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www.catalysts.basf.com/refining
3 A sunnier outlook
Chris Cunningham

5 ptq&a

15 Revamping crude and vacuum units to process bitumen
Tek Sutikno
Fluor Enterprises

23 Tube alloy degradation in a steam cracking furnace
Glen A Hay and Ghoncheh Rasouli Virtual Materials Group, Inc.
Toshiharu Morishita and Jinichiro Usami Mitsubishi Chemical Corporation

29 Overcoming the effects of ammonia in heat exchangers
Marcelo Senatore Sandvik Materials Technology

37 Enhancing energy efficiency in the CDU
Osman Kubilay Karan and Cansu Iner
TÜRAŞ Kirikkale Refinery

43 Improving energy efficiency in furnaces
Steve Chernack
Morgan Advanced Materials

47 Heat recovery from corrosive flue gas
Bart van den Berg
HeatMatrix

51 Optimisation of energy consumption
Farbod Rikhtegar PPG Consultant Engineering
Sepehr Sadighi RIPI

61 Best practice in energy efficiency
Ron Beck
AspenTech

65 Advanced process control in FCC and hydrocracking units
Grzegorz Oleszczuk and Marta Dylewska
Honeywell Advanced Solutions

71 Increasing distillate production at least capital cost
Joe Musumeci, Steven W Stupin, Brandon Olson and Carlos Wendler
Ascent Engineering

81 Advances in processing high naphthenic acid crudes
Parag Shah, Mahesh Subramaniyam, James Ondyak, James Noland and India Nagi-Hanspal
Dorf Ketal

89 Seven rules of sedimentation in hydrocracking
Scott Sayles, Robert Ohmes and Rick Manner
KBC Advanced Technologies

99 Catalytic strategies to meet gasoline sulphur limits
Patrick Gripka, Opinder Bhan, Wes Whitecotton and James Esteban
Criterion Catalysts & Technologies

107 Reducing vacuum tower pressure
Norman Lieberman
Process Improvement Engineering

113 Technology in Action

118 Achema 2015

Marathon's Canton refinery in Ohio has installed a new 25 000 b/d condensate splitter. Photo: Marathon Petroleum Corp.
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A sunnier outlook

Make firm predictions on the price of crude oil at your peril. But one thing is for certain: for the time being at least, petroleum refiners are doing pretty well out of cheaper feedstocks.

In a recent review of the outlook for oil prices, BofA Merrill Lynch pointed out that energy consumption as a percentage of global GDP is the lowest it has been in 13 years, although spare capacity in global production of oil is relatively low. The oil market these days is never in balance, but uncertainty over prices is especially high at present, given the range of uncertainties over production issues and geopolitics. The review cites shale output and current OPEC policy as having long lasting consequences for supply, favouring low-cost, flexible production over very large projects.

Shale oil output in the US is approaching a peak which may complicate the argument in favour of exports to stabilise prices on the wider market. However, as supplies of ‘conventional’, relatively expensive crude run down then the opportunities for stepping up production of shale oil should improve.

Apart from the favourable immediate impact of lower crude prices on refining margin, another piece of positive news posted by BofA Merrill Lynch is that demand will be “meaningfully altered” by a regime of low-cost crude. Continued high prices would have led to zero growth in global demand by 2025. The review estimates that if oil stays at $60-90/bbl, demand will increase over five years by 6.3 million b/d. Consumers will no longer rush to buy smaller and more fuel efficient cars, and growth in demand will speed up in South and East Asia as those markets catch up with efficiencies in consumption elsewhere.

Downward pressure on oil prices may have its origins in North America and the Middle East, but the biggest sigh of relief from refiners may well be in Europe where thoughts of the demise of the region’s refining industry appear, like Mark Twain’s obituary, to be premature. A report on Spain’s Repsol in the Wall Street Journal illustrates the switch in roles between production and refining as the chief money earner for energy companies. Repsol’s results for 2014 reveal a substantial write-down on its production sites, with an overall net loss for the year. But the company describes its rejuvenated refining arm as a “cash cow”. The price of crude delivered to Repsol’s refining sites is close to half its level in mid-2014 so that earnings per barrel in the final quarter of last year were $5.50, compared with the company’s year-ago earnings of $4.10 per barrel.

In no small measure, Repsol’s refining bounce back has been strengthened by substantial investments, as the pages of PTQ have demonstrated in recent years. This counters the European trend which has seen refineries performing relatively badly compared with their counterparts in North America and Asia. Repsol’s €4 billion spend was designed to eke some measure of profit from its refineries in a time of high-priced crude, with a view to survival amidst closures and cutbacks elsewhere in Europe. With barrels of raw material arriving at around $60 each, fourth-quarter downstream earnings were reported at €370 million.

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Leading minds. Advanced technologies.
Our heavy crude feed is causing problems with stable emulsions in the desalter. What are the possible causes and remedies?

Charles Radcliffe, Senior Tech Service Engineer-Europe, Johnson Matthey Process Technologies, Charles.Radcliffe@matthey.com

The stability of desalter emulsions is influenced by the relative density of the crude and wash water, pH of the wash water (hydroxyl ion concentration), desalter residence time, degree of polarity of the crude, and emulsion droplet size, electric field strength, and use of de-emulsifier additives. Dealing with these in turn:

a. The greater the density difference between the hydrocarbon and wash water, the quicker the emulsion will break. If possible, the desalter temperature can be adjusted to increase this difference, although Brownian motion at higher temperatures can cause the emulsion to be more stable.

b. Hydroxyl ions in the wash water act like soap and stabilise the emulsion. Phenols are a particular problem, as these tend to be deliberately routed to wash water from FCC overheads treatment to lower COD on wastewater. If possible, increased make-up water can be used but this will increase the total wastewater flow, and lower desalter residence time. Look at alternatives for spent caustic disposal.

c. Lowering crude rate and/or wash water rates will increase residence time, but are probably constrained by economics and wastewater quality issues.

d. The mix valve DP is the main controlling factor on droplet size, but reducing this may result in higher salt carry-over, and higher crude overheads treatment costs.

e. Electrode voltages should be maximised, and the current to all the electrodes should be a near as possible equal. Uneven currents indicate either damage or an overloaded desalter (too small).

f. Proprietary de-emulsifiers are available, but need to be carefully controlled because over-use can cause the salts in crude to increase. Refiners need to work closely with their supplier to ensure this is optimised.

Antonio Aulicino, Process Development & Marketing, CHIMEC, aaulicino@chimec.it

The water-oil separation mainly depends on the physical properties of the hydrocarbon phase. Heavy crudes consist of oil with API gravity lower than 20. These types of crudes are usually characterised by high viscosity, high conductivity, high solid loading as well as high asphaltenes content. All these characteristics can have a direct effect on the emulsification of the water in the oil, thus jeopardising the desalting operation.

The settling velocity of a water droplet in a hydrocarbon phase is directly proportional to the difference between water and oil density and inversely proportional to the oil viscosity. This means that the driving force of the water separation in a high density and high viscosity crude oil is lower. As a consequence, a higher residence time is required to reach the specification of salts and water in the desalted crude oil.

Heavy crude oils are often characterised by high conductivity. The crude oil conductivity plays an important role, often underestimated, in demulsification under electrostatic field. In high conductivity crude oils, the voltage decay reduces the average voltage gradient applied. In AC desalters, this results in a lower electrostatic field, with consequent less effective dehydration. AC/DC desalters are able to overcome this side effect.

Solids and asphaltenes are usually present in heavy crude oils. These compounds are able to stabilise the water-in-oil emulsion, because they remain at the water droplet interface, avoiding or however inhibiting the droplets coalescence. Asphaltenes, for example, are surface active compounds that are adsorbed at the oil-water interface, avoiding or however inhibiting water-in-oil emulsion, because they remain at the crude oils. These compounds are able to stabilise the interface.

A stable water-in-oil emulsion can lead to:

• High water content in the desalted crude oil, with consequent increase in energy consumptions

• High salt content in the desalted crude oil, that increases the risk of corrosion in the main fractionator overhead system, increases the fouling deposition in the crude distillation unit and in downstream processes, and increases the catalyst poisoning of residue hydrocracking (if present)

• High hydrocarbon content in the brine water, that can jeopardise the wastewater treatment.

It is clear that a proper management of the desalting system is crucial when processing heavy crude oils. An increase of the wash water is usually recommended in order to improve the desalting. 5–8% of wash water referred to the crude oil flow rate can be considered as a good range. To avoid emulsification, it is suggested to minimise the pressure drop of the mixing valve, without reducing the mix ratio to values lower than
0.5. The level of water inside the desalter vessel should be minimised, to assure an adequate residence time of the oil phase without compromising the brine water quality.

However, if a stable emulsion is present, the action on the process parameters may have only a limited effect. In these cases the application of a specific demulsifier is required. These chemicals are blends of surface active compounds, able to replace the emulsifiers at the oil-water interface, enhancing the coalescence and the flocculation.

Decades of researches and direct field applications allowed Chimec to develop a line of best in class demulsifiers, specifically designed for heavy crude oils and high sediment content crude oils. The application of these cutting edge technologies, together with the expertise of Chimec personnel, can enhance the desalting and the dewatering efficiency, smoothening the desalting operations and thus reducing the energy consumptions.

For more information, please contact us at procestreatments@chimec.it

**A Berthold Otzisk, Kurita Europe GmbH, Otzisk@kurita.de**

Heavy crude oils provide economic benefits to refineries, but their desalting is always a challenging operation. Many heavy feedstocks contain higher amounts of inorganic solids. They can accumulate in the desalter vessel and contribute to stabilised emulsion layers in the water/oil interface zone. Heavy crude oils have small density differentials with water and tend to form diffuse interface layers.

The sedimentation of the water droplets is adversely affected, causing emulsion problems as the driving force for separation is small.

If solid based sediments continue to increase in depth, action must be taken to remove them from the desalter vessel. Mud-washing procedures, interface sludge drains and agitating the water layer are useful tools to remove these sediments. It is one of the most difficult items to control the interface level of heavy crude oils, and why conventional interface controls such as displacers or weighted floats are unsuitable.

The asphaltene concentration in heavy crude oils is significantly higher than in lighter crude oils and can reach concentrations of up to 30 wt% or more. Asphaltenes are polycyclic molecules, which have the tendency to form stacked aggregates. They are surface-active components and can interact and reorganise at the oil/water interface, which stabilises the emulsion. The higher viscosity of heavy crude oil feedstocks can be a critical factor as it limits the sedimentation rate. The agitation with wash water will not break up the water phase into numerous and fine droplets, which would be the case with lighter crude oils. Larger drops of dispersed water are kept in suspension while smaller dispersed droplets show a greater resistance to settling. Temperature is the primary control of heavy crude oil viscosity. The required higher temperature is usually limited by the temperature tolerance of the insulators of the electrical grids.

A chemical treatment programme can provide significant benefits to improve the desalting and dehydration efficiency. Demulsifiers (emulsion breaker programmes) accelerate the separation of suspended solids from the heavy oil by forcing them into the water layer. These demulsifiers are often blends of different components with various actions to achieve a complete treatment. They work by providing a far better coalescence efficiency of the water drops, combined with destabilisation of the formed emulsion phase. Compared to lighter crude oils, much higher demulsifier dosing rates are required, because natural emulsifiers such as asphaltenes are often present in large quantities. Kurita delivers customised demulsifier programmes for heavy crude oil treatment.

**A Vivek Srinivasan, Senior Engineer, Technical Services of Dorf Ketal Chemicals**

Stable emulsions can be attributed to several reasons while processing heavy crudes. The viscous nature of heavy crude demands optimised mix valve adjustment and use of superior demulsifier technology to augment emulsion breaking. Filterable solids that are neither oil soluble nor water soluble stay in the emulsion, causing rag layer formation, which can be overcome by using good tankage preparation practice. Dorf Ketal’s proprietary dewatering aid and solid wetting agents manage crude solids up to >1500 ppm. Stable emulsions are also caused by alkaline wash water pH due to the presence of ammonia and amine. Dorf Ketal’s pH management aid will give good desalting performance. Asphaltenes precipitation arising out of incompatible crude blend causes stable emulsion. This can be overcome by understanding the compatibility of the crude to be blended using oil compatibility studies. Dorf Ketal has conducted compatibility studies for more than 200 crudes. Last but not the least, stable emulsion is also caused by high calcium crudes, due to the poor solubility of calcium salts. Dorf Ketal has proprietary calcium removal aids (acid and non-acid chemistry) to tackle calcium naphthenate problems.

Slop processing along with heavy crude also creates stable emulsion in desalters. It is important to know which kind of slop it is (cracked or straight run) and to what extent it is being processed through crude distillers in order to provide suitable remedies. Ideally, cracked slopes should not be processed through crude distillers, to avoid emulsion problem in desalters and fouling downstream.

**Q We are encountering high levels of fines and jagged particle formation in our FCC catalyst bed. Could this be the result of some gas jetting effect in the fluid bed?**

**A Charles Radcliffe, Senior Tech Service Engineer-Europe, Johnson Matthey Process Technologies, Charles.Radcliffe@matthey.com**
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Jagged particles in fines and higher fines formation are certainly indicative of higher catalyst attrition. This is most likely due to a high velocity jet somewhere in the reactor regenerator circuit. Tracerco can provide diagnostic information using Gamma scans and radio tracer studies but, before embarking on this, basic troubleshooting should be carried out:

a. Compare the fines level trends from the reactor and regenerator.
b. Check all steam and air purge flows and back pressure, in particular feed nozzles and stripper steam.
c. Check for changes in conversion that could indicate feed nozzle damage.
d. Check for changes in radial regenerator temperatures (cyclone temperatures in particular are useful) that could be indicative of air distributor damage or plugging.
e. Check for changes in catalyst attrition index.
f. Check the cyclone and distributor nozzle velocities against design.

g. Compare samples of fresh catalyst before and after problem, for their morphology. Optical and electron microscopy can be used. Also compare the fines morphology. Jet erosion tends to produce random shapes, while poor catalyst morphology tends to increase the number of segmental shapes.

We believe arsenic contamination is the cause of loss of activity in our diesel hydrotreater. How do we address this?

Robert Bliss, Mid-Distillates HPC Specialist, Albemarle, Robert.Bliss@Albemarle.com

Arsenic concentrations in crude oils vary significantly across the globe and crudes containing high levels (>300 ppb) are typically associated with specific geographical production regions. Some of the regions known to have the highest concentrations of arsenic include the Canadian Alberta Oil Sands bitumen deposits, the Venezuelan Orinoco Belt extra heavy crude deposits and Russian crudes from the Western Urals. Theories suggest petroleum plays derived from vast marine animal deposits are typically high in arsenic due to arsenic concentrating in marine species thousands of times above the 1.5 ppb level typically found in ocean water.

Arsenic compounds found in petroleum are primarily derived from aryl and alkyl substituted arsine. These organoarsenic compounds can vary greatly in structure and molecular weight; as a result they distribute evenly across all petroleum distillate fractions (naphtha, diesel, VGO) and negatively impact hydrotreating units across all application segments (for instance, NHTs, DHTs, HCUs).

Arsenic is one of the most severe poisons for base metal (NiMo, CoMo) hydrotreating catalysts (HPC). Studies have shown activity losses exceeding 50% at arsenic loadings as low as 0.8 wt% on catalyst. This is very severe compared to a moderate poison such as silicon where catalyst activity losses do not exceed 50% until loadings in

Side-feed entry, center-feed results.

Extend coke drum life with DeltaValve’s new retractable center-feed injection technology.

Side-feed entry has been shown to negatively impact traditional resid flow patterns in coke drums. DeltaValve has responded with the introduction of an innovative retractable center-feed injection device utilizing side-feed entry. This technology transforms side-feed entry back to the center of the coke drum, generating stream flow patterns similar to traditional bottom-feed injection. Recent thermal and strain measurement data and subsequent calculations indicate a significant increase in coke drum life may be achieved when utilizing DeltaValve’s new retractable center-feed technology.

Contact us at 1.807.984.1000 or visit http://deltavalve.curtis.com
excess of 8 wt% on catalyst are realised. Arsenic is a permanent poison; once it is on the catalyst it cannot be removed and it will prevent catalyst regeneration at loadings as low as 0.3 wt% on catalyst.

Arsenic bonds directly with nickel and cobalt promoter atoms on molybdenum disulphide (MoS₂) HPC active sites forming nickel arsenides (NiAsₙy) and cobalt arsenides (CoAsₙy). Once formed, these arsenide compounds do not destroy the MoS₂ structure; however they do alter its electronic state resulting in substantial catalyst deactivation. Further, it has been shown that arsenic has a higher affinity towards nickel than cobalt. Thus catalysts designed with larger amounts of nickel will ‘trap’ larger amounts of arsenic.

Because catalyst deactivation from arsenic poisoning is so severe, it is critical in hydroprocessing applications known to have arsenic contaminated feedstocks to employ an arsenic specific trapping catalyst layer in the top bed guard system to protect the main bed HPC below. Albemarle has extensive experience in the design and application of arsenic traps; our two latest arsenic traps include KG 8, commercialised in 2011, and KG 16-MAC (maximum arsenic capture), commercialised in 2014. The best way to determine which arsenic trap and the quantity required to address the loss of activity in your unit is to utilise the application knowledge of your Albemarle technical service team to design a catalyst system solution that will exceed your objectives. Albemarle also offers analytical services to quantify the level of arsenic contamination in your feedstock.

Reference

We are encountering compressor performance issues as a result of condensation from the hydrogen stream from our catalytic reformer. Any solutions for this problem?

A Charles Radcliffe, Senior Tech Service Engineer-Europe, Johnson Matthey Process Technologies, Charles.Radcliffe@matthey.com

Catalytic reformer compressor fouling is normally due to chloride deposition. Chlorides can be removed using a chloride guard bed, but this will influence the chloride balance and continuous injection rates will need to change.

How do recombination problems involving a hydrotreater effluent steam and H₂S occur and what effect can it have on ULSD product specification?

A Andrea Battiston, Technical Specialist Hydrotreating, Albemarle, Andrea.Battiston@Albemarle.com

Recombination problems are due to the reaction of olefins with H₂S, leading to the formation of mercap-

tans. If trapped in the effluent product, mercaptans would increase sulphur concentration, typically by a few ppm, and could cause the ULSD product to fail target sulphur specification as a result.

The key factor for recombination is olefins’ saturation equilibrium. Olefins are very reactive species and their saturation by hydrogen is favoured at low temperature. In hydrotreaters, olefins saturation occurs below 260°C and is typically completed already in the top layers of the reactor. Thermodynamic equilibrium conversion for olefins, though, decreases with increasing temperature and, depending on H₂ pressure, dehydrogenation may take place, with olefins being formed again.

The risk is highest close to the reactor bottom, in particular at end of run, if temperature is sufficiently high, >380°C. Traces of olefins formed close to the reactor outlet, or even downstream when contacting hot surfaces, could react further with H₂S, producing mercaptans that could enter the effluent product.

Recombination problems are encountered quite regularly in naphtha and in ULSD hydrotreaters as the impact on product quality is high in view of the very tight sulphur specification.

In hydrotreating ULSD operations, recombination is not encountered very frequently, or, at least, is less often recognised. Heat exchangers leakage is, in fact, a far more common problem in ULSD production for product sulphur specification. In ULSD operations that include a (mild) hydrocracking function, on the other hand, olefins are typically generated as a result of cleaving C-C bonds, and with them mercaptans. For this reason, a layer of finishing hydrotreating catalyst is positioned below the cracking catalyst layer to convert the mercaptans.

A typical way to recognise the presence of mercaptans recombination is to check the response of product sulphur to the variation of the unit operating temperature. Failing to reduce sulphur product when increasing operating temperature is a sign that mercaptans recombination may indeed be occurring. This can be easily verified by analysing the product effluent, for instance by GCXGC-SCD, to identify specific sulphur species. If mercaptans are found in the product, the conclusion is that recombination is very likely the reason for failing sulphur specification. In such a case, reducing operating temperature may be the only solution at hand. Measuring effluent samples at different positions in the section downstream of the reactor, for instance right after the reactor outlet or in the rundown line, may allow identifying where recombination takes place.

The exchangers cooling output from our visbreaker have particular problems with fouling. Can we resolve this upstream or through exchanger design?

A Marcello Ferrara, President, ITW, mferrara@itwtechnologies.com

ITW Online Cleaning can clean the equipment in as
little as 24 hours on an oil-to-oil basis without extracting the bundles.

Additionally, the fractionator, the lines, the filters will all benefit from Online Cleaning.

By applying ITW Online Cleaning proactively, there is no need to redesign the exchangers or to revamp the unit (as far as fouling concerns) because its regular application will allow a run under clean conditions. This is a mind shift from the normal ‘run to death’ mode of running a unit.

The advantages of online cleaning over hydroblasting include:
• Reduced downtime
• Simultaneous cleaning of multiple equipment/units
• No waste generation
• No emissions.

Q What advice do you have on upgrading our CDU internals to increase throughput?

A Celso Parejo, Manager APT Refinery Applications & Process Technology, Sulzer Chemtech USA, celso.pajaro@sulzer.com
This is a general question so we would provide some guidelines:
• There are several tray options: high capacity trays like VGPlus that can be used in the pumparounds and fractionation sections; antifouling trays like VG AF are used in the column upper (where salt deposition can be a problem) and bottom (where solids coming with the crude can deposit) sections
• Structured packing has also been used in a variety of columns and column sections. A CDU wash zone revamped with structured packing increases capacity while minimising residue entrainment
• Please check all the transitions like changing from one- to two-, or four-pass trays as well as the liquid collection below the flash zone
• Verify liquid velocity in all draw-off nozzles. High velocities can limit the draw rate and possibly premature pump cavitation during start-ups
• Check the side-stripper vapour return line pressure drop to eliminate bottlenecks
• Verify transfer line velocity and the momentum of the feed going into the column. High feed velocity can create erosion problems inside the column and/or produce high residue entrainment with rising vapours.

A Charles Radcliffe, Senior Tech Service Engineer-Europe, Johnson Matthey Process Technologies, Charles.Radcliffe@matthey.com
The normal route to debottlenecking crude tower internals is to replace trays with packing. Random packing is cheaper but structured packing is more efficient. Normally the packing manufacturers can study and advise on what the options are and their relative cost. Things to consider include:
a. Which section is the nearest to flood.
b. What can be done by adjusting pumparound and reflux rates by increasing heat transfer and reducing their temperatures.

Q Can reducing atmospheric tower top temperatures to maximise middle distillate production introduce new corrosion problems? If so, how are they overcome?

A Antonio Aulicino, Process Development & Marketing, CHIMEC, aaulicino@chimec.it

Corrosion is the most critical issue for refineries in terms of safety and costs. Among the various processes, corrosion control in crude distillation units is one of the most challenging, due to the particular and complex nature of the system.

A distillation column overhead stream contains a changeable quantity of steam, in addition to different kinds of hydrocarbons. The concentration of several chemical compounds, such as hydrogen sulphide, chlorides, ammonia and light organic acids present in the water and hydrocarbon phase, changes according to the characteristics of the plant feed, the efficiency of the desalting system as well as the wash water used.

As a consequence of the cooling and condensation process occurring in the column overhead system, these species go to the water phase, according to their solubility, partial pressure, temperature and pH value.

Depending on the temperature and pH values in the overhead system, the combined action of sulphides, chlorides, light organic acids, amines and ammonia determines water solution corrosion potential. Besides the generalised corrosion phenomena, salt deposition can occur and may lead to under-deposit corrosion. Being of pitting type, under-deposit is particularly risky for safety and operations because it can produce leakages.

Salts are formed by the reaction between ammonia/amine and hydrogen chloride. This reaction can also occur in the gas phase. In this case the reaction is heterogeneous (the product is solid or liquid) and exothermic (as all the neutralisation reactions), so it is possible to determine a limit temperature: the so-called salt point. If the temperature is higher than the salt point, the reaction does not occur. If it is lower, the reaction occurs and in theory it continues until the exhaustion of the limiting reactant. The salt point depends on the partial pressures of ammonia/amine and hydrogen chloride: the higher the partial pressures are, the higher the salt point is.

If the salt point is higher than the water dew point, salt deposition occurs in the anhydrous area. The salts stick on the metal surface; being hygroscopic they adsorb water, promoting the typical pitting of the under-deposit corrosion. Besides corrosion, salts create an insulating layer on the heat exchanger surfaces, reducing the heat transfer efficiency. Moreover, this layer reduces the flow area, increasing the pressure drop and limiting the unit operability.

Refineries that want to maximise middle distillates reduce the atmospheric tower top temperature to adapt their production. The top temperature reduction reduces the hydrocarbon fraction in the vapour line. As a consequence, the partial pressures of water, ammonia, amines and hydrogen chloride increase. This results in higher water dew point, ammonium chloride and amines hydrochloride salt points. The increase of the salt points is stronger than the one of the water dew point, with a consequent increase of salt deposition risk in the anhydrous zone. Plugging and under-deposit corrosion are common issues for refineries that reduce the top temperature.

The traditional approach applied to remove salts is the injection of wash water. This method in many cases is effective in removing the water-soluble salts, but on the other hand wash water implies operating costs and operational difficulties. Without a proper distribution, water remains on the bottom of the line without washing the whole surface. By applying the wash water, we are able to reduce the hydrocarbon residence time in the overhead accumulator, thus increasing the risk of water carry-over in the reflux naphtha. This could promote huge corrosion phenomena in the top trays of the column.

The patented Chimec Salt Dispersant Technology is the result of years of research that led to the most effective and unique chemical formulation, successfully applied worldwide. The application of Chimec Salt Dispersant in a continuous way avoids salts formation and deposition, by keeping the micro-crystals dispersed. It is clear that, compared to wash water, Salt Dispersant can also provide a preventive action. Moreover, being oil dispersible and water soluble, it is able to reach the whole surface, assuring a proper and complete washing. In columns with low top temperature and high concentrations of ammonia/amines and hydrogen chloride, Salt Dispersant can be applied also on the reflux, to completely protect the top trays from plugging and under-deposit corrosion, and can also be applied by shock dosages to clean the unit and remove the already formed salts directly online without affecting normal operations.

For more information, please contact us at processtreatments@chimec.it

A Parag Shah, Head of Technical Services, Dorf Ketal Chemicals, paragshah@dorfketal.com

We understand that maximising naphtha or middle distillate enhances the profit margin of every refiner but at the cost of breaching desublimation temperature. Amine and ammonia are sourced from H₂S scavengers in crude, desalter wash water from under-designed strippers and overhead neutralisers. At alkaline wash water pH, these basic species partition to the crude phase, ultimately landing in the crude column. When operated at a lower temperature, there can be risk of desublimation temperature breaching, causing ammonium chloride deposition in the mid-section, thereby causing under-deposit corrosion. Overcoming such problems includes mitigating a vicious ammonia/amine cycle at the source level, selecting suitable neutralisers, and maintaining a good margin between...
relentless

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Pilot plants. A true commitment to fast, thorough research and development. A vast team of experienced, dedicated engineers and scientists. The reasons to choose UOP catalysts are many, but perhaps the biggest of all is that UOP never quits innovating. When you use UOP catalysts, you'll know you're using products specifically designed to help optimize your operation. UOP invented the refining and petrochemical technology used in most operations today, and that knowledge and expertise comes through in every catalyst we develop. You'll always get the high stability and global support your business needs, and you'll be working with a company that will keep you on the leading edge year after year.

For more information about UOP catalysts, visit www.uop.com/catalysts.

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tower temperature and de-sublimation temperatures. Chemical mitigation plans include use of Dorf Ketal’s proprietary amine removal aids and top pumparound filming corrosion inhibitors. When one operates at a low top temperature, cold reflux temperature further reduces. Ensuring reflux is as dry as possible using drier/filters helps in improving corrosion control in the top section with a lower top temperature.

Celso Parejo, Manager APT Refinery Applications & Process Technology, Sulzer Chemtech USA, celso.pajaro@sulzer.com
In order to reduce top temperature, the column will require a higher reflux. This reduces the residence time in the overhead drum which can lead to poor separation of the water from the naphtha. If allowed to proceed, it can carry over with the reflux to the column. Once inside, the water will vaporise, leaving the salts that can create under-deposit corrosion. Coalescing internals like Mellaplate have been successfully used in atmospheric overhead drum accumulators to improve the water-naphtha separation.

Another potential corrosion problem occurs when the column temperature is low enough for water to condense, forming concentrated acids such as HCl, creating a highly corrosive environment. Often this problem can be mitigated with the use of corrosion resistant tray metallurgy such as Zeron 100, AL6XN, 254 SMO, Monel, Alloy 825, C-276 ( Hastelloy), 625 (Inconel), C-22, and so on.

Charles Radcliffe, Senior Tech Service Engineer-Europe, Johnson Matthey Process Technologies, Charles.Radcliffe@matthey.com
Lower crude tower top temperature will move the point where the acid condensate dew point occurs, and you will need to identify this and check the metallurgy is suitable, and that neutralising and filming amine injection points are before this point. The main problem will be if the dew point is actually moved to within the tower. The amine suppliers should be able to help with analysis and advice. Switch to caustic for overheads corrosion control. This is not advisable if feeding resid to the FCC because this will increase the sodium in the FCC feed.

The CO₂ content of our SWS gases results in a high reagent turnover in the caustic scrubber. Solutions please.

Marcello Ferrara, President, ITW, mferrara@itwtechnologies.com
Reagent turnover depends basically on stoichiometry and scrubber efficiency. While stoichiometry is related to gas composition only, operational scrubber efficiency is affected by fouling. Fouling of caustic scrubbers is quite common, as the composition of treated gases normally contains unsaturated compounds. ITW can help solve fouling problems of caustic scrubbers by implementing Online Cleaning and cleaning the equipment in as little as 24 hours on a process-out/process-in basis.

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Opportunity or Annoyance?

Price differentials between conventional and opportunity crudes compel refiners to process increasing percentages of lower valued opportunity crude. However, as many refiners have learned the hard way, opportunity crudes are tied to unique processing challenges. Furthermore, existing crude unit configurations may limit high-profit opportunity crude to a disappointingly small proportion of the total unit blend.

Processing a changing slate of opportunity crudes of varying compositions requires a CDU/VDU design that is flexible, reliable, and commercially proven. A good design must control chronic problems associated with many of these crudes including corrosion, exchanger fouling, tray plugging, vacuum heater and wash bed coking, and unreliable product quality prediction. CDU/VDU designs for challenging crudes should be based on proven best-practices rather than simply on a low-CAPEX strategy. For example, a poorly designed heat exchanger may operate well initially, but high fouling will quickly lower efficiency and eventually limit throughput. Up front investment in engineering experience and know-how pays dividends when units meet capacity and run-length targets.

Over the course of 20 years, Process Consulting Services has completed more than 130 revamp and grassroots designs supported by over 75 detailed test runs. An extensive collection of test run equipment performance data and feed/product analyses enables confident prediction of real-world opportunity crude performance. PCS has enabled refiners worldwide to extend crude unit run lengths from months to years while improving yields and operability.
Revamping crude and vacuum units to process bitumen

Revamping crude and vacuum units to process dilbit can involve extensive equipment replacement as well as major changes to the crude preheating scheme

TEK SUTIKNO
Fluor Enterprises

Bitumen has become an increasingly significant source of raw crudes for refineries, especially in North America. About 170 billion barrels of proven reserves are economically recoverable with the latest methods, as reported in 2010 for Alberta oil sands in Canada. In addition to this vast bitumen reserve, the regional market price difference between light WTI crude and Canadian bitumen-based heavy crude, for example, reached $30/bbl in April 2012. Processing bitumen crudes can be financially lucrative for refineries located in the market regions of these crudes.

The typical API gravity of bitumen is in the range of about 7° to 12°. For pipeline transportation, up to 35 vol% of diluent is added to become diluted bitumen (dilbit) with API gravity in the range of 21 to 23, which is at the high end for API gravity in typical heavy crudes. Sulphur compounds, naphthenic acid and viscosity are all high in dilbit, in addition to other undesired characteristics including high asphaltene and fine solid contents. An existing refinery will generally need to be revamped to process dilbit or crude blends with high percentages of dilbit, and the extent of the requirement for revamping depends on the targeted dilbit percentage in the crude feed and the complexity of the existing refinery. Typically, revamping crude and vacuum units is necessary for processing 100% dilbit, and revamps for these units are discussed next.

Refining scheme and dilbit capacity

Planning the revamp scope for crude and vacuum units should be developed with timely consideration of the overall refinery revamp plan which will depend on market assessment and the targeted product slates. For a given design feed capacity, higher percentages of dilbit in the crude feed increase the rates of heavy products from crude and vacuum units. For example, atmospheric residue and vacuum bottoms rates increase with higher percentages of heavy or dilbit crudes. These require capacity expansion of the vacuum unit and the downstream coking unit. Other downstream units such as hydro-processing or even catalytic cracking units will require performance evaluation and/or modification as processing dilbit results in changes of operating parameters such as feed rates and compositions, sulphur concentration, microwoven residue, solid contaminants, and metal contents.

The capital costs necessary for modifying downstream units affect the economics of a crude and vacuum unit revamp project to process dilbit. To identify the overall required scope for modification, evaluation of equipment performance in the crude and vacuum units, along with the impacted downstream units, will need to be completed. The associated costs of the overall refinery modification will need to be thoroughly assessed in parallel to using linear programming and simulation models as decision supporting tools for evaluating the product slate from the crude feed. Generally, the design capacity target for processing dilbit could potentially be specified in accordance with existing equipment capacities and plot space limitations to minimise capital investment and possibly maximise the associated rate of return on investment, but this minimised approach to investment will not necessarily generate maximum revenues when dilbit market prices are favourable.

Metallurgical upgrade

Lower percentages of dilbit in the crude feed could minimise the need for material upgrade in the crude and vacuum units. Bitumen contains high levels of naphthenic acid compounds which are corrosive to carbon steel in an operating temperature range of 400-750°F (200-400°C). The rate of corrosion increases as operating temperature and naphthenic acid content become higher. Processing higher percentages of dilbit in the crude feed increases naphthenic acid content and consequently the corrosion rate. Generally, the required scope for material upgrade could potentially be reduced by lowering the percentage of dilbit in the crude feed. Additionally, to reduce sulphidic corrosion through processing conventional sour crudes, low alloy steels with chromium and/or molybdenum contents are typically used in sections of crude and vacuum units. Naphthenic corrosion rate reduces with increasing content of chromium or molybdenum in steels. Existing sections with adequate chromium content may not require replacement if the naphthenic acid content of the crude is sufficiently low at reduced percentages of dilbit in the crude.
Maximize Reliability in Grassroots Crude Units

Crude unit operators are far too familiar with a long list of crude unit reliability problems including fouling in heat exchangers and fired heaters, poor desalting, corrosion of piping and equipment, and coking in the vacuum column wash zone. Many millions of dollars have been spent fighting these problems, yet they continue to force unplanned shutdowns with depressing regularity.

Revamps must address reliability issues, but project scope is hindered by the limitations of existing equipment. Grassroots design of crude and vacuum units presents an opportunity to get everything right the first time. Here are a few tips for designing a reliable and profitable crude/vacuum unit.

Heat Exchanger and Heater Fouling

High velocities in heat exchanger tubes produce high shear at the walls, preventing foulants from accumulating. High shell-side velocities, coupled with exchanger designs that minimize dead zones in the flow, eliminate shell-side fouling. In fired heaters, high mass fluxes maximize wall shear, shorten residence time, and lower wall film temperatures, all of which reduce coking. Furthermore, reliable heaters must have correctly sized burners with proper burner-to-burner and burner-to-tube spacing.

Desalting

Desalter size is highly dependent on crude blend due to dramatic variation in required centerline velocity. A unit must be designed with the flexibility to carefully control desalter temperature, which can range from 110°C to 150°C, by shifting heat from upstream to downstream of the desalters. Vendors are often judged on cost alone, which results in minimum sizing for the design crudes and rates. Carefully consider whether long-term crude trends will soon render these desalters inadequate.

Corrosion

In grassroots design, be realistic about metallurgy. Because modern refineries do not run a steady diet of the same crude, consider the sulfur and TAN numbers of potential crudes outside the unit’s design blend. Chronic corrosion issues, or the inability to process high-margin opportunity crudes, will quickly overshadow the initial savings from choosing too low of a metallurgy.

Vacuum Column Wash Zone Coking

Wash zones are not for fractionation, they are for de-entrainment! Pursuing fractionation efficiency by specifying a deep bed with small crimp packing is a recipe for rapid coking. The correct choice of packing combined with the right wash rate and good distribution will properly de-entrain while preventing coke formation.
Stability of crude blends
Crude blend stability may need to be assessed when processing less than 100% dilbit crude blends. Mainly as a result of the asphaltene content of bitumen, dilbit has been reported to have stability issues with phase separation and high fouling rates. Blending dilbit with other compatible crudes reduces or minimises these stability issues and associated increases in the operating costs. If the objective of a revamp is to refine less than 100% dilbit crude blends, crudes compatible with dilbit should be considered as the blending components when these can be made available at competitive prices. Methods to characterise the stability of dilbit blends include analysis of the saturates, aromatics, resins and asphaltenes (SARA) contents of the blend, determination of insolubility number (I_n) and solubility blending number (SBN), and others such as the ASTM D7157 test method for instability determination and ASTM D2007-80 procedures for separating asphaltenes.

Crude preheating and desalting
As Figure 1 shows, the raw crude (or cold) preheat train upstream of the desalters and the hot (desalted crude) preheat train downstream of the desalters recover heat supplied through the crude and/or vacuum furnace heaters. Improved heat recovery in these trains will reduce the net energy or fuel consumption of the crude and vacuum units, and optimised design of these preheat trains enhances the economics of the refinery. Revamping crude units for processing dilbits typically includes modifications to the preheat train exchangers.

The high viscosities (at ambient temperatures more than 100 times more viscous than light crude) of dilbits cause excessive crude-side pressure drops in exchangers and significant reduction in the overall heat transfer coefficients. Replacement preheat exchangers may also be required for metallurgical upgrade to improve resistance to naphthenic acid corrosion. These replacement exchangers need to be designed with reasonably high velocities (typically 3 ft/sec shell side and 6 ft/sec tube side) on the dilbit side to minimise fouling and improve overall heat transfer. High velocity design, however, results in high pressure drops which increase the discharge pressure requirement of the raw crude charge pump. For a given allowable pressure drop, special design exchangers such as helical baffle exchangers may offer relatively higher overall heat transfer coefficients and reduce the required exchanger surface areas. For existing crude units with limited plot space available for revamping the preheat trains, specially designed exchangers with high heat transfer coefficients can be evaluated.
The raw crude (cold) preheat train heats the raw crude to the required inlet temperature of the desalters, which remove salts in the raw crude. Poor desalting performance accelerates the rate of corrosion, especially in the crude overhead system. Flowing through a mixing valve, raw crude at the required temperature is mixed with desalting water, forming a water in oil emulsion. A demulsifying chemical is added to enhance the desalting process where crude salt content is extracted into the water droplets of the water in oil emulsion. The desalter’s electric field coalesces these water droplets which settle by gravity to form a brine phase. The settling rate is directly proportional to the differential density of the brine droplet and the oil emulsion and inversely proportional to the emulsion viscosity.

Due to its high specific gravity and excessive viscosity, desalting dilbit requires a longer residence time for separation, and high desalter inlet temperatures, typically in the range 280-310°F (140-155°C), mainly for reducing the viscosity effect. The requirement for a longer residence time necessitates replacement or expansion of desalters intended for conventional light crudes.

Desalting conventional light crudes (API >30) requires inlet temperatures in the range of 200°F (or lower) to 250°F (90-120°C). Higher desalter inlet temperatures in the 280-310°F (140-155°C) range result in higher duties for the cold preheat train. Modification or expansion of the existing train is needed to meet the requirement for higher desalter inlet temperatures. Moreover, high desalter inlet temperatures increase the desalter operating pressure necessary to keep the crude below its vapour pressure within the targeted design margin. This high operating pressure, together with high preheat exchanger pressure drops necessary to maintain reasonable heat transfer coefficients and minimise fouling, may require replacement of the raw crude charge pumps and result in a higher flange pressure rating of the cold preheat piping. Additionally, the associated make-up and recycle desalting water systems intended for light or medium crudes become inadequate for desalting dilbit. Make-up desalting water, for example, will generally need to be increased from 4 vol% to 7 vol% of the feed rates when processing light to intermediate crudes to higher than 8 vol% for desalting dilbit.

In addition to meeting the requirement for higher desalter inlet temperatures, designing a new preheat train capable of swinging the heating duty from cold preheat train to hot preheat train should also be considered if processing lighter crudes in the future remains a probability for the refinery. Distribution of pumparound duties in the crude tower will change when switching from 100% dilbit to light crudes. The desalter may be operated satisfactorily at inlet temperatures much lower than 280°F when desalting light crudes. As such, the pumparound cooling duty in excess of the required cold preheat duty needs to be transferred from the cold preheat train to the hot preheat train. Not only does this reduce the crude furnace heat input, this duty swinging capability is necessary to meet the higher crude pumparound duties associated with processing lighter crudes.

All pumparound streams from both the crude and vacuum towers typically supply the heat required in the preheat train. As crude slates become heavier, the total pumparound cooling duty of the crude tower will reduce for a given crude furnace outlet temperature. Relative to light crudes, heavy crudes will have less vapourisation at the furnace outlet and require less total pumparound duty. With this reduced pumparound duty available for crude preheat, additional heat sources are necessary to meet the requirement for a high desalter inlet temperature. This increased cold preheat duty can be supplemented by the vacuum tower pumparound duties, but this could increase the crude furnace duty as the available heat source for the hot preheat will be less.

For existing crude units where heat from the crude tower overhead system is rejected to the ambient, the amount of crude tower overhead cooling duty is essentially as much as that of the total pumparound duty. Revamping the crude tower overhead system to utilise the overhead cooling duty for heating the cold preheat train will significantly increase the energy efficiency of the crude unit. However, this option is capital intensive as the crude tower overhead is typically constructed with costly alloys for corrosion resistance. This corrosion is mainly due to hydrolysis of inorganic salts such as calcium chloride and magnesium chloride. At high temperatures in the crude furnace, these salts form hydrogen chloride which is soluble in water and becomes corrosive hydrochloric acid. To minimise crude tower top and overhead corrosion, desalters need to reduce the crude salt contents to less than 1 pound per thousand barrels and keep the salt content of the crude tower overhead water to less than 20 ppmw. Maintaining crude tower top temperatures above the water dew point and salt formation temperature, or ‘salt point’, is essential to minimise corrosion.

Desalting dilbit could also form a rag layer which needs to be intermittently removed and results in an appreciable loss of the crude feed if oil in rag is not properly recovered. High levels of microfines or ultrafines solids in bitumen, typically clay particles less than 5 micron in size and suspended in dilbit, cause equipment fouling and increase coking tendency. These solids accumulating in desalters will need to be intermittently removed through mud-washing and rag layer removal. Working with the desalter vendor to perform laboratory testing of 100% dilbit, or the design crude slates containing the target percentage of dilbit, could minimise or mitigate rag formation issues and verify the proposed desalting technology, the demulsifying chemicals, operating range of pH and volume percent of the desalting water, and others as required. For
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example, the typical desalting water optimum pH range of about 6-8 may need to be adjusted to avoid excessive formation of naphthenate soaps.

**Crude distillation**

Relative to processing lighter crudes, switching to dilbit at the same crude feed rate to the crude tower will generally produce less light distillate products – heavy naphtha, kerosene, LGO, and possibly HGO. Atmospheric bottoms (ATB) rate from the tower increases significantly and results in a higher feed rate to the downstream vacuum unit. Changes in the distribution rates of crude tower liquid product can result in a greater revamp requirement for the crude tower system. For example, the product pumping/delivery system needs to be assessed as part of developing an economically viable overall revamp scope for the existing refinery processing scheme. Obviously, an excessively higher crude tower product rate requires capacity expansion of the associated downstream units, and a reduced rate results in under-capacity operation of the subsequent units. Crude towers processing dilbit could result in higher naphtha rates as the volume percent of naphtha boiling range diluted in the dilbit increases. This naphtha stream can be recycled as diluent or further refined to meet product specifications such as boiling point limits. Crude tower top section internals and/or their operation may require modification to meet product specifications for the naphtha boiling range.

Dilbit contains much higher metal content (for instance, nickel and vanadium) than conventional crudes such as WTI. These metals, concentrating in high boiling fractions of dilbit, are poisonous to catalysts in the downstream fluid catalytic cracking (FCC) and hydroprocessing operations. To minimise increases in metal content beyond the design limits of the feed streams to the catalytic processes, options for enhancing fractionation of the relevant crude tower sections should be considered for processing dilbit to minimise catalyst lifetime reduction in the affected downstream units. Separation of gas oil from the atmospheric bottoms, for example, will affect the concentrations of metals in feed streams to the FCC or the gas oil hydrotreater.

As the rate of ATB from crude tower in dilbit service increases, the capacity limits of the downstream vacuum unit may be exceeded, and this unit will subsequently generate higher vacuum tower bottoms (VTB) rates, increasing the operating capacity of the downstream coking unit. While it may be desirable to reduce the ATB rate from the crude tower to minimise the required modifications of the vacuum unit and coking unit, options for ATB reduction are generally ineffective and problematic. Common options include higher crude furnace outlet (CFO) temperatures or increased rates of stripping steam to the ATB section. However, a lower ATB rate means higher AGO yield cut points which inherently results in lower AGO quality. Moreover, higher CFO temperatures increase the coking rate of the crude furnace; CFO typically needs to be reduced when processing dilbit to avoid shutdown due to coking of the furnace. As an existing crude tower typically operates at optimal stripping steam rates, higher stripping rates in the ATB section do not effectively reduce the ATB rate.

**Crude furnace and preflash drum**

Retubing or replacement of the crude furnace heater with 317L becomes common when processing dilbits with high naphthenic acid contents. If plot space is available, replacement heaters should be designed with a lower maximum heat flux to reduce fluid film temperature and subsequently minimise cracking of dilbit which could polymerise and plug the tubes. Installing a decoking facility and velocity steam injection points for the new heater should also be considered.

An existing crude unit sometimes includes a pre-flash or surge drum mainly for reducing pressure drops through the hot (desalted crude) preheat train and the crude furnace. The amount of vapour flashed depends on the operating pressure and temperature of the drum, in addition to the crude characteristics. When processing dilbit, the existing drum at the same operating conditions could vaporise more, primarily due to the diluent content of the dilbit, and this higher vapourisation rate could make the existing pre-flash drum under-sized and result in excessive liquid entrainment or foaming. Poor vapour-liquid separation in the pre-flash drum could affect the crude tower fractionation and product properties, especially for crude unit design where the pre-flash drum vapour is routed to an elevated tower section with similar boiling range fluid. As such, the performance of the existing pre-flash drum in dilbit service should be assessed to identify whether modifying equipment or adjusting operating conditions is necessary to prevent reduction in the performance of the crude tower.

**Vacuum distillation**

With higher rates of ATB through processing dilbit, the vacuum unit needs to operate at a much higher capacity which could necessitate new replacement of the vacuum charge pumps, vacuum furnace, and/or vacuum tower. As with the crude furnace, retubing or replacement of the vacuum furnace is required to minimise naphthenic acid corrosion. As high boiling point components and asphaltenes of dilbit remain in ATB, vacuum heaters in dilbit service have high cracking or coking tendency and should be designed to minimise the possibility of coking. Options to minimise asphaltene coking in the vacuum furnace include:

1. Consider a low heat flux heater such as a double fired heater if plot space is available
2. Specify an adequately high furnace pressure drop sufficient to increase tube fluid velocities
3. Increase velocity steam rate
4. Prevent furnace operation with excessive high outlet temperatures

Options 1 and 2 reduce fluid film temperatures within tubes and
been planned, adding a diesel recovery section to the new vacuum tower should be considered. This recovery section could recover diesel boiling range product about 3% to 5% of the total dilbit feed rate to the crude unit. Additionally, the wash bed of the new vacuum tower should be designed with plenty of wash oil rate, and the effects of entrainment and vaporisation due to superheated feed stream to the flash zone should be accounted for when specifying the wash oil rate, to prevent plugging.

**Conclusion**

Revamping crude and vacuum units to process dilbit could involve extensive equipment replacement as well as major modifications to the crude preheating scheme, especially for an existing refinery designed for processing lighter crudes. The targeted design percentage of dilbit in crude feed blends directly determines the extent of requirements for modification which should be identified and evaluated before deciding the targeted percentage of dilbit. The targeted percentage of dilbit to be processed in crude and vacuum units should also be defined only after assessing the impact of processing dilbit on the existing overall refinery and identifying the revamp requirements of the downstream processing units.

Capital costs for revamping existing crude and vacuum units will generally increase as the targeted design percentage of dilbit in the crude feed increases. While a revamp objective for processing 100% dilbit could potentially maximise gross profit, the revamp investment may not necessarily result in maximum rate of return.

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In order to optimise service run length for a steam cracking furnace it is essential to understand the conditions surrounding and including the tube coil for that run. These running conditions, such as temperatures, pressures and steam dilution, allow coke growth trends to be predicted and minimised to ensure the most favourable plant operational economics. In order to understand and optimise trending of multiple service runs throughout the life span of the tube coils, different considerations must be taken into account. This article reviews a simulated case study using the software package VMGSim to explain the mechanisms causing reduced run times over the lifespan of a tube coil at a Mitsubishi Chemical plant site in Kashima, Japan.

Coke formation mechanisms
Coke formation in an ethylene cracker reduces the tube cross section, the heat flux to the reacting gas mixture and yield; it increases pressure drop and consequently reduces service time. Coke growth can happen through pyrolytic and catalytic mechanisms. Both mechanisms play an important part in the formation of coke within tube coils in a cracking furnace. At the early stages, coke formation mainly occurs through the catalytic mechanism. This type of coke growth is driven by the tube alloy itself when metal sites such as iron or nickel are contacted by process material and filamentous coke is produced. Detailed kinetic models of this can be developed by including surface reactions, segregation processes, and the diffusion of carbon through specific metal particles such as nickel. Chromium content in the tubes can be used to inhibit the catalysing effects of tube metals and is often found in higher service temperature tube coil materials such as Inconel or HK40. One must be careful regarding less obvious effects of trace components in the tube alloys such as silicon and aluminum and the interactions between iron, nickel and chromium content that make any direct correlations cumulatively incorrect (see Table 1).

Over time, pyrolytic coke growth soon becomes the dominant mechanism within the remaining service time of the furnace tube coils. This mechanism is directly related to the concentration of components within the process material and the running pressure and temperature. The simulation model developed and used for the analysis within VMGSim applied a molecular structure-type model for prediction of the coke growth rate profiles throughout the tube coil using the PIONA oil characterisation environment. Coke formation from each type of molecular group is predicted and general kinetic rates could be derived from open literature using this generalised structure. The classifications and groupings for kinetic rates in many of the papers available showed types of molecular structures from olefin to more dehydrogenated and ringed components were already recognised as different influences towards overall pyrolytic coke growth rates.

A combined equation to determine coke growth is shown (see Equation 1) where the first term consists solely of pyrolytic coke formation and provides an asymptotic growth rate:

\[
r_{\text{Coke}} = r_{\text{Asym}} + r_{\text{Cat}} \times \left(1 + r_{\text{Cat}} \times l_{\text{Thick}}\right)
\]

where \(r_{\text{Asym}}\) is asymptotic coke growth due to pyrolytic coke formation, which is a function of the local temperature, pressure, and composition; \(r_{\text{Cat}}\) is catalytic rate of coke formation, which is a function of the tube alloy material; and \(l_{\text{Thick}}\) is thickness effect related to coke thickness, that is a function of the local coke thickness.

<table>
<thead>
<tr>
<th>Alloy composition inputs for a simulated coke growth model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal content, %</strong></td>
</tr>
<tr>
<td>15Mo3</td>
</tr>
<tr>
<td>13CrMo4.4</td>
</tr>
<tr>
<td>X8CrNi18.10</td>
</tr>
<tr>
<td>X50CrNi30.30</td>
</tr>
<tr>
<td>X5CrNi20.80</td>
</tr>
<tr>
<td>Inconel 600</td>
</tr>
<tr>
<td>Inconel 800</td>
</tr>
</tbody>
</table>

Table 1

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WHEN CONDITIONS HEAT UP
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Alloy degradation effects on service run times

As coke builds on the inside of the tube coils, the added roughness, reduced internal diameter and heat flux resistance cause the inlet coil pressure and furnace box temperatures to increase to keep outlet product specifications constant. Once a maximum tube coil temperature or pressure drop is reached, the inner tube coil must be cleaned. In this process of decoking, the tube coil metallurgy is affected and the metal content of the surface of the tube coil changes. Regular operation of the cracking furnace also alters the composition of the tube surface as iron, nickel, chromium and other elements can be found in coke formed within the coil during service time.

Possibilities of tube coating and feed inhibitors

Tube coatings come in the form of aluminum, magnesium, zinc, and other metals and their associated oxides. These coatings are specifically good at reducing catalytic coke growth since they hide the iron and nickel sites that would typically catalyse the coke formation surface reactions. Inhibitors used are commonly sulphur, phosphorus, aluminium, or silicon based and also focus on reducing the catalytic coke growth by passivating the metal surface.

In order to bring the effect of tube coatings or feed inhibitors into the simulation model, the overall coke growth rate is calculated using Equation 2:

\[
    r_{\text{Coke}} = r_{\text{Asym}} \times r_{\text{AsymInhib}} \times (1 + r_{\text{Cat}} \times l_{\text{Thick}} \times r_{\text{CatInhib}})
\]

where \( r_{\text{AsymInhib}} \) is a reduction in asymptotic coke formation due to using inhibitors or coatings; and \( r_{\text{CatInhib}} \) is a reduction in catalytic coke formation due to using inhibitors or coatings, which is a function of tube coating or feed inhibitor effects on the catalysed coke growth mechanism.

Although this study focused mostly on the changing content of tube alloy, the roughness of the tubes is also suspected of playing a role in the reduced service time seen in older tube coils. In addition, the metals deposit as oxide films and their effect is not as simple as direct weight percentages, as described here, and carburised layers are created where carbon can more easily intrude. These are two details of the service time performance over tube aging that could potentially be further refined if more performance data and analysis were available.

Results

The built layer of coke thickness within the tubes also acts as a major parameter of how catalytic coke growth rates are determined. As the coke layer becomes thicker, diffusion rates through the coke slow the rates of material mass transfer to a point where this catalyst type coke growth becomes negligible. This transition from where catalyst growth is dominant to that where it is negligible depends on the growth rates of the coke itself, but can range from hours to days in an ethylene cracking furnace. Figure 1 shows model predictions of coke growth rates as compared to literature from the catalytic dominated regions to the pyrolytic dominated region for different tube alloys. It is obvious how the effects of chromium content for the inhibition of coke growth – from the metal contents used as input into the model given in Table 1 – compared to observations from specific tube alloys provided by Zimmermann et al. in Figure 1.

Unfortunately, the chromium content of the tube can decrease quicker than the iron and nickel contents, and the simulation model predicted higher initial catalytic coke growth from the new apparent tube coil metal content with less inhibiting make-up. Service times can be heavily over-predicted over the lifespan of the tube coils if this alloy degradation is left out of a coking simulation model for the reactor. Analysis of tube coil from the Kashima plant confirmed this type of tube alloy degradation and showed chromium content on the
tube’s inner surface falling from 30-35 wt% in a new tube coil to 4-6 wt% at the end of the tube’s life. Figure 2 shows the results from two separate simulation model runs where initial and older tube content was entered for the service time runs. If the resulting furnace temperature and pressure drop are dependent on a set coke maximum thickness, 20% differences in service time can easily be encountered. The constant coke growth rate after initial catalyst coke growth is due to equivalent operational inputs being used and therefore equal pyrolytic growth rates were determined.

The speed at which the chromium content decreased, therefore reducing the length of each service run, could be trended when looking at the plant’s operational data. Figure 3 shows the operational service runs versus the run number for one of the ethane cracking furnaces. The severity of service runs being reduced by more than half is shown and points to the importance of understanding and planning for these trends. A similar trend could be observed in the simulation model when the tube alloy content used as input was updated per run. This was mainly due to a sharp increase in the coke thickness at the start of the run times as seen in the older tube profile in Figure 2.

In Figure 4, the coke formation rate as a function of dimethyl disulphide (DMDS) inhibitor is shown for asymptotic and catalytic coke types from experimental data and correlated using equation 2. Figure 4 shows that the correlation used in VMGSim agrees well with experimental data and illustrates the reducing effects of DMDS on coke growth rate for either asymptotic or catalytic conditions.11

Even though the tube’s metal content changes during the life of tube coils there are still inhibiting solutions available to keep longer run times. These solutions include tube coating and feed inhibitors since they do not directly relate to the operational conditions. Solutions such as increased steam dilution work to a limited degree, but keeping constant outlet yields with the resulting reduced residence times requires increased coil temperatures and decreases any significant advantages gained.

Conclusions
In this study the inevitable degradation of tube coil alloy over time was reviewed alongside measured alloy...
compositions and recorded service run lengths. Chromium depletion in the inner tube coil surface and resulting increased catalytic coke growth rates caused the service run length times to decrease over time. Plant data showed chromium content falling from 30-35 wt% down to 4-6 wt% over the tube's life. During this time, run lengths were found to decrease to less than half the possible days when the tubes were new. The use of different tube coatings and feed inhibitors was then suggested as a potential application to mitigate this problem and prolong tube coil lifespan without altering operational conditions. Addition of dilution steam as a solution to prolong service times was seen as less effective due to increased coil temperatures and therefore faster coke growth rates in order to match product yields. Further improvements to the simulation model of coke growth over tube coils would potentially come from the addition of roughness and metal oxide formation details, although more data would be required for confirmation of these effects to coke growth and their quantification.

Acknowledgement
The authors are grateful for the suggestions, support, and overall contribution of knowledge from Ota-san of Mitsubishi Chemical Corporation throughout the creation of the coke growth simulation model. His enthusiasm for better understanding the complexities of coke growth gave ongoing drive to further enhance the details and rigorousness of the developed model.

References
3 Alloy Data Sheet, Kubota Metal Corporation, 2015.

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Overcoming the effects of ammonia in heat exchangers

Forensic testing revealed the mechanism of under-deposit corrosion in exchanger tubes, a problem solved by replacement with hyper-duplex steel

MARCELO SENATORE
Sandvik Materials Technology

Overhead condensers (OHC) are critical to oil refineries. The OHC is essentially a large heat exchanger used for cooling and condensing the crude oil distillation tower (CDU), the first processing unit in virtually all petroleum refineries, by exchanging heat with the incoming crude oil via either an air cooled or water cooled condenser.

Selecting the best performing available materials for OHCs has become ever more critical and complicated due to issues of under-deposit corrosion which is caused by the presence of hydrochloric acid (HCl) and ammonium chloride (NH₄Cl). In particular, oil refineries are seeking new materials that can provide higher levels of safety and reliability for more cost effective long term operations.

Today, many different materials are used on OHCs and their effective performance depends greatly on the local service conditions and each refinery’s operational requirements. The combined effects of these causes must be taken into consideration when selecting materials for longer term and more cost effective performance.

Corrosion media in OHCs
Stainless steel components within OHCs are subjected to several corrosion mechanisms during operations. Documented causes of corrosion include HCl dew point, chloride pitting, hydrogen sulphide (H₂S) and, in particular, NH₄Cl deposits.

HCl is also often present in the OHC in crude oil refineries and is well known for being very corrosive because it lowers the levels of pH at the same time as chlorides are present. In order to control the pH in the OHC, it has become common practice to inject ammonia (NH₃) or neutralising amines into the system. This method increases the pH of the media but will also lead to the formation of dissolved NH₄Cl, also known as salmiac, which has very high solubility in water. Since the water content at the inlet of the OHC is usually low, and the amounts of HCl and NH₃ can be high in units which do not utilise water wash, there is a risk of salmiac precipitation in the OHC.

Precipitation of salmiac can form deposits in the OHC and, in really bad cases, causes complete blockage of the equipment.

Salmiac deposits are not harmful in themselves, but can create a crevice-like situation on the heat exchanger tubes which may in turn cause harmful under-deposit corrosion. Consequently, the situation can become very bad because part of the salmiac deposit may dissolve and lead to very high local chloride concentrations. It is because of these factors that under-deposit corrosion is a common problem within oil refineries’ OHCs.

Case study
A number of refineries around the world have reported severe corrosion problems in their OHCs. These include one Canadian heavy oil operator that had experienced premature failure with the duplex overhead condenser tubes in its crude unit. The material was supposed to last for about 10 years, yet had only been in service for 18 months when an inspection team spotted leaks in the tube wall.

To find a solution, the operator approached Sandvik Materials Technology to identify an alternative material that could exhibit superior performance while also proving more cost effective and reliable for long term operations. While the existing equipment was replaced with a spare unit, two failed tubes were sent to a laboratory for failure analysis. Each damaged tube was made of duplex stainless steel (UNS S31803 or S32205) and thereafter referred to as 22% Cr.

The first step towards determining the cause of equipment failure was to thoroughly assess the operational conditions of the tube. Both of the failed tubes oriented horizontally in the crude column overhead heat exchanger. It was reported that approximately 500 m³/h of diluted crude liquid had passed through the heat exchanger tubes entering at gauge pressure of approximately 2000 kilopascals (kPag) and 44°C. The outlet temperature for the tube side medium was approximately 77°C while the shell side media comprised approximately 93% naphtha and 7% water from the column stripping steam. The total liquid flow on the shell side upstream of the wash water injection point was 144 m³/h.

Water at the downstream separator typically contained 80 ppm chlorides. NH₃ had been injected into the overhead system as a pH neutraliser, while the shell side fluids entered at approximately 44 kPag at 130°C and exited at approximately 78°C.

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NH₄Cl deposits had not been expected during operations, as these should have been avoided by proper washing; wash water was also injected just prior to the shell side of each heat exchanger inlet to wash away any salt that might have formed as the vapour condensed. Nevertheless, it was clear from the significant amount of loose deposits present on the tubes that the 22% Cr grade had been unable to withstand the severe conditions.

Failure analysis
For analysis, the two failed tubes were named Tube A and Tube B. Each had been located a few feet from the tube sheet and at the bottom of the heat exchanger while in service. Figure 1 shows the tubes in as-received condition alongside a pail of the deposit material.

A leak was observed in Tube A (see Figure 2) and the area immediately surrounding the leak was roughened due to external corrosion damage. This corrosion scale was submitted to an X-ray diffraction (XRD) analysis that did not identify any significant corrosion products located immediately around the leak. This result, or lack thereof, can be explained by the rapid release of higher pressure tube side fluids which had probably rushed through the perforation and caused erosive removal of the corrosion scale in this region.

No leaks were readily visible in Tube B, but similar external corrosion damage was visible on portions of the tube (see Figure 3). Due to the apparent similarity of the corrosion damage, further examination was limited to Tube A.

In order to detect any acid soluble sulphides or carbonates, chemical spot testing was performed on both the interior and exterior of the heat exchanger tubes. A similar test was also performed in order to detect possible chlorides. The interior and exterior surfaces of the tube were then sandblasted to remove all scale and debris, and to reveal the extent of the corrosion attack. It was discovered that the most severe corrosion damage, including the leak, tended to be concentrated on one side of the tube exterior (see Figure 4). This was likely the top side of the tube where deposit formation may have occurred due to sedimentation.

Chemical analysis
Chemical spot testing of the failed tube gave no positive indications for either acid soluble sulphides or carbonates. However, it should be mentioned that such a test is not totally conclusive because all sulphides are not acid soluble. Tests to detect the presence of chlorides yielded mildly positive indications on both the interior and exterior of the tubes. The cross section of the tube (see Figure 5) illustrates the external nature of the corrosion attack. It can be clearly seen that the inside surface is relatively smooth and has not been subject to corrosion except very close to the leak.

The microstructure of the investigated tube was considered typical for a duplex stainless steel, and no unusual phases or defects could be observed (see Figure 6).

Energy-dispersive X-ray spectroscopy (EDS) analysis of Tube A (see
Figure 7) indicated that the material composition was consistent with a 22% Cr duplex stainless steel such as UNS S31803 and UNS S32205. This is indicated by relatively strong iron and chromium peaks (the major alloying elements), with lesser peaks for nickel, molybdenum, manganese and silicon. An average measured microhardness of 268 HV 500 gf was also considered typical for this type of material.

X-ray differentiation (XRD) measurements of the deposit found in the heat exchanger (see Table 1) revealed that the most abundant compound present was salmiac formed by reaction between HCl present in the water and NH3 injected in order to maintain the pH neutrality of the water phase. A significant amount of elemental sulphur and a small amount of quartz (sand) were also detected in the loose deposit material. There is no data about the amount of sulphur in the incoming media on the shell side of the heat exchanger.

A summary of the results from XRD analysis performed on the corrosion scale found on the exterior of tube is shown in Table 2. More than half of the sample was made up of austenite/ferrite duplex material metal scrapings collected along with the corrosion scale. The most abundant corrosion product detected was greigite (Fe3S4) which, together with FeS and Fe2S, is a corrosion product of iron based metals in the presence of H2S and/or sulphur corrosion.

Another conventional explanation for the participation of sulphur species in accelerating corrosion in this case is its participation in an autocatalytic reaction which regenerates HCl:

\[
\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{HCl}
\]

Synthetic hazlewoodite (Ni3S2) was also detected; this is a nickel sulphide corrosion product that can form during corrosion of duplex stainless steels associated with exposure to H2S and chlorides.

Corrosion of the 22% Cr tube

Results from the investigation of

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Approximate amount %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenite</td>
<td>Fe-Cr-Ni-N</td>
<td>47</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Fe-Cr</td>
<td>5</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe3S4</td>
<td>22</td>
</tr>
<tr>
<td>Hazlewoodite</td>
<td>Ni3S2</td>
<td>13</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>FeO(OH,Cl) (general)</td>
<td>9</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe3O4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2

Such phenomena would explain the presence of sulphur containing iron and nickel salts in the corrosion products. The presence of Iron(II) oxide FeO (OH,Cl), a corrosion product associated with acidic, chloride containing environments, corroborated the idea of a chloride induced corrosion mechanism. Since sulphur containing salts do not passivate the stainless steel surface, the steel would be prone to further corrosion attacks. Repassivation could be slow or even being completely inhibited.

Hyper-duplex stainless steel

Based on failure analysis of the 22% Cr tube, hyper-duplex grade Sandvik SAF 2707 HD (UNS S32707) was recommended as the best material for the application. Designed for highly corrosive conditions, the material was initially developed as an advanced replacement for super-duplex grades. However, the grade’s high strength, corrosion resistance and cost efficiency properties were better than expected, especially in

Results of XRD analysis of the corrosion products found around the leak

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</tbody>
</table>

Table 2
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were performed on tubes corresponding to UNS S32707 in ASME SA 789-04. The tube dimensions were OD 25.4 mm × wall thickness 2.11 mm and were produced from heat number 501695.

All tests performed intended to show that the twisted material can maintain the same corrosion properties as the base material. Specific testing for SCC was not considered during this evaluation as the hardness results achieved after twisting were under the maximum level for the base metal specification. SCC tests will be considered for further evaluation.

Corrosion testing was performed in accordance with ASTM G48 A (2) on two samples cut from two different twisted tubes. The test solution was prepared in accordance with ASTM G48 A and each test specimen was tested in a one litre beaker maintained at 80ºC +/-2ºC for a period of 24 hours. After the 24-hour test period, the samples were rinsed and cleaned in an ultrasonic bath in order to remove deposits. They were then dried, weighed and examined at 20x magnification by stereomicroscope. A visual examination and photographic reproduction of specimen surfaces, along with specimen mass losses, are often sufficient to characterise the pitting and crevice resistance of duplex grades.

According to the standard if the material with superior corrosion resistance.

The material has a nominal PRE value of 49 which, compared to 22% Cr grades that usually have a PRE number of 30 to 35, provides the grade with superior pitting and crevice corrosion resistance in chloride containing environments. The higher the PRE number of a stainless steel, the lower the risk of chloride induced SCC. This is among the reasons why hyper-duplex grades are used successfully in atmospheric overhead condensers as a demonstrably cost effective solution for such applications.

Table 3 illustrates the chemical composition of Sandvik SAF 2707 HD, and compares it alongside the established super-duplex stainless steel grade UNS 32750. By contrast with unstable high Ni alloys, the Ni content of the hyper-duplex can be kept as low as 6.5% due to the grade’s nominal 0.4% nitrogen (N) content which also stabilises the austenitic structure.

Also important are the material levels of chromium (Cr), molybdenum (Mo) and nitrogen (N) which, in combination, reinforce the material’s superior pitting and crevice corrosion resistance in chloride contaminated media. The chemical balance imbues the steel with a duplex, austenitic-ferritic, microstructure that is 50% ferrite and 50% austenite. The austenitic-ferritic properties of the material imbue the grade improved mechanical strength, an ability to withstand greater external loads and pressures from all directions, and better fabricability.

Chromium is the most common element for enhancing a stainless steel’s resistance to general and localised corrosion.

After the twisting procedure, the corrosion resistance and the mechanical properties of the tubes were tested. All tests were performed at WH Laboratories in Houston, Texas. All qualifications were performed on tubes corresponding to UNS S32707 in ASME SA 789-04. The tube dimensions were OD 25.4 mm × wall thickness 2.11 mm and were produced from heat number 501695.

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material loss is above 0.0001 g/cm² or 10 mdd, indication of pitting corrosion is considered. The microstructure of two twisted tubes was analysed according to ASTM A923 A. The samples were polished to 0.3 micron surface and then electrolytically etched for 20 seconds at 2 volts using a sodium hydroxide electrolyte. The ferrite content of each sample was determined using manual point counting according to ASTM E562. Magnification used for the point counting was 1000x, the grid used was 5×5 squares and a total of 32 fields were counted for each sample.

Also measured was the Vickers hardness of the twisted tubes using a 10 kg weight. Two samples were analysed at the as-twisted section and at the straight section. Results of the Vickers hardness was converted to Rockwell C hardness using the standard API 938 C(3) curve for duplex stainless steel. During the hardness testing, the temperature was 24°C and the humidity 40%.

Corrosion rates achieved after the G 48A test were 3.1 mdd for sample A and 2.6 mdd for sample B, which is well below the allowed 10 mdd corrosion rate at 80°C for passing the test. Thus the samples passed the corrosion testing without remarks. Mechanical deformation of the tubes from the twisting procedure apparently does not affect the corrosion properties of the material. These were expected results as the corrosion resistance of stainless steel towards pitting and crevice corrosion are rarely affected by mechanical deformation.

Figure 8 shows the microstructures of samples A and B, respectively. Both tube samples display normal microstructures for a duplex stainless steel. The average percent of ferrite achieved for sample A was 40.3 ±1.2% and for sample B 42.3 ±1.8%. Both samples thus had ferrite content within the 35-65% range limit and were approved. The twisted section presented average hardness of HRC 28.4 measured at the tube’s ID and HRC 28.9 measured at the tube’s OD, while the straight section presented average hardness of HRC 27.2 measured at the tube’s ID and HRC 26.3 measured at the tube’s OD. All the results were approved as they were under the base metal specification limit of 34 HRC.

The material qualification has shown that the hyper-duplex grade UNS S32707 can indeed be twisted in the same way as the 22% Cr tubes. Results from corrosion and mechanical testing performed on the twisted hyper-duplex tubes show that the material properties are unaffected by the twisting operation. It is thus not necessary to perform any additional heat treatment of the tubes. This makes it possible to replace the original 22% Cr tubes with hyper-duplex ones without changing the design of the heat exchanger and with no extra costs due to additional fabrication steps. The heat transfer area of the heat exchanger will be the same.

Conclusion
The failed 22% Cr heat exchanger tubes were subjected to external chloride pitting corrosion attack. Cause of the attack was most likely due to an under-deposit corrosion mechanism triggered by precipitation of salmiac on the shell side of the heat exchanger. This was formed as a result of the addition of NH₃ in order to neutralise the HCl present. Deposits found in the heat exchanger contained, apart from salmiac, a significant amount of elemental sulphur. It is believed that the sulphur has probably taken an active part in the chloride pitting corrosion mechanism since both iron and nickel containing sulphur species were found in the corrosion products.

Hyper-duplex UNS S32707 has been chosen as the replacement material for the 22% Cr duplex grade. It has been shown that it can successfully be twisted by cold-working without altering the mechanical properties and corrosion resistance. The same heat exchanger design can thus be used with the new tubes and the fabrication procedure does not need to be altered.

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Crued distillation is probably the oldest process in any refinery configuration. In the early days of refining, ‘black oil’ in simple batch stills was used to produce lighting oil (kerosene) as the main product, beside asphalts to meet the needs of the times. Following the development of the internal combustion engine, the need for improved fractionation led to the use of simple fractionation columns. Demand for increased throughputs and higher quality products resulted in the development of continuous fractionation units.

A simple crude distillation unit constructed in earlier times included a basic heat exchanger train in which generally hot atmospheric residue was used for preheating, as well as a furnace and a column which would not have any pump-around flows. The only aim was to meet product demands and produce higher quality products. Lowering the energy consumption of the unit would not be considered an important issue in a time of abundant and low-cost crude.

Over the course of time, energy saving has become one of the most essential topics in the oil industry because of environmental considerations and high production costs due to fluctuations in the price of products. Some studies such as the pinch method, developed at the end of the 1970s and extended to heat and power systems, were accepted among standard applications for refinery projects related to energy savings after the 1980s.

In refineries, crude distillation units (CDUs) are the largest energy consumers, utilising around 20% of a refinery’s total energy consumption, depending on configuration and type of crude processed.

Tüpraş Kirikkale Refinery is a medium-sized refinery with a capacity of 5 million t/y which began operating in 1986 with a Romanian designed CDU. It is a conversion refinery whose other units were developed to meet local product demands for Turkey. It may be considered a typical example of its type and was a perfect candidate for an energy efficiency programme begun in 2006 after the privatisation of Turkish Petroleum Refineries.

Kirikkale refinery’s CDU
Kirikkale Refinery was designed to process 5 million t/y of 36 API Kirkuk crude. The unit design is a daily 18 000 m³ of crude oil. A simple flow scheme is shown in Figure 2.

Energy efficiency projects for the CDU
Change in diameter of air preheater tubes
As the regulations for emissions from industrial plants have tightened in the last 20 years, so the quality of the fuel oil burned in CDU furnaces has improved with reduced levels of sulphur and other impurities such as heavy metals. It was found that the two crude
charge furnaces’ air preheater tubes were designed with a large diameter (3in) to avoid plugging by the ‘dirty’ fuel oil utilised in the 1980s. A project was developed to reduce the diameter to 2in and to increase the number of air preheater tubes in order to increase the heat transfer area in the air preheaters. In this way, furnace efficiency was increased by transferring more heat to the air fed to the burners. This modification resulted in an increase in heat surface area of 283 m² in both furnace A and furnace B. By changing the heat surface area, the furnace efficiency was increased by 6.2°C and 7.8°C, respectively. Energy savings were about 1.9 Gcal/h in the furnaces.

Additionally, an increase in pumparound levels resulted in a decrease in top reflux since extra heat removal reduced heat losses from the column top air coolers. As a result of reducing the amount of top reflux, a pump was shut down since only one pump was needed to transfer liquid as top reflux and split column feed.

Installation of variable speed drive
Crude oil from the desalter is sent to the furnaces via G-1102 A and B pumps (see Figure 2), one of them (A) with an electric drive while the other has a steam turbine. Now that the rate of crude charge changes frequently in response to economic conditions, a 6 kV variable speed drive was installed in the electric motor. Variable speed drives for that level of voltage are known to be expensive but a feasibility study showed that the return on investment was satisfactory. After installation of the variable

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Figure 2 Original flow diagram of the Kirikkale CDU
speed drive, electricity consumption decreased by more than 50% (from 392 kWh to 180 kWh) for the same operating conditions.

Use of antifoulant
Crudes with a high asphaltene content cause more fouling in the second preheat train (after the desalter) because of its higher temperature compared to the first preheat train. Fouling in a preheat train directly affects the charge furnace inlet temperature and hence leads to greater fuel consumption. The loss of inlet temperature is measured as a decay rate of C/day and, by using an appropriate antifoulant in the second preheat train, it was found that the decay rate reduced to 0.0175 C/day from 0.08 C/day. The economic return on use of antifoulants is satisfactory and calculated at around $910 000/y. Using antifoulant also reduces cleaning time for the exchangers as a side benefit.

Tempered water system for cooling residues
In the original design of the CDU and VDU at Kirikkale refinery, cooling of atmospheric residue to storage was carried out by air coolers while vacuum residue run-down was cooled by a tempered water system. Cooling with air is not an efficient approach, especially for heavy products, since it depends on ambient temperatures which sometimes cause bottlenecks on hot summer days. A project was developed to combine the residue cooling systems of the CDU and VDU with tempered water cooling. Installing a combined tempered water circulation system removed the bottleneck in residue cooling and the recovered waste heat, about 3 Gcal/h, was transferred to crude oil before the first preheat train.

This also prevented shock condensation of chlorides and water in the naphtha pumparound in the first exchangers in the preheat train (E-1101 A-D in Figure 2) since crude from storage is at low temperatures (5-10°C) during winter. This sudden cooling of the naphtha pumparound was causing a corrosion mechanism involving HCl-water condensation, leading to heat exchanger tube leakage. This problem with the reliability of the heat exchangers was also prevented by increasing the inlet temperature of E-1101 A-D.

An old shell and tube heat exchanger taken from an unused reformer unit was rated by simulation and was retrofitted to be added to the first preheat train so that crude oil taken from tank is heated with tempered water from the residue cooling tempered water system. The approaches of ΔTs in the current systems were also checked so as not to cause a pinch problem due to over-heating of the crude charge. Only the cost of piping and valves applied to this project since the water circulation pumps were found to be adequate and continued to be used with the retrofitted old exchanger.

Using crude oil as a heat sink and transferring waste heat to the unit charge resulted in an increase in the desalter and furnace inlet temperatures and hence fuel savings in the furnaces. The inlet temperature of the furnaces increased by 4-5°C and the economic return of this project is $900 000/y. Because less fuel is consumed, emissions from the furnaces also decreased as another benefit of the project.

Additional pumparound flow
In the original flow scheme, two pumparound flows (naphtha and kerosene) were used for transferring heat from the column to the crude flowing to the furnace (see Figure 2). After a process study, an opportunity was discovered to install a new pumparound flow which utilises heavy gas oil draw from the column. It provided a heat duty of about 14.8 Gcal/h and was used for the reboiler requirement of the splitter column bottom. Because of this additional free heat source, the reboiler fired heater (F-1102 in Figure 2) was removed after a new shell and tube exchanger was installed. Overall fuel consumption reduced by 16.3 Gcal/h and a CO₂ equivalent saving of 43 617 t/y was realised.

Change in furnace air blowers
The refinery CDU’s charge furnaces originally had six air blowers which required 400 kW each. Since they in excess of requirement in the 1980s, only one is utilised with a bypass line for two furnaces. Sharing air from one blower with a bypass line caused an air distribution imbalance between the two furnaces, with a resulting decrease in furnace efficiencies and unreliable operation.

The refinery’s combustion division developed a project for furnace efficiencies in which the capacity of the air blowers was to be decreased with the installation of new blowers and a variable speed drive fitted to the air blowers’ motors, adjusting fan speeds according to oxygen demand in the furnaces determined via online oxygen analysers in the stacks.

The saving in electricity is calculated to be 3.2 million kWh/y, with expected fuel savings of 11.3 million kWh/year. Installation work is ongoing and start-up of the project is planned for the second quarter of 2015.

Preheat train optimisation and preflash drum
A heat integration study was started in 2014 utilising pinch analysis of the current flow scheme of the CDU, with the aim of finding out whether there is an opportunity to decrease hot-cold approaches and add a preflash drum. Using the SuperTarget tool (from KBC), an optimisation study of the preheat trains was carried out. Among many scenarios given by the model, the Hv. diesel vs crude heat exchanger (E-1104 AB in Figure 2) is to be relocated after the desalter and a new heavy gas oil pumparound heat exchanger will be added to the second preheat train. A preflash drum will also be placed before the charge heater to separate crude vapours which will be sent directly to the kerosene zone of the atmospheric distillation column. Bottom liquid will be sent to the furnace. After the preflash drum, crude oil will also be heated in another new heat exchanger with atmospheric residuum before enter-
ing the furnace. By changing the flow scheme and adding new equipments, fuel consumption of the fired heaters is calculated to be reduced by nearly 16 Gcal/h and the economic return of the project will be $6.9 million/y. Because of the high equipment cost, a preflash column was not selected, so two preflash drums will be placed to guarantee no entrainment by heavier products inside the column.

Detailed engineering of the project is continuing and start-up will probably be in 2016.

Conclusion

The refining industry faces a challenging situation when it cannot control its biggest cost item, crude prices, and many refiners have to be at their fittest to survive by cutting operational costs by evaluating hidden opportunities for energy savings in an increasingly competitive global business environment. Successful and cost-effective investments for energy efficiency technologies and practices will meet the challenge of both maintaining the high quality of products while reducing production costs.

Starting in 2008, Tüpraş Kirikkale Refinery developed an initiative for prioritising energy saving projects, not only for the CDU but also for other process units and utilities (see Figure 3). The CDU processes all of the crude oil charged to the refinery. It is a major energy user and the opportunities for energy efficiency it contains vary from heat integration, waste heat recovery, lower use of utilities and improving fractionation, though to other, smaller measures resulting in large gains. During such studies, it was seen that many possible energy saving opportunities generally require short payback times ranging between two years and as little as a few months.

Refiners monitoring such opportunities for savings will first need a benchmark of their CDU and other units to identify areas for improvements, and then an energy strategy and management programme to locate and apply the improvements according to their economic priorities. Even when such programmes are completed, there is a need to continue monitoring key performance indicators and discover further opportunities for savings.

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Improving energy efficiency in furnaces

Developments in refractory materials and design can contribute to reduced heat waste and higher energy savings

STEVE CHERNACK
Morgan Advanced Materials

Many companies in the hydrocarbon processing industry are making the transition to new generation designs of insulation for furnace linings to increase reliability, lower operating costs, prepare for expected future energy price increases, and position themselves to compete globally.

The main energy units in refineries and petrochemical plants, furnaces often consume more energy than any other single piece of equipment in the plant. So companies are focusing more closely on the efficiency of their fired heaters and looking for more efficient and reliable insulation linings for them, from the flooring to the stack, and all areas in between.

Fortunately, fibre and refractory manufacturers are developing lightweight, energy saving products with unique refractory designs to significantly minimise heat loss in these units.

Before launching into specific floor to ceiling tips, here are a few general refractory options for reducing energy consumption in fired heaters:

1. Use insulating firebrick (IFB) – it is generally about 25-50% more thermally efficient than castable options and actually has better thermal conductivity than fibre in temperatures over 2000°F.
2. Consider the use of pliable (compressible yet robust) monolithic ceramic fibre logs and modules made with a lubricant to allow compressibility in all four directions for easy installation. Then harden at moderate temperatures.
3. Take a look at using thin, lightweight, microporous insulations that offer the lowest thermal conductivity of any material available. This is an especially good choice for areas where tough geometries or older style linings make cold face temperatures higher than normal.
4. Use high density monolithic ceramic fibre modules manufactured specifically for flat flame burner block areas.
5. Monolithic ceramic fibre modules can be especially good choices, including those prefabricated in L-shapes to fit around corners such as radiant to transition, transition to convection sections, and on columns.

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Figure 1 Furnace areas benefiting from energy efficient solutions

Figure 1 is a simplified diagram of a fired heater, like those used in process heaters, reformers and pyrolysis.

Floors
Use insulating firebrick or monolithic ceramic fibre logs
Floors in fired heaters have traditionally been lined with hydraulically bonded refractory castables. Consider one of the following two more energy saving alternatives, known as dry solutions:

- A combination of high duty firebrick (HDFB) backed by insulating firebrick (IFB) augmented with back-up block type insulation
- A newer, more thermally efficient dry floor solution that starts with HDFB, backed by a levelling layer of high strength vacuum formed fibre board and efficient monolithic ceramic fibre log floors.

Floor linings made of IFB and ceramic fibre materials offer improved thermal efficiency and lower heat storage than those insulated with castables, allowing for a thinner lining.

Lightweight, economical IFB offers excellent thermal efficiency, low heat loss and good structural strength properties. When used to line floors, IFB is generally augmented with back-up stable block insulation like TR-19. However, if end users are still concerned about perceived floor strength, a thin layer (1.5-2.5in) of firebrick can be placed on the hot face.

The other cost effective alternative to hard refractories uses the newer monolithic ceramic fibre log
floor design, for example Pyro-Log fibre produced by Morgan Advanced Materials.

**Lower walls**
Consider microporous materials with low thermal conductivity
The lower walls of floor-fired units have traditionally been lined with insulating firebrick backed up by mineral wool block. These low temperature insulation blocks can be a suitable option; however, mineral wool-based blocks deteriorate over time, causing long term hot spots. Instead, opt for a combination of a stable back-up block (TR-19) and new microporous materials, which offer the lowest thermal conductivity around, delivering considerable insulation benefits. For instance, just one inch of microporous insulation, such as BTU-Block Board from Morgan Advanced Materials, delivers the same thermal efficiency as several inches of standard ceramic fibre blanket.

**Upper walls**
Switch to high density monolithic ceramic fibre modules
In floor-fired units, the upper walls are less prone to flame impingement, and traditional linings include ceramic fibre blanket or insulating firebrick with vacuum formed fibre peep sites. Another option is monolithic ceramic fibre modules, with temperature grades up to 1427°C (2600°F) and densities up to 15 pcf (240 kg/m³). Because of their high density, these fibre modules can also be cut and used as peep sites. They offer equal or better thermal conductivity and users can experience reduced heat flow and substantial energy savings.

**Side walls and burner blocks/peep sites**
Move away from castables to high density monolithic ceramic fibres
The side walls in side fired units have traditionally been lined with IFB with refractory castable burner blocks, but HPI companies have begun transitioning to ceramic fibre module linings to achieve improved energy efficiency. For example, Pyro-Bloc modules are the only monolithic ceramic fibre modules made specifically for burner blocks. Another option is robust vacuum formed boards and shapes made of Superwool fibre, which feature good hardness properties and thermal shock resistance, resistance to molten iron and steel, and are easy to machine into shapes for burner blocks and peepholes.

**Arch linings**
Use material that compresses in all four directions, and add a textile tube seal for penetration points
These areas are commonly insulated with folded ceramic fibre modules that only compress on two sides, which can cause issues where the corners are difficult to seal or the material falls out under vibration conditions. Consider using high density monolithic products which compress in all four directions. These modules are simple to install, do not require batten strips, seal well around adjacent modules, and reduce heat loss.

In areas where there are penetrations from pipework or valves outside the furnace, consider the addition of a textile tube seal, which is basically a removable, flexible thermal insulation designed to stop the influx of ambient air and remain a good seal even if the tube moves.

**Corner blocks**
Move away from material wasting options and consider solid pieces of monolithic fibre prefabricated to fit effectively
The areas around the external corners of fired heaters can be particularly difficult to insulate because they are subject to high velocity and mechanical abuse. Butt-jointed modules can easily slump and cause hot spots. Other options include compressing layers of L-shaped blanket together or using folded layers and cutting them to fit. However, these methods waste considerable material, and the layers can separate, resulting in inconsistent insulation, hot spots and heat loss.

Consider using products designed specifically for this application, like solid pieces of monolithic fibre prefabricated into L-shapes to fit more snugly around corners.

**Convection sections**
Use high density monolithic fibre and consider the use of structural insulation to replace the back-up layer
Convection sections experience considerable velocity and difficult service conditions with relatively high and turbulent velocities. This area has traditionally been lined with castables, but more recently many users are opting for more energy efficient high density monolithic fibre modules, like Pyro-Bloc. This option is not appropriate for areas with tubes designed to be steam cleaned, but it is fine for clean gas-fired units.

Another cost effective option includes using structural insulation, such as TR-19, as a replacement for a back-up layer to reduce thickness and achieve improved insulation. This has the added benefit of facilitating any work that has to be done in the area; with castables, it is not practical to do required maintenance or repair work while still operating the furnace. In addition, it eliminates the typical high water content of super-insulating castable (typically 150% water by weight), helping to make refractory dry-out much easier.

**Conclusion**
Engineers who want to upgrade the insulation design in fired heaters should consider all options before proceeding, not just the standard ones that have been used for decades. Think about reducing energy waste, heat loss and hot face temperature to find a cost-effective insulation system that will improve reliability, cut heat loss, reduce energy waste and offer long term savings.

**Steve Chernack** is Manager, Engineered Accounts, Morgan Advanced Materials Thermal Ceramics Business.
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During the conversion of primary energy, approximately 5-10% of the energy used is lost via hot flue gas. There is no need to emphasise that significant savings are within reach when 60-70% of refining operational costs consist of energy costs. Nowadays, many petrochemical companies are focusing their efforts on improving energy efficiency in order to remain competitive. Waste heat recovery from flue gas is the most cost effective way to contribute to this target. This article introduces an air preheater technology for reliable waste heat recovery from corrosive flue gas.

Corrosive flue gas
The corrosiveness of flue gas is the main reason why the energy efficiency of furnaces, fired heaters and steam boilers remains poor. Flue gas originating from sulphur containing fuel becomes corrosive below a temperature of approximately 150°C (acid dew point corrosion). Local cold spots in metal air preheaters will lead to rapid corrosion and breakdown of plates and tubes. Breakdown goes unnoticed for a while, but the shortcut between combustion air and flue gas leads to energy loss (reduced flue gas temperature at flue gas inlet), more power to the combustion air fan and limited throughput because of a maxed-out combustion air fan. These cold spots already occur when the flue gas bulk temperature is as high as 250°C because of cold ambient air at the other side of the heat exchanging surface, which results in a flue gas side surface temperature below the acid dew point.

Existing technologies
In order to lower flue gas outlet temperatures and improve energy efficiency, several techniques have been applied with mixed success. When cooling down flue gas to approximately 170°C, recycling of heated combustion air to the inlet of the forced draft fan will lift the air temperature and subsequent local cold spot temperature. Frequently, an air preheater driven by steam is also applied for additional heating during the winter. These measures cost energy and limit recovery to approximately 20°C above the acid dew point.

For the highest energy efficiency, flue gas has to be cooled below the acid dew point; for this, metal exchangers are not suitable any more, or they become very expensive. Alternatives, such as glass tube and polymer tube, have been applied but they are sensitive to flow induced vibrations and temperature shocks, which leads to tube breakage or rupture. The subsequent short cut between combustion air and flue gas leads...
The top end of the polymer tube bundles is fixed to the upper tube sheet and the lower end is allowed to expand in a sealing system connected to the lower tube sheet. The extra tube sheet in the middle of the exchanger prevents bypassing and directs combustion air into the polymer tube bundles.

The inlets and outlets of the exchanger are located at the side of the heat exchanger in order to allow easy access to the polymer tube bundles. These lightweight bundles are retractable from the top and can be cleaned or replaced without demounting the complete exchanger. In the case of fouling flue gas, each bundle can be equipped with an in-line spray nozzle, which thoroughly cleans each bundle in an alternating cleaning sequence during operation.

Hybrid air preheater design
For applications with a flue gas temperature below 200°C (such as steam boilers), integration of the polymer air preheater is straightforward. For applications with a flue gas temperature above 200°C a combination of a metal air preheater and polymer air preheater in series is required (see Figure 3). The polymer part protects the metal part against low air temperatures that lead to cold spot corrosion problems and the metal part protects the polymer part against high temperatures. This combination is available as an integrated exchanger with only one single shell or as a compact assembly containing a separate metal air preheater and a separate polymer air preheater. The latter can be equipped with an extra induced draft fan between the metal and polymer air preheater for independent control of flue gas towards the air preheater assembly and to overcome the extra pressure drop of the exchangers (see Figure 4).

Waste heat to liquid
Not all combustion processes can benefit from preheated combustion air as the outlet for waste heat from
corrosive flue gas. For example, the electrical efficiency of gas turbines will reduce dramatically when combustion air is preheated. Furthermore, some installations have limited space for large ducting and/or air preheater assemblies. For these applications a liquid outlet for waste heat can be utilised if available (for instance, preheating condensate, a city heating grid, or other process streams). Such a recovery system consists of a polymer gas-gas exchanger and a standard finned tube gas-liquid exchanger separated by a circulating air loop in order to separate corrosive flue gas from higher pressure liquid. This fail-safe and robust design prevents any upsets in either of the independent connected systems (see Figure 5).

Case study air preheating

The following example involves a typical furnace at a refinery. A flue gas flow of 95 000 kg/hr at 290°C was used to preheat combustion air in a hybrid configuration of a metal and polymer air preheater. The realised efficiency improvement is 9.6%, which corresponds to 5.8 MW in this specific case. Flue gas is cooled to 180°C in the metal exchanger and subsequently to 91°C in the polymer exchanger. The combustion air is first preheated to 122°C before it enters the metal exchanger and is further heated to a final temperature of 247°C.

Conclusion

In order to improve energy efficiency in the petrochemical industry, waste heat recovery from corrosive flue gas is the most cost effective source to look at. Cooling flue gas beyond the acid dew point is unconventional but, with a robust exchanger for the corrosive duty, significant savings can be realised in a reliable way. Additionally, this extra efficiency step contributes to a low carbon emission strategy.

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Optimisation of energy consumption

The true values of fuel, power and steam costs are needed for reliable estimation of energy saving projects

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Refineries add value to crude oil by converting feed into marketable products using energy. Figure 1 shows the net margin of a crude oil refinery.

In a typical refinery, the terms shown in Figure 1 can be described as follows:

• Product value is the value received from the sale of products. Because most refined products are commodity items, their values are related to their prices on the open market; thus, engineers can adjust the operation of the plant to maximise the most profitable stream. This is a good start point to develop process improvement projects
• Feedstock cost is the cost of the refinery feed stream, taking into account any transport costs
• Fixed costs are generally the costs of running the refinery, the infrastructure, taxes, people, and corporate costs
• Variable costs include fuels, catalysts, additives, purchased utilities, and maintenance costs.

Assume that a 100 000 b/d refinery consumes energy at a pacesetting level – roughly 5% of the feed input. Assuming the cost of fuel at about $100/t, the total energy bill is about $25 million/year. By contrast, an inefficient site consuming approximately 8% of purchased crude as energy receives an energy bill of $40 million/year, $15 million higher than the pacesetter site.

Figure 2 shows the change in crude oil cost, product slate value, and energy cost for the 100 000 b/d conversion refinery over a year. This figure uses data gathered from two refineries (one consuming 5% fuel and the other consuming 8% fuel on crude) at each end of the typical energy efficiency spectrum. During this period, the efficient refinery showed a mostly positive net margin, whilst the inefficient one operated mostly at a net loss, indicating the critical role of energy consumption on refining profitability. Depending on the fuel cost, the annualised loss of profit for the inefficient refinery is $20 million/y (around $50/bbl).

Assuming average energy consumption of 6.3% on crude for a refinery with 100 000 b/d crude oil processing capacity, total energy usage is 6300 b/d FOE or 400 Gcal/h. A breakdown of this is shown in Table 1.

The energy balance of this typical refinery is further illustrated in Figure 3. The assumed energy consumption – that is, 400 Gcal/h – includes all types of fuel which can be further broken down into three main categories (see Table 2).

Table 2 indicates the major area of interest. Burning fuels in
furnaces incurs the highest energy cost in a refinery. Consequently, this was the driving force for extensive research and development projects which were the beginning of a number of new design concepts in the early 1980s.

The useful power consumption of this average refinery accounts for only about 5% of total energy (24 MW or 20 Gcal/h), but incurs around 25% of the total energy cost (100/400 Gcal/h).

Some energy expenditures, such as those resulting from fired heater inefficiency or heat losses through insulation, are independent of process operations, and so can be independently managed for saving energy, regardless of how the processes operate. Some of the most typical methods are:

- Optimising overflash in distillation: too much overflash wastes energy; too little reduces distillate yields
- Pumparound duties: increased pumparound duty improves feed preheat and saves energy, but impairs fractionation quality above pumparound trays
- Use of stripping steam improves separation and therefore improves yields
- Increasing reflux ratios increases energy consumption for reboiling, but improves separation and product quality.

It can be concluded that optimising refinery energy systems requires an integrated approach comprising energy balancing, rigorous energy economics, process analysis, steam/power system analysis, analysis of process/energy interactions, and use of optimisation tools. These basic steps form a systematic approach to achieving the best energy management within the refinery. It is obvious that energy efficiency has a great impact on refining margins, and by increasing the cost of marginal fuel, the importance of sustaining an efficient operation increases. But how is energy-efficient operation defined, and can refineries be compared in terms of efficiency? Since more complex refineries are expected to consume more fuel than simpler ones, the percentage of crude input is obviously not a valid parameter. Therefore, the fuel consumption expressed as a percentage of crude input is a function of both the energy efficiency and the complexity.

**The basis of best technology**

Developing a method encapsulated in the ‘best technology’ (BT) concept, enables us to compare energy efficiencies between refineries with different configurations, capacities and performances.

Through process simulation, an optimised, energy-efficient design can be developed for all refinery processes, and the energy consumption of each process can be calculated as a function of throughput, feed quality, severity of operation, or other parameters. Therefore, the best economically justifiable design can be simulated according to the following rules:

- Preheat trains designed for a minimum network approach temperature of 20°C (36°F)
- All fired heaters at 92% efficiency
- Yield-efficient operation
- Efficient utility systems
- All power generated internally at 80% marginal efficiency.

Next, correlation of energy consumption for BT processes is applied to rank existing refineries. Moreover, BT allowances for individual units are calculated, taking into account actual throughput, feed quality, yields, and so on. To rationalise the comparison, energy efficiency is expressed as a single number, tonnes of equivalent fuel oil per hour (foet/h). All energy streams – fuels, steam, and power – are converted to foet/h using a systematic method of rigorous energy evaluation and costing. Their sum is the total BT (or %BT), and it can be compared with the actual refinery energy consumption. For example, an index of 180% BT means that the target refinery consumes 80% more energy than the energy consumption of a BT refinery with the same configuration, feed quality, and yield pattern. Existing refineries rarely approach the BT target, and it is not economical to bring them down to 100% BT. Practically, energy-efficient design is achievable and economically justifiable only in grassroots plants.

During the last few years, a greater focus has been put on building efficient new plants. These refineries, as well as some of the older refineries, have helped bring the average BT figure down towards the 180 point. Using the data in **Table 3**, refineries can be categorised according to their BT indexes.

**Figure 4** shows some of the initial BT indices and the achievable BT after implementing the recommended energy-saving projects. There is a wide range of opportunities for the enhancement of efficiency from 20 to about 80 points on the BT scale. However,
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The difference between the achievable improvements resulting from different energy costs and investment policies for each site limits the number of investment related energy saving projects. The potential for improvement can then be carried forward to a gap analysis in order to identify where the refinery is not meeting the BT energy performance. Trying to identify the gap, four main groups of operations should be apportioned:

- Fired heaters
- Heat integration
- Process
- Steam and power.

A typical breakdown of gap distribution is shown in Figure 5 in which:

- The fired heaters gap is the difference between ideal and actual efficiency of fired heaters. The BT of fired heaters should be at least 92% efficient, corresponding to 3% excess oxygen and a stack temperature of 160°C (320ºF). In practice, a significant portion of the gap is lost through poor stack heat recovery. Adding extra convection banks is difficult to justify economically.

- The heat integration gap can be easily identified as the difference between the actual performance and the pinch targeted energy consumption. There are normally a number of economically justifiable projects that can cover a large portion of this gap. But it is assumed that a small gap remains.

- The process gap refers to the actual design compared to the BT design. Unless the plant is state-of-the-art, gap-closing options can usually be identified, but they should be discussed with process specialists to guarantee no loss of yield.

- The steam and power gap is normally the largest gap and, after its implementation, an acceptable achievement can be readily made. Because all the previous projects affect the steam and power balance, this is usually the last to be addressed. The gap incorporates any inefficiency from steam letdowns and poor choices on turbines. Closing the gap usually significantly reduces the loss of efficiency from imported power.

Table 4 shows the impact of the BT score on the efficiency of refining units through gap analysis. Due to the scale of most refineries, it is often difficult to evaluate all the choices to reach optimum energy efficiency. A reliable approach to overcome this problem is to simulate the steam and power system using Thermo-flow (Bent Lorezenten) or Pro-Steam (KBC) software. The model can then lead to the introduction of a project roadmap, where interactions are considered and the best financial options can be realised. Moreover,
constraints within the refinery may also limit the opportunity to reduce energy consumption (see Figure 6).

Fuel costing
Energy conservation does not necessarily make money for the refinery. For example, venting steam or not repairing steam traps may increase refinery profitability whilst refinery heat recovery projects can reduce profitability. Therefore, energy cost reduction is the true objective. The first step in any programme is to develop a thorough understanding of the refinery’s energy economics and costs, from which appropriate cost reduction strategies can be planned.

When a modification affects the energy systems of a site, it is necessary to identify exactly what those effects are. The marginal mechanism may depend on where in the refinery the change is made. For example, reducing furnace firing may reduce refinery fuel consumption and result in additional fuel oil sales, or it may simply increase flaring. The following example can be used to illustrate the marginal cost mechanism.

If 1t/h of low pressure steam is saved somewhere in a process, this will normally reduce the amount of fuel burned in the boilers, but at the same time it will change the deaeration steam demand, the quantity of the returned condensate, and the amount of boiler blow-down or flash steam. The steam balance may be changed, perhaps reducing back pressure power generation through the turbogen and increasing condensing power generation or power import. Less boiler feed water may be required and this will reduce the pumping power. The related terms can be defined as follows:

- **Cost of fuel** This equals the sales value of fuel oil. If balancing fuel is an intermediate product (for example, the vacuum residue), the marginal fuel cost is the value of the vacuum residue when used as blending stock. It means that its value is evaluated from its sulphur content and viscosity, the ‘sulphur and viscosity parity’ calculation.
- **Carbon trading** The introduction of carbon (CO₂) trading schemes has presented a new aspect to marginal mechanisms. Its essence is to set limits on CO₂ emissions produced by industries. If a refinery can emit less CO₂ than the target value then it can sell this credit to an over-producer and gain additional revenue. Over-running the target value means that the refinery must pay additional credit. Nowadays, carbon credit is traded in the open market and is susceptible to price swings.
- **Power costing** In most cases, the mechanism for supplying incremental electric power is either increased power import or reduced power export. In the case of a self-balanced site, there may be an increase in the use of gas turbines or condensing turbine generators. Frequently, refineries have an option to choose between generating their own power and importing it.
- **Steam costing** Many refineries still evaluate steam on the basis of heat content or enthalpy. Since the enthalpy of steam does not vary considerably versus pressure, low pressure steam has slightly less value than high pressure steam. This concept may lead to a gross error of steam/power economics and may drive the refinery in the opposite direction from an economically sound energy strategy. The correct method for costing steam takes into account the amount and the cost of any power generated from the steam when its pressure is reduced. For high pressure steam, it normally increases the load on the marginal boiler. The marginal cost of high pressure steam is equal to the cost of its production, which is mainly the cost of fuel. Low pressure steam can be supplied either via back pressure turbines or simply through a letdown valve. Using the latter option, the potential for generating power from steam is irreversibly lost. In this case, the net cost of providing low pressure steam is calculated as follows:

\[
\text{LP steam value} = \text{HP steam value} - \text{Power credit}
\]

So the marginal value of low pressure steam is affected by a number of variables as follows:

- **Boiler cycle efficiency**: if the boiler cycle efficiency increases, the value of low pressure steam will decrease
- **Enthalpy of high pressure header**: if the enthalpy of the high pressure header decreases, the fuel requirement for boilers and power credit will decrease
- **Power price**: if the cost of power decreases, the power credit will also decrease. In contrast, the value of low pressure steam will increase.

Case study
Data gathering
An oil refinery located in the Middle East is selected to benchmark and develop an energy conservation programme. The programme follows these steps:

1. Data collection
2. Benchmarking
3. Calculation of complexity factors
4. Identification of inefficiency
5. Technoeconomic evaluation.
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A number of different techniques are used to validate and reconcile energy consumption data, which are: boiler and furnace efficiencies, boiler fuel consumption, refinery steam and power balance, measured fuel gas rates, gas turbine fuel consumption, and process data (for example, process furnace fuel consumption and heat exchanger duties). It is supposed that data are collected for both the hot and cold representative period of operation. Table 5 shows the period of operation for the target refinery.

To perform the study, the following data are gathered:

- Boiler steam production
- Refinery steam balance
- Power balance
- Furnace and boiler efficiency
- Fuel balance
- Process unit.

The data collected for the hot and cold operating periods are used to determine the total refinery energy consumption, such that:

Total energy = Total fuel consumption + Power import/Generation efficiency

Furthermore, the following assumptions are considered for this calculation:

- The required power is provided from an external site, generating power with an efficiency of 35% which is equal to fuel consumption of 2.46 Gcal/ MWh
- The monthly average energy consumption is calculated.

Measuring energy consumption

During the period of study, the target refinery consumed two types of fuel: fuel gas (includes some imported natural gas) and fuel oil (mostly heavy fuel oil). Table 6 shows the measured energy consumption collected from the target refinery before data reconciliation.

Reconciliation of energy consumption

Table 7 shows the energy consumption data after validation and reconciliation. It is assumed that the boilers consume 35% of the refinery’s total fuel oil consumption during summer operation, and the fuel gas burned in the utility boilers has a LHV equal to 10 470 kcal/kg. The reconciled data show that the total energy consumption of the target refinery for winter and summer is 1200 Gcal/h and 1279 Gcal/h, respectively, with an average value of 1239 Gcal/h. Total energy consumption in winter is about 6% higher than in summer because more energy is required for heating.

Specifying energy consumption A relatively simple method for determining the energy performance of a refinery is to calculate the existing specific energy consumption (SEC). SEC is the total energy consumption per unit mass or volume rate of crude. From the data provided (see Table 8), the SEC for the refinery is 0.55 Gcal/t in summer and 0.59 Gcal/t in winter, with an
average value of 0.57 Gcal/t.

Because the refinery configuration (complexity) and the process unit operation (for instance, hydrocracker conversion) are not considered, the energy performance of the refinery is not reliable. BT takes into account these factors, so benchmark energy performance is accurately estimated in the second step of this programme. Figure 7 shows the SEC and energy consumption of the target refinery for both summer and winter base case months.

Process unit feed rates and energy consumption
In addition to the overall energy consumption of the refinery, the energy consumed by individual units for both base cases is calculated. In order to develop a realistic heat balance for this refinery, it is essential to carry out data validation and reconciliation.

Energy intensive equipment
A number of the main energy intensive facilities contributing to the overall energy consumption of the refinery are identified. For each facility, the energy intensive items of equipment are listed in Table 9.

Comparison of the target refinery with other refineries
Figure 8 demonstrates the energy consumption and the existing SEC in the target refinery and in three others in the Middle East.

Conclusion
In this article, a method of calculating the true monetary benefit of saving energy was discussed. Moreover, the correct mechanism for estimating the price of energy, leading to better economic evaluation, was presented. It was shown that basic building blocks should be constructed before executing energy conservation programmes for a refinery.

Additionally, it was confirmed that best technology (BT) benchmarking can highlight the efficiency of a target refinery against BT to show the potential for optimisation programmes. In order to provide correct figures for energy efficiency
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Further reading
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Figure 8 Total energy consumption and SEC in the target refineries
Weir Minerals Lewis Pumps is known internationally in the sulphur, sulphuric acid and phosphoric acid industries with equipment installed in more than 120 countries worldwide. With new product innovations and a dedicated group of employees, Weir Minerals Lewis Pumps is the recognized world leader for pumps and valves in difficult applications.
Best practice in energy efficiency

Energy management software tools provide solutions for energy savings from design through operation

RON BECK  
AspenTech

Energy management is essential to the sustainability and profitability of an operation. Second to raw materials, energy is the largest expense in most chemical and refining processes. Those refineries and petrochemical companies that invest in energy efficiency gain a competitive advantage through improved operating margins, production flexibility and better carbon footprints. Improving energy consumption should be seen as a business opportunity and embedded within all aspects of the enterprise. External and internal factors make energy optimisation an on-going challenge in any operation. Energy sources, supply and costs are changing and evolving. Feedstock shifts impose adjustments in operating strategies. Sales contracts impose constraints. Environmental regulations and taxes can force operating shifts whilst equipment ages with time and its condition impacts operating effectiveness (for instance, heat exchangers age and get fouled).

So, how can refiners and petrochemicals companies keep energy efficiency foremost in mind in the midst of business complexity and uncertainty?

Tackling energy inefficiency is divided into supply-side and demand-side areas. On the demand side, there are various strategies for reducing energy demand. Fundamentally, making more efficient use of all heating and cooling sources presents opportunities in a plant. This is known as heat integration and is tackled during design, but also on any operating facility. Demand can be reduced through better operation and maintenance of process equipment. Heat exchangers encounter a variety of operating challenges ranging from fouling on heat transfer surfaces, vibration and hydraulic issues. Process strategies can have a significant impact on energy use – for instance, adjusting operating temperatures, tuning and adjusting column tray and flow. Reducing process variability (through optimisation and real time control) can significantly improve efficiency. On the supply side, actively managing the available utility sources based effectively to the issues in energy efficiency and carbon footprint.

Design for energy efficiency

Process engineering design faces a range of design objectives, starting with yield and quality targets, feedstocks, flexibility to handle changes in feedstock and product over time, safety and emissions compliance, operating stability and capital cost minimisation. When energy efficiency is relegated down the priority list there will be a negative impact over the life of the plant.

The enemy of energy efficient designs is time. Most projects today, whether large or small, are under huge pressure with regard to schedule. The most proven or easiest to design process (from a functional point of view) gets developed. Incorporating heat integration (pinch) analysis into this early stage can yield important lifecycle benefits. Energy efficient processes not only save lifecycle costs, but also capital through reduction in required ratings. This will help also to save hot and cold utilities.

Ways to improve energy optimisation at the early design stage include:

• Intuitive heat integration (pinch) analysis and optimisation software embedded within the process simulation enables the conceptual designer to rapidly investigate, screen and select better designs from an energy point of view.
• Detailed heat exchanger modeling within the process simulation enables the conceptual designer to look at trade-offs between heat exchanger size, efficiency and oper-
ability to achieve the best balance of capital and operating cost

- Optimisation of the interaction between heating and cooling block and key process units, such as separation columns, using optimisation methods within leading process simulators such as Aspen Plus and Aspen Hysys.

Energy conservation is important, not only to large petrochemical processes, but also to new bio-conversion processes seeking commercial viability. Liquid Light is a start-up company which is commercialising patented bio-to-chemicals processes and Pan Pacific is a company addressing conceptual process design of algal biofuels production. Both organisations have made use of these early design approaches to improve the economics of their novel processes. Braskem has developed an innovative energy efficient process for synthesising isopropanol from sugarcane by utilising the above approach. Some 30% energy saving is achieved in the early stage of process design with the right combination of process knowledge and software tools like energy analysis inside Aspen Plus.

Revamping existing facilities

Diverse opportunities are available to improve energy use in existing facilities and many of these alternatives fortuitously improve yields. The same tools, which are available during front end design, are similarly available to the engineer looking at energy conservation and plant improvement. Several of the key opportunity areas are reconfiguration of heat exchangers; replacement and addition of heat exchangers; more aggressive preventative maintenance strategies to reduce heat exchanger fouling; process changes in operating parameters and configuration to improve efficiency.

A comprehensive energy analysis of an existing process facility may identify dozens of individual opportunities for improvement.

- Heat exchanger maintenance
  Heat exchanger fouling imposes both energy and yield penalties. Tuned process and heat exchanger models can be used in combination with real-time plant data to predict heat exchanger fouling and to drive improved maintenance schedules that reduce plant outages, energy use and yields. Organisations, such as Ineos and Dow Chemical, have documented significant impact from these strategies.

- Efficient production/energy planning and scheduling
  Establishing a link between production and energy scheduling ensures secure energy supply for plants; reduces the need for flaring of surplus fuel gas and venting of surplus steam; and helps forecast possible bottlenecks. Better daily scheduling and reacting to changes quickly with enhanced execution is crucial. Aspen PIMS, Petroleum Scheduler and Aspen Utilities Planner are the toolsets that provide a comprehensive ability to synchronise the production planning, scheduling and energy planning for these complicated objectives. Supply-side management in the production planning process, energy costs and emissions targets are becoming an integral part of planning. Operational benefits can be gained by planning for inbound and outbound energy use (that is, energy use in process equipment and facilities, feedstock scheduling, purchase of external utilities versus use of internally available sources). Forward planning tools can help evaluate the trade-offs between production, energy sources and costs and emissions, enabling a true optimal operation to be defined. Aspen Utilities Planner software can help plan the optimal utilities system’s setup and also advise operations personnel on actions they can take on a real-time basis to improve energy and economic performance. Rompetrol has realised significant values and improved the bottom line of refinery operation by adopting the approach above to close the gap between hydrocarbon planning and energy planning.

- Real-time optimisation combined with advanced control
  Advanced process control (APC) can manage a process to reduce variability and enable the plant to be run closer to its desired performance. This in turn can reduce the overall energy budget for the process and better manage emissions within permitted limits. Aspen DMC3 software is a new generation of APC that makes an advanced control system more intuitive and maintainable. Real-time optimisation can be combined with APC to further achieve energy reduction. By running an analytical process model continuously against plant data, operating strategies can be continuously revised, based on actual plant performance. Profertil is an example of an organ-
isation that achieved millions of dollars in annual benefit from this strategy.  

Making the difference
The priority that companies place on energy management fluctuates in concert with trends in energy prices and price uncertainty. This is a short sighted view. In the longer term, investments in minimising energy consumption will pay off over an asset’s lifecycle. By achieving the same outcomes through less energy usage, organisations can implement more efficient processes and embrace advanced technology to improve performance. Energy improvement has the side benefit of improving process yields. It also has sustainability benefits. Process plants as major energy consumers will be increasingly under regulatory and public scrutiny related to their carbon footprint.

For many enterprises, the value of energy reduction on profitability is usually evident. The challenge is in clearly identifying opportunities for improvement and their capital and operating implications. State-of-the-art process simulation, analysis, planning, scheduling, optimisation and control software optimise energy usage by managing operations across the enterprise. Capital savings can be made by implementing more energy efficient operational measures, resulting in increased production and reduced emissions.

Adopting best practice improves the way companies source, trade and use energy. Operating existing utilities with minimum cost and maximum reliability delivers the optimum production plan while considering ever-changing environmental, organisational and technical constraints. Managers can use best practice to make calculated, measured and sustainable decisions, while meeting regulations and improving production standards. By considering total energy and utilities systems, energy management software tools provide a process organisation the solution to energy savings from design through operation and help dramatically improve margins.

Case study: S-Oil
S-Oil Corporation is one of the largest producers of petroleum products, petrochemicals and lubricants in the Asia Pacific region. Achieving maximum energy efficiency in its processes was deemed critical by S-Oil. Specifically, the company wanted to be recognised as one of the leading refineries in the Asia Pacific region for energy efficiency, requiring a reduction in its rating on the Solomon Energy Intensity Index. In addition, the company set itself the goal of improving the refinery’s energy efficiency each year, despite an increase in crude processing in each of the four preceding years.

Using Aspen Hysys and Aspen Energy Analyzer, S-Oil was able to model its refining process, explore operating condition optimisation and bypass cooling units to accomplish its energy efficiency demands. The company achieved the goals of improving its energy efficiency and lowering its Solomon Energy Intensity Index, while ultimately identifying process revamp ideas worth total savings of $39 million throughout its refinery.

Improving energy efficiency to leading standards
Substantial rises in operating costs over a four year period led S-Oil to recognise that becoming as energy efficient as possible in its refinery, without affecting product output, would help to defray the increases in operating costs and lead to a significant growth in profits. For that reason, S-Oil set an annual target goal to improve its energy efficiency.

Process optimisation and heat recovery drive energy reduction
S-Oil modelled its process in Aspen Hysys, allowing for optimisation of energy performance in the distillation columns by reducing the total column pressure. The hot feed to the aromatics portion of the refinery was previously cooled in a heat exchanger using cooling water before being allowed to proceed throughout the process. Using Aspen Energy Analyzer, a better use for the energy contained in this hot feed was developed. The solution involved bypassing the coolers and transferring the hot aromatics feed elsewhere in the process where heating was required. This greatly decreased the total number of cooling units needed before the aromatics process section. Additional heat from the hot aromatics feed was also cascaded to downstream units to further cut heating demand in the process.

Using Aspen Hysys and Aspen Energy Analyzer helped generate more than 100 process revamp and optimisation ideas. After screening for feasibility, the company selected 35 of the ideas for implementation and the end results proved fruitful for its energy efficiency venture.

S-Oil abated its energy requirement by over 102 MW throughout the refinery and process revamps and optimisations saved $39 million. The payback period for all enhancements made in the refinery was under a year.

Implementing the changes developed in Aspen Hysys and Aspen Energy Analyzer led to a successful reduction of the company’s Solomon Energy Intensity Index, positioning the company as one of the Asia Pacific region’s leaders in energy efficiency.

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Advanced process control in FCC and hydrocracking units

Implementation of advanced process control of two major units produced significant savings with short payback times

GRZEGORZ OLESZCZUK and MARTA DYLEWSKA
Honeywell Advanced Solutions

Given the competitive and cost pressures facing refineries, solutions to boost company profits and reduce expenses are highly sought after. Advanced process control (APC) in this respect is among the most attractive solutions. Through process optimisation, APC not only delivers and often exceeds expectations for cost savings and productivity gains, but does so with relatively little outlay. Few technological changes in the units addressed are required, and there is no need to invest in new equipment.

Nevertheless, this should not diminish the importance of the implementation and the expertise required. The fact that APC does not require the investment or disruption associated with other options does not mean it is simpler. For every quick win there are complex problems that must be overcome. Two aspects are of particular note. First, the APC should reflect current market conditions for product margins, feed costs and other variables to ensure the process is effectively optimised. Second, empirical models should underpin the solution by employing step tests and real-world observations of plant responses. Results from solutions relying on analytical models of the process will invariably deliver disappointing results.

Two APC applications implemented at PKN Orlen in Plock, Poland, in 2013 illustrate these points. The refinery, Central Europe’s biggest, chose the hydrocracker and fluid catalytic cracking (FCC) units to act as pilot schemes with a view to implementation of APC throughout the group.

“We need to continuously improve our already high production standards, so we decided to undertake a production optimization program for the whole group. Advanced process control is one of the main components, because it impacts the production results very quickly and positively,” said Krystian Pater, Member of the Management Board for Production at PKN Orlen.

Technology used
Both projects used Honeywell’s Profit Suite of APC and optimisation applications. The key software, Profit Controller, reads process data from the existing control system and, based on the process model and its range control algorithm (RCA), sends optimum set point values back to the control system.

Three types of inputs and outputs are used:
- Controlled variables (CV) which are usually process values (such as qualities, flows, temperatures and pressures) that must be kept in safe and optimal ranges
- Disturbance variables (DV) which are read-only variables such as feed quality and ambient temperature, or parameters outside the local control system’s control such as disturbances from other process units
- Manipulated variables (MV), the

Figure 1 Fluidised catalytic cracking unit at PKN Orlen
values the APC sends back to the control systems, usually represented by the list of set point values for PID controllers.

The RCA algorithm calculates and predicts CV values based on the process model and MV movement. The objective of APC is to push the steady state MV values closer to the predetermined ideal operation point.

“Honeywell executed two very big APC projects on the HCK and FCC units in parallel. Both covered more than 10 multivariable controllers and several inferential calculations. Cooperation with Honeywell had a positive impact on our APC Team through sharing Honeywell’s experience and knowledge in the field of refinery process optimization,” said Marek Bożek, PKN Orlen APC Team Manager.

**FCC unit**

The FCC unit (see Figure 1) is among the most important process units in oil refineries, but it handles a physically complex process that is difficult to operate and control. The reactor, regenerator and main fractionator sections are highly sensitive to process dynamics and face multiple constraints. Units are also required to run under different operating modes, reflecting changing economics, market demand, mechanical constraints and refinery feedstock. The significant economic incentive to push FCC constraints close to limits is matched by operators’ reluctance to do so for fear of process upsets. In short, FCC units are ideally suited to advanced control solutions.

APC’s benefits derive from several sources:

- Feed maximisation: the FCC unit operates on various types of feed from different units in the refinery. Consequently, throughput can be a downstream constraint
- Conversion maximisation results in higher propylene yields by optimising the reaction severity in the reactor and regenerator section
- Distillation control and yield shift are achieved by producing more valuable products from the main fractionator and gas plant section. The most valuable products for the latter are propylene and light gasoline, which is routed downstream to the Prime-G desulphurisation unit.

In view of the specific processes in each section of the FCC unit, the APC’s targets were divided by operating area. The top three, for the unit feed system and reactor and regenerator section, for example, were to maximise throughput (taking into consideration unit constraints and planning requirements), improve conversion control and maximise propylene yield. Those for the fractionation section included: maximising the yield of the most valuable main fractionator distillates, subject to quality specifications; minimising CLO draw; maintaining the heat and liquid/vapour loading balance using pumparound streams; and reducing energy consumption. Objectives were similarly developed for all of the FCC unit’s sections.

Based on these objectives, six multivariable controllers were designed for the FCC unit. One controller divided into two subcontrollers covered the reactor/regenerator section and fractionation section. Another six were designed for the reactor/regenerator and main fractionator; the debutaniser; depropaniser; butylene splitter; the new propylene splitter; and the old propylene splitter.

All controllers were designed to execute their calculations at one-minute frequency. Underpinning the controllers were multivariable process models for each area.

**The role of inferentials**

Inferentials, or ‘soft sensors’, are crucial elements in many APC
projects. Calculations using historical data from lab samples and key process parameters can predict quality parameter values in place of lab analyses. A number of inferentials were implemented for the FCC unit to meet product quality specifications. Since the implemented inferentials predict lab values in just one minute, against the eight hours required for lab analysis, they enable more responsive control. Testing indicated that these inferentials were highly accurate. Figure 2 shows the trend for the inferential and real lab samples for 90% distillation of gasoline. Green dots represent lab samples; the brown line is the soft sensor prediction. Even lab samples far away from the main trend were accurately predicted (as in the sample with the green arrow).

Results
All requirements for the APC project were fully realised. A key objective – a 1% increase in throughput – was surpassed (see Figure 3). The multivariable controller increased feed smoothly despite oxygen constraints in the regenerator, compressor capacity, and product quality constraints measured after the main fractionating column.

The most valuable benefit, however, came from improving propylene purity, so boosting the yield. During test run, the propylene purity was approximately 99.63% (v/v, based on laboratory data), against a specification value maximum of 99.6%. Figure 3 shows the trend of propylene purity during APC start-up. The process stabilises immediately.

Finally, the standard deviation of the stabilised gasoline’s 90% (v/v) and light clarified oil’s 90% cut points decreased by more than 25%, allowing a 30-50% reduction in transition time from maximum naphtha production to maximum LCO production.

Overall, the benefits from the implementation at PKN’s FCC unit were calculated to be worth an annual $2 million, representing a payback period of less than two months.

The hydrocracker unit
Similar benefits were achieved in the hydrocracker unit. However, for this unit simply using a separate APC controller was not sufficient to adequately control the hydrocracking conversion process.

Hydrocracking is a versatile catalytic refining process that upgrades petroleum feedstock by adding hydrogen, removing impurities and cracking to a desired boiling range. The hydrocracking catalyst converts high boiling range material into diesel, jet fuel and lighter products. During this process, significant aromatic saturation and isomerisation occurs in addition to cracking. These reactions also take place in the presence of a recycle gas with high hydrogen content. Effluent from the cracking reactor is cooled and liquid products are separated from vapours. The vapour stream is compressed and recycled to the reactors; the liquids are sent to the fractionation section, where the various products are recovered.

In PKN Orlen’s hydrocracker unit (see Figure 5), fresh feed is routed from the vacuum unit or from a combination of the vacuum unit and storage tanks. The valuable products range from heavy diesel to light naphtha.

Application objectives
The primary objective of APC was...
Conversion control

The hydrocracker conversion is difficult. The conversion (CONV parameter) was calculated based on feed to the unit and flow of the hydrocarbon residue from the main fractionator column, using the following widely used formula:

\[
\text{CONV} = \left(1 - \frac{\text{Residue flow from MF}}{\text{Feed to the unit}}\right) \times 100\%
\]

However, while this provides a good indication of the hydrocracker operation, it is not always adequate:

- The hydrocarbon cracking conversion process takes place on reactor beds, so product flows from the main fractionator column (in this case residue flow) can introduce errors in the equation results, which depend on the main fractionator operation conditions.
- Residue flow on the main fractionator column was controlled in cascade with the column’s bottom level controller to promote stability, which makes conversion calculation noisy due to level fluctuations at the bottom.

### APC benefits for the hydrocracker

**amounted to millions of dollars a year, with the return on investment at less than three months**

- The response of the main fractionator draws lags the hydrocracking reactions on the reactor beds by five hours or more. To overcome this, another software tool, Profit Optimizer, was used for optimisation across multiple sections.² It reuses the APC controller models to provide steady state and dynamic optimisation across multiple process sections.
- Three ‘slave’ APC controllers work under one of these optimisers: two for hydrocracking reactor optimisation and control, and one for controlling and optimising the main fractionator column. The built-in optimisers in these controllers were configured for reactor product value optimisation, with hydrogen quench flows and products flows adjusted to maintain conversion and throughput. The multiple section optimiser above them controlled a number of variables: reactor conversion; WABT and reactor profiles (or bed temperatures); hydrogen quench valves; hydrogen make-up; and hydrogen/hydrocarbon ratios. The optimisation coefficient assigned for conversion was set very high to maximise it within unit constraints.

### Hydrocracker inferentials

Inferentials were again an integral part of the project, being implemented for the most important process quality parameters, such as nitrogen content after the first reactor, unstabilised gasoline (90% distillation), and heavy naphtha (95% distillation). Each inferential required a few days of bias updating, using calculations based on laboratory data to modify the inferential equation. This increases the inferential credibility and reliably represents actual lab samples.

### Results

All of the project’s objectives were met, and the APC and optimiser increased average cracking conversion by almost 3% (see Table 1). Diesel yields, meanwhile, increased by more than 0.8% (see Figure 6).

Implementation of APC also equalised heater outlet temperatures on the HCK furnace through an implementation algorithm commonly known as pass balancing. This reduces thermal convection between furnace streams, significantly extends heater efficiency, and prolongs
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Overall, APC benefits for the hydrocracker amounted to millions of dollars a year, with the return on investment for the project at less than three months. Combine these with the gains realised through the FCC project and, in total, a conservative calculation of the benefits of the pilot APC implementations at PKN Orlen exceeds $5 million a year.

Przemysław Hartliński, PKN Orlen Refinery Production Manager, concluded: “Within months both APC projects provided ROI and made our production process significantly smoother, achieving optimal ranges in the units’ KPIs.”

Pass balancing helped to deal with heater constraint by maintaining tube skin temperatures at the acceptable optimum level (see Figure 7).

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The authors thank PKN Orlen S.A. for analysing the operational data of post-APC samples and for permission to publish. Also, thanks to all operators and other PKN Orlen staff at the FCC and hydrocracking units for fruitful cooperation during both APC project implementations.

Figure 7 Pass balancing algorithm reconfiguration effect on outlet temperatures on HCK heater

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Increasing distillate production at least capital cost

Investing in improvements to the atmospheric crude unit can deliver increased distillate yields with short payback times

JOE MUSUMECI, STEVEN W STUPIN, BRANDON OLSON and CARLOS WENDLER
Ascent Engineering

This is the second of two articles which discuss changes to the crude unit to increase distillate production from each barrel of crude processed. The first article reviewed operational adjustments that require zero capital investment. This second article focuses on atmospheric crude unit improvements that require minimal investment with short payback to further increase distillate yield. Improvements to the vacuum unit, which are not discussed here and will be covered in a future article, can also offer tremendous gains to the refiner’s distillate production.

Historically, most US refineries have been designed and operated to maximise gasoline production as a response to the needs of transportation that have led the consumer market. However, shifts in worldwide fuel consumption patterns have caused a decrease in the demand for gasoline and an increase in the demand for diesel fuel. This trend, discussed in our first article (PTQ Revamps 2014), has led to a current diesel price differential of about $0.23/gal over gasoline and is expected to increase to over $0.70/gal by 2030 if the trends continue. Contributing factors to this changing consumption pattern include increased demand in developing countries, a focus on reducing greenhouse gas emissions that has led to more stringent automotive fuel efficiency standards, and increased blending of renewable fuels. Adjusting to these market conditions can allow refiners to maximise refinery profitability by producing higher yields of the most valuable distillate products.

Opportunities for increasing distillate yield range from operational tweaks that require no capital, as discussed in the first article, to simple modifications that can be potentially implemented without a unit shutdown, to major capital projects. Operational tweaks can be identified by test run most successfully with the help of process simulation, but are often limited by the capabilities of the existing equipment. A refiner who is willing to invest in capital projects may benefit the most from a well thought out design plan which will yield the greatest return on investment and maximum profitability.

A key to implementing any plant design plan is to have accurate simulation and design. A simulation tuned to actual plant data is often useful to benchmark the current operation and can be used to compare alternative concepts for optimisation of the proposed upgrades. The alternative cases should focus on variables which have the greatest impact on distillate yield with effort to minimise capital cost often by maximising the reuse of existing equipment. Refinery and unit product specifications should be reviewed to ensure they are current and their purpose understood. This process may require challenging some of the unit’s current target specifications by identifying unwarranted limits on unit operations and possibly resulting in unnecessary over-processing and increased operating costs. With these specific areas in mind, concepts can be assessed to narrow down options to those with the greatest financial incentives. Simulation and design experience, such as that provided by a skilled process design firm, is critical if the refiner wants to identify new ideas and the best projects to maximise profitability.

Atmospheric tower modifications to increase distillate production

Maximising the capability of the atmospheric tower is often the primary focus when considering crude unit modifications. Improving atmospheric tower operation usually requires the least amount of capital for a given increase in diesel yield. The following sections focus on atmospheric tower modifications that go beyond simple operational adjustments and will require some capital investment in order to improve distillate recovery.

Stripping steam in the atmospheric tower and side strippers

Increased stripping steam vaporises additional distillate range material from the crude; this requires adequate tower capacity and heat removal capabilities to condense and recover the additional distillate above the flash zone. The first article of this series included a case study demonstrating how, in one refinery, increasing the stripping steam rate (and the tower operating pressure, to offset the increase in percent of flood) significantly increased diesel yield and refinery profits. Other refineries may have similar equipment or hydraulic constraints which limit the ability to increase stripping steam rates as
a means to improve distillate product recovery. The extent of the equipment constraints could range from flooding in one or more tower sections or in a side stripper to limited condensing capacity or water dew point limitations in the overhead system. Specific modifications are required in order to tackle specific atmospheric tower system limitations which may exist when trying to maximise stripping steam.

Even though stripping steam rates represent a small portion of the tower’s vapour loadings, flooding in one or more atmospheric tower sections or in a side stripper can be the first limit encountered when increasing stripping steam flow. In this case, a designer may consider installing higher capacity trays or replacing trays with packing. Increasing tray spacing is another option for greater debottlenecking. However, the reduction in theoretical stages that can result from this type of modification should be evaluated to ensure that the fractionation remains acceptable.

A thorough review of all auxiliary equipment is necessary to ensure that the limits of the other equipment have not been exceeded. If increased tray spacing or high capacity trays are insufficient to relieve the tower flooding, more extensive modifications may be required. The tower or side stripper diameter may need to be replaced with a new, larger tower section. The additional capacity that results from these modifications will enable the refiner to take advantage of increased stripping stream rates and subsequent increased distillate recovery.

Another common obstacle that can prevent or limit an increase in stripping steam rate is the inability to remove additional energy from the atmospheric tower. Heat removal can be limited by insufficient capacity in the overhead condensing system and increased pumparound duty. Options for increasing overhead condensing capacity include adding exchanger surface area with new exchanger bundles, reconfiguring the existing exchanger train, and adding a new exchanger or air cooler. A designer can evaluate whether heat is currently being rejected to water or air that can instead be recovered into the crude preheat train. Modifications to the tower pumparound circuit(s) should also be considered. Modifications can include changes to the pumps, piping, control systems, and exchangers with a review of the tower’s pumparound section trays or packing. Lower cost options include new impellers, piping jump overs, and exchanger bundles. Larger investment might include new heat exchangers and air coolers along with a major reconfiguration of the crude preheat train.

An accurate simulation model is paramount for the optimisation of the complex interactions between the tower pumparound and the preheat train in order to maximise energy recovery and to minimise fractionation losses. If an accurate plant-matched simulation model does not already exist for the full crude unit, consider commissioning an experienced engineering firm to assist in developing this powerful and valuable tool.

**Reduce atmospheric tower operating pressure**

Like stripping steam, reducing the operating pressure of the atmospheric tower increases distillate recovery by reducing hydrocarbon partial pressure and increasing vapour rate, thereby allowing lighter range material to remain in the vapour phase at a given feed temperature. This helps to ‘lift’ heavier materials like distillate up the tower to increase recovery, but will increase vapour loadings because of the additional volumetric flow at lower density and therefore more volume which must be evaluated.

Lowering the pressure also has similar constraints to tower capacity and heat removal as in the previous stripping steam discussion. Lower pressures result in lower condensing temperatures, which lower the temperature driving force for heat transfer in pumparound and the overhead condenser. Having an accurate simulation of the system will help identify and quantify effects such as this. Aside from cooling capacity, hydraulic limitations can also bottleneck a tower overhead system. The lower cost solution for fixing hydraulic problems can include installing low pressure drop valves, new exchanger bundles, and adding a parallel piping line. Larger investments might include new exchanger systems, and new nozzles and piping. Often, the source of the overhead capacity limit can also be the tower off-gas compressor which should be evaluated.

**Improve atmospheric tower fractionation**

Equipment modifications to improve fractionation typically focus on the effective operation of tower internals and may include installation of high efficiency or high capacity trays or packing. Generally, all atmospheric tower sections should be reviewed with improved fractionation as a goal to increase distillate recovery. Also, the designer should keep in mind that certain tower sections may require or benefit from additional design consideration to help maximise run length or maintain operational efficiency, for instance anti-fouling features for trays or packing in the wash and stripping sections, particularly with certain crude types known to have fouling effects.

Packing should also be considered to replace trays where the advantage of low pressure drop can be beneficial. In low pressure systems, the advantage of lower pressure packing can be that the same amount of stripping occurs with lower stripping steam rates. When revamping from trays to high capacity packing, separation efficiency needs also to be evaluated. A loss in separation efficiency is sometimes unavoidable if high capacity packing with lower surface area is considered. Lower surface area packing has higher capacity and is more fouling resistant, but has lower separation efficiency.
While new or modified tower internals may be sufficient to achieve the desired fractionation improvement, more extensive modifications may be required if these options do not achieve the desired fractionation. For example, the addition of a stripper on an AGO side draw that does not currently have one can be a lucrative option to recover incremental distillate. Additional fractionation improvements may warrant more costly options including adding additional tower height to increase the number of distillation stages or installing a new larger tower section.

Often fractionation and tray or packing performance deteriorates, and may go unnoticed for some time. In one medium-sized US refinery, the authors worked with engineering staff to evaluate and specify new trays in the atmospheric tower to increase distillate yield by a predicted 3.1 LV% of crude. The refiner had been having problems reliably drawing a consistent volume and quality of AGO product, and product fractionation was poor. This condition continued for more than a year. A subsequent gamma scan of the atmospheric tower suggested some level of suspected damage to the wash and stripping section trays.

**Figure 1** shows the atmospheric tower configuration, with the suspected damage noted. The poor fractionation in the wash and stripping sections had severely limited the ability to recover distillate from the crude feed, resulting in losses via the atmospheric tower bottoms. Diesel range material that was lost to the vacuum tower tied up vacuum unit capacity and was recovered as LVGO, which was cracked to lower value products in the downstream hydrocracker unit. Additionally, the excess diesel in the vacuum tower feed resulted in worsened vacuum system performance. This increased the tower pressure which resulted in an undesirable increase in residue product yield.

**Table 1** shows the results of simulated cases for the plant match simulation, including predicted operation with the new trays and subsequent operational cases which increase the heater

![Atmospheric tower configuration](image-url)
Process Insight:

The design and optimization of separation processes is carried out using process simulators, which utilize various calculation approaches. Two techniques that are widely used for modeling distillation are the ideal stage model and the mass transfer model.

**Ideal Stage Models**

The ideal stage model requires a minimum amount of data—only equilibrium relationships and enthalpy data for the heat balance. The assumptions of the ideal stage approach are: 1) that the vapor and liquid are both perfectly mixed so that the vapor and liquid leaving a stage are at the same composition as the material on the stage and 2) that thermodynamic equilibrium is obtained on each stage. The equilibrium assumption also means liquid and vapor leaving a stage are at the same temperature. Ideal stage models can also account for non-ideal column performance through the use of reaction kinetics as is done for amine sweetening columns.

For most processes encountered in gas processing and other industries, the overall efficiencies are well established for proper operating conditions of the column. For systems that are unavailable, similar systems often exist to allow for efficiency estimation. If not, the mass transfer approach is available as an option.

**Mass Transfer Models**

For the end user, the notable feature made available via the mass transfer approach is the ability to model a column with the actual number of trays in the unit or the actual depth of packing. However, there are still several assumptions that are made in this approach that can have a significant impact on results. Two that are worth mentioning include the mixing model for trayed columns and the discretization of the packing depth for packed towers.

Application of the mass transfer model to random or structured packing requires the column height to be discretized into vertical segments or stages. For trayed columns, various mixing models can be used for the liquid and vapor phases. The most basic assumption is that of complete mixing in both the liquid and vapor phases. However, the concentration gradients that develop across operating trays can significantly impact the predictions made by this model since this gradient is the driving force for mass transfer. As the column diameter becomes larger, the perfectly mixed flow model is less applicable.

For modeling both liquid phase chemical reaction and mass transfer, the use of the Mass Transfer - Kinetic (MTK) technique may be considered. The enhancement factor describes the increased rate of absorption due to the effect of a chemical reaction. The material balance requires kinetic rate expressions for all chemical reactions occurring in the system. As with equations for a non-reacting system, an appropriate model for interface behavior must be used.

Mass transfer models require data necessary to calculate interphase mass and heat transfer coefficients and interfacial area based on correlations of the following transport and thermal properties: diffusivities, viscosities, densities, heat capacities, thermal conductivities, etc. Furthermore, mass transfer models require detailed information on the column internals. For trays, this includes information such as weir heights and fraction active area. For packing, this includes surface area per unit volume and void fraction.

If the simulator allows the user to select from various alternatives for these parameters, knowing the correct selection may be problematic. Further, the prediction of multicomponent mass transfer coefficients is of questionable accuracy. These facts prompt the recommendation that columns modeled with the mass transfer approach be checked against an ideal stage model with an expected efficiency until sufficient experience with the particular application is achieved.

**Conclusions**

When performed properly, the ideal stage, ideal stage - kinetic, mass transfer, and mass transfer - kinetic approaches as implemented in ProMax 4.0 can calculate accurate results for a variety of separation processes with and without reactions. The ideal stage approach can be used initially to determine appropriate equipment sizes and operating conditions. More detailed studies can be performed using the ideal stage approach, the mass transfer approach, or both.

The mass transfer approach requires more equipment design details and does not make use of overall efficiencies or HETP’s. More detailed composition and temperature profiles are produced by this method at the expense of longer calculation time. The mass transfer approach may appear more predictive in nature, but is not necessarily more accurate. It relies on more parameters that must be estimated using correlations for mass transfer coefficient, heat transfer coefficient and others. Many of these mass transfer parameters are of limited accuracy but also may be of limited sensitivity. Both techniques are useful tools in process simulation.

For more information about this study, see the full article at www.bre.com/support/technicalarticles

ProMax® process simulation software by Bryan Research & Engineering, Inc.

Engineering Solutions for the Oil, Gas, Refining & Chemical Industries
outlet temperature and tower stripping steam rate.

At this refinery, replacement of the atmospheric tower trays resulted in a predicted increase in kerosene and diesel yield by a total of 3.1 LV% of crude. Additional profits from this minor cost improvement are roughly $8.3 MM/year, based on this refiner’s estimated diesel recovery incentive of $30/bbl.

An additional benefit to replacing the trays was the reduction of the vacuum tower off-gas by a factor of 2.3, which significantly unloaded the refiner’s vacuum tower jets and improved vacuum, which allowed for increased gas oil recovery. The new atmospheric tower trays reduced the amount of lighter range material being sent to the vacuum tower, which relieved choking of the vacuum transfer line. Further modifications require a unit shutdown to improve the efficiency of the tower wash section internals.

Another modification that can be considered for the wash oil section is to replace the trays with a packed bed. Since wash trays require relatively high wash rates to de-entrain the vapours moving up the atmospheric tower from the flash zone, this option is best suited to atmospheric towers suffering from high overflash and subsequent loss of distillate to AGO range material. A packed bed allows for lower wash oil rates compared to trays, which in turn can minimise the loss of distillate and gas oil material in the overflash. For an existing tower, structured packing can increase the number of theoretical stages and improve fractionation, which can be advantageous if space is a concern. A packed bed of reduced diameter (in an internal cylinder) can further reduce wash oil requirements. The preferred combination for the wash bed is a combination of structured packing over grid. Any carefully vetted modification made to the wash oil section that results in reduced wash oil rate helps to minimise losses of distillate range material from the bottom of the atmospheric tower, which is critical for crude units that do not have distillate recovery in the vacuum tower section.

### Atmospheric tower pumparound modifications

Evaluation of a tower’s pumparound section requires thorough review of the crude unit as a whole, due to the complex interaction between the atmospheric tower and the preheat train exchangers and, in some cases, pumparound exchangers that are used as heat or reboiler sources for other towers. Generally, increased pumparound duty results in increased energy imparted to the cold crude charge, which increases heater inlet temperature. For heaters that were previously at their limit, the outlet temperature can then be raised to increase lift in the tower which can be used to recover more distillate. The effect of increased pumparound rates within the tower is that internal reflux will increase below the pumparound, which helps sharpen fractionation in this section, but decreases fractionation above the pumparound where reflux decreases due to the extra heat removal below. The first article of this series discussed the benefits of optimising atmospheric tower pumparound rates and included a case study demonstrating how, in one refinery, even small operational adjustments to the AGO and diesel pumparounds improved diesel yield and refinery profits.

Some refineries may have one or more equipment constraints which limit their ability to adjust tower pumparound rates. Equipment limitations can range from flooding (tower capacity), insufficient heat

<table>
<thead>
<tr>
<th>Atmospheric tower product flow rates, % change from base case</th>
</tr>
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<tbody>
<tr>
<td>New wash and stripping section trays</td>
</tr>
<tr>
<td>Atm tower products change in yield, %</td>
</tr>
<tr>
<td>Naphtha</td>
</tr>
<tr>
<td>Kerosene</td>
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<tr>
<td>Diesel</td>
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<td>AGO</td>
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<td>Kerosene + diesel</td>
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*The baseline AGO flow measurement was essentially zero. The improvements shown represent AGO yields ranging from 0.3 LV% to 3.2 LV% of crude charge rate.
removal (heat exchanger performance), and/or flow limitations (pump capacity). Lower cost pump-around modifications may include equipment rerate at higher design conditions, heat exchanger retube, or a new pump impeller. More extensive modifications may also include pump or heat exchanger replacement, or modifications to the tower internals in the pump-around section. It is important to review the changes and how they impact the rest of the crude unit, keeping in mind that the modifications should help the refiner achieve the end goal of increased distillate yield or capacity without sacrificing performance within the unit as a whole.

**Atmospheric tower overhead system modifications**

The atmospheric tower overhead system plays an important role in distillate yield. Minor changes to reflux rate or temperature can affect fractionation and subsequent distribution of the side cuts. The ability to maximise distillate production by means of increasing the reflux rate and lowering the overhead temperature to shift naphtha end range material into light distillates is typically limited by overhead condensing and pump capacity. Furthermore, care must be taken to avoid operating below the water dew point, which can increase localised corrosion and fouling in the overhead exchangers and on top tower trays due to acids and salts which concentrate in the first drops of water.

Lower cost upgrades to the overhead system may include rerated equipment, a bundle retube, or a new pump impeller or motor. More substantial capacity improvements may include replacement of exchangers, addition of air coolers, adding reflux or distillate pump services into independent operation, or installation of additional or larger reflux/distillate pumps. With sufficient condensing capacity available to reduce the reflux temperature, and with considerations made to avoid tower overhead system corrosion, a refiner can capitalise on increased distillate yield.

Any review that aims to minimise corrosion issues in the overhead system should begin at the desalter make adjustments to the overhead’s cutpoint in order to achieve increased distillate yield.

**Atmospheric heater and preheat train modifications**

For many refiners, the limiting piece of equipment in the preheat train is the atmospheric heater. Heaters are often run at or beyond their design limits, and any way that a refiner can unburden this key piece of equipment will significantly impact crude unit operations. The goal is to maximise the heating duty that is provided by the other equipment in the preheat train so that an increased heater inlet temperature with the same heater outlet temperature (lower furnace duty) or increased heater outlet temperature (constant furnace duty) can be realised. Optimising the balance of heat duty provided by the preheat train and by the atmospheric heater is often limited by preheat train capacity, atmospheric transfer line or tower inlet device capacity, atmospheric tower pump-around exchangers or overhead condensers, or fuel quality at the heater itself.

Potential preheat train modifications include many of the topics previously discussed, such as exchanger modifications (adding or relocating surface area, changing the order of heat sources, or balancing flows), pump modifications (new impeller or motor), or new, larger piping or equipment altogether. Some consideration must be made when assessing the preheat train as an integrated system. For example, adding a parallel heat exchanger reduces velocities in adjacent exchangers, which accelerates fouling, thereby reducing overall heat transfer and heat exchanger performance. The performance of preheat train heat exchangers may also be reduced when operating exchangers designed for two-phase flow below their vapourisation design basis, as lower fluid velocities result in reduced heat transfer coefficients. An improved crude preheat design can be achieved with simulation and a thorough understanding of the temperatures and duties of the process streams available for crude preheat. In some cases, a pinch study of the crude preheat train may be justified.

In addition to preheat train modifications, there are changes that can be made to the heater itself. Low cost options may include a review of the burner management system, fuel gas system, and other heater controls to ensure optimum operation, or burner elements may need to be replaced. A larger investment might include retubing the heater for increased capacity and surface area, but this would be subject to the heater’s permit limitations. Then, having unburdened the heater with preheat train or heater modifications, the refiner gains flexibility for future operations. The refiner may choose to increase
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Energy consumption?

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heater firing to raise the atmospheric tower flash zone temperature and lift more diesel. Alternatively, the refiner may choose to increase the crude charge while maintaining the same heater outlet temperature. It is important that the designer considers the preheat train modifications and the heater modifications together, while also considering future operational plans, in order to optimise the whole system for increased distillate yield.

Atmospheric preflash tower

A preflash tower is used to remove lighter material from the crude before it reaches the atmospheric tower. The overhead product and side draw streams may be bypassed around the atmospheric heater and tower and routed to downstream units for further processing. This configuration allows the refiner to unload the atmospheric heater and tower, which can increase distillate recovery. A preflash tower can suffer from some of the same capacity or heat removal issues that the atmospheric tower often sees, so the debottlenecking tactics are similar and include strategies such as stripping steam and operating pressure optimisation, retraying the tower with increased tray spacing or with high capacity trays, or expansion of overhead condensing capacity. More significant modifications include replacing an existing preflash tower with a larger tower, or installing a new preflash tower and auxiliary equipment if the system does not already exist.

If the crude unit does not currently include a preflash tower, the addition of such a tower could help to substantially increase distillate yields. A preflash drum is also an excellent option to consider for a refiner who desires a preflash system to debottleneck the crude unit but does not wish to immediately invest the capital required to install an entire tower and its auxiliary equipment. The drum serves as single stage flash, the vapour from which must be routed to the atmospheric tower for further fractionation. The flashed crude exits the bottom of the preflash drum and is routed to the atmospheric heater. The refiner has the option to convert the system to a preflash tower in the future, which would include the auxiliary equipment and may allow the overhead vapour and/or a side draw stream to bypass the atmospheric tower altogether and be routed directly to downstream processing units.

In one US refinery, the authors designed a new atmospheric preflash tower as part of a crude unit revamp which increases middle distillate production by 25%. This crude unit expansion project is driven by new crude opportunities which have more naphtha and middle distillates than current crude slates. The refinery’s desire to process lighter crude necessitates capacity improvements in the areas being overloaded by the new crude, which ultimately will allow for an increase in overall crude unit capacity. Thus, the recommended modifications will bring flexibility to refinery operations and allow for increased distillate production either by processing inherently lighter crude slates (such as tight oils) or by increasing the regular crude charge by roughly 30% compared to current operation.

In order to handle the lighter crude and increased throughput, this debottlenecking project includes a number of modifications requiring significant capital investment, including new exchangers in the preheat train, and a new preflash tower with overhead system. A simulation modelling the new crude slate showed severe flooding in multiple sections of the atmospheric tower and limited heat removal capacity.

The preflash tower affords increased separation capability for the crude unit and was less costly than installing a new larger atmospheric tower with more overhead condensing and pumparound capacity. Additionally, stripping steam was added to the new preflash tower which recovers some of the lighter material that would otherwise be sent to the atmospheric tower. This saves adding additional condensing and pumparound capacity to the atmospheric tower. The preflash tower will be installed at the end of the hot crude preheat train before the atmospheric heater.

Modifications to the existing atmospheric tower include increased capacity of the diesel packed bed. The structured packing in the diesel pumparound bed will be replaced with a higher capacity type to avoid flooding in this tower section. One tower cost modification, a new kerosene pumparound draw and exchanger, was evaluated and also incorporated into the revamp project. The modelling work for this modification showed that the new pumparound vs crude exchanger could reduce the charge heater duty by 13%.

At this refinery, the 25% increase in middle distillate products (kerosene and diesel) amounted to significantly increased profitability with a very short payback period.

Conclusion

The demand for diesel continues to rise, as does its price incentive over gasoline, and refiners are wise to consider making capital investments to increase distillate yield. The decision for which capital modifications to pursue depend on many factors unique to each refinery and include examination of available crude slates, product strategy, unit configuration, and equipment capabilities, though economics ultimately govern the decision. Once a refiner has exhausted zero capital opportunities by optimising existing crude unit capability, attention should be turned to capital projects that provide great opportunity for a large return on investment.

A simulation matched and tuned to plant operation is key for determining where the atmospheric tower is limited and for exploring the refiner’s options for upgrades. All areas of the atmospheric tower and its auxiliary equipment should be analysed thoroughly, including stripping steam rates, tower flooding, heat removal capabilities, operating pressures and temperatures, wash oil, pumparounds,
overhead system, and the preheat train including the atmospheric heater and preflash tower. Modifications to these subsystems can range from relatively inexpensive, such as replacing a pump impeller, to moderately priced, such as new tower internals or an additional exchanger shell, to major capital expenditure, such as major new equipment. Several examples were presented, showing how profitability was improved at several refineries. The authors have analysed atmospheric tower systems at numerous refineries and recommended modifications which have resulted in millions of dollars per year of increased profits. Modifications to the vacuum tower, which require a future article to fully address, represent another piece to maximising the refiner’s distillate yields. The current and future distillate premiums over gasoline present other significant unit configuration changes as compared to the historic crude and vacuum design intended to maximise gasoline instead of distillate yield. With the increased industry focus on distillate production, a refiner has a number of options across a range of price points to help him increase diesel recovery and maximise product profitability.

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ITW Innovative Technologies Worldwide

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Advances in processing high naphthenic acid crudes

High naphthenic acid crudes are cheaper and calcium removal aids and corrosion protection methods allow refiners to increase margins with better crude treatment

PARAG SHAH, MAHESH SUBRAMANIYAM, JAMES ONDYAK, JAMES NOLAND and INDIA NAGI-HANSPAL
Dorf Ketal

The corrosivity of naphthenic crudes raises challenges in refining, therefore naphthenic crudes are sold at a discount. Some of these crudes also contain oil soluble calcium naphthenate. The presence of calcium in naphthenic crude can lead to decreased desalter performance, and high calcium in the resid can affect coke quality, resid fuel oil quality and FCC catalysts, and can aggravate fouling. Relative to naphthenic acid crudes with low calcium, the presence of calcium results in additional crude price discounts. Heavily discounted naphthenic crudes are attractive for increasing refiner margins, but challenging for economic and reliable refining.

It is estimated that worldwide production of crudes containing high levels of naphthenic acids will increase almost four-fold, from 1.2 million b/d in 2000 to 4.5 million b/d in 2020. This article focuses on the category of high naphthenic acid crudes which also contain calcium. The authors present new chemistries for calcium removal and corrosion protection which reduce the risk to refiners from the two prevalent challenges in these crudes.

Calcium removal
Calcium is present in many crude oils in the form of brine soluble calcium salts that are removed within the desalter. However, in recent years the content of oil soluble calcium naphthenate in crude blends has increased in oils from the North Sea, West Africa and China. Calcium naphthenate is not water soluble and releases oil soluble naphthenic acids if treated with aqueous acid. The latter causes downstream corrosion problems in areas of high temperature. Crudes that contain calcium naphthenate include Doba, Kuito, Heidrun, Ciao Fao Dien and Shengli (see Table 1).

Calcium naphthenate tends to accumulate at the interface within the desalter. This results in water carry-over, and increased oil in brine has a negative impact on the wastewater treatment plant. Most refineries cannot afford to have an extra load on the wastewater treatment plant and, with more stringent environmental regulations, treating this brine can be a severe issue.

West African Doba crude sells at an attractive price, but it presents significant potential processing challenges due to a calcium content which averages over 200 ppm. Traditional design and process chemistries for desalting equipment on average can remove only approximately 15% of the calcium. Assuming 50% distillate, this means 340 ppm of calcium will be carried downstream in the resid which will affect coke quality, resid fuel oil quality and FCC catalysts, and will aggravate fouling. Dorf Ketal has developed three new calcium removal additives (CRA, see Figure 1) and has demonstrated

| Figure 1 Functionality and advantages of Dorf Ketal’s CRAs |

| Acid based calcium removal aids | Acid-free calcium removal aid |
| CRA-1 advantages | CRA-2 advantages |
| - Forms water soluble calcium salts | - For sour and heavy crude (high H₂S) |
| - Low oil solubility | - Forms water soluble calcium salts |
| - Includes corrosion and scale inhibitor to protect brine system | - Low oil solubility |
| - Biodegrades easily | - Includes corrosion and scale inhibitor to protect brine system |

| Advantages | |
| - Acid-free | |
| - Requires no separate corrosion inhibitor or scale inhibitor | |
| - Forms water soluble calcium adduct | |
| - Biodegrades easily | |

**Calcium naphthenate containing crudes and their properties**

<table>
<thead>
<tr>
<th>Crude</th>
<th>Country</th>
<th>API°</th>
<th>BS&amp;W, vol%</th>
<th>Sulphur, %</th>
<th>Asph., %</th>
<th>TAN, Mg KOH/g</th>
<th>Ni, ppm</th>
<th>V, ppm</th>
<th>Fe, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuito</td>
<td>Angola</td>
<td>19.7</td>
<td>0.30</td>
<td>0.05</td>
<td>1.87</td>
<td>2.41</td>
<td>43.8</td>
<td>38.7</td>
<td>48.5</td>
</tr>
<tr>
<td>Doba</td>
<td>Chad</td>
<td>21.1</td>
<td>0.50</td>
<td>0.12</td>
<td>0.06</td>
<td>5.18</td>
<td>9.38</td>
<td>0.48</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 1
brine. Desalted crude treated with these products typically contains so little calcium (less than 10% of inlet crude) that it does not cause downstream problems. The acid-free CRA forms a calcium adduct that is water soluble, biodegradable and non-corrosive. It does not require supplemental addition of a corrosion inhibitor or scale inhibitor.

**Case study 1**

An Asian refinery processing a heavy and sour crude blend demonstrates the benefits of using the correct calcium removal agent. This particular parcel of Doba had >200 ppm calcium in the crude. The refinery evaluated a competitor product against Dorf Ketal’s. The difference in calcium removal efficiency and oil content in brine was significant (see *Figures 2 and 3*). Dorf Ketal’s CRA-2 was selected for this crude blend and essentially eliminated effluent treatment plant overloads even with relatively high percentages of Doba in the blend. Higher calcium removal resulted in better coke quality, improved resid fuel oil quality, less FCC catalyst poisoning and a reduction in downstream fouling.

**Case study 2**

An Asian refinery processing Ciao Fao Dien is another situation where Dorf Ketal’s chemistry increased calcium removal. The crude’s properties are shown in *Table 2*.

The step-by-step reaction for the organic acid contained within CRA-2 is that it sequesters calcium naphthenate from the crude to distill overhead and cause further corrosion problems. In either case, the acid treatments release naphthenic acids back into the oil.

To avoid the problems experienced with such treatments, Dorf Ketal’s CRAs include two which are acid based formulations and one which is acid free. The acid based products are water soluble, organic acid based CRAs that hydrolyse calcium naphthenate to form water soluble calcium salts, which are removed via the desalter.

### Ciao Fao Dien crude properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>0.9199</td>
</tr>
<tr>
<td>API°</td>
<td>22.3</td>
</tr>
<tr>
<td>Total sulphur, wt%</td>
<td>0.18</td>
</tr>
<tr>
<td>BS&amp;W, vol%</td>
<td>0.10</td>
</tr>
<tr>
<td>TAN, mg KOH/g</td>
<td>2.3</td>
</tr>
<tr>
<td>Calcium, ppm</td>
<td>150</td>
</tr>
<tr>
<td>Viscosity @ 40°C, cSt</td>
<td>65.42</td>
</tr>
<tr>
<td>Filterable solids, ptb</td>
<td>16.0</td>
</tr>
<tr>
<td>Conductivity @ 1000 ppm in Isopar L, ps/m</td>
<td>5000</td>
</tr>
<tr>
<td>Salt, ptb</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Table 2*
reaction with the acid group of CRA-2 that forms a water soluble salt, which is easily removed from the desalter. Equilibria favour the acid group of CRA-2 over naphthenic acid. Naphthenic acid is soluble in the oil phase and hence will pass along with the crude to a downstream unit which is protected by high temperature corrosion inhibitor (HTCI). Low pH is expected downstream of acid injection; this was taken care of by the water soluble inhibitor present in CRA-2. Table 3 shows the performance of Dorf CRA-2 during processing of Ciao Fao Dien crude.

The Asian refiner achieved more than 75% calcium removal with CRA-2 and experienced no adverse effect in desalter downstream system or desalter performance.

Naphthenic acid corrosion protection
Crudes containing high levels of naphthenic acid (high TAN crudes) can cause severe corrosion at high temperatures (240-400°C). Total acid number (TAN) is a method for measuring the acidity of naphthenic acids in oils that are corrosive at high temperature, although some other naturally found components in crude oil can interfere.

There are three primary ways to manage the risk to capture the economic benefit of high TAN crudes:

- Blend down: determine the TAN limits of the existing metallurgy and flow characteristics and consistently operate at a safe limit without metallurgical modifications or corrosion inhibitors
- Metal up: invest in metallurgy and increase TAN limits and consistently operate at that new limit.
- Prevent: invest in corrosion inhibitors and increase TAN limits, and consistently operate at that

Table 3 shows CRA-2 performance.

<table>
<thead>
<tr>
<th>Date</th>
<th>CFD in blend, %</th>
<th>Ca in feed, ppm</th>
<th>Ca removal efficiency, %</th>
<th>Salt removal efficiency, %</th>
<th>Dehydration efficiency, %</th>
<th>Oil in brine, ppm</th>
<th>COD, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalter set</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Brine-ETP</td>
</tr>
<tr>
<td>KPI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>3.1</td>
<td>5.8</td>
<td>80.00</td>
<td>90.59</td>
<td>96.07</td>
<td>96.22</td>
<td>95.04</td>
</tr>
<tr>
<td>Day 2</td>
<td>3.1</td>
<td>8.5</td>
<td>80.00</td>
<td>90.59</td>
<td>97.07</td>
<td>96.22</td>
<td>96.10</td>
</tr>
<tr>
<td>Day 3</td>
<td>5.0</td>
<td>8.4</td>
<td>76.19</td>
<td>78.57</td>
<td>96.20</td>
<td>95.23</td>
<td>95.04</td>
</tr>
</tbody>
</table>

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new limit within the existing metallurgy. Incrementally invest in metallurgy when the cost is justified in terms of reduced chemical and monitoring costs.

The return on incremental investment in metallurgy requires significant capital expenditure and long payback periods which must also account for the cost through lost opportunity of waiting for a planned shutdown to install the metallurgy. An investment in a chemical solution has an immediate return on investment. Many factors can affect chemical costs, but generally these costs can be estimated to be 2-6% of the crude discount.

Historically, refiners have preferred to use metallurgy to increase TAN limits. However, new chemistry based upon technical insights into the limitations of current corrosion inhibitors has been developed by Dorf Ketal. Tanscient is proving to be a safer and more reliable corrosion inhibitor.

**Corrosion mechanism and protection**

The generally accepted mechanism for naphthenic acid corrosion of steel in the presence of sulphur is described in terms of diffusion through a porous, metal-deficient iron sulphide scale. Five steps have been identified for this type of naphthenic acid corrosion:

- Adsorption of naphthenic acid on the scale
- Diffusion of naphthenic acid through the scale to the base metal
- Reaction of naphthenic acid with iron to form ferrous naphthenate
- Diffusion of ferrous naphthenate to the scale’s surface
- Desorption of the ferrous naphthenate from the scale’s surface

Simultaneously, reactive sulphur compounds are being catalytically decomposed by iron on the scale’s surface, creating additional scale and scale defects. The net effect is that metal is lost from the steel surface into the bulk liquid while leaving the metal surface with a weak, stress-sensitive sulphide scale.

HTCI are designed to deliver phosphorus to provide polyphosphate corrosion protection. The attributes of the ideal HTCI are:

- Oil solubility: a homogeneous solution that ensures even surface distribution of P
- Thermal stability: ability to deliver the same active form of phosphorus to all treated surfaces
- Surface adsorption: possesses a strong affinity for wall surfaces
- Surface reaction: $(POx)$ released to form iron polyphosphate.

These attributes are the minimum requirements for effective corrosion protection. Increasing the safety of corrosion protection, the product must also be:

- Low or neutral in acidity: acidity is a key factor in the handling and delivery via quills into the process stream.
- Free of insoluble foulants: degradation of the delivery chemistry to form P precipitants increases the risk of downstream fouling
- Phosphorus efficient: over-dosing HTCI feed to compensate for thermal instability increases the risk of downstream impact.

**Tanscient’s thermal stability**

Competitive corrosion inhibitors are acidic monoesters or diesters
synthesized from blends of commercial alcohols. These inhibitors are thermally unstable and lack oil solubility. They are also highly acidic which complicates delivery to process streams and can break down sulphide scales. Tanscient is a polymeric phosphate triester with a synthesized custom alcohol which increases thermal stability and oil solubility. Ethoxylation of the phosphate ester to a triester renders it low in acidity which means it is easier to feed and does not attack the protective layer formed at the metal surface.

The difference is thermal stability; Table 4 compares Tanscient to a conventional phosphate ester and a thiophosphate.

Figure 4 shows that the phosphate ester loses over 50% of its phosphorus within the first five minutes of exposure to high temperature and the thiophosphate loses 50% within approximately 30 minutes. Conversely, thermally stable Tanscient retains over 90% of its phosphorus after two hours.

Performance in corrosion protection
Tanscient outperforms conventional HTCI products in both passivation and maintenance dosages of phosphorus. Figure 5 compares it with a traditional phosphate ester and a thiophosphate in a four-hour static test under severe conditions – 11.3
TAN at 290°C (554°F) with a baseline corrosion rate of 436 mpy. Dosages here are much higher than are required in field conditions; the test is designed to illustrate the relative difference in phosphorus efficiency. The x-axis shows different levels of phosphorus tested and the y-axis shows the percentage reduction in the baseline corrosion rate. Comparing Tanscient (1.2% phosphorus) at 3.6 ppm with the traditional phosphate ester (7.5% phosphorus) at 13.9 ppm, Tanscient has better protection with 75% less phosphorus. Compared with the thiophosphate product, Tanscient at 1.8 ppm has slightly better corrosion protection at 50% less phosphorus.

The corrosion performance shown in Figure 6 demonstrates that Tanscient recovers corrosion protection at much lower dosages should passivation be lost. The baseline (untreated) corrosion rate is 59.6 mpy. The competitive phosphate ester requires 13.5 times more phosphorous to achieve the same 5 mpy to 6 mpy. If a plant loses passivation, Tanscient is able to recover it with far lower dosages of phosphorus.

Figure 7 shows that Tanscient is less sensitive to decreasing passivation dosages than competitive phosphate esters. These results are from a short dynamic test designed to show the efficacy of passivation dosages under stress conditions. Passivation is done over a four-hour period and the passivated coupon is then exposed to 5 TAN at 345°C (653°F) with a product dosage of 50 ppm, also for four hours. Maintenance dosages and test conditions are constant; the only variable is passivation dosage. Product dosages are expressed as ppm phosphorus. In all tests, the dosages of Tanscient based on phosphorus are 1/6 the dosages of phosphorus for the traditional phosphate ester. In all cases, the corrosion rates on Tanscient are lower which means passivation is stronger at 1/6 the phosphorus level.

Risk of downstream fouling
Phosphorous fouling in the crude column leads to increased tower pressure drop and the potential to reduce throughput. This fouling potential has been recognised by refiners, downstream equipment suppliers and trade associations. The Canadian Association of Petroleum Producers has established a specification of 0.5 wppm volatile phosphorus in response to a phosphorus fouling study conducted by the Canadian Crude Quality Technical Association.

Fouling is not only limited to the crude tower. It can also be problematic in pumparound circuit exchangers and in tower beds where coking can be accelerated by high temperatures resulting from heat exchanger fouling.

If an iron phosphate scale with poor stability is formed by traditional acidic phosphate based chemistry, it can become dislodged from metal surfaces subjected to high velocities and wall shear stress. This dislodged scale fouls the heat exchangers and reduces heat transfer rates.

Hydrotreaters are becoming more common as a method for refiners to meet fuel specifications brought on by more stringent environmental regulations. High phosphorus has the potential to foul hydrotreaters which can lead to decreased run lengths. Additionally, phosphorous can also lead to impairment of hydrotreater catalysts, resulting in increased replenishment of fresh catalysts.
Changing perceptions
The incremental risk of phosphorous fouling from the inefficiency of conventional, thermally unstable acidic phosphate esters has been a major factor in limiting the use of chemical corrosion inhibitors. Tanscient is new chemistry that achieves the required corrosion protection at treat rates of 0.1 to 0.5 ppm phosphorus, which is up to 80% less phosphorus than in conventional phosphate esters. This high phosphorus efficiency is providing refiners with a safer option for corrosion protection and is changing refiners’ perceptions of HTCIs.

Conclusion
Integrating opportunity crudes into a refinery’s crude slate is an accepted strategy to drive incremental margin improvement. High naphthenic acid crudes present calcium removal and corrosion protection processing risks which has limited incremental profit improvement from these crudes. Dorf Ketal’s Calcium Removal Additives and Tanscient HTCIs are reducing process risks and providing refiners with safer, more reliable and less complex chemistry to increase high naphthenic acid crudes in their crude slate.

TANSIENT is a trademark of Dorf Ketal.

Reference
1 Study on oil refining and oil market prepared by Purvin and Gertz Inc. for the European Commission.

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Johnson Matthey is a global supplier of market leading hydrogen plant catalysts, FCC additives, technologies and services for the oil refining industry.

At Johnson Matthey we are committed to helping our customers find solutions to their toughest challenges and offer a full spectrum of value added products and services to improve the performance and profitability of their processes.
Seven rules of sedimentation in hydrocracking

Guidelines to mitigate sedimentation fouling in heavy sour crude processing together with case studies illustrating how the improvements are captured

SCOTT SAYLES, ROBERT OHMES and RICK MANNER
KBC Advanced Technologies

Conversion of heavy oils is still a major economic consideration for refiners around the world. Recent discoveries of light oil in North America have reduced the emphasis on heavy oil conversion processes but the balance of crudes being processed still contains a significant heavy crude fraction. One of the processes that is fundamental to upgrading heavy sour crude is the ebullated bed and slurry hydrocracker. One area of operational challenge is the formation of a solid phase that incurs fouling of equipment. The formation of the solid phase is commonly referred to as sedimentation. Sedimentation is difficult to define and so is consensus on theory, composition and the behaviour that causes its formation. Occurrence is verified by unit fouling, resulting in:

• Short runs for equipment clean out
• Loss of exchange performance
• Ebullation difficulties
• Limitations to unit performance.

Testing methods are solvent extraction based and are a reasonable way to monitor sedimentation but are not useful to predict its occurrence. The following ‘rules’ use typical methods to determine performance and provide guidance. The rules provide a basis to reduce sedimentation and improve unit performance.

Unit description

The ebullated bed and slurry hydrocracking processes utilise elevated temperatures and pressures to convert vacuum residua to lighter products. The ebullated bed unit uses a fluidised bed of catalyst with the ability to replace the catalyst on-line, while the slurry reactor has a continuous catalyst with the feed as a slurry through the reactor. The reactor configuration for an ebullated bed unit is shown in Figure 1. An ebullated bed design is shown in Figure 2 with locations for potential improvements indicated. These changes will be discussed, as well as how the improvements are captured using case studies.

Evaluation methodology

Understanding of the potential for sedimentation in a given unit configuration requires knowledge of the reaction chemistry, process design and operating goals. Hydrocracking residua chemistry is a function of thermal conversion. The catalyst’s role is to saturate the thermally cracked product. The reaction mechanism then is: first crack, then saturate. This leaves the process subject to a requirement to achieve close contact between the catalyst, oil and hydrogen. The evaluation of sedimentation is based upon experience and an understanding of the thermal cracking functionality as the determining factor in overall conversion.

Rule 1: reactor temperature

Increased temperature increases sedimentation. Options are available to achieve higher conversion without increased sedimentation and are affected by keeping reactor temperatures low. For example, recycling the vacuum residua allows higher conversion at lower reactor temperatures and lower sedimentation. Supporting observations are:

• Sedimentation increases as reactor temperature increases for constant space velocity
• Decreased reactor space velocity at the same reactor temperature decreases sedimentation
• Thermal kinetics controls the hydrocarbon conversion, not hydrocracking; this leads to production of unstabilised heavy streams that contribute to sedimentation
Rule 2: incompatibility

Hydrocracked products are incompatible with each other and form sediments. Mixing light hydrocracked products with heavy results in more sedimentation:

\[ \text{Light} + \text{Heavy} = \text{Sediment} \]

or

\[ L + H = S \]

For example:

\[ (0\% \times 1000^\circ F - ) + (100\% \times 1000^\circ F + ) \] less sediment

\[ (50\% \times 1000^\circ F - ) + (50\% \times 1000^\circ F + ) \] more sediment

Applying the rule indicates a light oil to quench the vacuum tower bottoms potentially creates sediment or poor vacuum tower fractionation may increase sedimentation.

HPS hydroclones

Removing light entrained gases from the high pressure separator (HPS) bottoms liquid reduces sediment. Rapid separation of the gas from the liquid can be accomplished using hydroclones in the hot separator. An example of a hydroclone from EGS Systems, Inc is shown in Figure 3.
The UOP Uniflex™ Process can double the diesel yield of other residue-upgrading technologies, helping maximize production and profits from every barrel.

Get the most from every barrel. The Uniflex Process is a high-conversion, commercially-proven technology that processes low-quality residue streams into high-quality distillate products—leading to refinery margin increases of 60-100%. Simply put, with the Uniflex Process from UOP, you’ll turn “bottom of the barrel” into more profit on your bottom line.
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At CRI, we provide catalyst and process solutions tailored for the petrochemical and refining industry. Our technology is an integral part in helping achieve success in a customer's application. Our strengths in R&D, catalyst manufacturing and technical service allow CRI to progress quickly from lab scale to production to customer results. We pride ourselves on developing lasting relationships with our customers through collaboration and successful implementation of catalytic solutions.

It is all part of our commitment to delivering innovation.
Separation efficiency is high and the light ends are removed from the heavy product, reducing sedimentation.

Rule 3: asphaltene conversion
High asphaltene conversion directionally reduces sedimentation, but not always. Sometimes asphaltene conversion removes the sedimentation component from the mix. Other times the partial conversion of asphaltene leaves it prone to sedimentation.

Catalyst effect
Some catalyst are reported to be effective in reducing asphaltenes. In general, lower asphaltene levels seem to relate to lower sediment and have the following effects:
- Lower sediment allows higher reactor temperatures and conversion to the sediment limit (Rule 1)
- Other catalysts have reduced asphaltenes without changing sedimentation.

LHSV effect
Lower liquid hourly space velocity (LHSV) increases asphaltene conversion, allowing higher temperatures and conversion at the same sediment level.

Feedstock
The contribution of feedstock is due to many factors and crudes with the same asphaltenes produce different sediments. KBC uses a statistical correlation for predicting crude’s contribution to sediment.

Asphaltene recycle effect
Recycling unconverted H-Oil bottoms increases conversion and reduces sediment. Demonstrated commercially, conversion reached 80% at reasonable fractionator bottoms sediment. Longer residence time to convert asphaltenes allowed higher conversions.

Reactor design changes were discussed earlier, along with increases in catalyst oil contacting potentially increasing asphaltene conversion and stabilisation with hydrogen saturation. Some catalysts have been reported to improve asphaltene stabilisation.

Rule 4: hydrogen partial pressure
High hydrogen partial pressure (H₂pp) favours saturation, but higher is not always better. The lower H₂pp limit to prevent high sediment is in the range 1600-1800 psia for high conversion units. The controlling factor is not the total pressure but the H₂pp in the reactor mix. Cracked gases are recycled with the ebulliating fluid and reduce the H₂pp unless they are removed in the pan or cup. Oil and gas maldistribution tends to provide high H₂pp in some zones but below the limit in other zones. Design improvements to increase gas and liquid contacting plus removing cracked gas recycle directionally increase the H₂pp and improve reactor performance. As a result, H₂pp levels in the reactor mix above about 1800 psia do not seem to have much of an effect on sedimentation. Improvements to the mix tee, cup design and plenum distribution reduce sediment by lowering the average reactor cracked gas hold-up, allowing higher H₂pp in the reactor at constant total pressure.

Increased metals content in equilibrium catalyst causes coke migration from the catalyst into the bulk fluid
with the ebulbating fluid and reduce the H₂pp unless they are removed in the pan or cup. Oil and gas maldistribution tends to provide high H₂pp in some zones but below the limit in other zones. Design improvements to increase gas and liquid contacting plus removing cracked gas recycle directionally increase the H₂pp and improve reactor performance. As a result, H₂pp levels in the reactor mix above about 1800 psia do not seem to have much of an effect on sedimentation. Improvements to the mix tee, cup design and plenum distribution reduce sediment by lowering the average reactor cracked gas hold-up, allowing higher H₂pp in the reactor at constant total pressure.

Rule 5: coke
Coke particles or pre-coke particles are a contributor to sedimentation. There are two sources of coke particles:
- Catalyst sloughing
- Thermal kinetic reactions

Catalyst coke sloughing
Increased metals content in equilibrium catalyst causes coke migration from the catalyst into the bulk fluid. As the metals increase on the catalyst, the coke and metal equilibrium on the catalyst changes, causing coke to be displaced and leaving the catalyst surface as a microscopic solid. Feedstock changes or changes in catalyst addition can cause the coke to be released. This source of sediment is transitory and difficult to detect as it occurs, but the results are seen by accumulation in downstream vessels.

Thermal kinetic reactions
Thermal reactions have the potential to make a low hydrogen solid or coke:
- Conversion is thermal (Rule 1)
- Thermal conversion making coke is a well known phenomenon
- H₂pp inhibits coke formation (Rule 4)
- But some coke still forms in the bulk fluid as small particles

Coke mitigation
Preventing coke formation is a desirable control technology. Design changes that reduce sedimentation also contribute to coke reduction. Lower temperature is
the primary contributor, with improvements in oil, gas and catalyst contacting being key contributors.

**Rule 6: solubility**
Sediment, once made, is difficult to resolubilise. Rule 2 says sediment is an incompatible material. Rule 5 says that it can also be a coke or coke precursor.

Some incompatible liquid phases can be placed back into solution by using aromatics as a solubiliser. Agglomerated asphaltenes can be dispersed by aromatics, reducing the size of particles in solution, but not dissolving the precipitated solid.

Solids are unable to dissolve back into the liquid using a solubiliser. Coke is an example of a solid that cannot be solubilised and prevention is the desirable control technology.

**Rule 7: aromatics**
Adding aromatic hydrocarbons to heavy product reduces the formation of sediment. Rule 2 says that hydrocracked products are incompatible:

$$L + H = S$$

This relationship can be modified such that:

$$L + H - A = S$$

where A = aromatics

Aromatics in the form of FCC slurry, lube oil extracts and other heavy streams can be used to solubilise incompatible liquid phases and disperse asphaltenes. Areas in the unit that can utilise these include:

- Aromatic quench to reduce the temperature of reacted products in place of hydrocracked product has a twofold effect:
  - Removes the liquid that unstabilises the mixture
  - Stabilises the mixture by adding an aromatic.

  The quantity of aromatics required to offset the effect of lighter hydrocracked products depends on the conversion and temperature levels.

**Case study: mix tee design**
Initially, hydrogen gas and liquid are combined externally to the reactor in the mix tee. The design uses separate oil and gas heaters. The oil outlet temperature is about 400°F (200°C) lower than that of the hydrogen heater and combination takes place in the mix tee. The measured mixture compared to the calculated temperature resulted in a difference of 10-20°F. Thermocouple location and other factors contributed to part of the difference but the primary cause was attributed to the mixer performance. Inspection during turnaround found coke deposits in several areas of the mix tee. A study was commenced to investigate the situation using computational fluid dynamics (CFD) and other techniques.

**No single item reduces sediment completely but, with a mitigation plan, multiple contributors can be reduced**

The design and operation of the mix tee uses the following rules:

- Rule 1: temperature
- Rule 4: H₂pp
- Rule 5: coke
- Rule 6: solubility
- Rule 7: aromatic.

Mix tee design requires a pressure drop high enough to shear the gas into the viscous liquid but not high enough to cause high energy use or the potential to erode the mixer. Low pressure drop allows better use of recycle gas compressor head and prevents damage to the mixer. Revamping existing mixers requires the following performance:

- Durable and reliable
- Redesign keeps these features
- Enhances the capability of the existing design.

The mixer was modified and the improvement resulted in closing the temperature differential to about 5°F. No coke deposition in the system has been observed. The conclusion is that a more uniform mixture was entering the plenum.

**Case study: hydroclones**
An ebullated bed unit was experiencing operational difficulties in the first vessel downstream of the reactors, the HPS. The overhead exchangers were receiving entrained heavy oil and the liquid flow from the bottom contained high levels of entrained light gases. A study was commenced to evaluate the HPS’s performance. The study recommended the installation of hydroclones in the HPS.

Hydroclones in the HPS increase the separation capacity of the vessel and use the following rules:

- **Rule 2: light + heavy = sedimentation**
- **Rule 4: H₂pp**
- **Rule 5: coke**
- **Rule 6: solubility**
- **Rule 7: aromatic.**

KBC provided the design considerations to allow installation of EGS Systems, Inc cyclones in an ebullated bed HPS. The cyclones have been in service for six years and have achieved the design objectives:

- Removes light from heavy, reducing sedimentation
- Removes residua entrainment into overhead exchangers
- Removes entrained hydrogen from bottoms
- Minimises control valve vibration
- Stabilises drum level, allowing faster start-up and better control during operation
- No welding or changes to the vessel
- Design is open at the top and bottom, minimising concerns about catalyst carry-over or internal coking
- Low installation cost.

Disadvantages include:

- Some external coking observed after a two-year run
- Vessel inspection requires removal.

**Evaluation included**:
- Unit simulation in Petro-SIM
- Hazop of major concepts
- Risk benefit analysis
- Selection of preferred design, cyclones
- Installed in one train to demonstrate concept
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The desired levels. This results in higher reactor temperatures at a given conversion. In addition the ebullation pump instability is reduced by the gas entering with the downcomer fluid. The circulation of cracked gases was believed to limit $H_2$ production, increasing sedimentation. The aim was to reduce the reactor cracked gas hold-up by redesigning the cup.

Using CFD techniques, a new cup was designed and the modified cup was put into service six years ago. Commercial data confirm lower gas hold-up and lower temperatures for the same level of conversion.

Conclusions

The seven rules of sedimentation are summarised in Table 1. Provided general agreement is reached on the seven rules, a sedimentation mitigation plan can be developed. The key is to review systems and subject them to the tests or rules discussed here. Those systems having multiple reasons for sedimentation are the priority designs. No single item reduces sediment completely but, with a mitigation plan, multiple contributors can be reduced, resulting in a significant reduction in sedimentation.

References

1. Sayles et al., Unconventional Crude Oil
power costs, and the high degree of spare parts to be kept in stock. The number of cylinders per stage can be reduced.

They show 

(Aerobacter, and Bacillus) and 

(Pseudomonas, and Ferrobacillus sp.) - sulphate reducing bacteria in soil, water and air. They show concerns related to conventional tank cleaning. The pounds of flow by the ratio of molecular weight of air, multiply cracked gas is different from the calculated above by approximately 30%

Table 1

| Sayles, Romero, Understand the differences between thermal and hydrocracking, Hydro. Proc., 9/11.
| Sayles, Bailor, Catalyst addition in ebullated bed units, PTQ, Q2 2005.
| Sayles, Ebullation Factor, Hydro. Eng., 3/06.
| McDaniel et al, AMOCO’s LC-Fining Resid Hydrocracking Yield and Performance


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### Summary of the seven rules of sedimentation

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<tbody>
<tr>
<td>1</td>
<td>Temperature</td>
<td>Yes</td>
<td>Lower</td>
<td>High asphaltene conversion</td>
<td>Mix temperature, plenum, cup</td>
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<tr>
<td>2</td>
<td>Incompatible</td>
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<td>Minimise</td>
<td>None</td>
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<td>Coke</td>
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Catalytic strategies to meet gasoline sulphur limits

Stricter regulations reducing average gasoline sulphur content will require further reduction of FCC gasoline sulphur

PATRICK GRIPKA, OPINDER BHAN, WES WHITECOTTON and JAMES ESTEBAN
Criterion Catalysts & Technologies

The US Environmental Protection Agency (EPA) has finalised new regulations designed to reduce air pollution from passenger cars and trucks. The regulations (commonly referred to as Tier 3) set new vehicle emission standards and lower the annual average sulphur content of gasoline from 30 ppm to 10 ppm (see Figure 1). Additionally, the regulations maintain the current 80 ppm refinery gate and 95 ppm downstream caps. The implementation date is 1 January 2017. These Tier 3 gasoline sulphur specifications are similar to levels already being achieved in California, Europe, Japan, South Korea and several other countries.

Implications for refinery processing
The gasoline pool is composed of gasoline boiling range hydrocarbons from several sources in the refinery. Typical gasoline pool blending components include butanes, ethanol, light straight run naphtha, isomerate, reformate, alkylate, FCC gasoline and hydrocracker gasoline. In addition, purchased blending components may also be present. Most of these components are very low in sulphur (typically <1 ppm) except for the FCC gasoline. Not only does the FCC gasoline have the highest sulphur content, but it is typically also the largest volume component of the gasoline pool. As a result, FCC gasoline sulphur will have to be reduced to 20-30 ppm in order for a typical refinery to meet the proposed Tier 3 regulations.

At present few, if any, refineries are able to blend significant amounts of FCC gasoline into the gasoline pool without employing hydrotreating to reduce sulphur. Options refiners are currently utilising to meet current Tier 2 regulations include:

- Pretreatment of FCC feed: pretreatment reduces the sulphur of the FCC feed, which in turn lowers the sulphur of the FCC products including FCC gasoline
- Post-treat FCC gasoline: post-treatment directly reduces FCC gasoline sulphur
- Combination of FCC feed pretreatment and FCC gasoline post-treatment.

Current unit constraints and relative economics of the available options will determine the technology selection for meeting Tier 3 regulations.

Catalyst developments in FCC pretreatment
To meet the demand for improved catalysts in FCC pretreatment service to meet Tier 2 regulations, Criterion Catalysts & Technologies L.P. (Criterion) developed and commercialised the Ascent family of catalysts with DN-3551 NiMo and DC-2551 CoMo. Criterion has also developed and commercialised the Centera family of catalysts for FCC pretreatment: DN-3651 NiMo and DC-2650 CoMo.

Figure 2 highlights the continuing evolution of FCC pretreatment NiMo catalyst development by Criterion. Refiners were able to take advantage of the increased activity of DN-3551 to meet Tier 2 regulations and still achieve long catalyst life; similarly, the increased activity of the recently commercialised Centera DN-3651 will assist refiners in meeting the proposed Tier 3 regulations.

Criterion’s newest CoMo FCC pretreatment catalyst, Centera DC-2650, is often used in conjunction with Centera DN-3651, especially in lower pressure units to optimise hydrodesulphurisation (HDS) and hydrodenitification (HDN) performance.

These new catalytic developments allow current FCC
pretreatment units to produce lower product sulphur at the same operating conditions and minimise the investments required to meet Tier 3 requirements.

**Capital avoidance from developments in FCC pretreatment**

Many refiners have invested heavily in robust FCC pretreatment units to meet Tier 2 regulations as well as MACT standards for FCC emissions. Leveraging advanced catalyst technologies with existing assets can, in many cases, provide attractive solutions to both minimise capital investment as well as improve refinery profitability. The FCC pretreatment unit plays a critical role in optimising FCC performance. Removal of sulphur from FCC feed improves FCC product quality while the removal of nitrogen and contaminant metals improves FCC catalyst performance and reduces catalyst usage. Additionally, hydrogenation of the FCC feed improves conversion by reducing the concentration of polynuclear aromatic species. In many applications, drop-in catalytic solutions for FCC pretreatment units can achieve higher severity with little to no capital investment and minimal change in cycle life.

There are several key factors to consider when evaluating FCC pretreatment units for higher severity operations:
- Hydrogen availability including recycle gas capacity to account for additional consumption
- Heat balance for operation at higher reactor temperatures
- Cycle life targets
- Current and future capacity targets as it relates to reactor space velocity
- Operating constraints such as fractionation limitations.

**Table 1** is derived from Criterion’s industry-wide database to illustrate a comparative analysis of the performance improvements expected for FCC pretreatment units using drop-in catalytic solutions with Centera products. In addition to product quality improvements, estimated improvements for FCC conversion are provided.

For a medium pressure unit with average feed properties and a typical 36-month cycle life currently producing 1000 ppm product sulphur, the more severe FCC pretreatment operation to produce FCC gasoline sulphur in the 20-30 ppm range requires FCC pretreatment product sulphur to be in the 300 ppm range and when using Centera catalyst, a cycle life of 24 months or more can be achieved. In addition, the product nitrogen is reduced significantly and hydrogen consumption, FCC pretreatment volume gain and FCC conversion are increased.

The improvements in FCC performance and yields from higher severity operation of the FCC pretreatment unit are linked to the increased saturation of polynuclear aromatics. The saturation of aromatic rings in these complex molecules determines both the product distribution and the relative sulphur distribution in the FCC products. In the FCC, aromatic rings do not crack while functional groups attached to the aromatic rings can be removed. The number of unsaturated rings adjacent to each other is critical in determining the boiling range of the final FCC product. Molecules with one ring end up in the FCC naphtha cut, two- and some three-ring molecules go to the LCO cut while most three-ring and greater molecules are either found in the HCO and clarified oil streams or deposit as coke. Saturation of aromatics results in higher value products and greater conversion in the FCC. Saturation of aromatic rings starts from the centre of the molecule with a decrease in relative reaction rate as polynuclear aromatics are hydrogenated.
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  - +44 (0) 203 772 6091 (London)

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The critical operating parameters that influence these reaction rates are hydrogen partial pressure and operating temperature. In order to maximise aromatics saturation for a given unit, it is important to maximise hydrogen purity and hydrogen availability to optimise hydrogen partial pressure, particularly at the reactor outlet. In addition to maximising hydrogen partial pressure, operating temperatures must be increased to maximise saturation. However, saturation of aromatics is equilibrium limited at constant hydrogen partial pressure so there is an optimum temperature range for maximum saturation. This optimum temperature range is often referred to as the kinetic region or the aromatics saturation plateau.

Operating in the kinetic region provides the best quality feed for the FCC.

When evaluating an increase in severity of a FCC pretreatment unit, there is typically a synergy between the additional temperature required and maximum aromatics saturation operating mode. The elevated desulphurisation severity drives the unit closer to maximum aromatics saturation mode, which results in improved yields in the FCC product slate. Additionally, the elevated desulphurisation severity early in the cycle capitalises on the maximum aromatic saturation activity of the catalyst system throughout the cycle which maximises overall yields.

Increased aromatic saturation has an impact on the distribution of the sulphur containing aromatic molecules in FCC products. The following discussion illustrates the impact of FCC pretreatment severity on a typical polynuclear aromatic species and the impacts on product sulphur distribution.

**Untreated feed (no FCC pretreatment)**

For an untreated aromatic molecule, the FCC simply removes the functional group chains attached to the compound and leaves most of the molecule unconverted, resulting in higher coke and or cycle oil yield. This results in higher sulphur in the unconverted cycle oils or higher SOx in the flue gas after coke is burned off the catalyst. There is a low probability of secondary thiophene cracking in the FCC, thus the sulphur in this molecule ends up in the cycle oil or coke. This is illustrated in *Figure 3*.

**Low severity FCC pretreatment**

When the same molecule is treated, but in a low severity operation, the resulting aromatic saturation result is an increase in gasoline yield. But

---

**Figure 3** Impact of untreated aromatic molecule on FCC products

**Figure 4** Impact of low severity aromatic treatment on FCC products

**Figure 5** Impact of higher severity aromatic treatment on FCC products
Catalyst developments in FCC post-treatment
Likewise Criterion has continued the development of FCC gasoline post-treatment catalysts with focus on maximising desulphurisation activity and selectivity with minimal olefin saturation. The company currently produces a Generation 1 FCC post-treatment catalyst that is employed in FCC gasoline post-treatment with a new catalyst in the development stage. The new catalyst is designed for maximum sulphur reduction while minimising octane loss.

The key challenge has been to develop catalyst nanostructures that selectively maximise desulphurisation sites while suppressing olefin saturation, thereby further improving the economics.

Higher severity FCC pretreatment
Increased aromatic saturation by increasing severity in the FCC pretreatment unit converts the polynuclear aromatic (PNA) to a single ring compound. Secondary cracking of the thiophene yields H₂S, which removes the sulphur from the gasoline boiling range. This is illustrated in Figure 5.

This secondary thiophene cracking in the FCC is inhibited by the basic nitrogen in the FCC feed and, in the presence of basic nitrogen, the inhibition decreases the amount of sulphur removed from the gasoline fraction. This is illustrated in Figure 6.

The higher severity FCC pretreatment operation thus provides additional advantages by increasing the nitrogen and basic nitrogen removal from FCC feed. This impacts FCC cracking reactions and influences the distribution of sulphur in the FCC products. Thus, improved nitrogen removal also leads to a reduction in gasoline sulphur.

In conclusion, the increased HDS achieved by increased FCC pretreatment severity along with the higher saturation and denitritication are critical in reducing FCC gasoline sulphur while still achieving reasonable cycle life. Applying best available catalyst technologies opens the door to improved product quality and maximum profitability.

Several US refiners are already using Criterion’s industry leading catalysts to increase severity and are capturing the yield improvements while also producing low sulphur FCC gasoline streams that are suitable for blending to Tier 3 specifications. With the increased severity, the diesel side-stream off the FCC pretreatment unit has, in several cases, been of ULSD quality, because the sulphur atom remains integrated with the aromatic benzothiophene, the probability of secondary cracking is low and it remains in the gasoline boiling range. This is illustrated in Figure 4.

<table>
<thead>
<tr>
<th>Polishing reactor feed properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sulphur, ppmw</td>
<td>159</td>
</tr>
<tr>
<td>Mercaptan sulphur, ppmw</td>
<td>52</td>
</tr>
<tr>
<td>Bromine number</td>
<td>24</td>
</tr>
<tr>
<td>API</td>
<td>47.0</td>
</tr>
<tr>
<td>PINOA analysis, wt%</td>
<td>14.55</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>21.32</td>
</tr>
<tr>
<td>n-paraffins</td>
<td>8.47</td>
</tr>
<tr>
<td>Cyclic olefins</td>
<td>4.62</td>
</tr>
<tr>
<td>iso-olefins</td>
<td>4.37</td>
</tr>
<tr>
<td>n-olefins</td>
<td>2.86</td>
</tr>
<tr>
<td>Aromatics</td>
<td>44.12</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Simulated distillation D-3710C-7890</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP, 5, wt%</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>164</td>
</tr>
<tr>
<td>30</td>
<td>183</td>
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<td>90</td>
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<tr>
<td>99</td>
<td>395</td>
</tr>
<tr>
<td>FBP</td>
<td>438</td>
</tr>
</tbody>
</table>

Figure 6 Impact of basic nitrogen inhibition on FCC products
Selective post-treatment HDS is generally conducted in multiple stage reactors: in the first stage, some diolefins are removed and high mercaptan and high sulphur compounds are converted to heavier sulphur compounds. The effluent is fractionated to produce an olefin-rich light naphtha stream and a sulphur-rich heavy naphtha stream. In the second stage, the heavy naphtha fraction is desulphurised using selective catalysts. Depending on the process employed, effluent sulphur from this section can vary from tens to hundreds of ppm. Post-treatment processing in fixed bed units is employed in some processes to further reduce sulphur content of this effluent.

Catalyst development for the finishing catalyst was conducted at Criterion’s R&D centres, where enhanced experimentation equipment was employed. This experimentation technique allows multiple experiments to be conducted simultaneously, while analysing and statistically organis- ing data, thus enhancing the chances of a significant catalyst development breakthrough. Our focus in the development of this catalyst was to reduce the sites involved in hydrogenation and enhance the sites involved in the direct desulphurisation route. This involved both the development of new support material and enhanced surface metal chemistry to maximise selective desulphurisation, while minimising undesirable reactions.

Table 2 shows the properties of the feed used for post-treatment catalyst testing. This feed was collected from a Gulf Coast refiner and represented feed to a polishing reactor to reduce sulphur content. Table 3 shows the product properties for two catalyst generations collected at various process operating conditions. Various studies were conducted where process parameters such as catalyst temperature, hydrogen partial pressure, gas circulation rate and system pressure were varied over an applicable range. Under all process conditions, the new generation catalyst showed superior activity for sulphur removal and olefin retention compared to the previous catalyst generation.

Conclusion

Proposed Tier 3 regulations reducing average gasoline sulphur content to 10 ppm will require further reduction of the FCC gasoline sulphur. Refiners are currently evaluating their options which include: increasing FCC pretreatment severity or expanding FCC pretreatment assets; increasing FCC gasoline post-treatment severity or expanding FCC post-treatment assets or a combination of the two.

Opportunities exist to minimise or eliminate these investments by use of advanced catalyst technologies to attain the longest possible cycle life at the increased desulphurisation requirements in the FCC pretreatment unit or to reduce the FCC gasoline sulphur in the FCC gasoline post-treatment unit while minimising octane loss.

Several US refiners are already using Criterion’s catalysts to increase severity and are capturing yield improvements while also producing low sulphur FCC gasoline streams that are suitable for blending to Tier 3 specifications.

Further reading


Patrick Griepka is Regional Technical Services Manager for the Americas with Criterion Catalysts & Technologies. With over 25 years of experience, he provides technical support for Criterion’s customers via estimates, design bases, start-ups, unit monitoring, troubleshooting and value creation opportunities, primarily in the NHT, DHT and CFH technology areas. He holds BS and MS degrees in chemical engineering from the University of Missouri – Rolla.

Opinder Bhan is a Senior Principal Advisor in the Catalysis Group at Shell. With over 27 years of experience with Shell, he has spent most of his career in catalyst research and development and is currently working on processes for more efficient removal of sulphur from petroleum feedstocks. He has received over 50 US patents, has commercialised over 20 catalysts, and holds a doctoral degree in chemical engineering.

Wes Whitecotton is Criterion Catalysts & Technologies’ Regional Marketing & Business Development Manager for the Americas. He started his career with Criterion over 22 years ago and focuses on providing business support within Criterion and sales account management to customers via estimates, unit monitoring, troubleshooting and value creation opportunities primarily in refining technology. He holds a BS degree in business.

James Esteban is a Senior Technical Service Engineer with Criterion Catalysts and Technologies, specialising in technical service and solutions for hydrosprocessing applications, and is the global Subject Matter Expert for naphtha hydrosprocessing with extensive experience in hydrosprocessing applications for FCC, FCCP, ULSD, ULSK and naphtha. He holds a BS degree in chemical and petroleum refining engineering from the Colorado School of Mines.
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Tower Technical Bulletin
3-Pass Trays: Profitable niche designs

Introduction
Over approximately 60 years of supplying trays to the industry, Sulzer has found that only 0.5% of those trays have been 3-Pass trays. However, in light of several articles on the topic, there has been a renewed interest in 3-Pass trays.(1,2)

3-Pass trays have an economic advantage over 2 and 4-pass trays because they employ only a single tray layout in any given column section, where 2 and 4-Pass trays have a totally different tray design for the odd and even numbered trays in a tower. Also, 3-pass trays can handle more liquid than 2-Pass trays because of their longer weir length. There is an optimum diameter range for the use of 3-Pass trays. This is between 7’ (2.1m) and 12’ (3.6m) ID. In this range, 3-Pass trays can have sufficient flow path length to allow placement of tray manways on the tray deck where 4-Pass trays cannot.

3-Pass tray application
In 2012, Sulzer provided a set of 3-Pass trays into a 102” (2.6m) ID Refinery Debutanizer Tower. The tray decks employed the UFMTM valve, our latest development in High Capacity/High Turndown tray technology. The plant has been operating successfully with excellent tray efficiency and capacity for 2 years now.

As with all multi-pass designs, once you take the necessary measures to balance the vapor and liquid flows, the number of passes becomes a non-issue. For those in-between applications where weir loads are too high for a 2-Pass tray and the column diameter is too small for a 4-Pass tray, 3-Pass trays can be a reliable and profitable option.

(2) H.Z. Kister and M. Olsson, “Understanding Maldistribution in 3-Pass Trays”, Distillation and Absorption 2010, Eindhoven, Netherlands, September 2010

Design Considerations: Balance is the Key
Knowledge of the column thermodynamic and hydraulic functions is the key starting point. Any problem that develops that does not allow the vapor and liquid to contact each other in the manner for which the device was designed, or keeps the vapor and liquid from separating after contact, will adversely affect column performance. For example, the packing shown below will not provide good flow or vapor/liquid contacting efficiency because some of the packing is blocked off by fouling.

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Reducing vacuum tower pressure

To create a better vacuum the vapour load to the ejector has to be reduced

NORMAN LIEBERMAN
Process Improvement Engineering

In a previous issue of PTQ, we discussed several troubleshooting opportunities in correcting vacuum system ejector and condenser malfunctions. In this article, several field-proven techniques to improve vacuum by process changes are detailed. While none of these techniques are common, they do work and are not proprietary.

Slipping HVGO into LVGO pumparound

The purpose of the LVGO pumparound is to minimise the vacuum tower overhead vapour flow to the vacuum system. The vapour flow from the top of the vacuum tower is proportional to:

\[ \text{Absorption factor} = \frac{L}{V} = \frac{L}{V} \cdot \frac{P_{T}}{P_{V_i}} \]  

where
- \( V \) = Moles of vapour
- \( L \) = Moles of liquid
- \( P_{T} \) = Pressure
- \( P_{V_i} \) = Vapour pressure of the \( i \)th component

The bigger the absorption factor, the lower the amount of vapour to the ejectors. One way to increase the absorption factor is a colder tower top temperature. The other way is to increase \( L \) in the above equation. This can be done in two ways (see Figure 1):

1. Reduce the HVGO pumparound heat duty and increase the LVGO pumparound heat duty. \( L \) in Equation 1 is not the LVGO pumparound rate, but the net LVGO product rate. However, reducing the HVGO pumparound heat duty will also, most likely, diminish the crude preheat. Also, the increase in the top temperature can offset the beneficial effect of the increased LVGO circulation rate. That is, the vapour pressure of the components (see Equation 1) may increase faster than the moles of liquid. Our field experiments have indeed shown that sometimes raising the tower top temperature, by reducing the HVGO circulation rate, improves vacuum, and sometimes it degrades vacuum.

2. Our second method of increasing \( L \) (the LVGO net product rate) in Equation 1 allows for an increase in vacuum, but without loss of HVGO pumparound heat duty and crude preheat. However, this method will not be possible if the LVGO product is flowing to a hydrocracker and the HVGO product is being used as FCC unit feed. However, if this is not the case, and both LVGO and HVGO products are combined, then we have directed a small portion of the HVGO product to the LVGO pumparound return. We have

![Figure 1](image1)

![Figure 2](image2)
This increases $L$, the moles of absorber oil, in the pre-condenser, and thus reduces the moles of vapour ($V$) flowing to the first stage ejector.

However, we have also observed that if the vacuum tower top temperature is raised too far then the pre-condenser outlet temperature will also begin to increase excessively. The net effect is similar to reducing the HVGO pump-around duty too much. That is, the moles of vapour escaping from the pre-condenser will increase as the vacuum tower top temperature is increased too much.

As Figure 2 shows, we have injected a naphtha stream as an absorption oil (akin to the sponge or lean oil in an absorber) to the inlet of the pre-condenser, to increase $L$ in Equation 1. A word of caution: the first time we did this, we unfortunately used a light naphtha product, rather than heavy naphtha or kerosene. The light naphtha injection led to a loss in vacuum, as it largely vaporised in the vacuum tower (see Figure 2), raising the tower top temperature up to a point improves vacuum. The reason for this again has to do with Equation 1. Raising the top temperature increases the moles of heavy naphtha and kerosene (180-240°C boiling range hydrocarbon components) distilled overhead.

We have observed that on most vacuum towers with a pre-condenser (see Figure 2), raising the tower top temperature up to a point improves vacuum. The reason for this again has to do with Equation 1. Raising the top temperature increases the moles of heavy naphtha and kerosene (180-240°C boiling range hydrocarbon components) distilled overhead. A word of caution: the first time we did this, we unfortunately used a light naphtha product, rather than heavy naphtha or kerosene. The light naphtha injection led to a loss in vacuum, as it largely vaporised in the vacuum tower.
the pre-condenser. To avoid the ire of our clients, we now calculate the vapour-liquid equilibrium flash in the pre-condenser before, rather than after, implementing process changes in the field.

The heavy naphtha injected will typically be recycled through the condensate seal drum along with the steam condensate and directed to a downstream hydrotreater without prior prefractionation.

**H₂S extraction from vacuum tower off-gas**

We have often sampled vacuum tower off-gas from the seal drum. Assuming that:

- Air leaks are small (less than 5% nitrogen in the off-gas sample)
- Vacuum tower feed is well stripped for light ends removal (less than 6% propane in the off-gas sample)
- High sulphur crude is being run (1.5-2% sulphur).

Then, the amount of H₂S in the off-gas (on a dry basis) will typically be 30-40 mole%. (Caution: H₂S at a concentration of 0.1 mole% is quite fatal to breathe, so fresh air equipment is advisable when obtaining this sample.)

Extraction of this H₂S with an amine (MDEA) would then reduce the vapour load to the downstream jet by a very large amount, somewhat greater than 30-40%, as the H₂S has a greater molecular weight than steam or air. This can be done as shown in **Figure 3**. The H₂S scrubber depicted would be identical to the now obsolete barometric condenser design.

The author has never actually used amine as an H₂S absorption agent, as suggested here. However, he has used NH₃ in the same manner as the proposed use of the amine. The NH₃ connection was intended as an HCl neutraliser. By using the NH₃ at a rate hundreds of times above that which was intended for HCl neutralisation, the vacuum was vastly improved.

Unfortunately, this benefit only lasted for half a day. That is, until the supply of neutralising NH₃ was exhausted. As the client summarised, “this was a technical success, but an economic fiasco”.

Of course, the off-gas has to be scrubbed with amine regardless, to extract the H₂S, so the use of amine, as opposed to NH₃, ought to be an economically viable project.

**Raising the top temperature increases the moles of heavy naphtha and kerosene distilled overhead**

A safety note: CO₂ will also be extracted by the amine. But CO₂ in the vacuum tower off-gas is an indication of an air leak in the vacuum heater transfer line. This is a serious safety issue because, when vacuum is lost, 400°C resid can, and has, blow out of this leak, auto-ignite, and burn down the vacuum tower. This happened to a vacuum tower that the author revamped in a plant in the Baltics several years ago. CO₂ on the other hand, is just an indication of the thermal degradation of naphthenic acids, which is unavoidable and is not a sign of any avoidable problem.

**Cracked gas evolution in boot**

On some refinery vacuum towers, especially those that lack a boot quench, we have measured by varying the boot level that the non-condensable vapour load due to thermal cracking in the boot may be 30-40% of the total non-condensables.

Reduction of the boot residence time to a minimum is an alternative means to reduce this thermal cracking. This is a less desirable but more cost effective alternative to the boot quench.

There are two approaches to minimising the level of vacuum resid in the boot. They can be used together:

- Control the vacuum tower bottoms pump, not on level, but on suction pressure control (see **Figure 4**). The set point pressure is found by experimentation. It is that pressure below which the pump discharge pressure declines by 0.5-1.0 barg
- Operate both the primary and the spare pumps in parallel. On one unit, the author found that the required suction head to prevent cavitation was reduced from about 4.5 metres to roughly 2.5 metres, when both vacuum tower bottoms pumps were run in parallel.

**Virgin components in the vacuum tower off-gas**

Typically, a sample of gas obtained from the seal drum should have 2-4% propane and 1-2% propylene. If the seal drum off-gas is 8-10% propane and 1-2% propylene, virgin crude components are entering the vacuum tower. Typically, this happens due to:

- Exchanger leaks in the boot quench vs crude preheat
- Exchanger leaks in the HVGO pumparound loop vs crude preheat
- Most commonly, poorly steam stripped crude tower bottoms that are feeding the vacuum tower.

On one plant in Northern Alberta, the author found excessive propane in the vacuum tower seal drum off-gas. Attempts to increase the stripping steam to the upstream fractionator bottoms made the vacuum worse. The problem was the fractionator pressure increased.
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due to a lack of overhead condenser capacity in the fractionator aerial coolers. The higher pressure increased the C₃s and C₄s in the fractionator bottoms. This incident took place with ambient conditions at -20°C.

Steam in heater passes
Most of the cracked gas to the first stage jet originates in the vacuum heater tubes, due to thermal cracking. Especially for vacuum towers equipped with a pre-condenser (see Figure 2), increasing coil steam up to a point will reduce oil residence time in the tubes. This will also reduce cracked gas formation and improve vacuum. The author has had substantial success in increasing HVGO production from bottoms using this technique for a vacuum tower equipped with a pre-condenser in California, but not for towers with a jet upstream of the first condenser.

Too much coil steam will overload the pre-condenser and thus increase both the temperature and gas flow to the lead jet, which will then degrade the vacuum. A typical coil steam rate is 1.5 lb/bbl. However, in practice the author proceeds on a purely trial and error basis. This works well for towers equipped with pre-condensers, but has caused jets to surge on towers without a pre-condenser, as the coil steam is increased past a point.

Conclusion
Frequently, the cause of poor vacuum is not due to any malfunction of the ejectors or condensers. The jets are usually operating on their vendor performance curves. To create a better vacuum, the vapour load to the jets has to be reduced, especially to the first stage ejector. As far as malfunctions of the ejectors and condensers themselves are concerned, we have discussed this in detail in a book on this subject.3

An abbreviated list of these malfunctions is:
- Hardness deposits in the ejector steam nozzles
- Erosion of the threads, where the steam nozzles screw into the body of the ejector
- Wet steam
- Leaking leaf seals in the condensers
- Leaks in the seal leg lines
- Condenser pass partition baffle leaking
- Non-condensable gas recirculation, between parallel ejectors, sharing a common condenser.

References
1 PTQ, Q4, 2014.
3 Troubleshooting Vacuum Systems, Wiley Publications.

Norman Lieberman is a chemical engineer who specialises in troubleshooting refinery non-catalytic process equipment and in retrofit process design. He has taught his Troubleshooting Seminar, which emphasises field observations, since 1983 to over 18 000 engineers and plant operators. The first of his eight books, Troubleshooting Process Operations, has been in print for 35 years. He previously worked for Amoco Oil and the Good Hope refinery. He graduated from Cooper Union in New York City in 1964.
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Pemex has successfully started up a SmartSulf unit treating amine acid gas and sour water stripper gas at a refinery in Salamanca, Mexico. This is the first example of a second generation SmartSulf unit, applying thermoplates for reactor temperature control, and is installed in Pemex’s Ing. Antonio M. Amor refinery.

The technology, acquired by Prosernat in 2014 and developed for many years by German company ITS Reaktor Technik GmbH, targets high efficiency in performance at least investment cost. The Salamanca plant was designed by Worley Parsons under licence from ITS Reaktor Technik and has a nominal sulphur capacity of 80 t/d.

SmartSulf delivers sulphur recovery efficiency in excess of 99.5% from a two-stage Claus unit configuration (one thermal stage and two catalytic stages). The main difference from a conventional Claus configuration, as Figure 1 shows, is the use of isothermal reactors, which enable the second reactor to operate as a dry sub-dewpoint reactor to achieve very high sulphur recovery efficiency. A key benefit of the technology, reflected in industrial feedback, is its high reliability and easy operation. For the 72 hours guarantee test run at the refinery, the unit had to operate as the only sulphur recovery unit in the refinery and therefore had to cope with the feed gas fluctuations typical of refinery operations. As a consequence, the sulphur load varied and the unit operated at around 110% of design capacity for most of the initial operation and performance test period. Nevertheless, the plant operated flawlessly, realising an average sulphur recovery efficiency of 99.5% and meeting the guaranteed design figure.

For the operation of a SmartSulf unit, utility requirements are low, quite similar to those of a conventional Claus unit. The only products are bright yellow sulphur and steam, with no by-products formed.

Prosernat: vsimonneau@prosernat.com

In sulphur recovery units (SRU), adequate protection of the waste heat boiler (WHB) tube sheet is needed. Many protection systems have failed either due to incorrect designs or operational problems. As existing facilities seek to increase throughput, oxygen enrichment is being implemented more often. Because the Claus furnace with oxygen enrichment can reach continuous temperatures of 1500°C, a good and reliable WHB protection system is needed.

Jacobs Comprimo Sulphur Solutions has long experience with the design of WHB protection systems, and uses modern simulation tools to verify the designs. The following case study involves a facility with oxygen enrichment.

Jacobs Comprimo was asked to implement oxygen enrichment to increase the SRU capacity. The tube sheet protection system selected for this case consists of a two-piece square head ferrule which can be easily installed and replaced. Additionally, a two-piece ferrule provides resistance against thermal cycling. The ceramic ferrule is made from a high purity alumina. A ceramic felt gasket and ceramic paper wrap act as critical heat barriers in this design. The ceramic paper also ensures that the ferrule is positioned in the centre of the tube and that movement is limited. Additionally, bypass of hot gas is prevented as the ceramic paper located in between the square heads seals off possible flow paths.

The two-piece ferrule was analysed in a finite element (FE) model in order to calculate the highest tube sheet temperature. The model discretisation can be seen in Figure 1a. By inserting the actual geometry and physical properties, the model is able to predict which part of the tube sheet will have the highest temperature.

Figure 1 shows the results of the FE simulation. The highest metal temperature is expected near the tube-to-tube sheet weld. The model clearly indicates a large temperature gradient over the ceramic paper wrap at this position. The thickness of the ceramic paper wrap should be large enough to maintain a low metal skin temperature. A maximum metal temperature of 310°C is expected for this design as shown in Figure 2, which is well within the safe limit for corrosion and strength.

Other WHB problems may originate from the boiler design. As large heat fluxes have to be accommodated, good waterside boiler design is essential. Steam blanketing can occur which causes a rise in metal temperature with severe H2S corrosion as a consequence. The Jacobs Comprimo design uses a square pitch for the tubes.
Sweden’s largest refiner, Preem AB, expects optimum performance from all elements of its refinery, which is one of the most modern in Europe. Consequently, the company went to the market for new reactor internals when it discovered there was scope to improve the catalyst utilisation in its hydrocracker and maximise diesel yield.

Preem operates a single-stage, two reactor, 142 bar, 53 000 b/d hydrocracker at its 220 000 b/d Preemraff Lysekil facility. Studies showed, however, that only about 85% of the two reactors’ catalyst volume was being utilised owing to thermal maldistribution. Thermal maldistribution in pretreatment and cracking reactors is a common issue that can cause performance limiting hot spots and dry areas. In an effort to boost catalyst utilisation, Preem’s technologists called on catalyst vendors to suggest their best catalyst option and reactor internals to solve this problem. The proposed catalysts were then tested competitively, back to back, at an independent pilot plant testing laboratory. After successful testing, Shell Global Solutions’ reactor internals and catalysts offered through Criterion Catalysts & Technologies (Criterion) were selected and implemented at Preem’s refinery during a 2013 shutdown.

Shell’s internals include high dispersion (HD) trays, which provide ultra-uniform vapour-liquid distribution and excellent thermal distribution; ultra-flat quench (UFQ) interbed internals for uniform process and quench mixing at the interbeds; catalyst support grids for improved catalyst retention and better fouling handling; and a skirt to raise the HD tray and provide more catalyst volume.

Installing the new internals has led to a 10% increase in the amount of catalyst that can be loaded into the reactor and, because of the improved dispersion, nearly 100% of the catalyst is now being used. The quick to open and close design also means that the time spent on any future maintenance of the new reactor internals will be less, which means more on-stream days for the hydrocracker. Criterion also provided its most active and stable pretreatment catalyst, Centera DN-3620 Z-2513, which offers outstanding selectivity for middle distillates; and guard beds and grading to protect the pretreatment catalyst from fouling. The catalyst and the internals are already improving performance and helping Preem to run its hydrocracker at a higher conversion rate. “The results so far are all in line with Criterion’s catalyst offer and the pilot plant tests. They are not due only to the internals, although we do have an excellent temperature profile in all four beds. The internals ensure that we can benefit from the new, improved catalyst throughout the cycle,” says Mats Hörnfelt, Senior Process Engineer with Preemraff Lysekil. “The advantage of the catalyst is its selectivity towards diesel with lower yields of fuel gas and naphtha, which were limiting the throughput of the
When Valero Energy Corporation needed to replace a boiler at its Memphis plant four years ago, it selected one from Rentech Boiler Systems, Inc. of Abilene, Texas. It has since ordered three other boilers from the company for other refineries.

Over the years, Valero has purchased many refineries. When it does so, it typically makes upgrades to the equipment. For example, as part of its purchase of Premcor, Valero acquired four refineries including one located on 250 acres alongside the Mississippi River’s Lake McKellar, just outside of Memphis. Originally built in 1941, the Valero Memphis Refinery has a rated capacity of 195,000 b/d of light, low sulphur crude oil, and produces light products including gasoline, diesel, jet fuel and petrochemicals. After acquiring the refinery, Valero invested about $250 million upgrading the now 70-year-old plant to modernise it and increase its efficiency. Among those improvements was a new boiler. Valero put the job out for competitive bid and selected Rentech based on both the economic and technical proposal.

“Valero’s corporate philosophy is to be very conservative with the boiler design, since a conservative boiler design translates into greater reliability,” says Paul Brown, a Sales Engineer operating out of Rentech’s office in Lincoln, Nebraska. “They request things like very large furnaces, very large steam drums, and we are able to accommodate that with some very big boilers.”

Typically there are two choices in selecting a boiler. One can get a package boiler, fabricated in the factory and shipped to the site for installation or one can get a ‘stick-built’ boiler which is built on site. Package boilers are the less expensive option, but they come in standard sizes and are not optimised for specific site conditions and requirements. Stick-built boilers are far more costly and take longer to install, but are designed for that particular application.

Rentech takes the best of both approaches. Each boiler is custom built to the customer’s specifications, preassembled and tested at an in-house 100,000 square foot manufacturing plant in Abilene, Texas. The boiler can be shipped to the site in one or more pieces for final installation and commissioning. Since the boilers are factory built, they do not require the extensive site work required for stick-built boilers.

“Valero is very concerned about being environmentally friendly,” says Brown. “That is why we keep the furnaces as big as we can, which makes it easier to achieve lower NOx emissions. By integrating the boiler and SCR, we can make sure all the components work together to reduce emissions.”

The Memphis boiler was a 250,000 lb/hr unit and a similar sized unit was installed at Valero’s Three Rivers Refinery – a 100,000 b/d plant located midway between Houston and San Antonio – at around the same time. The company has since installed two more Rentech boilers, a 250,000 lb/hr unit at the Texas City Refinery, and a 350,000 lb/hr unit in Corpus Christi.

All four boilers are designed to follow steam load, firing up and down with the demand, and typically produce 750° steam at 450-650 psi. But there are other differences unique to the needs of each site. For example, with refineries dating back to 1908 and acquired from different companies, the control systems vary from one location to the next. Typically the boilers are controlled separately though a distributed control system (DCS), with the plant management system distributing the load among the boilers. But this varies from refinery to refinery with some plants being more manual and others relying more on their control system.

The functions of the boilers are also different. Two of the units are designed as high turndown units that can run reliably at low fire and then ramp up when needed. Even though the new boilers are more efficient than the other units, since the older units cannot be turned down as reliably, the boilers are kept at the minimum level until needed.

Walker Garrison, Technical Advisor for Utility Infrastructure at Valero, says that the boilers have been operating reliably in an environmentally friendly manner. “The older boilers have about 85% to 87% lower heating value efficiency, but the newer ones have 91-92% efficiency,” he says. “And, while we were EPA compliant before, these take us from an older emissions control technology to Best Available Control Technology (BACT).”

Rentech Boiler Systems: hkumpula@rentechboilers.com

Acid gas treatment for giant LNG plant

Prosernat, an engineering company and licensor of Total’s amine based technology portfolio, AdvAmine, has announced the successful start-up of a major integrated acid gas removal and tail gas treatment unit designed using AdvAmine MDEAmax (selective MDEA) technology. The unit is part of Qatargas 1 and
is a major debottlenecking project known as the Plateau Maintenance Project (PMP). The purpose of the project is to maintain LNG production while coping with increased levels of H$_2$S and CO$_2$ in the inlet feed gas streams. A new pretreatment acid gas removal unit (AGRU), upstream of the existing gas sweetening facilities, and an additional sulphur recovery unit (SRU) were selected for the debottlenecking.

The PMP project involves the construction of an additional AGRU treating, in a single train, 1100 million cu ft/day of natural gas, and an associated SRU and tail gas treatment unit (TGTU). An AGRU with integrated TGTU amine was considered the most effective solution to install a new compact plant inside the existing facilities of Qatargas 1 LNG plant at Ras Laffan, Qatar.

After an international bidding contest for the design of the process units, AdvAmine MDEAmax, licensed by Prosernat, was selected for the design of the integrated AGRU + TGTU absorber. The proposed design based on MDEA solvent offers a fully integrated unit meeting multiple process requirements with high operational flexibility.

The process includes the following steps:

- Partial removal of H$_2$S and CO$_2$ from the 1100 million cu ft/day inlet gas, in a high pressure absorber, to meet required specifications to feed the downstream existing sweetening units
- Clean up of H$_2$S from tail gas by TGTU amine, installed downstream of the 880 tonnes of sulphur per day SRU, to meet environmental emissions specifications
- Control of the H$_2$S, RSH and BTX content of the acid gas by partial enrichment of the acid gas in a selective hot preflash column upstream the MDEA regenerator, in order to meet the inlet specifications of the SRU
- Semi-lean solvent recycle from the TGT column to the HP absorber giving benefits in term of reduced solvent circulation and minimised solvent regeneration duty
- A MDEA regeneration section in one single common regenerator.

The overall process scheme is shown in Figure 1.

Performance tests were performed at the beginning of 2015, and all of the guarantees associated with the operation of the AGRU and TGT amine section at design and turndown capacities have been demonstrated without operational issues (see Table 1). Operators have reported simple management of the H$_2$S content of acid gas by the preflash column.

Prosernat: lnormand@prosernat.com

Ruhr Oel refineries in Germany are among the first to employ the world’s first ATEX-certified portable flowmeter, the F Fluxus F/G608 from Flexim. At the Ruhr Oel GmbH refinery in Gelsenkirchen-Scholven, Paul Freynik is among the first to employ the new explosion protected flowmeter in their work.

BP Gelsenkirchen GmbH manages Ruhr Oel GmbH’s two refineries in Scholven and Gelsenkirchen-Horst. Freynik works in the maintenance department of BP Gelsenkirchen and looks after the plants in the southern area of the Scholven factory, amongst them an atmospheric distillation unit, a visbreaker, an aromatics plant and the raffinate storage tank. The measuring tasks that arise are equally diverse: sometimes the efficiency of a pump must be monitored or existing measuring equipment must be tested. With the Fluxus FG08, Freynik has immediate access to the measuring point, which previously would have required applying for a transfer certificate.

Since the revised version of explosion protection directives, there was no longer any portable ultrasonic flow measurement system that met current ATEX standards. Flexim says that with its ‘Ex-portables’ it is continuing to develop extreme ranges. There were

<table>
<thead>
<tr>
<th>Project guarantees approval check list</th>
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<tbody>
<tr>
<td>AGR4 design capacity</td>
</tr>
<tr>
<td>AGR4 turndown capacity</td>
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<tr>
<td>Treated HP gas H$_2$S content</td>
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<tr>
<td>Treated HP gas CO$_2$ content</td>
</tr>
<tr>
<td>Flash gas H$_2$S content</td>
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<td>Flash gas pressure (upstream of PCV)</td>
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<td>Acid gas pressure (upstream of PCV)</td>
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<tr>
<td>Acid gas H$_2$S minimum content</td>
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<td>Maximum reboiler duty</td>
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Table 1

Figure 1 Process scheme for an integrated acid gas removal and tail gas treatment unit at Qatargas 1

Explosion protected portable flow metering
already quite a few measuring points where, the company says, its instruments were the only ones able to measure the flow rate non-invasively, be it due to the particularly large or small nominal widths or due to extreme temperatures.

Stefan Hoffterheide is a colleague of Paul Freynik. He also works at the Ruhr Oel GmbH refinery in Gelsenkirchen-Scholven in the preventative maintenance department which is responsible for ensuring maximum availability of the plants by carrying out regular inspections of large-scale equipment such as pumps and air blowers. There is also a Fluxus ADM 6725 in the department’s equipment storage. The department decided to purchase another of Flexim’s portable Fluxus F601 Energy, not least because of the reliability of the old acoustic flowmeter.

**With the Fluxus F601 Energy, flow rates and the effective power of liquid based thermal consumers can be measured non-invasively**

With the Fluxus F601 Energy, flow rates and the effective power of liquid based thermal consumers can be measured non-invasively. For this purpose, the temperature of the fluid which transports heat must be recorded in the supply and in the return line. This is also done non-invasively using Pt100 sensors which are clamped onto the pipe. These sensors calculate the current thermal and cooling capacity from the temperature difference, from the volume flow rate measured in the return line and on the basis of physical media parameters stored in the internal database of the measuring transmitter. Due to the totaliser function integrated into the measuring transmitter, the Fluxus F601 Energy can also be used as an energy meter. This is how Stefan Hoffterheide tests the efficiency of heat exchangers in order to ensure they are well maintained. Another feature is the fact that the flowmeter can also be used to determine the cooling capacity of the buffer liquid circulation on the mechanical seals of pumps.

With the meter, two pairs of transducers are sufficient to measure the flow rate non-invasively in the most common nominal size range from DN10 to DN2500. There are other transducers available for a nominal size range from DN6 bis DN6500. The measuring transmitter automatically detects the transducers when they are connected and loads their calibration data. As a result, setup takes a matter of minutes and incorrect parameter settings are avoided.

*Flexim: flexim@flexim.com*
Clamp-on flowmeters
Flexim’s Fluxus range of clamp-on ultrasonic flowmeters measures independently of pipe size, the flowing medium, pipe material, wall thickness and internal pressurization. The WaveInjector transducer mounting fixture enables operation in temperatures from -170°C up to +600°C.

As the transducers are mounted in rugged stainless steel mounting fixtures onto the outside of the pipe wall, they are never in contact with the flowing medium, can never be a source for potential line clogging and are not prone to wear and abrasion. For installation, no pipe cutting or process shutdows are required and maintenance is virtually zero.

Due to transducer matching, calibration and internal temperature compensation (to ANSI/ASME MFC-5M-1985(R2011)), the flow meters are zero point stable and precise, allowing flow measurements down to 0.001 m/s.

Fluxus clamp-on flow meters operate at many downstream facilities in applications such as at distillation columns and coker feed flows.

Mass transfer and mist elimination
Koch-Glitsch’s mass transfer and mist elimination products include trays, random packing, structured packing, severe service grid, column internals, mist eliminators, and liquid-liquid coalescers. The following products will be showcased at Achema.

Proflux severe service grid combines the efficiency and de-entrainment performance of a conventional structured packing, with the ruggedness and fouling resistance of a conventional grid packing that outperforms both. The assembly provides durability in severe operating applications, such as fouling, coking, erosion, corrosion, and frequent upsets.

Intalox Ultra random packing can help to increase the capacity of a random packing tower by up to 10% while maintaining the same efficiency compared to previous high capacity random packings. This packing allows smaller diameters for new columns, reduces energy consumption for revamps, reduces foam generation, and reduces carryover and solvent losses with high vapour handling capacity.

Superfrac trays can be used in new construction and revamp opportunities for virtually any service in which conventional sieve and valve trays are used, such as applications requiring a large number of mass transfer stages or where mass transfer efficiency is critical, as in superfractionators. Use of Provalve tray decks combines performance with fouling resistance for applications such as coker fractionators and sour water strippers.

Demister-Plus technology combines the efficiency of the Demister mist eliminator with the capacity of the Flexichevron mist eliminator. When revamping for additional capacity, Demister-Plus mist eliminators can be installed into existing separator drums to achieve higher throughput. When new separator drums are required, this technology can optimise the overall size of the drum when the size is set by the requirement of the mist eliminator itself.
New process for bursting disks
Rembe has developed a new manufacturing process for bursting disks, for greater precision and resistance to alternating pressure. The process is based on special laser-cutting and abrasion methods to make both tensile-loaded and reverse-acting bursting disks with precision. According to Rembe, clean cuts and notches allow minimum tolerances and extraordinary levels of resistance. Instead of attacking the bursting disk material with chemicals, as has been common, a Rembe 3D Contour Precision Lasering method called CPL-3 is applied whereby the relevant bursting points are entered – surgically, as it were – into the spherical cap of the bursting membrane. The result is a longer service life and optimum opening characteristics. For operators, this means primarily a reduction of downtimes.

Rembe’s non-invasive monitoring unit (NIMU) signalling unit provides information about the way a bursting disk responds to positive and negative pressure. It is attached within a blind hole in the bursting disk holder, thus isolating it from the process medium. The unit can be serviced and replaced without opening the pipeline. This signalling method is suited to critical processes and applications which require the entire system to be completely impermeable.

NIMU can be integrated into an existing process control system using terminal boxes and isolating amplifiers, and meets all certification and zoning requirements.

Elemental analytical Instruments
Spectro Analytical Instruments supplies analytical instruments for optical emission and X-ray fluorescence spectrometry. At Achema 2015, Spectro will exhibit models from its line of ICP and XRF spectrometers for the elemental analysis of liquids, powders and solids:

Spectro Arcos The Spectro Arcos ICP-OES analyser is an inductively coupled plasma optical emission spectrometer for elemental analysis of metals, chemicals, petrochemicals, and other materials. Its MultiView plasma interface option provides axial-view and radial-view plasma observation in a single instrument.

Spectroscout Spectroscout is a portable, energy-dispersive X-ray fluorescence (ED-XRF) analyser for lab quality results at low cost. Predefined application packages are designed for all laboratory-grade analysis in the field.

Spectro xSort The Spectro xSort family of handheld ED-XRF spectrometers supplies elemental testing and spectrochemical analysis of many materials in widely varying conditions. They provide metals or non-metals identification in seconds.

Spectro Midex The Spectro Midex is an X-ray fluorescence spectrometer for fast, non-destructive analysis of small spots and the rapid mapping of large surfaces. It is suited to elemental analysis tasks in industry, research and the sciences that require a non-destructive measuring technique that is sensitive and offers a small measuring spot.

High performance ceramic tower packing
Vereinigte Füllkörper-Fabriken GmbH & Co. KG (VFF) is Europe’s largest producer of catalyst support material and tower packings. At Achema, VFF will present a new ceramic tower packing which features the design and benefits of a random packing, and performance that may be compared to a structured packing.

VFF’s ceramic tower packing fits into the series of VFF’s high performance tower packings, featuring best mass transfer and a very low pressure drop; for example, the metal VFF-Twin-Pak or the VFF-NetBall made of plastic. A new quality of Duranit Inert Balls, a catalyst support material, the Duranit X500 will also be shown, illustrating how its various materials and different sizes may be combined with VFF’s bed topping material DuraTop.

Valves for non-standard conditions
Zwick’s Tri-Con metal-seated triple offset butterfly valve series includes Tri-Check check valves, and the Tri-Block Double Block and Bleed design.

The triple offset butterfly valves are designed for critical services as shut-off and control valves. Tri-Con valves incorporate a third offset design with a true cone-in-cone seating with zero leakage performance and bi-directional tightness. Zwick valves are used for industrial and exhaust gases, liquids, hot water or steam at low temperatures as well as at temperatures up to 815°C.

Tri-Block Double Block and Bleed design requires only one actuator or gearbox With Zwick’s design of the linkage between the two shafts, the user is able to actuate both shafts with only one actuator and reach zero leakage with the two available sealing surfaces.

Tri-Shark control valves are able to achieve a nearly equal percentage inherent characteristic which extends the control rangeability. They feature cavitation reduction and noise attenuation, as well as dynamic torque reduction, and are suitable for services from -196°C up to +815°C, for liquids, gases and steam.
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Bryan Research & Engineering 74  
Cat-Tech 70  
CB&I 7  
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CRI International 92  
Criterion Catalyst & Technologies 4  
CS Combustion Solutions 49  
Delta Valve 8  
Dunn Heat Exchangers 59  
ExxonMobil Research and Engineering Company 41  
Flexim 27  
Gastech 101  
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Grabner Instruments 87  
Hoerbiger Kompressortechnik Holding 45  
ITW Technologies 80  
John Zink 50  
Johnson Matthey Process Technologies 88  
KBC Advanced Technologies 2  
Kidextractor 34  
Koch-Glitsch 77  
Kurita Europe 95  
Magnetrol International 64  
Merichem Company 98  
OHL Gutermuth Industrial Valves 97  
Optimised Gas Treating 83  
Paqell 46  
Process Consulting Services 14 & 16  
RefComm Galveston 2015 108  
Rembe Safety + Control 85  
Rentech Boiler Systems 32  
Sabin Metal Corporation 22  
Sandvik Materials Technology 24  
Spectro Analytical Instruments 79  
Streamlight 69  
Sulzer Chemtech 106  
ThyssenKrupp Industrial Solutions 36  
UOP 12,19 & 91  
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