospheric tower overhead water is used as desalter wash water, some of the amine will partition to the crude oil phase in the desalter and end up in the atmospheric tower. Routing the overhead water to the sour water stripper (SWS) can greatly reduce the risk through dilution, but it will also consume additional energy and SWS capacity. If stripped sour water (SSW) is then used as desalter wash water there will still be neutralising amines in the SSW, but at a lower concentration than if the overhead water were routed directly to the desalter. The neutralising amines will have been diluted by other water sources feeding the SWS.

Figures 2 and **3** show the typical partitioning behaviour of a variety of amines in a desalter.[3] The actual percentage of a given amine that goes out with the desalted crude will depend on the amine, the percentage of wash water used, the temperature in the desalter, and the pH of the desalter water. The crude oil used may potentially have a small impact as well. These figures are indicative only because they were generated for a system with a specific hydrocarbon composition, percentage of wash water, and temperature.

These figures clearly show that both the pH and nature of the amine compound play critical roles in determining how the amine will behave in a desalter. Alkyl amines tend to have a much stronger affinity for hydrocarbon than do the alkanol amines. The oxygen functionality in alkanol amines greatly enhances their affinity for the aqueous phase in a desalter. When selecting the neutralising amine, it is important to understand where the crude tower overhead water is going to be routed and the overall quality of the wash water (pH) used in the desalter. Routing overhead water directly to the desalter and running the desalter with high pH wash water both tend to reduce the flexibility in neutralising amine selection. Routing overhead water to the SWS and maintaining low desalter wash water pH allow greater flexibility in neutraliser selection at the cost of creating additional SWS feed, and potentially the need to acidify the desalter wash water.

Some refineries will inject an acid into the desalter to lower the wash water pH and reduce the partitioning of amines into crude oil. Acids commonly used for this purpose are citric, acetic, and hydroxy acids such as glycolic acid. Besides adding substantially to the refinery chemical costs, the acids can each create their own set of negative side effects.[4] Desalter acidification can lead to overhead corrosion, increased neutraliser consumption, fouling, and increased BOD/COD loading on the wastewater system. While use of acids to lower desalter wash water pH can be beneficial, it is critical that the refiner makes sure that the cure is not worse than the problem being addressed.

More recently, Dorf Ketal has introduced an aldehyde based reactive adjunct chemistry into the market. The chemistry converts the amine to a non-salt forming, water soluble imine. The amine conversion has the beneficial side effect of lowering the pH of the water in the desalter without the need for acid injection and its negative side effects. Initial trials of the new chemistry have been promising, but more time is required to fully evaluate the impact of this new chemistry on refinery operation.

When deciding how to design and operate the crude unit, the operating objectives can sometimes be in conflict with each other, thus requiring costs and benefits to be weighed very carefully. To minimise the amount of neutraliser that goes to the desalter, it would be desirable to route the overhead water to the sour water stripper first instead of going directly to the desalter. Sour water strippers, however, often inject caustic into the feed to enhance ammonia stripping, resulting in relatively high pH stripped sour water. The benefit of reduced amine to the desalter must be weighed against any negative impacts on partitioning behaviour due to higher pH of stripped sour water feed to the desalter instead of tower overhead water. Also, the impact on sour water stripper capacity utilisation and operating cost need to be factored into the analysis.

With these key considerations in neutraliser selection in mind, let us look at some basic principles in the design of overhead systems and some examples of how to apply this information.

Design principles for overhead corrosion control

Some basic principles in the design of the corrosion control system for crude tower overheads are:

- Inject the neutralising amine ahead of the first point where it is possible to form liquid water in the system.
- Select a neutralising amine that does not form a separate salt phase ahead of the water dew point
- If the second criteria cannot be met a water wash is needed to prevent corrosion and fouling.

There are also a number of additional design considerations that are beyond the scope of this article, such as filmer injection and water wash system design.

Other factors such as shock condensation, neutraliser injection location, and variable operating conditions can also impact neutraliser selection. Failure to properly consider the actual conditions that can exist either in normal operation or during abnormal operational periods can result in corrosion from improper neutraliser selection or through injecting the neutraliser at the wrong location.

These issues can best be illustrated through the use of some real life case studies.

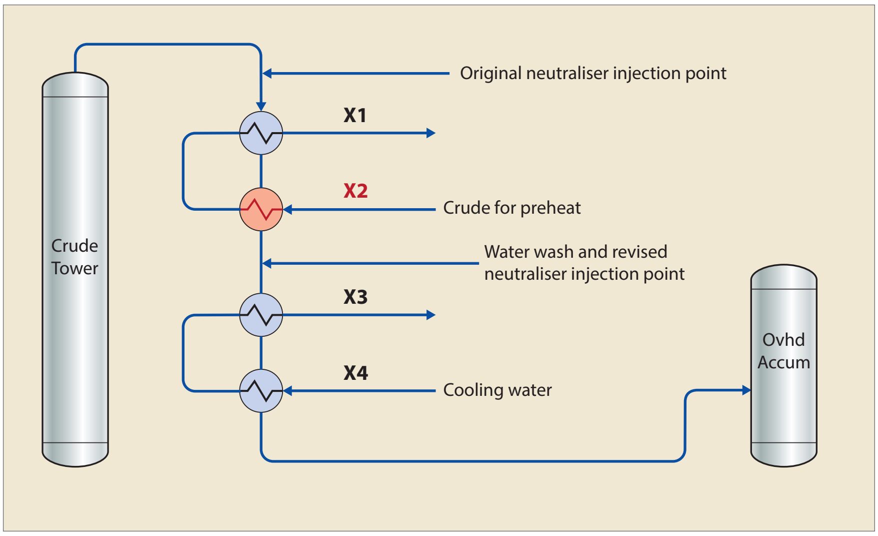

Figure 4 Overhead system for Case 1

Case 1

The refinery in Case 1 has a crude tower overhead system (see **Figure 4**). The unit processes a high salt content crude in a single stage desalter, and overhead chlorides average 150 ppm. The overhead temperature at the time when the problems occurred ranged between 280°F and 300°F (138-149°C). The first two exchangers in the overhead system, X1 and X2, are raw crude vs overhead exchangers with titanium bundles and carbon steel shells.

To maximise crude preheat and to reduce the quantity of wash water required, the wash water is injected

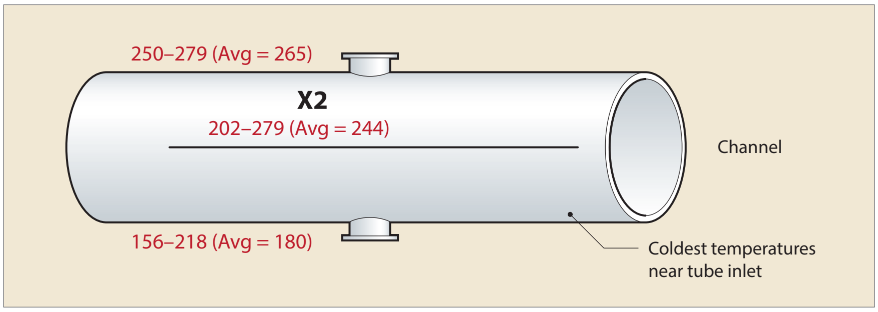

Figure 5 Skin temperature profile on X-2

between the crude vs overhead exchangers and the water coolers.

Historically, the neutralising amine had been injected ahead of the first exchanger. Because of the high chlorides, amine chloride salts formed in the first two exchangers, and they suffered high, chronic corrosion rates of 0.75-2 mm/y on the shells and outlet piping. The titanium bundles did not corrode, but the neutraliser formed liquid amine chloride salts which flowed off of the bundles and onto the CS shells and outlet piping where aggressive corrosion occurred. The chemical supplier modelled the system and determined that the water dew point would not occur in the first two exchangers so that, if no neutraliser were present, the corrosion should go away.

Two months after the neutraliser injection was moved to the water wash downstream of the first two exchangers, X-1 and X-2 were taken out of service during a planned shutdown to replace X-1's shell. During that downtime, corrosion was discovered on the X-2 shell and corroded areas were built up with weld overlay to full shell thickness of 0.28 in. Six weeks after the exchangers were put back in service, the X-2 shell holed through.

During the root cause analysis that followed the event, several interesting contributing factors came into play. Firstly, the chemical supplier based water dew point calculations on normal operation of the tower overhead system. With more detailed analysis of the operating data, it was determined that about 2% of the time the water dew point would actually be expected to occur in X-2 based on the vendor's predicted minimum tube wall temperature in X-2.

The second finding was that temperatures in the exchangers were significantly cooler than the chemical supplier had predicted. Their calculations had predicted a minimum tube wall temperature of 214°F (101°C) and a water dew point of 204°F (96°C, from which the conclusion was that shock condensation of water was not a concern.

In reality, though, the lowest tube wall temperature had to be much lower than predicted as evidenced by the temperature survey results shown in **Figure 5**. During a time period when the insulation was off X-2 for an automated ultrasonic thickness (AUT) inspection, an infrared temperature survey of the shell was also performed. The most interesting thing to note was that the temperature along the bottom of the shell averaged only 180°F (82°C) compared to a measured outlet temperature of over 260°F (127°C). This temperature data indicates that the liquid which condensed on the upper tubes in the bundle continued to subcool as it flowed down the bundle and that it did not mix uniformly with the rest of the vapour in the exchanger.

This temperature along the bottom of the exchanger is representative of the liquid film that forms on the tube surface, which is significantly different from the bulk temperature that a process simulator would calculate or the temperature indicator in the outlet line would measure.

One approach to estimating the coldest tube wall temperature is to take the average of the cold stream inlet temperature and the hot stream outlet temperature. In this example, if the outlet temperature is 260°F (127°C) and the crude inlet temperature is 80°F (27°C), this is first exchanger coming in from the tank farm, the coldest tube wall temperature would be estimated at 170°F (77°C), which is reasonably close to the temperature measured along the bottom of the shell in this case.

In this case, when the neutraliser injection was relocated, the neutraliser was no longer being injected ahead of the water dew point, and extremely aggressive corrosion occurred. In many systems without a water wash, the second objective cannot be met and corrosion will occur due to salt formation, which was the case in this system before the neutraliser relocation was done. In some systems, there is a lot of

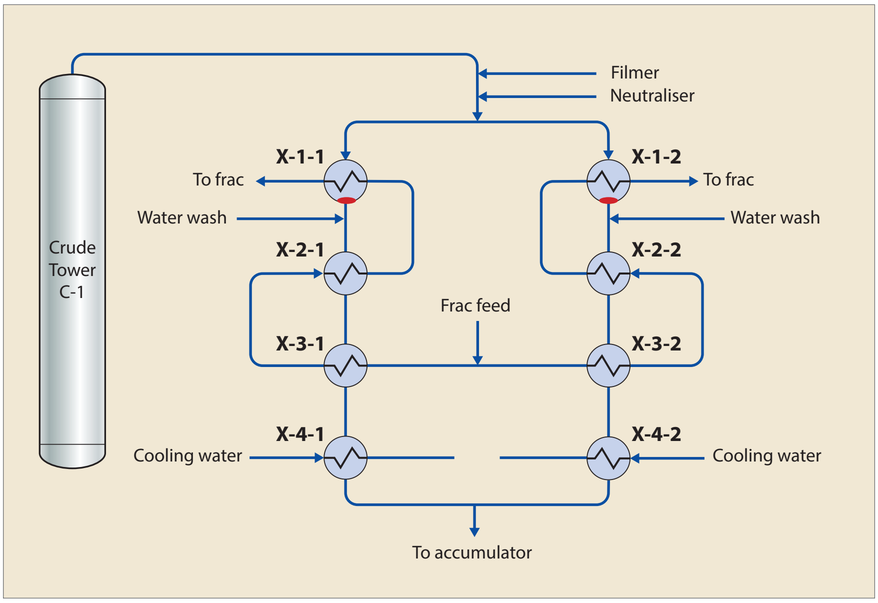

Figure 6 Overhead system for Case 2

naturally occurring ammonia or there are tramp amines present, and a salt point is reached ahead of the neutraliser salt point. In such systems, a water wash is the only practical approach to preventing salt formation.

Case 2

This crude unit had two banks of exchangers that used crude tower overhead to preheat feed to another column (see **Figure 6**). Water wash was injected between the first and second exchanger in each bank. The exchangers had titanium bundles and carbon steel shells, and the top exchangers in each bank (X-1-1 and X-1-2) had long term corrosion rates of approximately 0.38 mm/y.

A routine inspection a year after a turnaround revealed that the average corrosion rate since the previous turnaround had accelerated to over 3.8 mm/y in the area highlighted in red in **Figure 6**. This change in corrosion triggered much more frequent inspection, which soon determined that the real corrosion rate was more like 12.5 mm/y.

A number of possible causes were explored, but the final conclusion was that a neutraliser change that had occurred when the refinery changed chemical suppliers caused the corrosion in these exchangers. Neither supplier had been routinely tracking salt points in the overhead system, which made the analysis more difficult. During the time frame in question, there did not appear to be any change in overhead chlorides or other key variables that could be linked to corrosion in these exchangers.

After the turnaround, the overhead temperature averaged 8°F hotter than it had before the turnaround, which normally would reduce corrosion risk, although the change in estimated tube wall temperature was small (see **Figure 7**). Supplier 1 had been using a three-amine blend (amines A, B and C). Supplier 2 elected to use a single amine product that used only amine A. As part of supplier 2's troubleshooting effort, they did several salt point calculations that showed a typical salt point of about 215°F (102°C) for neutralising amine A. It was estimated that the lower concentration of amine A in supplier 1's product reduced the salt point of A by about 15°F.

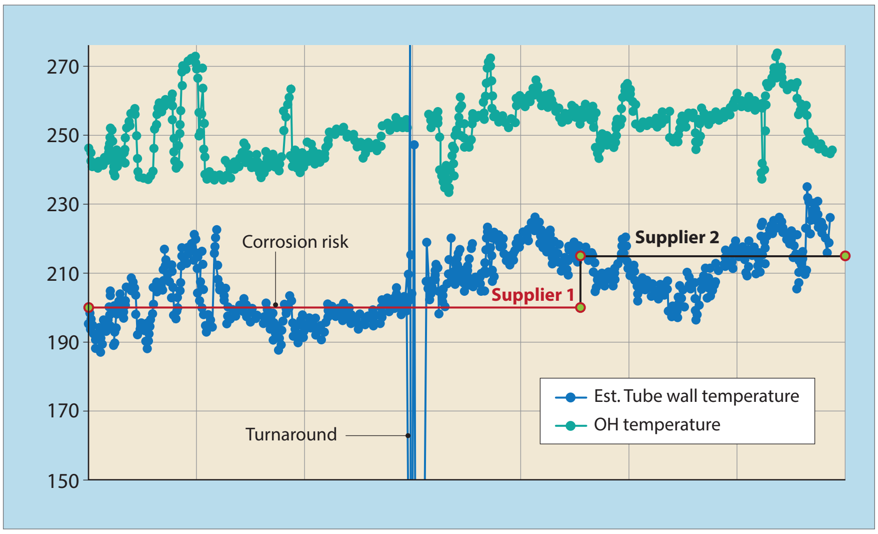

Figure 7 This graph indicates that after the neutraliser change there was an extended period of time when the estimated salt point was significantly higher than the tube wall temperature

Those approximate salt points are plotted along with the estimated minimum tube wall temperature in **Figure 7**. In the time before the turnaround, the minimum wall temperature and the salt point were very close to each other. When supplier 2 took over and switched neutraliser products, the salt point became significantly higher than the minimum tube wall temperature, which significantly increased the amount of salt that would have formed and thus the amount of corrosion.

As an interim measure, the chemical supplier switched to a multiple amine blended neutraliser product to at least get back to historic corrosion rates. Ultimately, the refinery decided to upgrade the metallurgy on the shells to eliminate the chronic corrosion problems and to increase operating flexibility.

Conclusions

Making the proper selection of neutralising amine chemistry is a challenging task at many refineries, especially with the wide range of opportunity crudes available in the marketplace. Besides traditional considerations like cost and base strength, a number of other factors need also to be considered. Making good decisions also requires a detailed understanding of the full range of process conditions and actual local conditions in the piping and exchangers. Simply relying on a bulk temperature predicted from a simulation or temperature indicator output may not accurately represent the actual conditions when corrosion may occur. Additionally, the presence of tramp amines in the unit and the potential to recycle amines to the crude tower via the desalter can further complicate the neutraliser selection process. If the refiner and chemical supplier make the effort to consider all of these factors when selecting their neutralising amine, a lot of future problems can be avoided.

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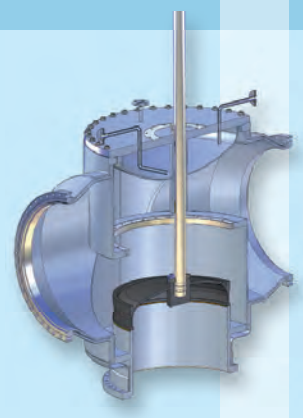

Energy network monitoring and optimisation

A software program for optimisation of an energy network supports decisions on equipment use in refineries that produce and import power

ELIF GÜL GÖÇER, ELIF MELEK ÖZTÜRK, GÜLŞEN ŞAHIN ANDAŞ, YAHYA AKTAŞ and ELIF METE
Tüpraş

Optimisation of energy costs and use is among the most important factors affecting operating expenditure and competitiveness in the refining sector. In order to reduce energy costs, there are many options to consider such as benchmarking internal and external best practices and optimising the use of existing capacity.

We think we can do this through a new conceptual framework, energy optimisation, which means using – and not using – energy in the refinery to maximise the reliability of processes for both safety and economic performance. For this reason, Tüpraş refineries operate their own power plants to meet energy demand.

In these power plants, energy is produced by conventional and waste heat boilers, and gas and steam turbines with different capacities and efficiencies which have been commissioned at different times. The refineries are also connected to the local grid. Thus, electricity traded between the refineries and the electricity grid is an option. In refineries, there is energy consuming equipment including furnaces, boilers, exchangers, pumps, and compressors. Different types of fuel can be fired in the furnaces and boilers. The energy demand of pumps and compressors is supplied by turbines or electrically driven motors. When electricity and steam demand and production costs are considered, the need for a decision support tool which ensures effective management of the utility system arises. Hence the Energy Network Monitoring and Optimization Program has been developed.

Previously, energy optimisation was performed via commercial software. However, the software did not exactly match refinery configurations, and software updates could not be adapted by the end user. Eventually, the expected results could not be achieved by the software. The most important objective of the program developed here is to provide a decision support system that reflects the refinery in a realistic way, and determines the load at which equipment should operate with which type of fuel. In addition, the program is able to produce, buy, or sell output for electricity trade on an hourly basis by taking into account the electricity/steam balance in the refinery and current electricity purchase/sell unit prices.

Methodology

Within the scope of the Energy Network Monitoring and Optimization Program, an interface has been developed wherein 25 different items of equipment can be selected from the palette by means of drag and drop. Power plant and process units are defined.

When modelling process units, energy conservation, mass conservation, and data collected from the field are used. Gas turbine modelling is described in this section. A gas turbine compresses air for the combustion process. High pressure and high velocity gas expand through the turbine to produce work. During the compression of air, the ratio of compression is calculated by:[1]

$$r_p = P_{r2}/P_{r1}$$

where, r_p is the compression ratio, and P_{r1} and P_{r2} are the inlet and outlet pressure of the compressor. The isentropic efficiency is calculated by: [1]

$$n_c = (T_{2s}-T_1)/(T_2-T_1)$$

where T_{2s} is the isentropic outlet temperature of the compressor, and T_1 and T_2 are the inlet and outlet temperature of the compressor.

The work done by the compressor is calculated using:

$$W_C = C_{pa}T_1(r_p^{\gamma_a - \frac{1}{\gamma_a}} - 1)/n_m n_c$$

where C_{pa} is the specific heat of air, γ_a is a constant(1.4), n_m and n_c are the mechanical and isentropic efficiency of the compressor. Energy balance around the combustion chamber is expressed using:[1]

$$m_a C_{pa} T_2 + m_f HV_f + m_f C_{pf} + T_f = (m_a + m_f)TIT$$

where m_a is the mass flow of air, m_f is the mass flow of fuel, C_{pf} is the specific heat of the fuel, HV_f is the heating value of the fuel, T_f is the fuel temperature, and TIT is the inlet temperature of the turbine. The shaft work produced in the turbine is calculated by:[1]

$$W_t = C_{pf} TIT n_t (1 - \frac{1}{r_p^{\gamma_g - \frac{1}{\gamma_a}}})/n_m$$

where n_t is the efficiency of the turbine and γ_g is a constant value of 1.33. The network can be calculated from the difference between W_t and W_c.

Steps in optimisation

The optimisation program consists of three main components:

- The database
- Modelling and optimisation
- Interface and reporting

The database

At this stage of the project, adapters that are independent of each other and which collect data from different data sources were developed. The process data measurements are impaired due to errors in measurement, processing, and transmission. These errors can be classified as gross errors and random errors. Gross errors include major errors caused by sensor calibration shifts, sensor surface contamination, and sensor failure. Random errors are minor errors caused by noise and external conditions. These errors lead to inconsistency in measurement and refinery applications, such as simulation and optimisation, and decision support systems that use these measurements produce false results.

The detection of gross errors is performed using various filters for these data. The data is filtered according to upper and lower limits and measurement quality. The effect of an error is reduced by using the last good value or a safe value instead of the detected error. In addition, data received in different units is adapted to the SI system to ensure integrity between data.

The equipment in the energy network is defined in the diagram developed within the program. The identified equipment, rings, and parameters are stored in the SQL database. Refinery, process, and equipment ontologies are designed in order to make collected data meaningful. In this way, how much utility each equipment produces or consumes and the total energy demand of a refinery for a given time are determined. The data warehouse had been designed for the storage of collected and semantically related data. The average hourly data from process is stored in the data warehouse. This archive provides the opportunity to conduct studies related to past data.

Modelling and optimisation

Equipment that produces and consumes energy, such as boilers, gas and steam turbines, waste heat boilers, turbines, and electrically driven motors, are defined within the scope of the program. In order to build an optimisation model, firstly the independent and dependent variables of equipment and the relationship between them must be determined. Therefore detailed thermodynamic analyses were performed for the equipment in the system, and independent variables that could affect their performance were determined. Through the process data source, historical data of determined dependent and independent variables was collected. By means of regression analysis based on the historical data, dependent variables that affect equipment performance and their strength of impact were determined. As a result of this study conducted on a SPSS statistics program, the sensitivity of models was compared with the field data.

In order to create equipment models, an infrastructure was developed in which the thermodynamic properties of water, steam, and fuel rings can be defined. Thus composition, density, enthalpy, entropy, and heat capacity are calculated instantly. The efficiencies of equipment and model parameters may vary according to the characteristics of the utility ring. Thanks to this infrastructure, models of equipment compatible with the field have been created.

After a detailed regression analysis for each item of equipment, an optimisation model covering the whole utility system was developed. The objective of optimisation is to assemble a production plan in order to produce steam and electricity which are required by the refinery at the lowest cost. The methods and practices in this context are:

- The constraints of equipment and process units have been identified. At this stage, the operating ranges of equipment, emission limits, and risks that could endanger refinery operations were studied.
- Independent variables to be used in optimisation were decided. These variables include whether an item of equipment is operated, its operating load, and its mode of operation.
- Algorithms that perform sensitivity analyses for the optimisation algorithm and achieve global minima instead of local minima have been tested in complex equation systems.
- The objective function of an optimisation model is to minimise the sum of fuel costs, costs occurring during equipment switch, and risk costs.
- The optimisation results were compared with past production plans, and software deficiencies were eliminated.

In the program, general algebraic modelling system (GAMS) software is used as the platform for an optimisation solver. The objective function, parameters, and linear equipment models were transferred to the platform. The objective function, the models of equipment, and other constraints consist of linear equations and inequalities. Since the decision variables are continuous and consist of integer variables, a mixed integer linear programming (MILP) method was preferred and the CPLEX 12 solver was used. The GAMS based CPLEX solver uses branch-bound and branch-cut algorithms.

User interface and reporting

The interface and reporting were developed as user friendly models. Some 25 different items of equipment could be chosen from the palette by a drag and drop method, flow diagrams could be created, and there is access to online field data. Optimisation results could be compared by reports.

Equipment on the palette could be easily identified visually to add it to flow diagrams. Simple flow diagrams are created by adding equipment to the diagram. Each time a new item of equipment is added, the system requests and records its name, unit, and equipment specific data. The names and connection points of equipment can be easily revised or deleted.

There are equipment pages including design and technical parameters. Detailed data required for modelling and optimisation can be entered, controlled, and revised through these equipment pages.

Using the interface, a user can list all online field data and optimisation reports including a required optimisation action list. In addition, since the previous data is stored, the user can obtain the field data of any defined time period using the interface. Besides optimisation of online field data, the user can study the optimisation of offline case studies, what-if scenarios, and feasibility analysis for future investments:

1. Reporting stack gas emissions: emissions from the stack gases of furnaces and boilers can be followed by the program. Also, any limits of emissions can be defined.

2. Diagram application: using the diagram, equipment can be added by a drag and drop method, defining any connections between equipment. Models of the equipment can be entered or recalled from the database, and their parameters can be defined to equipment models. Setting up flow diagrams using the equipment's optimisation studies can be applied.

3. Sensitivity and cost analysis: electricity is produced from gas turbines and steam turbine generators, and steam is produced from conventional boilers and waste heat boilers of gas turbines. Since each item of equipment has a different efficiency, it is difficult to separate the fuel costs for steam and electricity. Using this software, marginal costs and average costs of steam and electricity can be easily calculated and reported.

4. Equipment library: there is an equipment library containing data for 25 different types of equipment. When new equipment is added to the diagram, default parameters and formulations can be taken from the library and any revisions can be applied.

5. Integrated historical database: the application automatically obtains the hourly average only field data and keeps it in the database. This provides the opportunity to make calculations using any previous hourly field data. All historical data is kept in storage, available for future possible project evaluations.

6. Functional reporting: in order to meet the different needs of users, it is possible to generate different reports using calculation results made using field data as well as optimisation results.

7. Detection and filtering of incorrect field data: this is the process of passing data taken from the field through various filters within the error detection mechanism. Measurement error, communication error, and other user types are informed.

8. Offline scenario analysis: for a feasibility study for a planned investment in the field or to study different scenarios, the user can change the diagram, run the optimisation, and observe the effects of the changes on refinery balances and energy costs.

9. Energy performance indicators: as in the other applications, it is possible to calculate and report key performance indicators such as equipment efficiencies and energy consumption.

10. Live access to field data: unlike other software, it is able to communicate with different refinery databases without requiring manual access to other historian databases and applying adapter software at the stage of accessing field data.

11. Data filtering: as in other applications, the minimum and maximum limits for field data are defined and the data is filtered. The major advantage of the program developed for Tüpraş is that it eliminates dependency on outside and is open for new development. If needed, below properties can be added to the program and usage range can be expanded.

12. Electricity cost management: the software can be run iteratively by the user to create different scenarios for different electricity prices and quantities. However, the user has to create the proposals based on the program's results, submit them to the market financial reconciliation centre (PMUM), and enter the accepted proposal as input to the software. It is useful to automate this process given that it will be repeated every day routinely and every time the production plan is changed. In future, a tool can be developed that will communicate with the PMUM's web server to run the process and require only user approval.

13. Integration of carbon market: the developed software can foresee flue gas emissions arising from planned actions. This information can be used in the carbon market, in which Turkey may be included.

14. Multi-period optimisation: the program has a sub-structure of hourly period optimisation instead of instant optimisation.

15. Closed circle application: optimisation results can be applied in the field by control tools without an operator. Tüpraş' process security procedures do not allow this kind of application.

Output and results

The Energy Network Monitoring and Optimization Program is a decision support system to enable the supply of refinery steam and electricity at minimum cost and least environmental effect by live monitoring of energy producer and consumer equipment in the energy network. In the scope of the developed user interface:
- Equipment relationships are established from the flow diagram created by drag and drop.
- Equipment models and model parameters are determined.
- Different sources of field data are accessed.
- Optimisation study reports are obtained for required time intervals.

The aim of the optimisation studies is that the refinery's energy needs are met by using fuel resources more efficiently. Increased energy efficiency by optimisation also decreases flue gas emissions.

With the help of a SOx limit defined in the system, the use of fuels with high sulphur content is restricted. Therefore environmental damage is avoided and penalties are limited.

Efficient management of the energy network enables the use of water resources more efficiently and so decreases water consumption. The amount of water lost in the system or becoming dirty is monitored live.

Tüpraş is both producer and consumer of electrical energy. Therefore it is imperative to minimise costs by using the electricity market efficiently. Because prices agreed in the market change periodically and

Base case and optimisation results of case study

	Base case	Optimisation result
Steam Turbine Generator-1, MW	5.0	0.0
Steam Turbine Generator-2, MW	6.5	0.0
Steam Turbine Generator-3, MW	0.0	6,0
Steam Turbine Generator-4, MW	2.4	4.7
Gas Turbine-1, MW	19.9	19.9
Gas Turbine-2, MW	21.3	21.3
Import power from grid, MW	4.8	8.0
Refinery electricity demand, MW	59.9	59.9
Steam turbine generators total, t/h	201	177.5
Steam consumption		
Boiler-1 steam production, t/h	0.0	0.0
Boiler-2 steam production, t/h	41.0	62.0
Boiler-3 steam production, t/h	0.0	0.0
Boiler-4 steam production, t/h	0.0	0.0
Boiler-5 steam production, t/h	0.0	0.0
Boiler-7 steam production, t/h	0.0	0,0
Boiler-8 steam production, t/h	78.0	63.9
Boiler-9 steam production, t/h	80.7	50.0
Total steam production from boilers, t/h	199.7	175.9
Total utility operating cost, $/hr	8522.6	8114.0

Table 1

hourly, the optimisation program creates an output by taking into account the refinery's capacity for electricity production and network electricity purchase and sale price. As a result, the profitability ratio obtained from trade with the electricity market has increased.

Case study

In this scenario, the effect of an increase in the import limit for electricity from the grid is studied to establish optimum working conditions (see **Table 1**).

The refinery's electricity import limit is increased from 5 MW to 8 MW, and two gas turbines and four steam turbine generators are opened to optimisation for electricity production. Three of the steam turbine generators have both medium pressure steam extraction and condensate stages while the fourth has only medium pressure steam extraction. The boilers' load and on/off status is opened to optimisation for steam production.

Conclusion

The developed program has a modular structure that can be applied to different sectors. It has potential for use in refining, petrochemicals, steel, paper, chemicals, and electricity production. In order to protect the intellectual property rights of the project, a patent application has been made.

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Delayed coking as a sustainable refinery solution

Fuel grade coke is a serious environmental pollutant but the producer, the delayed coking process, can be a contributor to future sustainable development in refineries

MARCIO WAGNER DA SILVA *Petrobras*
JOHN CLARK *Coke Consulting Company*

The challenge facing the refining industry in the medium term will be to remain economically relevant in the face of increasing process costs (heavier, higher sulphur crudes and environmental emission restrictions of its final products). Refinery production of automotive fuels produces heavy petroleum residuals, for example vacuum residue (VR). The viability of refineries has historically been primarily based on revenues generated by lighter fuels (LPG, petrol, diesel, and jet fuel). However, as heavier crude oils are increasingly processed, the volumes of straight run VR are expected to increase. As a consequence, refineries will have to rely on hydrocracking and carbon rejection technologies to augment lighter hydrocarbon distillates, with associated costs. Nowadays, the capacity to add value to the bottom barrel streams represents great competitive advantage among refiners, especially considering such stricter regulations as IMO 2020. This imposes a significant reduction in the sulphur content of marine fuel oils, requiring even more capacity to treat bottom barrel streams, especially for refiners processing heavier crude oils.

In this scenario, process units called bottom barrel processing, which are able to improve the quality of crude oil residue streams (VR, gas oils, and so on) or convert them to higher added value products, gain strategic importance, mainly in countries that have large heavy crude oil reserves. These process units are fundamental to comply with environmental and quality regulations, as well as to ensure profitability and competitiveness for refiners through higher refining margin.

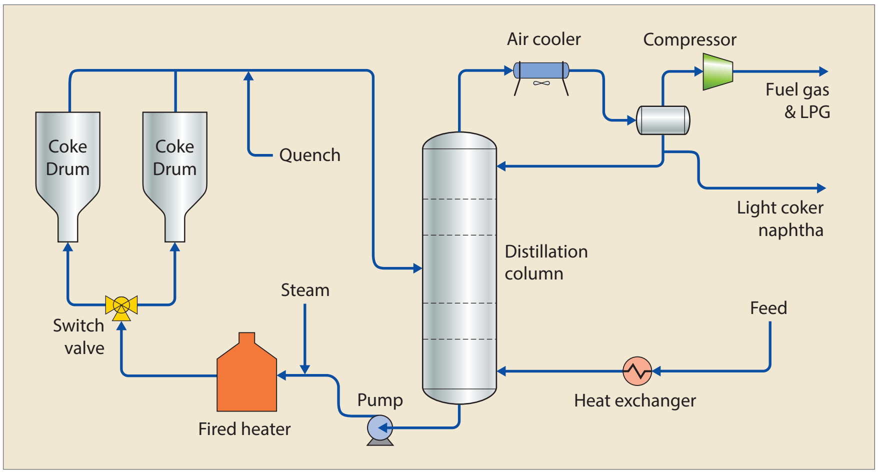

Figure 1 Typical arrangement of a delayed coking unit

Delayed coking is a carbon rejection technology using heavy petroleum residues to produce lighter hydrocarbon distillates (inclusive of naphtha and coker gasoil) and green coke as a solid by-product. While production philosophy over the delayed coking process has historically maximised lighter distillate production, its potential role as both a business and environmental enabler has to date not fully been exploited. This article examines the role of delayed coking in the context of generating environmentally sustainable refinery solutions for heavy petroleum residues to address future market reforms, specifically in the case of fuel grade coke.

Delayed coking technologies – a general overview

Delayed coking employs the thermal cracking concept under controlled conditions to produce light and middle streams (LPG, naphtha, and gasoils) from residual streams which would normally be used as diluents in fuel oils production.

The typical feed stream for delayed coking units is the residue from the vacuum distillation process that contains the heavier fractions of processed crude oil. However, streams like decanted oil from the FCC unit and asphaltic residue produced in solvent deasphalting can be in the feed stream to the delayed coking unit, depending upon the refining scheme adopted by the refiner. Another possibility is to send the residue from atmospheric distillation directly to the delayed coking unit; in this case, the unit design is modified, demanding greater robustness in the fractionating and gas compression section.

Due to their thermal cracking characteristics (low availability of hydrogen during the reactions), the streams produced by a delayed coking unit have a high concentration of olefinic compounds which are chemically unstable. Furthermore, due to the processing of residual streams that have high contaminants content like nitrogen, sulphur, and metals, refiners that apply delayed coking units need high hydrotreating capacity to convert these streams into added value products which meet contaminants levels according to the environmental regulation. **Figure 1** shows the process flow scheme for a typical delayed coking unit.

The feed stream is fed into the bottom of the main fractionating tower. Here it is mixed with the heavier fraction of the thermal cracking products and then sent to the fired heater, where thermal cracking reactions are initiated. The conditions are controlled so that the reactions are completed in the coke drums. The residence time in the fired heater must be the lowest possible to minimise coke precipitation in the fired heater tubes. A way of minimising coke formation in the walls of tubes is steam injection to raise the velocity and consequently reduce the residence time.

After the fired heater, the feed stream is sent to the coke drum or reactor, where the thermal reactions are completed and coke is deposited. The thermal cracking products are removed from the top of the reactor and receive an injection of quench with a cold process stream (normally heavy or middle gasoil) and directed to the main fractionators, where the products are separated. Coke deposited in the reactor is removed through a cut with water under high pressure (about 250 bar).

Delayed coking is a process that occurs in batch. In order to make a semi-continuous process, it is always employed as pairs of reactors, wherein one reactor is under reaction, the other is in the decoking step, and so on. The delayed coking process occurs in cycles that can vary from 14 to 24 hours.

The main operational variables of the delayed coking unit are: recycle ratio, which is the quantity of the total feed stream that corresponds to the heavier fraction of the reaction products mixed with the fresh feed; reactor temperature, normally considered in the top of the coke drum; pressure in the top of the reactor; and the time of the reactor cycle.

The recycle ratio varies normally between 5% and 10% (in units dedicated to producing fuels) and the refiner seeks to operate the unit with as low a recycle ratio as possible in order to maximise the capacity of the plant in processing residual streams. The reactor temperature is close to 430°C and is linked to the fired heater temperature. Throughout the thermal cracking reactions, the temperature falls due to the endothermic characteristics of the reactions.

The pressure in the reactor can vary from 1 bar to 3.5 bar. In units optimised for producing fuels, the variable is maintained at lower levels. When the unit is dedicated to producing high quality coke, the unit is operated at higher pressures.

Reactor cycle time is linked to the function performed by delayed coking in the refining scheme. Units dedicated to producing fuels operate in shorter cycles, and units optimised to produce high quality coke operate in longer cycles.

The coke produced normally is seen as a by-product of the delayed coking unit; however, in some cases, the delayed coking process is optimised to produce high quality coke, and coke becomes the principal product of the process.

Depending on the feedstock quality to be processed, three types of coke can be produced:

- Shot coke/fuel grade coke is poor quality coke produced from feedstock with a high asphaltenes and contaminants (sulphur, nitrogen, and metals) content; normally, this type of coke is commercialised as fuel.
- Sponge coke: in this case, the feedstock has a lower asphaltenes and contaminants content, and the coke can be directed as raw material for anodes production in the aluminium industry.
- Needle coke production requires the processing of feedstock with a high aromatics content (decanted oil from the FCC, for example), and these products are sent as raw material for producing anodes in the steel industry.

Production of high quality coke requires quality control of the feed stream. In most cases, refiners choose to install delayed coking units focusing on the production of middle and light distillates. Therefore unit optimisation to produce needle coke occurs only in specific cases.

While lighter distillates generated by delayed coking are further processed within the refinery (to meet stringent petrol and diesel specifications), green coke may be sold to market as-is (fuel grade or shot coke), or calcined (needle or sponge coke) prior to sale. The chemistry of the delayed coking process involves thermal cracking of heavy refinery residuals at 450-510°C in the heater tubes, producing lighter distillates (naphtha, coker gasoil, and residual oil). The process also produces higher molecular weight radicals which rapidly polycondense in the reactor at 430-490°C, forming solid green coke.

For the most part, process conditions are tailored to maximise distillate over fuel grade coke production ('white product' mode). This involves higher temperatures, lower pressures, and lower recycle ratios, and is enhanced by lighter feeds. The green coke produced is largely sold as fuel grade coke in the energy market, which is the subject of this discussion. Alternatively, process conditions may be altered to favour coke laydown ('carbon' mode) in the case of sponge or needle coke production.

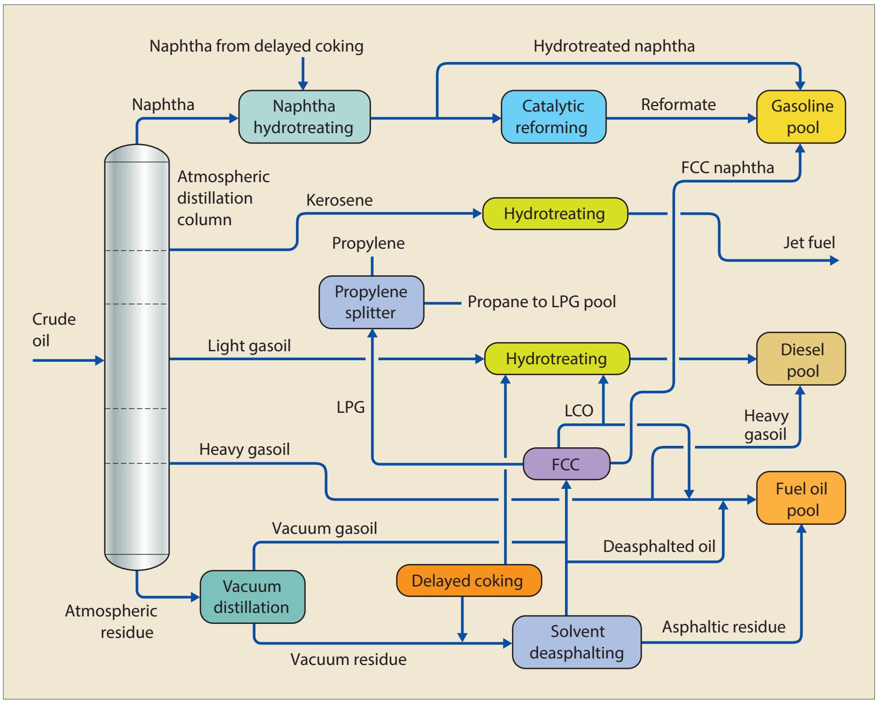

Figure 2 Refining configuration relying on solvent deasphalting and delayed coking units

Fuel grade coke

Although considered a low value by-product, fuel grade coke has specific potential to enhance the role of delayed coking as an environmental enabler. Fuel grade coke (typically 18-25% of delayed coker production) acts as a contaminant 'sink', concentrating sulphur, nitrogen, metals, and asphaltenes within the solid carbon matrix. As its name implies, it is sold into the solid energy market based on its comparatively high calorific value and low ash content. It is sold as green (raw) coke and not calcined, to maximise the calorific value aided by hydrocarbon volatiles (8-18%). A combination of high contaminant (especially sulphur, vanadium, and nickel) levels and isotropic microstructure usually excludes it from higher value non-fuel markets (sponge or needle coke).

Approximately 91 million tonnes of fuel grade coke are produced annually. While this represents over 70% of global coke production, it commands the lowest market value while generating the highest SOx emissions. Fuel grade coke is utilised as a solid fuel (in cement kilns and power stations), releasing particulate matter, metals, SOX, NOx, and CO_2 into the atmosphere.

The value of fuel grade coke compared to coal (based on substantial variation in coal qualities, averaged data reported in literature has been used) for incineration in power stations may be compared:

- Fuel grade coke has a substantially higher calorific value than coal given its lower ash content, although it has a higher greenhouse gas component (emitting 10% more CO_2 per unit of energy produced).
- Fuel grade coke has a higher sulphur content (up to 7%) compared to coal (typically 1-4%).
- Globally, annual use of coal in power stations is in the region of 8 billion tonnes. Annual production of fuel grade coke is orders of magnitude lower at approximately 91 million tonnes.
- Although coal (by sheer volume) is the largest source of global sulphur based emissions, fuel grade coke combustion contributes in excess of 11 million tonnes of SOx on an annual basis.
- Although the calorific value of fuel grade coke is substantially higher than that of coal, it commands only 60-70% of its market value.
- In future, if coal is replaced by cleaner/renewable energy technologies, it is simply not mined. However, fuel grade coke is produced as a by-product of the refinery value chain. Thus, even if it is removed from the solid fuel market, it will still be produced. Thus to reduce its environmental footprint a non-fuel application would be beneficial.

Synergies between delayed coking and other residue upgrading technologies

In some refining schemes, deasphalting and delayed coking units can be complementary technologies (see **Figure 2**).

In the refining scheme shown in **Figure 2**, deasphalted oil is fed to the FCC unit to produce LPG, naphtha, LCO, and so on, while the asphaltic residue is applied to produce fuel oil and asphalt. It is fundamental to understand that, in the current scenario, the combination of solvent deasphalting and FCC

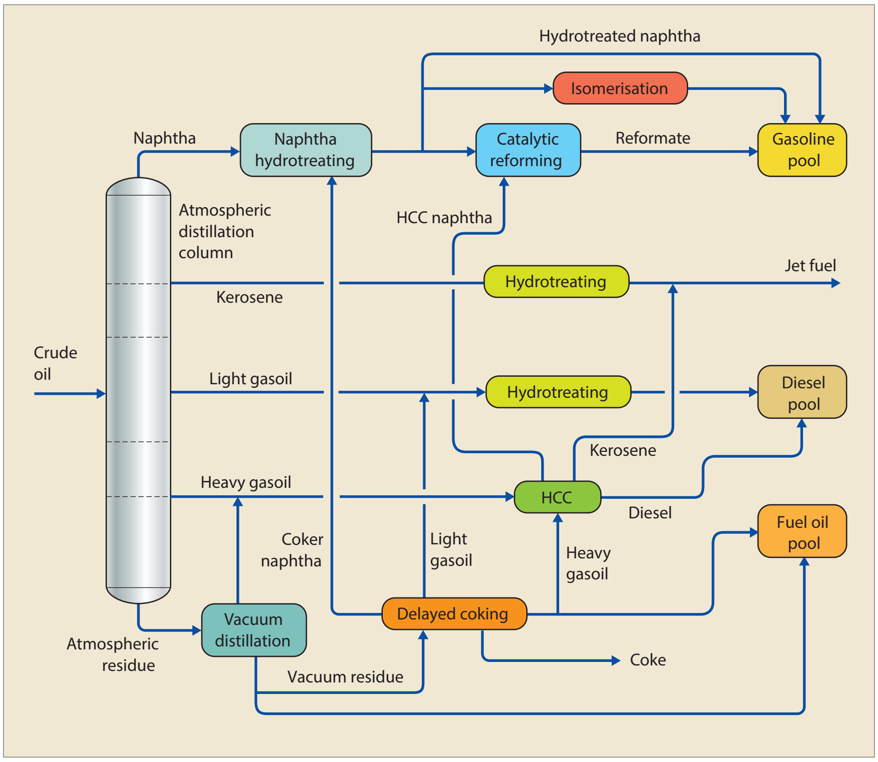

Figure 3 Process arrangement with a coking/hydrocracking configuration

is possible only for refiners with access to low sulphur crude oils. Both processes are unable to reduce drastically the sulphur content in the final derivatives, hence in the refining scheme shown in **Figure 3** significant hydrotreating capacity is needed to produce marketable crude oil derivatives. Despite this restriction, the synergy between FCC and solvent deasphalting units offers a relatively low capital and operating cost alternative by comparison with hydrogen addition alternatives for bottom barrel upgrading such as deep hydrotreating or hydrocracking units. Refiners operating in markets with high demand for transportation fuels can achieve high yields of middle distillates (higher than 40%), a good result considering the relatively low capital investment when compared to the hydrocracking alternative.

Despite the high capital cost, the synergy between delayed coking and hydrocracking can significantly raise capacity to add value to bottom barrel streams, especially for refiners processing heavier and sourer crude oils. **Figure 3** shows a coking/hydrocracking configuration to reach high bottom barrel conversion.

In the case of the coking/hydrocracking refining scheme, fuel oil production is reduced to the minimum necessary. Delayed coking and hydrocracking units raise the production of higher value products, like naphtha, diesel, and jet fuel.

The role of a delayed coking unit to process vacuum residue and produce streams capable of conversion to high quality transportation fuels after adequate hydrotreating reveals another interesting possible synergy between residue upgrading technologies. While in some cases delayed coking and solvent deasphalting technologies can be regarded as competitors since both units process vacuum residue, they can also be complementary (see **Figure 2**). In some cases, the asphaltic residue produced by a solvent deasphalting unit can be fed to a delayed coking unit to maximise yields of higher added value streams and minimise the production of fuel oils.

The choice of residue upgrading technology by refiners normally involves an economic analysis which takes into account the refinery production focus (middle distillates, light products, or lubricants), the market that will be served, and the synergy between processes that will be applied in the chosen refining scheme.

The influence of sulphur compounds on refinery products

Sulphur may be present in many natural forms in crude oil. Understanding its nuances contributes to understanding its distribution throughout refinery processes and products. Sulphur is present in three main forms: thiols, organic sulphides, and thiophenes.

Sulphur may be present as thermally unstable thiols (R-SH or Ar-SH). These may be associated with aliphatics or aromatics (as side chains such as thiophenols). Given their thermal instability, they are typically destroyed by thermal hydrocracking or FCC reactions to form H_2S. Higher molecular weight thiols may form reactive radicals (during delayed coking), crosslinking with adjacent heavy aromatics to form stable high molecular weight sulphides (Ar-S-Ar). Because sulphur has the same valency as oxygen, the cross-linking reactions of phenols and thiophenols are remarkably similar. These organic sulphides typically report to the coke fraction.

Thermally stable sulphur species may even survive severe FCC reaction conditions. They include organic sulphides (dibenzosulphide and dibenzodisulphide derivatives) and orthiophene derivatives (a five-membered condensed ring structure, C_4H_4S technically classified as aromatic heterocycles). Processing heavier crude oils increases the concentration of stable sulphur species (sulphide or thiophene derivatives) both in straight run vacuum residues and consequently in green coke.

Delayed coking as an environmental solution and market enabler

The coke fraction acts as a sulphur 'sink' (within the stable carbon matrix) by virtue of the delayed coking process. While the environmental potential of concentrating and stabilising sulphur in the coke fraction (to reduce SOx emissions) is evident, incinerating it as a solid fuel essentially reverses this benefit. However, in contrast, refineries go to great lengths (with associated costs) to remove sulphur (as H_2S) from petrol and diesel derivatives to

comply with stringent environmental legislation. Thus, the efficacy of the aforementioned regulations on absolute SOx atmospheric emission reductions is largely diminished by incinerating fuel grade coke.

Given the ability of delayed coking to concentrate and stabilise sulphur within the carbon matrix, the value of fuel grade coke may in future be interpreted less by virtue of its low market value but rather as a stable environmental vehicle to reduce absolute SOx emissions by finding a non-fuel application.

To reduce its environmental footprint, the volatiles content of fuel grade coke (8-18%) would require low temperature calcination (approximately 900°C). While carbon is a naturally inert material, calcination would densify the microstructure while stabilising the sulphur, nitrogen, and metal contaminants within the carbon matrix. Low temperature calcination (especially in a reducing atmosphere) would not release volatile sulphur compounds as the kinetics of their dissociation from the carbon matrix are associated with higher temperatures (1500°C-1800°C). From an environmental viewpoint, this would reduce the potential for volatile leaching into ground water and substantially increase the flashpoint. The coke could be used as a filler in asphalt roads, construction material, resin encapsulation, or landfill.

Finding a non-fuel based sustainable application for fuel grade coke will require an examination of its environmental stability. The US Environmental Protection Agency (EPA) has classified the environmental stability of coke (as a calcined variant) in the following manner:

- Does not vaporise in ambient atmospheric conditions
- Does not react with or dissolve in water
- Is chemically inert
- Sulphur bound within the carbon matrix is chemically and physically stable at ambient temperatures
- Does not degrade when exposed to light
- Is not biodegradable
- The potential environmental harm based on eco-toxicology reports is considered extremely low

Finding a non-fuel application for fuel grade coke permanently eliminates it as a potential SOx emission source. This 'cradle to grave' elimination approach reinforces the potential for oil companies to adopt a philosophy of sulphur stewardship over refinery processes. In a highly competitive market, oil companies may benefit by diversifying their product offering and marketing this sustainable initiative. However, holding oil companies accountable for the costs of currently unlegislated emission initiatives would not be reasonable or economically viable.

Over the past two decades, the environmental drive to reduce SOx emissions from petrol and diesel has largely exhausted the probability that these products could be further regulated. However, national governments rely on environmental sustainability mandates to cement their service offering to an increasingly climate conscious electorate, while at the same time guaranteeing a sustainable petrol and diesel market (at least over the medium term) to their electorate. Thus it is reasonable that future SOx regulation will be enforced over high impact markets (including fuel grade coke, shipping bunker fuels, low efficiency heavy residue fuels, and coal). Partnerships between oil companies and governments (in the form of performance based incentives) to reduce absolute SOx emissions may prove beneficial with regard to sustainability targets while protecting economic refinery viability.

As an enabling process, delayed coking offers several economic and sustainable benefits. As heavy petroleum residues are slowly removed from energy markets (burner fuels or bunker fuels) due to energy efficiency and emissions concerns, delayed coking offers a sustainable processing option, thus negating the immense costs incurred by disposal in an environmentally appropriate manner.

When processing heavier crudes (on a straight run distillation basis), delayed coking is able to accommodate increased volumes of potentially 'distressed' heavy petroleum residue volumes to augment the production of lighter hydrocarbons.

Apart from hydrogenation processes, delayed coking is the only other process with the potential to stabilise sulphur. A non-fuel coke application would substantially reduce SOx emissions.

While other carbon rejection processes such as FCC produce liquid volumes of by-product heavier residues, delayed coking is able to stabilise these high molecular weight molecules within an inert solid carbon matrix.

Removing heavy petroleum residues from the energy market further enables fast-track implementation of cleaner medium term technologies such as natural gas, with specific emphasis on energy efficiency and SOx emissions. Whilst there is a market demand for petrol and diesel, heavy petroleum residues will be produced irrespective of current or future market disposal requirements.

Apart from delayed coking, another sustainable option may be to convert vacuum residuals to bitumen for the production of asphalt roads. As a non-fuel application, it stabilises sulphur in a thermoelastic polymer matrix, eliminating SOx emissions. There is a global drive to build reliable roads, thereby enhancing national transport networks. Additionally, there is a direct correlation between the development of road networks and national economic prosperity. Both a bitumen application and delayed coking will provide sustainable solutions to accommodate potentially distressed heavy residue volumes as they are removed from energy markets.

Conclusion

The production of heavy petroleum residues is an inevitable consequence of demand for gasoline and diesel. In future, energy market outlets for heavy petroleum residues may be curtailed due to emission concerns and competition from cleaner technologies. The potential financial and environmental benefits of delayed coking to process these heavy residues are immense, although they have as yet not been fully exploited. In as much as green coke enables delayed coking to provide a stable 'sink' for sulphur, its incineration effectively reverses this benefit, contributing to substantial SOx emissions, negating initiatives to restrict sulphur levels in automotive fuels. As cleaner, more efficient energy technologies replace heavy petroleum residues in fuel markets, they will need to be processed in an environmentally sustainable manner to affect an absolute reduction of SOx emissions. Delayed coking offers a realistic enabling option in terms of refinery integration, distressed heavy residues, SOx emission targets, and lighter hydrocarbon production to drive business initiatives in an increasingly environmentally restricted market. By removing fuel grade coke from energy markets, significant contributions are made to reduce absolute SOx emissions.

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John Clark is a fossil fuel scientist and industrial development specialist. He has substantial experience in fossil fuels research and sustainable product and business development. He specialises in delayed coking chemistry and coke markets, and has made considerable contributions in aluminium, steel, bunker fuel, heavy petroleum residues, coal to oil, bitumen, and energy value chains. He has lectured as an honorary professor on a pro bono basis at the University of the Witwatersrand (South Africa) and held a seat on the executive council of an international coal industry consortium in the USA. A seasoned international lecturer and industrial adviser to academic, industry, and government audiences, he holds a BSc in chemistry, MSc (Eng) in heavy petroleum shipping fuels and a PhD (Applied Materials Engineering) in sustainable needle coke.

Boosting tube-side heat transfer

Tube insert technologies can improve heat exchanger performance by enhancing tube-side heat transfer coefficients in two-phase applications

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CALGAVIN

For single-phase applications, it is generally understood that tube inserts will yield the greatest benefits in viscous or otherwise slow-moving fluids, due to the low heat transfer coefficients arising in laminar and transitional flow. In such cases, it can be possible to significantly optimise the design or performance of the heat exchanger.

The criteria which determine whether tube inserts could be effective in two-phase flow conditions are more complex than for single phase. The presence of a second phase necessarily introduces concerns about phase change equilibria, flow separation, and mass transport. The design engineer first needs to consider how these factors contribute to the overall thermal performance, to determine whether the enhancement mechanism of a particular tube insert will usefully improve or change the flow conditions.

This article will identify some general examples of two-phase applications where tube-side enhancement with Calgavin's hiTRAN Thermal Systems can be particularly effective. We will discuss the underlying flow regimes in these cases and how they are augmented. This will allow us to define some basic criteria to help the design engineer decide if it would be worthwhile to consider using tube-side enhancement.

Various forms of tube-side heat transfer enhancement technologies have been used widely in industry to help improve the performance of tubular heat exchangers. The adoption of these technologies is driven by the need to reduce the overall cost of new equipment and to increase the efficiency of existing processes. Using tube-side enhancement can be an attractive proposition if the tube-side heat transfer is a limiting factor, and provides an additional degree of freedom in the design.

Figure 1 hiTRAN wire matrix element being inserted into a tube

Figure 2 Dye injection test showing (A) laminar and (B) pseudo-turbulent

hiTRAN is one example of a tube-side enhancement technology. It is a type of removable tube insert which consists of a matrix of wire loops supported with a central core wire (see **Figure 1**). The wire matrix generates turbulence by interrupting the normal fluid flow, which increases the rate of convective heat transfer and virtually eliminates the transition between laminar and turbulent flow (see **Figure 2**). The packing density of the wire matrix can be finely adjusted to suit a prescribed pressure drop, and the geometry of the loops is varied to achieve optimum performance.

For applications with single-phase fluids, the criteria to decide the suitability of tube inserts are straightforward. Laminar and transitional flow conditions typically yield poor tube-side heat transfer coefficients, which subsequently limit the overall performance of the heat exchanger. In these conditions, tube inserts can often provide significant increases in the heat transfer coefficient. Calgavin provides a freely downloadable software tool, hiTRAN.SP, which can assist with the specification of hiTRAN elements in single-phase applications.

While multi-phase streams are preferentially allocated to the shell-side of a heat exchanger – owing to the greater volume and design adjustability – there are nevertheless many exceptions where allocation to the tube-side is necessary. For example, in air-cooled heat exchangers, operating with a high pressure fluid, when using expensive corrosion-resistant materials, or where such allocation would yield a more optimal thermal design.

In two-phase applications, there are additional factors to consider due to the added complexities of mass transport, phase separation, and vapour-liquid equilibrium. A tube insert will not only generate turbulence but will also disrupt the interface between the two phases, provide additional contact surface for the liquid phase, and alter the phase change behaviour due to the increased pressure drop. Therefore, it is important to consider which phenomenon controls the performance of a given heat exchanger, and how this may be affected by the enhancement mechanism of a tube insert.

Through studying cases where hiTRAN has been used in two-phase fluids, it has been possible to determine some criteria for cases where it is likely to provide measurable and significant improvements in performance.

Vaporisers

Although there is no rigorous definition of a vaporiser, the term is typically applied to heat exchangers where a liquid stream is converted completely into a vapour. Some vaporisers also require sensible heating of the sub-cooled liquid, and super-heating of the vapour.

In many cases, the process fluid will arrive at sub-zero temperatures, with the heating medium significantly hotter. The local temperature differences can exceed 100°K, which often leads to the occurrence of film boiling – a condition where the liquid at the heat transfer surface rapidly vaporises and forms an insulating vapour layer. In regions of film boiling, the heat transfer coefficient is very low and can significantly limit the performance of the heat exchanger.

Additionally, at near-complete levels of vaporisation, high velocities can cause liquid droplets to become suspended within the vapour and form a mist. The liquid droplets do not easily evaporate, because the rate of heat transfer through the vapour phase and into the droplets is relatively poor. Consequently, the presence of mist flow can lead to liquid carry-over in the outlet of the heat exchanger. In applications where liquid cannot be tolerated in subsequent parts of the process, mist flow must be avoided.

Film boiling and mist flow can not only reduce the effectiveness of a vaporiser, but also create significant uncertainties in the prediction of the performance. hiTRAN offers a potential solution for an affected vaporiser. The increased convective heat transfer cools the internal surface of the tubes, and the wire matrix introduces a physical disruption within the vapour film. The combination of these effects suppresses the onset of film boiling, increasing the local heat flux. The technology can also disperse mist flow by increasing the rate of heat transfer through the vapour into the droplets and breaking them up through collisions with the wire matrix.

Revamp of an ethylene vaporiser with hiTRAN

	Before retrofit	hiTRAN (after retrofit)
Ethylene flow rate, kg/s	14.5	21.1
Temperature in/out, °C	-100/-1 (sat.)	-100/30 (superheated)
Pressure in/out, bar	40/39.9	40/39.7
Heat transfer coefficient, W/m²K	613	2390
Duty, kW	261	618

Table 1

Case study

A tube-side ethylene vaporiser, designed as a BEU-type shell-and-tube heat exchanger (702 tubes, 4m straight length), was found to perform below the required duty when in service. Analysis of the process conditions and thermal design indicated significant areas of film boiling were present. The exchanger was retrofitted with hiTRAN, and the subsequent increase in heat transfer performance indicated the suppression of film boiling. After the retrofit, the vaporiser was able to meet its required duty (see **Table 1**).

Vertical thermosyphon reboilers

A thermosyphon reboiler (calandria) is a common case of a distillation column reboiler, whereby the force driving the circulation is due to the density change of the boiling fluid. In a vertical thermosyphon, the process fluid is assigned to the tube-side and partially boils along the tube length.

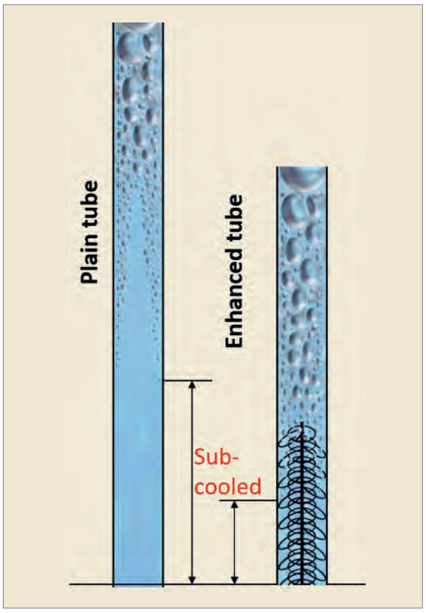

Figure 3 hiTRAN element used to reduce the sub-cooled length in a thermosyphon tube

In lower pressure applications, a disadvantage of the vertical thermosyphon is the high static pressure head which effectively sub-cools the liquid at the inlet. Therefore, a certain portion of the tube length is needed to first heat the liquid to its boiling point. This reduces the total amount of surface area available for carrying out the intended process of boiling the liquid.

The performance of a thermosyphon can be optimised by minimising the tube length filled with sub-cooled liquid. However, this may be difficult to achieve if the liquid is viscous or if the recirculation rate is low, as laminar flow can occur and limit the local heat transfer coefficient. This can be compounded during periods of low duty operation, where there can be a significant decrease in performance relative to the design condition.

Installation of a hiTRAN matrix only into the sub-cooled liquid zone can improve the rate of heat transfer into the liquid (see **Figure 3**). This allows the liquid to reach boiling point earlier, extending the surface area available for boiling and improving the achievable duty for a given size heat exchanger. The boiling zone is kept free of the matrix to ensure minimal impact on the total pressure drop, which could otherwise affect the recirculation rate through the reboiler.

Forced flow reboilers

A forced flow reboiler is similar in operation to a thermosyphon, except in this case a pump is used to deliver a controlled flow rate through the heat exchanger tubes.

The considerations for applying hiTRAN in a forced flow reboiler

Figure 4 hiTRAN induces turbulence in a liquid film

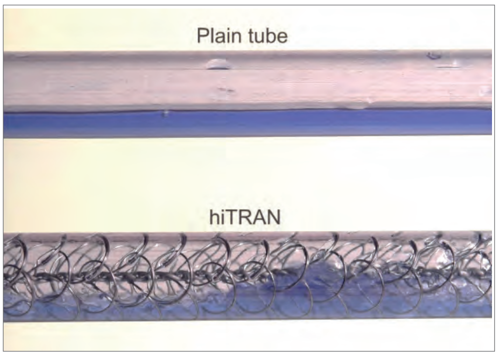

Figure 5 Comparison of phase stratification between plain tubes and hiTRAN

are generally similar to the vertical thermosyphon. The most significant improvements are made by reducing the tube length filled with subcooled liquid. However, as the flow rate is controlled by the pumping force, the pressure drop becomes less of a controlling factor. If sufficient capability is available from the pump, additional enhancement along more of the tube length may be possible.

Furthermore, the enhanced heat transfer coefficient varies more evenly with the flow rate, and fluctuations will cause a more significant change in pressure drop. This can improve the stability of both forced flow and thermosyphon reboilers at varying loads.

Falling film evaporators

In a tube-side falling film evaporator, a thin film of liquid descends the inside surface of the tubes and gradually evaporates. Falling film evaporation is usually employed when the process fluid is temperature-sensitive, necessitating the use of a heating medium which is not significantly hotter than the product. However, this low mean temperature difference can be a limiting factor for the thermal design.

A consequence of using only convective boiling (evaporation) is that the heat transfer coefficient of this process can be low, in comparison with nucleate boiling. When processing fluids with high viscosities or low mass flow rates, the flow regime within the liquid film can be laminar. The heat transfer is then controlled by thermal conduction through the film which, combined with the low temperature difference, significantly limits the overall effectiveness of the heat exchanger.

Falling film evaporators can be improved by ensuring good convective heat transfer in the liquid film, and fully distributing the liquid around the tube wall. hiTRAN can help to introduce turbulence in the liquid film, improving the rate of heat transfer. Additionally, when fitted in the opposite direction to the fluid flow, the wire matrix provides a solid route for entrained liquid to travel towards the tube walls, which helps maintain the film.

Vertical condensers

When a condensing fluid is required on the tube-side, a vertical orientation may be preferred to allow natural drainage of the liquid under gravity. Here, a film of condensate forms on the tube surface and falls down the tube walls. The condensing process is usually very effective, however there are certain situations when the heat transfer can be limiting and where hiTRAN may be beneficial.

For the condensation of pure substances, the heat transfer is dominated by the removal of latent heat and resistance through the liquid film. The application of hiTRAN must be carefully considered against the sensitivity of the fluid's boiling point to the operating pressure. The increased pressure drop may lower the boiling point, which will offset any improvements in heat transfer. hiTRAN is applied effectively in conditions where vapour velocities are low, and where the condensate film is found to be in laminar flow (see **Figure 4**). In such cases, there is a lower pressure drop penalty and a more significant increase in the heat transfer coefficient due to the induced turbulence in the liquid film.

The condensation of multiple-component mixtures introduces a simultaneous requirement for sensible cooling of the vapour, as well as removal of the latent heat. The sensible cooling requirement can be substantial for mixtures with a wide boiling range. Furthermore, accumulation of the more volatile or non-condensable components near the vapour-liquid interface creates a mass transfer resistance as the condensation process proceeds. The heat transfer through the liquid film may also be poor, particularly in cases where the condensate is viscous.

In addition to enhancement of the convective heat transfer coefficients in the bulk vapour and liquid film, the turbulence generated by a hiTRAN matrix more thoroughly mixes the various components in the vapour. This prevents the build-up of volatile and non-condensing components at the heat transfer surface.

Horizontal condensers

Horizontal tube-side condensation may be necessary where the geometry of the heat exchanger is constrained in this orientation, for example air-cooled heat exchangers and U-type shell-and-tube units. The general considerations for vertical condensation also apply to horizontal condensation. However, in horizontal tubes, the force of gravity acts tangentially to the direction of flow and can therefore significantly affect the fluid distribution within the tube.

If the fluid velocity or vapour fraction is high enough, the flow regime is regarded as shear-controlled. The effect of gravity is negligible compared to the momentum of the fluid, and turbulent flow results in high heat transfer coefficients. Application of hiTRAN in these conditions is not advisable due to the high pressure drop penalty.

On the other hand, gravity-controlled flow tends to occur in regions of low fluid velocity and low vapour fraction. Stratification of the two phases creates a pool of liquid at the bottom of the tube, which effectively reduces the surface area available for condensing the remaining vapour. Furthermore, a low velocity results in poor heat transfer through the vapour phase.

In gravity-controlled conditions, hiTRAN proves to be effective as it induces a significant change in flow behaviour (see **Figure 5**). The wire matrix breaks up the liquid-vapour interface and increases the formation of liquid slugs. This continuously refreshes vapour onto the heat transfer surface, aiding further condensation. There is also enhancement of the convective heat transfer coefficients due to increased turbulence.

The flow regime within a condenser will vary continuously along the tube length. The conditions may be shear-controlled near the inlet but become gravity-controlled as the vapour fraction and velocity decrease. The hiTRAN matrix may be partially installed only in the areas where maximum enhancement is possible, to minimise the penalty in pressure drop.

Case study

A horizontal BXM-type shell-and-tube heat exchanger (490 tubes, 5m long), condensing a mixture of aromatic hydrocarbons and inert components using cooling water, suffered from excessive vapour carry-over. A region of gravity-controlled flow was suspected near the outlet of the condenser, with poor heat transfer. hiTRAN matrix was partially installed in the final 2m of the tube length. The heat transfer performance was improved, resulting in a 45% reduction in the outlet vapour mass fraction. This allowed for increased economy of the process due to improved product recovery.

Conclusion

Tube inserts can be an attractive and beneficial solution when designing a tubular heat exchanger with poor heat transfer properties on the tube-side. Two-phase streams introduce additional complications and limitations due to phase separation and vapour-liquid equilibrium. Calgavin's hiTRAN Thermal Systems may be able to provide benefits by improving the convective heat transfer, achieving a more homogeneous fluid mixture, and disrupting the interface between the phases. In each case, it is important to identify the controlling phenomena, in order to define the potential scope for enhancement.

A selection of general examples is presented where hiTRAN has been found to be successful in achieving increased overall heat transfer. This may serve as a guide to the design engineer to consider some of the common limitations of two-phase flow, and the opportunities for using the technology to optimise or improve heat exchanger designs.

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Crude logistics scheduling

Upgraded crude scheduling enabled a refiner to increase its use of opportunity crudes for higher margin

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Generation of a refinery's operations plan requires the capability to monitor and determine the quality and the composition of crude oil to be processed in the crude unit as well as its availability date. Batches fed to the CDU must fit both quality constraints set by the operations department and simultaneously maximise the content of opportunity crude oils for the best processing margin.

Poor scheduling can erode up to 5% of the theoretical monthly result predicted by linear programming planning models and can result in higher ship demurrage costs. Thus, optimisation of crude oil logistics is fundamental, especially when the available crude inventories are limited and it is difficult to segregate crude quality.

Prometheus has developed a tool, Proraf, which offers an innovative algorithm to concurrently manage crude oil logistic events (reception, transfer, and processing) and predict the hourly evolution of the status of all tanks.

Crude data, simulation, and optimisation techniques are integrated by an algorithm which is also able to work high-level transfer instructions where the sequences of tank loading/unloading operations are not detailed.

The calculation engine manages the service requests associated with material transfers according to specified priorities and selection criteria, to bring each event to completion as fast as possible. This simulation highlights real bottlenecks to manage to prevent operational problems.

The software can solve autonomously the major components of the scheduling problem, requiring the user's intervention only to manage significant issues requiring appropriate action.

Furthermore, integration of economically driven optimisation methods generates operational plans to maximise the processing of opportunity crudes while meeting the CDU's feedstock quality requirements.

Significant time saving enables schedulers to explore a greater number of options, resulting in a more effective and optimised scheduling plan. It is a tool that supports, in the same environment and with the same model, development of both long and short term scheduling tasks:

- Long term scheduling models can calculate and update in a few minutes the evolution of the status of all tanks and pipelines in the logistic network. It is able to define cargo arrival dates and to identify solutions in case of unforeseen operational changes.
- Short term scheduling models enable detailed instruction reports to be issued and store validated operational results (that is, actually executed operations) into a centralised historical database which can provide the information to reproduce details of past activity.

This article describes the technology and reports a case study illustrating its implementation for the scheduling of crude supply operations for an Indian petrochemical refining complex.

The operator's maritime depot receives a variety of crude oils of variable quality (in terms of sulphur content, acidity, and API). The number of available tanks does not enable proper quality segregation, therefore each tank's evolving composition must be tracked.

Concurrently with cargo reception, some tanks are unloaded and fed in parallel (three to five pumping channels) to a pipeline. The blend resulting from parallel pumping must respect the quality constraints required for CDU processing at the other end of the pipeline. Batches exiting the pipeline can either be fed directly to the crude unit or go to refinery storage.

DSS modules

Prometheus has developed a set of technologies for crude oil characterisation, plant simulation, and blending calculations and has integrated them into five modules, designed to support the most relevant planning and scheduling tasks.

These modules can work standalone to perform a specific set of scheduling tasks, or share data and processes in case of extended solutions:

- CUTS is a crude assay data elaboration for database building and recutting. This module provides crude oil data for all the other modules.
- Simraf refinery LP optimisation is integrated with process plant simulation models for yield and quality calculations. This module supports ordinary and strategic planning tasks.
- Proraf provides modelling and optimisation of logistics.
- Prolav provides modelling and optimisation of processing operations.
- Ottmix provides LP optimisation of blending operations.

These modules support short term scheduling tasks.

The crude scheduling model described in this article applies the CUTS and Proraf modules. Further integration with other DSS modules to model crude oil processing and finished product blending operations is in the design phase.

Crude scheduling

Figure 1 summarises the findings of a study carried out to identify the refining operations which mostly impact the difference between the theoretical result expected from the business plan and the actual result.

According to these results and for various reasons, the actual refinery margin can decrease, compared to the planning figure, by up to 25%. One of these reasons is improper crude logistics management (reception facilities, deposits, and pipelines) which can represent, for a mid-sized refinery, an annual \$15-20 million loss: this is particularly true when variability of feedstocks forces operators to monitor the quality of their crude refinery tanks or to store different crude types separately to prevent quality contamination.

Typically, the average residence time of crude oil in refinery inventories is too low to enable proper quality segregation, and it is fundamental to improve the intelligence of tools dedicated to the scheduling of logistic assets, to manage the quality of the stocks finally fed to refinery crude units. In such cases, the crude scheduling process becomes critical, and great effort and investment is made to improve performance in this area.

Figure 2 lists the leading causes of economic losses arising from poor scheduling of crude oil logistics. In practice, LP models assume the capability to process optimal crude mixes in refinery crude units for the whole period, while in fact feedstock availability depends on the supply schedule and the logistic constraints involve unforeseen quality contamination.

In this case, the refiner must exploit all degrees of freedom available during the operational planning and scheduling process to maximise the final result. Crude batches fed to the CDU must fit the quality constraints set by the operations department and maximise the content of opportunity crude oils for the best processing margin.

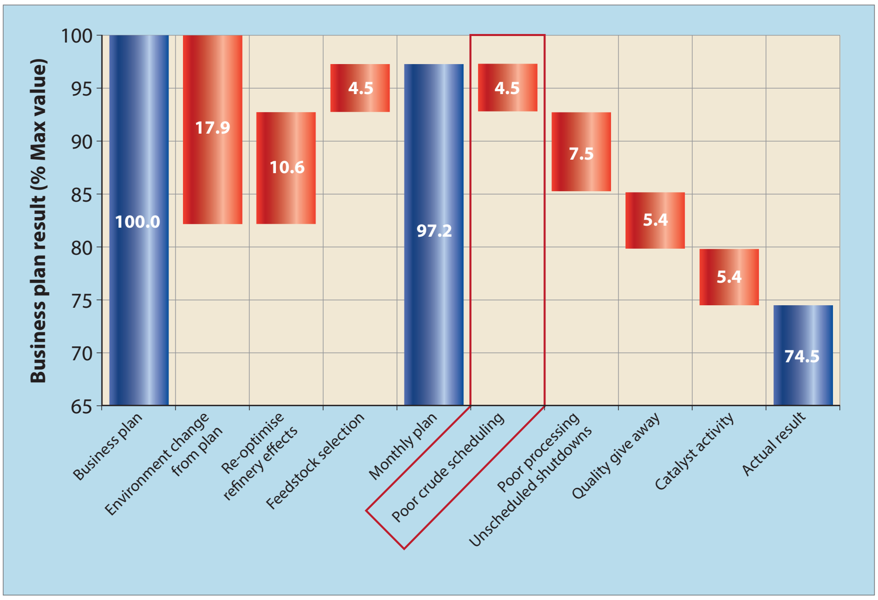

Figure 1 Actual refinery result versus original business plan

Typically in this framework, crude quality and cargo size is input from planning while scheduling can define the arrival dates of cargoes as well as handling operations throughout the logistics network up to the crude unit.

In the case of definition of cargo arrival dates, the impact of this material intake on crude logistics must be foreseen.

Given the supply programme, it is crucial to plan handling operations to avoid undesirable contamination, especially in the case of different operating modes based on different crude qualities, and to optimise batches by maximising the use of opportunity crudes.

The two main classes of scheduling activities differ by specific objective and time horizon; they are long term scheduling and short term scheduling. Proper execution of both activities requires the capability to simulate the evolution over time of the status of crude logistic assets (tanks, tank farms, pipelines), depending on supply programme, transfer operations and processing runs.

Long term scheduling

Long term scheduling assesses the feasibility of crude reception and transfer operations, in terms of blend quality and reliability, within a time horizon of a few months for a given schedule of crude cargo arrivals. The goal is to assure an ordered cargo arrival plan, timely unloading of cargoes at the maritime terminal with no demurrage costs, and blending to maximise consumption of heavy/opportunity crudes. A typical time horizon is 90-120 days. For example:
- **M:** current month, day 0-30 (Short term horizon).

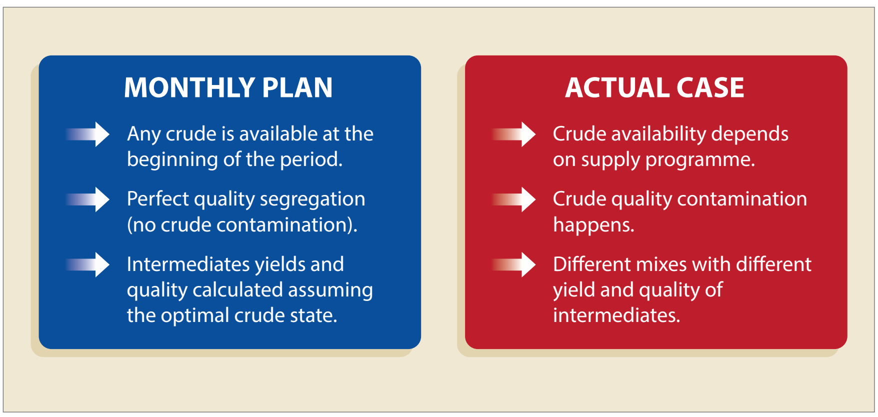

Figure 2 Monthly plan vs actual case

- Crude arrivals gates and dates are fixed (with three days variability)
- Once an actual cargo reception date and time is available, the simulation must be re-run

• **M+1:** next month, day 31-60 (nomination horizon).
- Known: quality, size, and number of cargoes (nominated cargoes)
- Unknown: arrival gates
- Task: to define the contractual arrival dates

• **M+2/M+3:** following month(s), day 61 to 90-120 (buy horizon).
- No information available
- Task: suggest the quality and the size of the cargoes to be purchased

With this activity, the scheduler defines the arrival dates of the crude cargoes to be nominated (typically at M+1) and finalises cargo grades, quantity, and arrival dates for the months M+2 and M+3.

For these purposes, the scheduler sets up a model of the logistic network and uses it to:

• Simulate the evolution in time of tank content considering arrivals, pipeline dispatches, and processing. The simulation aims to check the feasibility of cargoes' reception schedule considering the status of the tanks at reception dates (volume and quality) and contemporary transfer and processing activities.

• Plan the composition of the crude batches. The scheduler must track the composition of the batches fed to pipelines and crude units to prevent issues during processing steps.

• Define contractual arrival dates for 'nominated' cargoes for the four months covered by the simulation.

• Estimate arrival dates for 'to buy' cargoes, providing feedback to the planning department and trading departments charged with the purchase of new cargoes.

The long term simulation of a crude logistics operation is a time-consuming activity and the availability of a fast simulation tool is fundamental to enable the evaluation of alternative scenarios.

Short term scheduling

Short term scheduling aims to update the status of tanks during the current month, considering deviations from the original schedule that occurred in the period. Actual operations are set in the model and recalculated to align to reality the status of the tanks and to check the feasibility of the scheduled blends. Short term scheduling supports the publication of daily operative instructions as well as the historicisation of actual movements. The typical time horizon for short term scheduling is one month (30 days).

In this case, the scheduler uses a model to:

• Re-schedule short term operations to handle unexpected events (minor changes, delays, or unforeseen shutdowns) and to update the simulation baseline accordingly.

• Calculate the status of the tanks based on actual operation accounting for schedule deviations: the logistic model can be used to keep track of the crude composition of the tanks.

• Reconcile operations: for each planned transfer, the scheduler adjusts the planned quantity to the actual one.

• Store the results of the past operation (after reconciliation) to data historian so that they can be retrieved to support future scheduling activities.

• Publish operating instructions for a horizon of about 10 days.

Even though the horizon is shorter than in the case of long term scheduling, this activity is also time consuming (the input required is much more detailed). Thus, using a tool supporting the reconciliation activities is particularly useful.

Logistic simulation

Requirements

Both long and short term scheduling require the availability of a model able to calculate the evolution of the status of the logistics assets depending on the events occurring in the simulation period.

Tools used to develop and run such models usually feature a time consuming modelling phase (all transfer data must be manually entered), and need to update such data when any deviation from the plan occurs. Basically, instead of spending time evaluating alternative scenarios, a lot of it is wasted inputting and updating data.

The Prometheus algorithm applies a paradigm change. In fact, it autonomously proposes a solution (that is, the origin and destination tank of a given service) after processing 'high level' instructions from the user. Setting the criteria for tank selection in different situations is much faster than preparing the detail of every transfer; this potentially reduces the time for modelling tremendously. On the other hand, the tool must provide the user with the flexibility to orientate the solution to account also for constraints which are not explicit in the model but which are taken into account while generating the schedule.

To enable the software to propose reliable and feasible solutions, Prometheus has made available in the same environment crude characterisation data and MIP optimisation, and has developed a simulation algorithm which is able to exploit these tools to generate the schedule automatically.

Following research based on user feedback, Prometheus was able to develop a fast and effective algorithm based on deep integration of crude assay data (bulk and fraction properties, economics), and a sophisticated simulation engine enabling, at the same time, high level set-up of transfer events, the flexibility to change and orientate the solution, and economics-driven MIP optimisation models to run automatically to optimise batches.

This simulation engine takes into account operational and quality constraints, suggests the sequence of handling operations, and requires only a few minutes for a long term scheduling solution.

Crude assay data

CUTS is the Prometheus module for the construction and management of the crude oil characterisation database. This application features a proprietary technology (multidimensional regression) specifically developed to elaborate crude assay information to produce a consistent library which can provide the data for all the properties of any fraction of any crude blend, irrespective of the source, form, and consistency of the input assay.

CUTS characterises every crude oil as a mixture of pure components (C_{5-}) and 'pseudo-components' (C_{6+}), which cover the entire crude boiling range. Each pseudo-component includes pure components boiling in a narrow range of 10°C. For each property, CUTS uses multidimensional regression to create distribution curves and allows harmonisation of the shape of the resulting curves.

Table 1 lists the fundamental properties managed, the relative blending rule, and a meaningful boiling range (with property values estimated for each pseudo-component).

Proraf enables the user to define the list of quality specifications to be considered to track the quality of tank contents or to set up quality constraints for tanks or crude blends (in case of quality-controlled parallel sequences).

It is possible to consider almost any characterisation property but, since a high number of quality specifications involves longer computing time, it is recommended to find a good trade-off between the constraints needed to characterise the tanks and the calculation resources.

Proraf foresees four types of quality specifications. For each type, it is necessary to define a specific set of parameters to enable their retrieval from the CUTS library:

- Bulk: a whole crude referring property. It can be either a generic property (density, sulphur, viscosity) or the yield of a fraction.
- Cut: a crude oil's fraction referring property (for example, the acidity of the 150-250°C fraction).
- Crude: the amount of a given crude oil in the mix.
- Crude type: the amount of a given crude type in the mix.

The simulation algorithm

Proraf differs from other scheduling tools because the detailed list of operations associated with each transfer event is an output of the simulation instead of an input. While other systems simulate the impact of the set of transfer operations input by the user on the status

CUTS fundamental properties

Property unit	Blending rule	Boiling range
Weight TBP Yield, wt%	Linear weight	Whole crude
Volume TBP Yield, vol%	Linear volume	Whole crude
Density@15°C, kg/dm^3	Linear volume	Whole crude
Sulphur content, wt%	Linear weight	Whole crude
Mercaptan sulphur content, wt%	Linear weight	Whole crude
Kinematic viscosity @50°C, CST	Index weight	Whole crude
Kinematic viscosity @100°C, CST	Index weight	Whole crude
Acidity, mg KOH/gr	Linear weight	Whole crude
Aromatics content (FIA), vol%	Linear volume	Gasoline
Naphthenic content (FIA), vol%	Linear volume	Gasoline
Paraffin content (FIA), vol%	Linear volume	Gasoline
Aromatics content (gas chromatography), wt%	Linear weight	Gasoline
Naphthenic content (gas chromatography), wt%	Linear weight	Gasoline
Paraffin content (gas chromatography), wt%	Linear weight	Gasoline
Octane Number Motor Method (MON)	Linear volume	Gasoline
Octane Number Research Method (RON)	Index volume	Gasoline
RON+ Tetra Ethyl Lead 0.5	Index volume	Gasoline
RON+ Tetra Methyl Lead 0.5	Index volume	Gasoline
Reid Vapour pressure, psia	Index volume	Gasoline
Cyclopentane content, wt%	Linear weight	Gasoline
Cyclohexane content, wt%	Linear weight	Gasoline
i-Hexanes content, wt%	Linear weight	Gasoline
n-Hexane content, wt%	Linear weight	Gasoline
Benzene content, wt%	Linear weight	Gasoline
Methylcyclopentane content, wt%	Linear weight	Gasoline
Naphthalenes, vol%	Linear volume	Mid Distillates
Freezing Point, °C	Index volume	Mid Distillates
Cloud Point, °C	Index volume	Mid Distillates
CFPP, °C	Index volume	Mid Distillates
Pour Point, °C	Index volume	Mid Distillates
Refraction Index @20°C	Index volume	Mid Distillates
Refraction Index @70°C	Index volume	Mid Distillates
Aniline Point, °C	Linear weight	Mid Distillates
Total nitrogen content, ppm wt	Linear weight	Mid Distillates and residua
Basic nitrogen content, ppm wt	Linear weight	Mid Distillates and residua
Ash content, ppm wt	Linear weight	Mid Distillates and residua
Asphaltenes C_5 content, wt%	Linear weight	Mid Distillates and residua
Asphaltenes C_7 content, wt%	Linear weight	Mid Distillates and residua
Conradson Carbon residue, wt%	Linear weight	Mid Distillates and residua
Nickel content, ppm wt	Linear weight	Mid Distillates and residua
Vanadium content, ppm wt	Linear weight	Mid Distillates and residua
Wax content, wt%	Linear weight	Mid Distillates and residua

Table 1

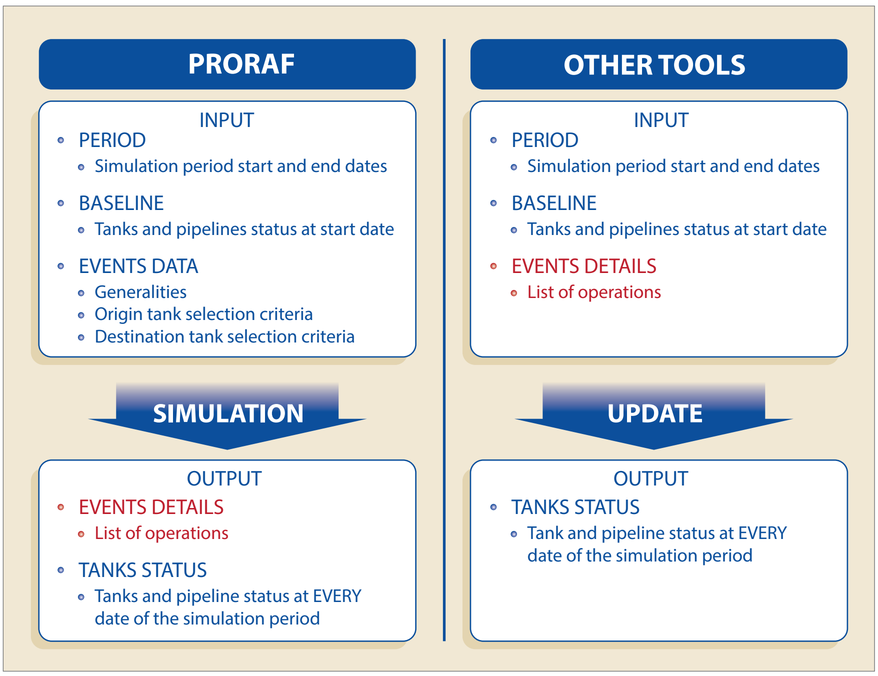

Figure 3 Proraf approach compared to other scheduling tools

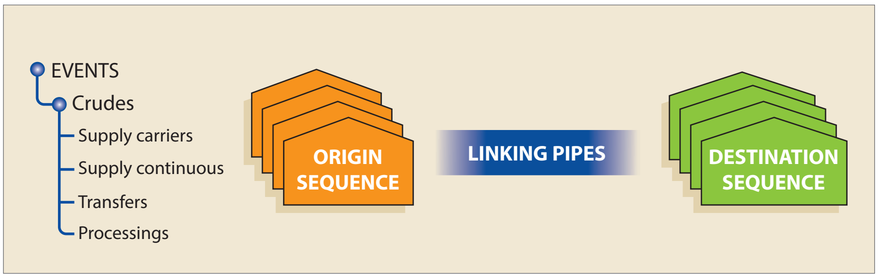

Figure 4 Event structure

of the tanks, Proraf can generate the set of transfer operations based on the high level instructions provided (see **Figure 3**).

This difference reduces tremendously the time needed to produce/update the scheduling plan, both for long and short term scheduling.

The simulation algorithm of Proraf can handle 'high level' instructions and propose a solution without needing to specify in detail the sequences of origin and destination for tanks involved in a transfer.

The user can specify in detail origin, destination quantity, and flow rate (as in the case of other scheduling tools) but can also delegate to the algorithm the selection from a set of tanks of which tank to use at a given moment ('Sequence'). In this case, Proraf suggests the best tank for the requested service, based on user criteria.

The algorithm splits the simulation period into time slots and elaborates them in series from first to last. For each transfer event, the engine generates a list of service requests to the connected objects (tanks, tank farms, pipelines) represented in the logistic structure and manages these requests according to specified priorities and selection criteria, to bring each event to completion as fast as possible.

The system manages various types of transfer events such as carrier and pipeline crude reception, transfers, and processing. The following information defines each event:

- General data (start date, flow rate, quantity, calendars)
- Origin and destination sequences (set of tanks and selection criteria)
- Linking pipes

The algorithm selects origin and destination tanks from the specified sequences and defines the transfer flow rate based on:

- Volume and pumping (load/unload) constraints
- Status (volume and content) and availability
- Handling operations (drainage, measurements)
- Quality specifications (quality constraints set for the receiving tank)
- Batch quality targets (in case of parallel pumping)
- Pipeline quality tracking
- Tank selection logics and exceptions

The calculation run generates the details of the operations associated with each transfer event as well as the time evolution of the status of any asset in the logistic network.

Batch optimisation engine

Proraf uses an optimised blending function, enabling it to determine origin tanks and blending ratios in the case of automatic parallel origin sequences. When required, the algorithm automatically formalises a mixed integer programming optimisation problem applying the constraints set, and solves it to find the origin tank of each pumping channel and the related pumping flow rate.

The simulation algorithm then uses this result to elaborate on the transfer event until the solution is applicable. When for some reason the solution becomes unfeasible (for example, one of the origin tanks empties) a new problem is formalised based on the updated scenario.

Model set-up

The simulation model foresees the preliminary set-up of a logistic network; Proraf features the following modelling objects:

- Tank: modelled with their actual geometrical properties, pumping constraints, and quality specifications
- Pipeline: connecting tanks can be one way, two-way or a simple connection
- Tank operations: to model operations triggered by loading or unloading
- Docks: cargo mooring points
- Ships' templates: different types of available crude carriers
- Crude types: crude oil associations
- Quality specifications: modelling the quality of crude oil batches
- Calendars: defining timetables for tank operations or events

The logistic network groups tanks in tank farms which can be actual or logical, depending on the simulation. It is easy to modify and update: Proraf's graphical user interface enables the user to customise the behaviour of each object to reproduce actual operating procedures.

Once the logistics are defined, it is necessary to define the transfer events occurring during the simulation period. Proraf features four types of events that model all types of operation; each event is defined by general information (start date, flow rate, quantity, calendars), origin sequence (set of origin tanks and selection criteria), destination sequence (set of destination tanks and selection criteria), and linking pipes (see **Figure 4**).

The algorithm uses this information to select, for each time slot, the origin and destination tanks as well as transfer flow rate. The events editor enables the definition of each transfer as well as the related parameters (type, calculation mode, origin, destination, volume, flow rate, and quality constraints). In this environment, it is also possible to set high level transfer instructions.

Results

The simulation calculates, with hourly resolution, the evolution of the status of all the tanks as well as the detail of material transfers. An exhaustive report section is also featured.

Examples of the different types of reports generated by the simulation – all exportable in Excel – include:

- Gantt chart reporting the events with transfer origin and destination

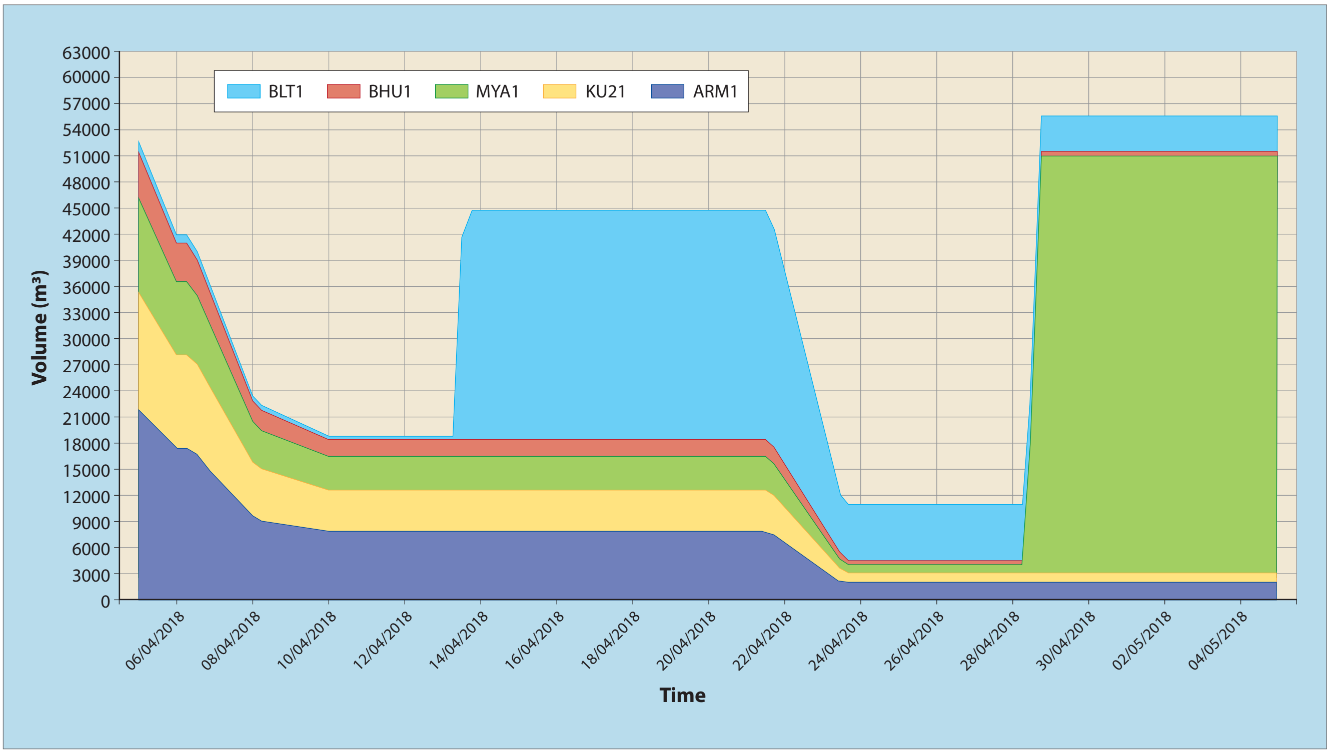

Figure 5 HMEL overview – tank status with graphical evolution of composition

details and highlighting transfer issues of any kind.

- Quality, composition, and origin tanks of all the crude oil batches fed to the pipelines and CDUs during the simulated period, both on a daily average and a batch base.
- Status (volume, composition, and quality) of all inventories at a selected date/time with hourly resolution.
- Graphical representation of ship discharge events with detail of the activity of the receiving tanks (loading, unloading, locked, on hold).
- Tank status table with graphical and tabular evolution of the status of all tanks.
- Tank graph with overall evolution of the composition of the selected tank.
- Pipeline line fill at any selected time during the simulation period.

Case study

Guru Gobind Singh refinery (GGSR) is owned by HPCL-Mittal Energy Limited (HMEL), a joint venture between HPCL and Mittal Energy Investment Pte Ltd, and is located at Phulokhari, Bathinda, Punjab, India. The current annual crude oil processing capacity is 11.3 million tonnes (225 000 b/d) and the refinery became operational in 2012.

GGSR receives its crude oil supply from a crude oil terminal situated at Mundra via a pipeline. The oil is imported from abroad and serves the domestic market, providing motor fuels to Euro-VI specifications and petrochemical products.

The refinery has a complex multi-unit configuration, plus utilities and offsites, cross country pipeline, crude oil terminal, and marine facilities. Its crude supply logistics enable the reception of crude feedstocks from the world market. Cargoes are unloaded into the tanks of the maritime terminal, then pumped to the refinery's crude oil tank farm via a 1000 km pipeline. The volume of the tank farm is 240 000 m^3 (see **Figure 5**).

The refinery receives crude oils which are highly variable in quality in terms of sulphur, API value, acidity, and asphaltenes and which must be blended appropriately to meet the quality constraints set by the operations department.

The blending operation is carried out in the maritime terminal. The goal of the scheduling process is to meet the quality requirements set by operations and planning, and to maximise the use of heavy/opportunity crude oils to provide higher margins than with lighter crude oils.

Blending is realised by parallel feeding of more tanks – typically four or five channels – to the pipeline. For every crude batch fed to the pipeline, the scheduler must decide the best pumping composition.

The scheduling tool must track the quality of the tanks as well as their availability at the moment in which it is necessary to generate a new crude blend and identify the most economical recipe.

HMEL was already using a crude scheduling tool but in 2017 the company began cooperating with Prometheus to develop a new tool better fitted to its requirements and aiming to:

- Accelerate development of the scheduling plan, especially for long term scheduling.
- Support the scheduler for better control of the quality of blended crude-mix batches entering the pipeline as feedstock for the CDU.
- Provide quick analysis of alternate scenarios for an early response plan to manage an unexpected event such as delayed arrival of a cargo (see **Figure 6**).

The implementation project started in November 2018, and

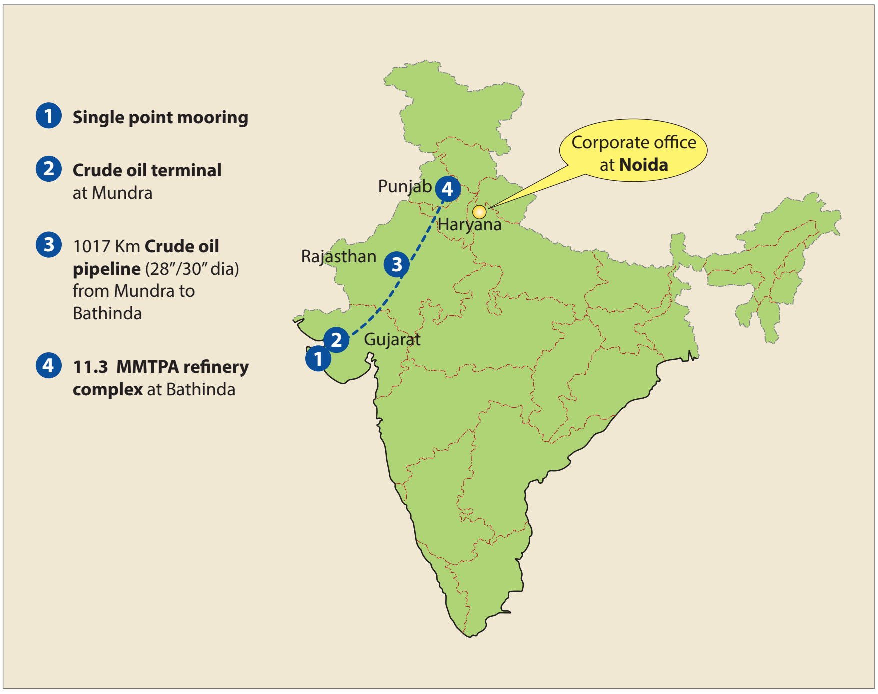

Figure 6 HMEL refinery crude reception scheme

the last module was delivered in August 2019.

Benefits

The economic objective function applied by the automatic optimisation engine available in Proraf tends to maximise the use of low value opportunity crude oils, corresponding to an increase in refinery margin by 1-2 cents/bbl.

The automatic calculation algorithm enabled updating the scheduling plan in a few minutes enabling: a precise cargo arrival sequencing plan for uninterrupted crude availability in optimum cargo parcels; and a quick analysis of different scenarios for an effective response to unexpected events such as a cargo's arrival delay, or a supplier confirms for a loading date different to the nominated one. This helps to minimise demurrage costs by 1-2 days every quarter. The algorithm enables a quick blend feasibility check for timely decisions on opportunity cargo purchases.

Conclusion

Integrating crude characterisation, simulation, and optimisation technologies, Proraf is a decision support system to optimise management of ship discharge and coastal storage tanks automatically with minimum user intervention. It assesses optimal crude blends for the pipeline or CDU, maximising the use of heavy/opportunity crude oils in compliance with feed quality constraints.

The system enables:

- CDU/pipeline feed quality tracking.
- Automatic calculation of a scheduling solution and CDU product yields and qualities.
- Obtaining a solution to crude scheduling problems in less time.
- Analysis of alternative scenarios.
- Better economics compared to other scheduling tools.
- Using the same tool and model can be used for long and short term scheduling.

HMEL - Guru Gobind Singh refinery successfully implemented this tool in 2019 and now uses it to support its crude oil scheduling activities.

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Q **What are the likely causes and solutions for severe fouling in a vacuum unit's preheat section?**

A **Celso Pajaro, Head Engineered Solutions Refinery AME, Sulzer Chemtech,** celso.pajaro@sulzer.com

The question is not so clear about the nature of the atmospheric residue and/or the streams that exchange heat with it. These are some potential causes:

- Low velocity of the atmospheric residue in the tubes (it should be above 6 ft/s)
- Leakage in the heat exchanger that allows the hot stream into the residue creating compatibility problems
- Mixing different types of atmospheric residues (paraffinic and non-paraffinic sources) that have compatibility problems leading to asphaltene precipitation.
- Paraffinic residues stored at low temperatures which allow the precipitation of solid wax.

A **Marco Roncato, Senior Product Manager Process Development & Marketing, CHIMEC SpA,** mroncato@chimec.it

The fouling affecting a vacuum distillation unit (VDU) HEX train depends a lot on the VDU's position in the process stream:

1) Downstream of a crude unit
2) Downstream of a cracking unit (for instance a visbreaking)

Case 1 (downstream a crude unit)

In this case, the fouling content of the VDU feed can be both:

- Inorganic (everything not removed at desalter stage will end up – concentrated – in the atmospheric residue, that is VDU feed)
    - sediment deposits
    - sand
    - corrosion products
    - salts
    - caustic injected in the crude oil after the desalter
- Organic
    - slops
    - sludges
    - destabilised asphaltenes
    - heavy paraffins

Which of the two will be predominant depends on the intrinsic nature of the crude diet (more or less clean, more or less stable) and on desalter performance.

Cleaning of VDU feed

For the inorganic part, the first measure is to maximise desalting efficiency: with lower basic sediment and water, and lower caustic injection in the desalted crude, their concentration in the VDU feed will be lower as will their role in reducing the heat exchangers' performance.

For more than four decades, Chimec has developed a programme – based on demulsifiers together with analytical and software tools – aimed at helping refineries in improving the desalter's performance.

But after this first step, despite good desalting efficiency, a further improvement can be achieved by injecting a caustic replacer in the desalted crude.

Caustic injection downstream of the desalter is recognised as a cheap and effective method to reduce overhead corrosion, but unfortunately at the same time NaOH can be detrimental because it can contaminate the bottom streams affecting the downstream units.

Caustic is itself a foulant agent; moreover, sodium is a well-known dehydrogenation catalyst, hence it is a coke promoter – it increases the coking rate in the downstream unit (for instance VDU) HEX train and furnaces.

Together with this, it is worth mentioning that caustic is also responsible for catalyst poisoning in downstream catalytic plants (FCC unit, hydrocracking unit, residue desulphurisation and, so on) and for the production of low-quality fuel oil (fouling problems in the burners, for instance in the power station or in the fuel oil furnaces).

In order to manage all issues, Chimec has developed a caustic replacer, Chimec 3034, to substitute completely or partially the injection of NaOH downstream of the desalter; it is completely organic and metal free which means it has no impact on coke promotion and catalyst deactivation.

The overall effect is the reduction of caustic and sodium content in the atmospheric residue.

This implies no risk of NaOH induced fouling in the preheat trains.

Managing fouling precursors

After 'cleaning' the VDU feed (by maximising the desalter's efficiency and reducing NaOH injection), the following action is to inject a suitable dispersant chemical in the VDU feed able to provide protection from both organic fouling (mainly due to asphaltenes deposition) and the inorganic variety.

Case 2 (downstream a cracking unit)

In this case, together with inorganic and organic fouling, there is also the strong presence of a further fouling portion, which usually becomes predominant – coke deriving from cracking processes and heavy gums due to olefinic polymerisation reactions.

For such units, usually the situation is more severe, because of the presence of coke and the higher amount of asphaltenes in the feed and generally lower stability.

Therefore, the dispersant must be more specific and stronger compared to the one injected into the feed of VDUs processing atmospheric residue.

Moreover, it is necessary to tackle the polymerisation reactions through the injection of a stabiliser, so the olefins cannot form heavy gums.

In such a situation, if possible the chemicals have to be injected directly into the cracking unit's MF bottom so that they can act from the very beginning, before coke and asphaltenes can settle and polymers are formed, fouling downstream equipment.

Alphabetical list of advertisers