Does your raw natural gas contain hydrogen sulfide, carbon dioxide, mercaptans or more?

Whatever the impurity, whatever the composition, Air Liquide Global E&C Solutions has the right treatment.

The composition of natural gas varies tremendously: almost every source contains a different blend of impurities. The options for treatment are almost as diverse. That’s why offering a solution specifically designed for your gas field is crucial. We as your partner of choice provide solutions for all types of natural gas, including associated and unconventional gas, from a single source. Customised and efficient.

www.engineering-solutions.airliquide.com
3 Fencing with rules
Chris Cunningham

5 ptq&a

21 Tail gas catalyst performance: part 2
Michael Huffmaster Consultant
Fernando Maldonado Criterion Catalysts

37 Predicting future FCC operations via analytics
Patrick J Christensen, Touseef Habib, Thomas B Garrett and Thomas W Yeung
Hydrocarbon Publishing Company

47 Predicting reactive heavy oil process operation
Glen A Hay, Herbert Loria and Marco A Satyro Virtual Materials Group, Inc
Hideki Nagata Fuji Oil Company Ltd

55 Integrated hydrogen management
Saša Polovina, Danijela Harmina and Ana Granic Šarac INA Rijeka refinery

69 Structured packing in a CO₂ absorber
Ralph Weiland and Nathan Hatcher Optimized Gas Treating, Inc.

75 Reflux in a gas dehydration plant
Sajad Mirian and Hossein Anisi Nitel Pars Co (Fateh Group)
Xiang Yu Hengye Chemical Co
Sepehr Sadighi Research Institute of Petroleum Industry

81 Override control of fuel gas
Rainer Scheuring Cologne University of Applied Sciences
Albrecht Minges and Simon Griesbaum MiRO Mineralöleraffinierie Oberhein
Michael Brodkorb Honeywell Process Solutions

87 'Snakes and ladders' for maximising propylene
Bart De Graaf, Mehdi Allahverdi, Martin Evans and Paul Diddams
Johnson Matthey Process Technologies

97 Troubleshooting a C₃ splitter tower. Part 1: evaluation
Henry Z Kister Fluor
Brian Clancy-Jundt and Randy Miller PetroLogistics

105 Overcoming tight emulsion problems
Hernando Salgado Cartagena Refinery, Ecopetrol
Luis Mariño Ramgus S. A. – Pall Corp.
Rosángela Pacheco Barrancabermeja Refinery, Ecopetrol

111 Enhancing bottoms cracking and process flexibility
Yee-Young Cher, Rosann Schiller and Jeff Koebel Grace Catalysts Technologies

119 Preventing emissions in coke removal
Artur Krueger, Bernd Lankers and Josef Wadle TriPlan AG

125 Troubleshooting steam ejectors
Norman Lieberman Process Improvement Engineering

131 Asphalt quality prediction and control
Zak Friedman Petrocontrol

137 Technology in Action

Marathon Petroleum’s Detroit, Michigan refinery.

Photo: Marathon Petroleum Corporation

©2014. The entire content of this publication is protected by copyright full details of which are available from the publishers. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, mechanical, photocopying, recording or otherwise – without the prior permission of the copyright owner.

The opinions and views expressed by the authors in this publication are not necessarily those of the editor or publisher and while every care has been taken in the preparation of all material included in Petroleum Technology Quarterly and its supplements the publisher cannot be held responsible for any statements, opinions or views or for any inaccuracies.
DEDICATED TO MAKING OUR CLIENTS IN THE HYDROCARBON INDUSTRY WORLD-CLASS BY DRIVING A NEW STANDARD IN OPERATIONAL EXCELLENCE THROUGH EXPERT CONSULTING AND ADVANCED TECHNOLOGY.

PROCESS CONSULTING
Optimisation and Profit
Improvement from pore to pump from a deep understanding of the chemical engineering of assets.

TECHNOLOGY
PVT, thermal hydraulics and process facility simulation from well bore through refining and petrochemicals in an open platform, which is enabled for workflows across the assets.

BUSINESS TRANSFORMATION
Sustainable operational excellence from strategic and organisational consulting, focused on people and processes that make the assets work hard.

KBC uses its 35+ years of history working in hundreds of oil and gas facilities worldwide to bring practical, sustainable solutions to its clients to improve their bottom line performance by using proven best practices and unit optimisation tools and techniques.

KBC Advanced Technologies
AMER: +1 281 293 8200 ASIA: +65 6735 5488 EMEA: +44 1932 242424
answers@kbcat.com • www.kbcat.com • blog.kbcat.com
Environmental regulation is the mother of invention in refining technology. The impact of successive clean fuels measures, originating in Europe and the US, continues to reverberate at refinery sites around the world as the technology developers’ output works to continually upgrade the refining industry’s impact on air quality, directly or via its products. With poorer quality crudes entering the mainstream of raw material flows into refineries, the pressure for further and better invention does not cease up.

This all, of course, means additional expenditure for the refiners themselves. It is no surprise when they demand a long, hard look at any proposal to require that cleaner products or cleaner emissions leave a refinery.

The latest significant step along the road to regulation in the US was due late in October when the call for evidence was scheduled to close on the Environmental Protection Agency’s (EPA) proposed extension of emissions limits from refineries. Introduced in May, the proposed rule arises from the EPA’s risk and technology review of two existing emissions standards for refineries. This extension of the rules calls for additional emission control requirements for storage tanks, flares and coking units at petroleum refineries, as well as a requirement – with refineries’ neighbours in mind – to monitor air concentrations at the fence line to check for accidental emissions.

According to the EPA, implementing the rule will result in a reduction in the US of 5600 t/y of air pollutants, and 52 000 t/y of volatile organic compounds (VOC). More specifically, the EPA wants to amend the operating requirements for refinery flares to ensure a “high level” of combustion efficiency for waste gases that go to flare. The agency also wants controls on delayed coking units with the aim of preventing exemptions to emission limits during start-up and shutdown. It expects that the measures will lead to a reduction in emissions of BTX of 1800 t/y and VOC emissions would fall by 19 000 t/y. The additional flaring measures would result in significant reductions in particulate emissions and VOCs.

Upgrading and tweaking the technologies to achieve all of this would also, says the EPA, lead to 700 000 t/y less carbon dioxide entering the atmosphere. The all-in cost of implementing the rule would be $240 million, with annual running costs of $40 million, with resulting “negligible impact” on product costs.

Refiners are not so sure about the EPA’s latest certainties. The American Fuel & Petrochemical Manufacturers (AFPM), the US refiners’ trade body and voice in Washington, takes the view that further tightening of the emissions rules is not cost effective. The AFPM said earlier in the year that it had evaluated the EPA’s analysis of risk on the basis of emissions data provided to the agency. That analysis, according to the AFPM, showed that risk levels were “not appreciably higher” than they were when the rule was applied first time around, pointing out that the EPA determined at that time that further action was unnecessary.

The AFPM went on to say that the level of concern for risks expressed in the original rule does not justify the further actions that the EPA wants to put forward. Fenceline monitors, for instance, are “not justified” by the latest risk analysis. This critique signed off by saying that the EPA’s latest proposed steps are neither cost effective, nor do they provide substantial health benefits.
“Advanced R & D means results, like our newest tail gas catalyst: C-834.”

Meet Karl Krueger:
Research Scientist. Tail Gas Catalyst Expert.

Activity, pressure drop, cost... According to Karl Krueger, Criterion research scientist, these among other factors are critical considerations when selecting a tail gas catalyst. He should know. Karl and his colleagues have just designed C-834, specifically to provide exceptionally high activity in low temperature operations while continuing to help refiners realize lower operating costs and extended cycle lengths. This breakthrough catalyst joins the ranks of Criterion’s range of advanced tail gas treating catalysts including C-234, C-534 and C-734, which account for the majority of the world’s installed capacity.

Leading minds. Advanced technologies.
Suspended catalyst in our FCC fractionator is accumulating in the bottom fraction. What is the most effective way of clarifying this slurry oil?

A Zhe Cui, FCC Technologist, zhe.cui@shell.com, Bob Ludolph, Principal Technologist - Catalytic Cracking, Robert.ludolph@shell.com and Kevin Kunz, Team Lead, FCC Design & Licensing, Kevin.kunz@shell.com, Shell Global Solutions

The suspended catalyst in the FCC fractionator bottom fraction (slurry oil) is uncaptured catalyst leaving with the reactor overhead vapour (feed for main fractionator). The slurry yield is determined by the FCC unit’s riser/reactor design, feed and catalyst properties, reactor conditions, desuperheating section temperatures, and by the design and operation of the bottoms circulating reflux and bottom quench. With a properly operating reactor cyclone system, a catalyst in slurry concentration of 0.15% is usually achieved (typical bunker fuel oil, 0.03-0.15 wt% catalyst in slurry). However, if the solid concentration in the slurry oil is higher, either some slurry clean-up system is needed, or the operating condition of the FCC unit needs to be reassessed and optimised. This could include redesign or repair of the existing reactor cyclones.

Shell has evaluated all major technologies for application in removing catalyst fines from the slurry oil. These options include hydrocyclone, electrostatic separator, backwash filtering, and centrifugation.

A hydrocyclone separates FCC particles from slurry oil based on centripetal force and fluid resistance. Due to the advantages of low cost, no moving parts, low pressure drop and low maintenance requirement, hydrocyclones are the first choice for resolving slurry ash issues when a cyclone redesign is not possible. However, the performance of the hydrocyclone is relative sensitive to the feed parameters (temperature, flow rate, solid concentration). So hydrocyclones are specifically designed for individual FCCs.

Electrostatic separators are designed and made specifically for slurry oil so they can provide the required separation with fairly low pressure drop. But the capital cost and footprint requirement can limit the application. Also, direct experimentation is required for a good design for a specific FCC system.

Backwash filtration can also provide highly efficient solid separation. Backwash filtration does require high energy consumption, higher pressure drop, and higher capital cost than hydrocyclones.

Centrifugation technology has advantages of small volume and low pressure drop. Also, it can provide some of the best solid separation performance. However, the capital cost and operating cost (energy consumption) need to be considered. Furthermore, the maintenance of a centrifugal slurry separator is more extensive compared to other separation technologies.

Each technology has its advantages and disadvantages, and applications are unit specific. For a specific application, a comprehensive analysis, including the source of the catalyst fines, temperature, residence time, pressure drop, fines concentration, flow rates, unit capacity, particle size distribution, and desired capital cost budget is necessary. Working closely with vendors of the various solutions will provide guidance in resolving the excessive fines content in slurry oil effectively and economically.

The catalyst concentration in the slurry oil should be minimised not only from an erosion point of view; it can also impact the sale value of the slurry oil. Therefore, it is of great importance to select a proper solid separation technology especially when higher catalyst concentration is observed, which can happen later in the FCC operating cycle. In Shell units, as the first barrier, a high efficiency cyclone system is installed in the reactor to minimise the catalyst fines loss to the main fractionator. Furthermore, with the help of the technologies mentioned, catalyst concentration in the slurry oil can be controlled to below 0.05%.

A Joe Nguyen, Research Associate, Baker Hughes, Joe.Nguyen@bakerhughes.com

Slurry oil has historically been clarified – that is, reduced in solids content – by one of three general methods. These are centrifuging, filtration, and longer-term passive settling. Centrifuging is not as effective as other methods since the particulate solids in a slurry oil (mostly FCC catalyst fines) are not removed by the FCC reactor’s cyclones and are finely divided and light. Filtration systems can be effective at removing solids, but these filtration systems can also be costly in terms of equipment and operation. The most cost-effective method is passive settling in storage vessels aided by temperature and slurry settling chemicals. Elevated storage temperature reduces viscosity, allowing solids to settle more easily. Chemical surfactants added to the slurry oil can promote agglomeration of smaller fines into larger particles, which settle at faster rates. The one drawback to passive settling is that time is required for slurry settling, even allowing for the temperature and chemical aids.

Additional Q&A can be found at www.eptq.com/QandA
Charles Radcliffe, Technical Service Engineer Europe, johnson Matthey, Charles.Radcliffe@Matthey.com

I read this as being a problem of catalyst fines settling in the bottom of the main fractionator. The important thing with handling slurry oil is to maintain a high enough velocity to ensure that catalyst cannot settle. High velocities also reduce residence times and so reduce coke formation due to thermal cracking. For this reason, main fractionator slurry systems are normally designed with a small diameter, <50% of the main column diameter heel. A short-term fix for the questioner is to try and increase slurry pumparound, and if they have a large heel to install a lining in the bottom of the fractionator with steel skinned refractory.

Catalyst fines can be removed using a gravity settler or filter system. The problem with settlers is that to work efficiently they need to have residence time at high temperature to lower viscosity. This leads to coke formation and potentially flash point problems on slurry product. There is also the problem of what to do with the settler underflow. Recycling will increase FCC delta coke. Filtration systems reduce the amount of high fine material (from back washing) but are high maintenance equipment.

Most refiners work to ensure good reactor cyclone efficiency to minimise fines carry-over, and purge this with the slurry product.

Eva Andersson, Market Manager Refinery, Alfa Laval, evae.andersson@alfalaval.com

High speed centrifugation technologies have been used for decades to remove cat fines onboard marine vessels, where engines demand less than 10-15 ppm cat fines in the oil. The same technology can be applied on unblended FCC slurry in refineries but the high speed centrifuge used must be designed to handle higher temperatures in combination with more abrasive sludge.

Is there an effective way of cleaning contaminants from deasphalted oil so that it can be used as a feed to a hydrocracker?

Deepak RD, Hydrocracking Technical Service Engineer, Deepak.Rd@CRI-Criterion.com, and Deepak Agarwal, Hydrocracking Technical Service Engineer, D.Agwal@CRI-Criterion.com, Criterion Catalysts & Technologies

In order to maximise the margin of upgrading heavy fuel oil into lighter products, one operation variable that has been leveraged by refiners is the degree of ‘lift’ employed at the deasphalting unit. Further, depending on DAO application and yield requirements, SDA (solvent deasphalting) units are designed with solvents ranging from propane to hexane. The type of solvent used is based on the contaminant level and yield of DAO from the unit. For base oil production, propane deasphaltenes is used to produce high quality and low yield DAO. Normally, CɅ and heavier hydrocarbon is used as a solvent when the DAO is processed in a hydrocracker and higher DAO yield is desired. This scenario increases both feed severity and catalyst deactivation rate in the hydrocracker processing the DAO stream. Typical DAO stream composition metals (5-100 wppm), Conradson carbon (2–10 wt%), asphaltene (heptane insolubles of 500-1000 wppm or more) and distillation end-point (1300-1500°F or more) are detrimental to achieving economic catalyst life and conversion at hydrocrackers. There are several ways to reduce contaminants in a DAO stream. Once the process to reduce contaminant carry-over is in place, effective use of catalysts is the key factor to success.

For new unit design, a separate guard reactor could be designed for contaminant removal. For an existing hydrocracker, a proper choice of the Demet catalyst system will be required to handle the contaminants in the DAO stream. From a hydrocracking perspective, the ‘contaminants’ most detrimental to pretreat and cracking catalyst performance are metals and asphaltene. Fortunately, both show the sharpest partitioning in SDA units, with DAO, even from deep extraction, often having a lower CɅ-insolubles (asphaltene) value than the corresponding HVGO. With proper understanding of the DAO chemistry, a ‘demetallisation’ catalyst system can be individually designed to protect the downstream hydrocracking catalysts. This has been fully proven by the successful operation at a European refinery of the combination of a KBR ROSE solvent deasphalting unit with a Shell fixed-bed hydrocracker, specifically designed to process a high percentage of deeply extracted DAO in combination with VGO. The upgrading complex delivers high conversion coupled with high distillate yields of high quality and with a long, sustained run length. After three years’ continuous operation, the demetallisation catalyst was replaced, while both pretreat and cracking catalysts were retained for the ‘next’ cycle.

It is important to know the level of removal of metals, heteroatoms, Conradson carbon residue (CCR) and asphaltene. The feed composition and operating conditions determine the right catalyst choice. These variables determine the factors to tailor make catalyst systems that meet each refinery’s needs. In an existing unit with existing HCU reactors, there would be a maximum reactor volume available for the demetallisation catalysts which then restricts the maximum amount of DAO that could be processed in the HCU feed based on the DAO quality. The performance of Criterion’s demetallisation catalyst system has been the key factor that enables ULSD and high quality jet fuel to be produced directly from DAO over economic cycle lengths. In addition, Criterion has developed step-out HDM/HDN/HDCR catalysts with exceptionally high HDN and HDCCR activities, good contaminant metals tolerance and excellent stability. Using innovative manufacturing technology, Criterion has additionally developed a new type of active site that resists metal and coke deactivation. In applications used, it has demonstrated stable activity at high metal deposition levels. Metal species compete with each other and hence the effective use of customised layering of catalysts is vital to sustain effectiveness.

www.ptq.com
STRATEGIES THAT DELIVER SOLUTIONS
Profiting from Refinery/Petrochemical Integration

With changing feedstock supplies and flat or declining demand for gasoline, it’s more important than ever that refiners derive maximum value from every molecule.

CB&I’s integrated hydrocarbon processing solutions enable refiners to handle varied feedstock supplies, maximize clean distillate fuels production and increase FCC light olefin yield to take advantage of growing petrochemical feedstock demand.

Our broad portfolio of both refining and petrochemical technologies, combined with our execution expertise, will help you maximize unit flexibility and achieve margin benefits in the widest range of scenarios.

PROCESS PLANNING AND DEVELOPMENT
LICENSED TECHNOLOGY AND CATALYSTS
FULL-SCOPE EPFC SERVICES
PROJECT MANAGEMENT AND CONSULTING
AFTERMARKET SERVICES
require more of these contaminant removal catalysts which then reduces the reactor volume available for other hydrotreating and hydrocracking catalysts. A refiner wishing to extend cycle length can increase loading of high macro/mesoporosity catalysts, but this reduces the volume of hydrotreating catalysts.

To alleviate the downside of the trade-off, ART has also developed and begun deploying next generation catalysts that exhibit two to three times the relative volume activity of conventional catalysts for this type of service. With this next generation technology in the catalyst load, the reduced hydrotreating catalyst volume will exhibit longer cycle length. A refiner wishing to process more DAO can also utilise this next generation technology in a similar way to improve profitability. An optimum catalyst loading for maximum performance requires close cooperation of refinery operating staff and catalyst supplier experts.

Alex Yoon, Senior Technology Advisor for Advanced Refining Technologies, alex.yoon@grace.com

The solvent deasphalting (SDA) process is itself a way of cleaning contaminants from a portion of vacuum resid – the deasphalted oil (DAO) – to be processed in a hydrocracker. Depending on the severity of SDA operation (extraction target of DAO), contaminant levels can vary significantly. The most common contaminants are Ni and V containing resid molecules. These can vary typically from 1 ppm to 30 ppm. There are also asphaltenes and other high CCR causing molecules which would be considered contaminants in a hydrocracker operation. The former can be as high as 1000 wppm while the latter can be as high as 13 wt%.

High sulphur, high nitrogen and low API are also typical characteristics of the DAO.

DAO contaminant removal for the hydrocracker is accomplished within the hydrocracker using appropriately designed catalysts, typically in the first two beds of the reactor. Advanced Refining Technologies utilises catalysts with high macro- and mesoporosity that have been successfully used in many vacuum resid processing units worldwide. These catalysts have successfully processed various DAOs with up to 12 wt% CCR, 30 ppm metals, and up to 75% DAO blended in the feed.

These catalysts also have excellent hydrotreating functionality. However, high contaminant levels can rapidly reduce their activity and this results in a trade-off with downstream hydrocracking catalysts. Higher contaminant levels with a given operating target
Helping refiners transform difficult feeds into the cleanest products possible.

The global hydroprocessing partner of choice.

Recent partnerships include:

- Saudi Aramco-Total: Jubail, Saudi Arabia, ISOCRACKING Technology
- GS-Caltex: Yeosu, Korea, LC-FINING Technology
- ROSNEFT: Novokuybyshhev, Russia, ISOCRACKING, ISODEWAXING and ISOFINISHING Technologies
- PetroChina: Sichuan, China, UFR and VRDS Technologies

Chevron Lummus Global
Hydroprocessing Technologies and Catalysts
www.chevronlummus.com
reactor. Similarly, special contaminant traps such as KF 16 MAC can be used in the guard zone of the HC-PT catalyst system to remove poisons (in this case maximum arsenic capture) from the feed and protect the active catalysts. Finally, wide-pore HDM catalysts (for instance, KFR 22) can be effectively employed to remove Ni and V from the HCU feed. With this protective guard zone up front in the HC-PT reactor, high activity NiMo catalysts can then be utilised to remove nitrogen (N) and sulphur from the DAO/VGO feed blend to enable proper performance of the cracking catalyst(s) and hydrogenate aromatics to make the feed more ‘crackable’.

Feeds containing DAO tend to have very high back-end boiling points, which implies they will have relatively high Ni and V content and high PNA content. In addition to requiring a larger guard zone than typically needed for most VGO feeds, it is important to ensure that an active NiMo HDN catalyst with relatively large median pore diameter (MPD) be used in a significant portion of the HC-PT catalyst bed to avoid accelerated deactivation of the catalyst due to coking and pore mouth plugging. KF 860 has excellent HC-PT activity stability in applications where feeds have very heavy back-end boiling points.

We need to replace the hydrocarbon gas detectors and associated wiring in our tank farm. Is a wireless set-up reliable enough for this critical safety system and what capital cost savings would a wireless option offer?

A Diederik Mols, Business Manager Industrial Wireless, Honeywell Process Solutions, diederik.mols@honeywell.com

Wireless technology based on the ISA100 wireless industry standard is technically able to provide a better than wired performance. Of course it will be essential that the wireless network is properly designed and implemented. Reliability can be further enhanced by designing in redundant communication paths, redundant gateways and network management. As a rule of thumb on a given project, wireless technology realises capital cost savings up to 50% and reduces execution time by up to 80%.

Wireless technology as an integral part of safety systems is in operation at oil and gas facilities both offshore and onshore. Wireless stationary gas detectors are in operation at multiple offshore platforms in Norway. Wireless stationary gas detectors combined with solar power panels, sounders and beacons serve as perimeter monitoring system at a gas producing plant in Qatar, meeting a stringent end to end latency requirement of three seconds. Wireless personal gas detection is selected and in the process of being commissioned at a large sour gas producing facility in the UAE, providing near real time data of gas levels as well as gas- and man-down alarms of personnel. Honeywell Process Solutions delivered turnkey solutions to each of these three examples. In 2003, Honeywell was the first vendor to introduce industrial wireless enabled technology.

How do we effectively remove aerosols from the hydrogen stream leaving our catalytic reformer?

A Srvan Pappu, Refinery Purification Manager, Johnson Matthey, Srvan.Pappu@matthey.com

Typically, aerosols found in the hydrogen product stream of the catalytic reformer are removed through engineering methods. In design, a flash separator should be sized to give adequate disengassing time for vapour-liquid separation. For those anticipating problems or experiencing such problems with the design of the flash vessel, which is expensive to replace, a demister pad is used to prevent liquid droplets from propagating with the vapour stream. Long or poorly insulated runs of piping around the hydrogen product stream can cause stream cooling and subsequent condensation. Such liquid can have an adverse effect on chloride guard performance as well as carrying over unwanted liquids to downstream users via a hydrogen header.

Given that most catalytic reformers utilise a chloride guard on the hydrogen product, many end users have removed aerosols to both protect downstream users and maximise performance of the chloride guard bed. This is done using a three-step system similar to those employed in recontacting sections. The first is a cooler which condenses out any heavier components that would have condensed out later in the line. Next, a knockout pot is used to drain accumulated liquids, many times for useful recovery. Finally, the third is a superheater which heats the gas above dewpoint. The end result of this system is a super-heated, dry, hydrogen-rich stream.

Since a switch to heavier crude blends we are losing around 25°C from our HVGO cutpoint. Are there any process schemes to overcome this?

A Charles Radcliffe, Technical Service Engineer Europe, Johnson Matthey, Charles.Radcliffe@Matthey.com

The lowering of the HVGO cut point could be caused by a number of problems:

1. Overloaded packing, possibly due to coking in the bottom of the HVGO and top of the wash oil sections. A switch to structured packing may help, otherwise talk to the packing manufacturers.
2. Overloaded draw tray – due to inadequate pump capacity or increased vapour/liquid traffic. If pumps are fully loaded, try running the spare(s) to see if the cut point is improved – if so debottleneck the pump(s). If the tray is flooding, this will require a revamp to fix.
3. Flooding will increase the tower DP lower cut point at a given flash zone temperature. Raising this will result in increased cracking which will increase the vacuum package loading and further reduce the cut point.
4. As well as reviewing the design and operation, Tracerco could be invited to scan the tower for evidence of flooding or maldistribution problems.
We create chemistry that makes tight oil feedstocks love flexible catalyst technology.

BASF’s flexible catalyst technology and advanced technical services provide solutions to improve product yields, solve heat balance problems, and improve metals tolerance for refineries processing tight oils. BASF, the leading supplier of FCC catalysts to the tight oil market, provides a broad foundation of knowledge and operating strategy to deliver value to your refinery.

www.catalysts.basf.com/refining
The Myth of the 1000°F Vacuum Unit Cutpoint

Canadian Synbit and Dilbit crudes will come to make up a substantial fraction of feedstocks to North American refineries. Today, however, for the most part refiners both north and south of the 40° parallel seem to be unaware of the extreme challenges this change will present.

To run an oil sands crude in a vacuum unit designed for conventional heavy feedstocks and to expect a 1000°F cutpoint for a 5-6 year run is like believing in the Tooth Fairy. Bitumen based crudes are ultra-heavy, fouling, hard to desalt, corrosive, thermally unstable and tough to vaporize in the vacuum column flash zone even at elevated temperatures. Can any crude oils be nastier to cope with?

First and foremost, heater outlet temperature can be no higher than 725°F and possibly lower to avoid extremely high cracked gas rates and rapid coke laydown. Even at these reduced temperatures the heater tubes must be double-fired, coil steam rates high, coil layout correct, oil mass velocity high and heater outlet pressure selected properly. But won’t lower heater outlet temperature increase the coker charge rate by 25% or more? Yes ... with current unrealistic vacuum column design! The proper design is one which can provide minimum coker charge with design features that incorporate efficient residue stripping and low column operating pressure.

If you design your vacuum unit correctly you can indeed expect to achieve a 975°F VGO cutpoint and a 5-6 year run length. But it won’t come from conventional cheap unit designs. If the wrong designs are used it could mean replacing the heater, having to add residue stripping and new ejector systems. The revamp can cost 40% of a new unit. The choice is yours. Pay now or pay through the nose later.

A last word: Because process and equipment design is critical when processing oil sands crudes, know-how and actual experience designing units to process these feedstocks can make the difference between success or possibly disastrous reliability and yields.

For a more thorough discussion of cutpoint ask for Technical Papers 236 and 237.
Q Heat stable salts forming in our amine plant circulation loop are leading to frequent unplanned shutdowns. Is there a means of continuous removal of these contaminants without shutdown and amine clean-up?

A Nate Hatcher, Vice President, Technology Development, Optimized Gas Treating, nate.hatcher@ogttr.com

There are at least two non-distillation technologies for continuous removal of HSSs from amine systems: one is based on ion exchange (EcoTec in Canada and MPR Services in the USA), the other uses electro-dialysis (Dow and ElectroSep) although it may not be continuous. HSSs are generated in the amine unit itself from components coming in with the gas. HCN is a typical and common source for HSS formation and once in the amine there is not much you can do to prevent its hydrolysis to formate. However, another source is oxygen incursion and yet another is SO₂ breakthrough in TGTUs. These generate cyanate and thiocyanate which can be prevented by keeping out oxygen and SO₂. Care must be taken not to over or underclean the system of HSSs. Some residual HSS can be beneficial for assisting the amine regeneration and result in improved treating in lean-end pinched columns. The optimal HSS level can be predicted with the ProTreat rate-based gas treating simulator.

A Charles Radcliffe, Technical Service Engineer Europe, Johnson Matthey, Charles.Radcliffe@matthey.com

Most amine systems include a slip stream filter, which normally treats about 10% of the circulation. A well designed filter should be able to maintain the solids at a level which minimises fouling. S ponge oil absorbers are prone to foaming, resulting in LCO carry-over into the downstream amine scrubber. LCO contaminated amine will tend to increase fouling and foaming in other scrubbers. Antifoam additives are quite effective in minimising this.

Where packed beds foul, refiners will often bypass them for 12-24 hours and steam clean the packing.

Q Is there a means of online pH testing of process water from our crude unit?

A Ralph Kajdasz – Senior Area Manager, Baker Hughes, Ralph.Kajdasz@bakerhughes.com

Baker Hughes operates a closed-loop pH control system to regulate the injection of overhead amine on a real-time basis. Overhead water is directed through a cooler and past a pH probe. The amine feed pump is connected to the pH controller and varies the feed of amine as required. As a safety precaution, the overhead pH is tested by each shift to ensure that the calibration of the overhead unit is still acceptable. Deviations of more than 0.5 pH units trigger immediate recalibration of the pH control unit. The overhead unit is also calibrated on a monthly basis as a preventative maintenance function.

Proper design is a critical element for a successful, online pH system. Maintaining adequate water flow is necessary. Managing the potential for contaminants to interfere is also important. Oil is the most serious threat to reliable operation. To manage that, devices can be included to maintain the probes in a clean condition, although at some sites, these are not required.

The first benefit of an online pH measurement is to provide an alarm when the system goes out of the control target. For online pH measurement, an alarm for low or high pH should trigger an investigation. The closed-loop control of amine injection is automatic when low pH events occur; however, occasional events of acid-bearing crude oils can lead to maximum pump flow, leaving the system below the minimum pH target. Operator intervention is then required to determine the best course of action. For systems with tramp amine in the crude feed, the upper pH target can be exceeded. For refiners where this is a common occurrence, the upper alarm limit may need to be adjusted to accommodate the nature of the operations with amine contamination.

Note that the pH that is analysed is only a look at the bulk overhead water. The distribution of both acid and amine through the overhead is a function of many different variables. A thorough analysis should be conducted to ensure that the proper amines are used to minimise overhead corrosion, featuring the Baker Hughes Topguard corrosion risk monitor. Assuming the proper amines are used and other parameters, such as wash water, are properly applied, an online pH system is an excellent method of controlling the feed of amine to the overhead system.

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

There is a wide range of corrosive components which can damage the equipment of a crude unit. Hydrogen chloride (HCl) is an acid gas, which is very aggressive, when it is dissolved in condensed water to form hydrochloric acid. The corrosivity of hydrochloric acid depends on its concentration, measured by pH. Regular pH online monitoring is a fundamental component of controlling corrosion potential by keeping pH in the optimum corrosion control range. The optimum pH control range of the overhead accumulator water is between 5.5 and 6.5. It is common practice to inject a neutralising amine such as Kurita CI-6110, which is a very powerful blend of selected amine-based corrosion inhibitors. Such corrosion inhibitors

www.eptq.com

PTQ Q4 2014
Nasty Stuff

Heavy crudes are here to stay. As long as oil prices remain high, Canadian, Venezuelan, Deep Water Gulf of Mexico, Mexican and other low API gravity crude oils will play an ever more important role in supplying world refineries. And prices promise to remain high because gainsayers notwithstanding, Hubbert was right.

A big question is how to best handle these nasty crudes? Do you revamp existing units or invest in new capacity? With refineries now running flat out, the balance might seem to favor grass roots expansion, but given the substantial cost multiplier over revamps, this could be questioned. Whichever the case, however, an inescapable fact is that the process design of the project will prove crucial. Between the charge pump, the desalter and the units' distillation columns there are many places where miscalculations in the process design could wreck the entire project.

Can you really be sure of attaining desired crude rates? Desalting viscous crude is extremely difficult. Minimizing coking or asphaltene precipitation in the heaters demands extreme care. Can you reasonably expect high diesel and HVGO recoveries, acceptable levels of nickel, vanadium, and microcarbon residue (MCR)? Refiners who cut deep should not be surprised when the HVGO product MCR is over 2 wt % and the vanadium content is in excess of 10 ppmw. Any one of such difficulties can result in lower revenue, unstable operation or even unit shutdown. It is critical to understand that the inherent properties of these low API gravity crudes dictate that exact process design is of paramount importance.

The point of this litany of possible problems is to remind you not to skimp in the early phases of engineering. From the start of the LP work through the completion of front-end process engineering, actual product yield and qualities depend on the process design.

The message is clear. Nasty crudes will continue to make up an increasing proportion of refineries' crude slates. But time is precious. The sooner we face this fact, unwelcome as it may be, the more expeditiously we can adapt.

For a more in depth review of heavy crude challenges, ask us for Technical Papers 173, 185 and 197.
significantly reduce the corrosion potential by neutralising the acids and elevating the pH of water condensate.

A side-stream of the process water can be routed from the overhead accumulator drum to an online pH meter (ATEX Eex). If the pH meter is connected to the neutralising amine pump it is possible to avoid under-dosage or over-dosage. It is an additional benefit to optimise the neutralising amine consumption. The neutralised process water can be used as wash water for the desalter or crude unit overhead heat exchangers.

**Charles Radcliffe, Technical Service Engineer Europe, CHIMEC, Charles.Radcliffe@matthey.com**

Online pH probes are commonly used in monitoring refinery sour water streams. They are quite reliable but are vulnerable to probe breakage and fouling, and so need regular checking (weekly is common). Buffering can also be a problem if they are used to control acid/alkali dosing using standard PID control. A more sophisticated control algorithm may be required if off-line titration indicates there is significant buffering.

**Q** Our heavy crude feed is delivering very high chloride levels downstream of the desalter and caustic injection cannot cope. What further treatment do you recommend?

**Andrea Fina, Process Technological Unit, CHIMEC, afina@chimec.it**

Certainly the best way to reduce the chloride content in a main fractionator overhead system is to maximise the performance of the desalting system by means of a proper tuning of the process parameters and the chemical treatment:

- Revise the mix valve pressure drop to find the lowest achievable value of salt downstream the desalter
- For heavy and very viscous crudes, a higher wash water flow rate is advisable (up to 7 wt% vs crude flow rate). A proper wash water flow rate assures higher mixing between the wash water and the salts in the crude oil
- Split the wash water injection into two different points: before the cold train (20-30% of wash water) and before the mix valve (80-70% of wash water). This configuration is aimed to improve the mixing between the wash water and the salts, thus better salt removal in the desalting vessel
- Maximise the oil residence time by decreasing the interface level, on condition of maintaining the effluent water free of oil
- Revise the demulsifier program for a higher dewatering and desalting efficiency.

A further strategy would be to implement a dewatering program on the crude oil directly in the storage tank. Being chloride salts mainly dissolved in water, by applying a demulsifying programme directly in the storage tank, an important amount of chloride will be discharged during the tank water draining operation, thus a lower load of chloride will be processed in the desalting system. CHIMEC has developed specific demulsifiers to be applied in the crude storage tank.

A high salt content downstream of the desalter leads to increased chloride content in the main fractionator overhead system. If the partial pressures of HCl, NH₃ and amines in the overhead system are high, depending on the temperature, ammonium and/or amine chloride salts are formed. Once precipitated, these salts promote fouling and under-deposit corrosion.

CHIMEC has developed an innovative and referenced technology, Salt Dispersant Technology. Applied together with a corrosion inhibitor program (neutraliser and film forming corrosion inhibitor), this technology assures complete protection against fouling and corrosion, promoted by salt precipitation above the water dew point and wherever the condensed water is not enough for removing precipitate salts.

**A Gerald Hoffman – Technical Manager, Baker Hughes, Gerald.Hoffman@bakerhughes.com**

As crude slates change to more attractively priced crudes, such as heavy Canadian crudes and shale oils, desalting can present increased challenges. Salt removal may suffer due to a variety of factors, such as incoming complex emulsions, asphaltene instability, increased solids loadings (and smaller particle sizes), and the presence of high melting waxes. Solids, waxes, and asphaltynes can concentrate at the interface, causing the interface to grow. As the interface grows downward, water residence time decreases, which can lead to oily solids in the effluent brine. If the level is increased to clean up the brine, electrical grids can short out. Of greater consequence, emulsion carryover with the desalted crude leads to a variety of downstream impacts, including higher overhead chlorides, preheat and furnace fouling, and metals contamination of downstream catalyst and products.

When processing heavy crudes, the first reaction to these negative impacts is often to reduce mix valve pressure drop. While this can help reduce emulsion band size, it also reduces salt removal and dehydration efficiency. If oily under-carry is occurring, the desalter level may be raised, which only serves to reduce crude oil residence time and move the problem downstream; however, these are the wrong steps to take if good salt removal is the goal.

A more appropriate approach is to first understand the root cause of the problems. The Baker Hughes Crude Oil Management programme is a suite of tools and capabilities designed to better manage opportunity crude desalting. The toolkit includes both operational strategies (crude blending and desalting best practices) and treatment methods (primary emulsion breakers, tank pretreatment, asphaltene stabilisers, wax dispersants, acidification, and solids release additives). The philosophy behind Crude Oil Management is to treat the problem, not the symptom. A few of the tools are discussed below.

Crude pre-treatment technologies can address several of the challenges posed by heavy crude
processing. Pre-treatment chemicals are specifically designed to function at tank conditions, and can be used to address asphaltene instability, wax stabilised emulsions, and solids impacts.

Crude compatibility: the Baker Hughes Asphaltene Stability Index Test (ASIT) provides guidance on crude oil blending to minimise the risk of forming asphaltene solids. If a blend of poor compatibility is processed, asphaltene stabilisers can be injected to improve asphaltene stability.

Crystallised waxes: high melting point waxes in some crudes can stabilise emulsions. Wax dispersants are an effective means of managing these concerns.

Solids: oil coated inorganic solids are a major contributor to emulsion formation in the transport and storage of crude oils. These solids can be the primary cause of oily under-carry with the effluent brine. Pre-treatment chemicals are designed to break emulsions in the storage tank, de-oiling solids and improving the overall quality of the crude oil. This leads to improved tank dewatering, more consistent crude quality, and fewer desalter and crude unit upsets.

**Crude pre-treatment technologies can address several of the challenges posed by heavy crude processing**

Treatment of heavy crudes at the desalter requires specialty emulsion breaker technology. Xeric heavy oil demulsifiers are designed to manage the challenges posed by heavy crudes, providing exceptional salt removal and dehydration efficiency.

Last but not least are the adjunct technologies: acidification and solids release:

- **Desalter acidification:** Excalibur contaminant removal technology. Excalibur technology is designed to remove contaminants such as metals (calcium, iron) and amines from the crude oil. The acidification also improves emulsion resolution, yielding higher quality effluent brine
- **Solids release – Jettison solids release additives (SRA).** Solids are a major cause of desalter emulsions, downstream fouling, and catalyst poisoning. They also tend to carry oil out with the effluent brine. Patented Jettison SRA products are designed to aggressively de-oil solids and enable clean separation from the oil. The result is effluent brine high in oil-free solids, meaning these contaminants are no longer fouling up the refining processes.

The use of these technologies, in conjunction with best practice operation of desalters, allows the safe processing of heavy crudes, free of the negative downstream impacts.

---

**ASIT, Crude Oil Management, JETTISON, EXCALIBUR, and TOPGUARD are marks of Baker Hughes Incorporated.**

---

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

As a first step, I would recommend an optimisation of the desalter system. Salt removal from heavy crude oils has always been problematical due to difficulties in obtaining good mixing between brine and dilution water. Heavy crude oils have a high viscosity and low differential density between oil and dispersed matter. An improved mechanical mixing (delta pressure change) in combination with a higher desalter wash water rate can help to achieve a better contact performance for salt removal without producing stable emulsions. The utilisation of an emulsion breaker programme for heavy crude oils can offer additional benefits like improved dehydration and desalting efficiency.

Kurita’s patented ACF technology is an appropriate means, controlling the corrosion potential of the overhead system, when caustic cannot cope. The additives used for this technology are chemical liquid formulations, known in the market as ACF. The very strong organic base ACF contains no metals which may harm downstream processes. Magnesium chloride and calcium chloride can be easily converted to hydrochlorides of ACF. In the furnace, these chlorides thermally decompose into a non-corrosive, volatile organochloride gas and a neutralising amine with almost no hydrogen chloride produced. Both decomposition products are routed to the overhead system, where the neutralising amine leaves the system with the accumulator water and the volatile gas with the gas phase. This is a technical innovation, which significantly reduces the chloride concentration and corrosion potential in the overhead system, even when high chloride concentrations leave the desalter.

**A Charles Radcliffe, Technical Service Engineer Europe, Johnson Matthey, Charles.Radcliffe@matthey.com**

Ideally, the problem should be addressed at the desalter. Initial moves would be to increase wash water rate, increase mix valve DP, and ensure all the electrodes are working at full power. The source of the problem may also be due to the formation of a stable emulsion, and in this case reducing mix valve DP may help, and using de-emulsifier additives. This problem can be detected by taking a sample of desalter product and keeping it in a temperature controlled bath at desalter temperature for 24 hours then checking the relative volumes of hydrocarbon and aqueous fractions.

If the problem cannot be controlled at the desalter then increase the strength of the caustic and increase neutralising and film forming amine injection rates to the crude and FCC overheads, along with increased frequency of crude and FCC fractionator overhead water washes.

**A Nate Hatcher, Vice President, Technology Development, Optimized Gas Treating, nate.hatcher@ogtrt.com**

Poor separation in the desalter may be to blame due to emulsion carry-over. If stripped sour water is used as
MIDAS® GOLD
The Gold Standard for Resid Upgrading

MIDAS® FCC catalysts are Grace’s high matrix catalysts with proven success for deep conversion of resid. MIDAS® Gold, the latest member of the family, is a high activity formulation that delivers

▶ Superior coke-selective bottoms upgrading
▶ Stable activity against metals contamination
▶ Formulation flexibility for a customized yield profile

We offer several distinct MIDAS® formulas, suitable for a broad range of feed and operating objectives. Let Grace technical experts show you the best fit for your operation.

grace.com
make-up to the desalter, verify that the amine content is not excessive. Amines combine with fatty acids in heavy crudes to generate soap.

A India Nagi-Hanspal, Asst. Manager Technical Services, Dorf Ketal, indiannagi@dorfketal.com
Achieving good desalting performance is a challenge during heavy crude processing. Processing heavy crudes requires a good desalter optimisation plan and use of superior demulsifier chemistry. A good approach during heavy crude processing can be as follows:
• Optimise desalter wash water rate
• Optimise desalter temperature
• Optimise mix valve pressure drop
• Dorf Ketal’s proprietary desalter treatment programmes, comprising a demulsifier and co-additives, have helped refiners to process heavy crudes (<25 API) with optimum performance
• Optimisation of wash water upstream of the overhead condensers can also help reducing chlorides and corrosion rates in overhead system.

Q We are not getting the cycle life we were expecting from our hydrotreating catalyst after presulphiding. How should we be adjusting process conditions after presulphiding?

A George Anderson, Global Hydroprocessing Specialist, Albemarle Corporation, george.anderson@albemarle.com
There are several potential causes for not achieving expected hydrotreater cycle length after start-up, and each of these has different potential solutions. For instance, the problem could be due to higher than expected start-of-run (SOR) WABT, and/or due to higher than expected catalyst deactivation. Both of these ‘causes’ are really responses that may be due to multiple potential root causes. Insufficient information is provided to do a root cause analysis, so the answers provided here are very generic.

At a minimum, extending cycle length means that you should operate your unit at minimum WABT to meet product specifications for as long as possible. Thus, you should avoid over-treating so that product properties are significantly better than the product specifications.

Maximising activity stability generally implies that you should also maximise treat gas rate and purity to maximise hydrogen partial pressure (ppH₂). If possible, you should also reduce the most difficult components in the feed (heavy ends, cracked stocks, and so on) to lower hydrogen consumption, exotherms and coking tendency, and you should remove very light feed components (such as coker naphtha, FCC naphtha and light kerosene) to avoid excessive feed vapourisation that lowers ppH₂.

If these recommendations do not achieve the desired cycle length and/or it is not possible to implement them or to route an easier feed to your unit, you may be forced to make a choice between accepting a shorter cycle length or reducing throughput (lower LHSV and feed/product rates) for your unit. Obviously, neither of these options is desirable economically. Therefore, it is strongly recommended that a rigorous root cause analysis be conducted to find the real causes of the short cycle so that the problem does not occur again in subsequent cycles.

Q Is there a catalyst option for upgrading LCO to ULSD without an additional process step?

A George Anderson, Global Hydroprocessing Specialist, Albemarle Corporation, george.anderson@albemarle.com
LCO can be upgraded to ULSD in either an existing diesel hydrotreating (DHT) unit or in a hydrocracking pretreat (HC-PT) unit without adding an additional process step. HC-PT is a high pressure process with very high treat gas rates, and can upgrade LCO with relatively high throughputs and LCO contents in the feed. Dedicated LCO hydrotreaters operating at ≥85 bar ppH₂ inlet can successfully upgrade 100% LCO feed with ~three-year cycles (depending on LHSV).

Most DHT units tend to operate in the 15-55 ppH₂ inlet range. At the lowest pressures, very little (<10%) LCO can be co-processed to produce ULSD and achieve a one-year cycle length. As ppH₂ and hydrogen treat gas rate increase, higher percentages of LCO can be accommodated and longer cycle lengths can be achieved. However, as LCO content in the feed increases, higher exotherms are generated due to the greater hydrogenation of olefins and aromatics. The exotherms and required cycle length may determine the maximum LCO content in feed to avoid exceeding maximum temperature limitations for the reactor materials.

Selection of the preferred catalyst system to maximise ULSD throughput and upgrade to ULSD specifications is highly specific to the unit capabilities and limitations as well as the feed properties and ULSD specifications (especially cetane number, density and cold flow properties). Albemarle’s Stax technology can be used to optimise unit performance with the right combination of CoMo and/or NiMo catalysts to meet multiple refiner objectives in producing ULSD. For higher pressure units with inlet ppH₂ ≥40 bar, using 20-40 vol% Nebula as part of the Stax catalyst system has been proven to be especially effective in increasing LCO upgrade to ULSD.

It is strongly recommended that a rigorous root cause analysis be conducted to find the real causes of the short cycle so that the problem does not occur again
UOP’s propylene production technologies outshine the rest

Low cost feedstocks, high yield products. There’s no better combination for generating petrochemical profits. As an industry leader in petrochemical process technology for more than 70 years, UOP continues to deliver proven, flexible solutions with high-yield returns. UOP advanced Methanol-to-Olefins (MTO) and Oleflex™ processes provide a higher return on investment, smaller environmental footprint and innovation that is second to none. For advanced MTO, you can use alternative feedstocks such as coal, natural gas and more, and you can produce the high-value olefin of your choice, including propylene and ethylene. Recyclable, platinum-based Oleflex catalysts offer the best performance for environmentally friendly on-purpose propylene production. From low-energy solutions to eco-friendly innovations, UOP sets a standard that shines.

UOP
A Honeywell Company

1914 - 2014 A Century of Innovation in the Oil and Gas Industry

Looking for exclusive information on olefins technology? Scan the code to register for the UOP Portal.
© 2014 Honeywell International, Inc. All rights reserved.
Take advantage of the world’s broadest range of hydraulic and instrumentation tubing.

A broader range of in-stock tubing gives you added flexibility. Within 24 hours, you can rest assured that we’ll process your order and ship you just the right high-performance tubing.

When it comes to seamless stainless tubing, we supply corrosion-resistant grades in outer diameters 1.59 to 50mm (0.0625 to 1.968 in), with larger diameters available upon request. At last count, we had exactly 3,768 unique items in stock, including premium tubes, pipes and control lines. With dedicated mills on three continents, as well as strategically located warehouses and distribution centers, we can deliver the widest array of in-stock hydraulic and instrumentation tubing to nearly any site in the world.

More than just giving you access to a broad range, we pride ourselves in providing a consistent level of high-quality tubing in every batch. Having served some of the world’s most demanding industries for 150 years, we have no choice but to set very high standards. So if you demand six-star quality, logistics and service, give us a call. Experience what we call the Peace of Mind Standard.
The tail gas unit (TGU) process has been developed to remove sulphur compounds from Claus tail gas in order to comply with stringent emission regulations. From the early 1970s to today, TGUs have been improved to meet higher levels of performance for ever tighter environmental requirements and to reduce capital or operating cost. Reactor performance is a critical parameter in achieving TGU environmental performance. Conversion of sulphur species to H₂S is a function of catalyst activity, reactor space velocity and temperature. Assessment of the impact of these principal variables on both catalyst bed design and performance is the subject of this article, presented in two parts. The first part of the article (PTQ, Q3 2014) provided an introduction to reactor modelling, process and catalyst development history, and chemical equilibrium. The second part develops reactor modelling with a kinetic reaction model, the effects of temperature and space velocity, catalyst activation, catalyst deactivation, and determining TGU catalyst health from a commercial unit temperature profile.

The influence of temperature on performance has competing effects.

To predict the performance of TGU reactor systems, a basic framework of chemical equilibrium, reaction chemistry and catalyst activity is used in kinetics and equilibrium, impacting conversion. The kinetics for reactions of importance are favourably influenced by higher temperature, proceeding to higher conversion at a given space velocity. Equilibrium effects from higher temperatures usually result in higher equilibrium concentrations for the species, which the system is designed to destroy, limiting lower values for outlet concentration. Equilibrium considerations were addressed in the first part of the article and this part deals with kinetics.

Conversion is a term of frequent reference in this article. Conversion for CO (or COS) is expressed as disappearance across the reactor and is adjusted for the equilibrium ‘back pressure’ of the reacting component:

\[
\text{Conversion} = 1 - \frac{\text{CO}_{\text{out}} - \text{CO}_{\text{equilibrium}}}{\text{CO}_{\text{in}} - \text{CO}_{\text{equilibrium}}}
\]

Tail gas reactor temperature has historically ranged between 200°C and 325°C. This fits within the region of active catalyst functions and meets the required minimum temperature for catalytic activity function, about 200°C for low temperature catalysts and 240-300°C for conventional tail gas catalysts. Maximum temperature is generally limited to 345°C (650°F).

Kinetics: first order reaction model
Reaction kinetics describes how fast a reaction proceeds and allows prediction of how far a reaction proceeds toward equilibrium in a reactor system. The reactor system is defined by gas composition, gas flow rate, and catalyst type and volume. A first order reaction kinetic model with equilibrium is useful to describe the conversion of reactants in the tail gas reactor system and is helpful to understand performance effects of operating variables.

Tail gas reaction kinetics can be represented reasonably with first order reaction models as a useful representation of tail gas reaction kinetics. Experimental data for a Criterion C-534 tail gas catalyst is fitted into the reaction modelling.

www.eptq.com
Reactor loading is represented in the kinetic expression as gas hourly space velocity (GHSV), a ratio of the gas rate per unit of catalyst. The basis used for these expressions is actual volumetric gas flow rate per hour divided by catalyst volumetric inventory.

The relationship between conversion, actual gas hourly space velocity, GHSV and catalyst activity, $k$, is defined in first order reaction model as:

$$\text{rate of disappearance of component a} = \frac{dC_a}{dt} = k \cdot C_a$$

and overall for the reactor, the equilibrium conversion is given by:

$$\ln (1-\text{Conversion eq}) = -k \cdot \frac{3600}{\text{GHSV}},$$

Equilibrium conversion (Conversion eq) represents the amount of component a, which can be actually converted, adjusting for equilibrium residual:

$$\text{Conversion}_{eq} = 1 - \frac{(C_{a_{in}} - C_{a_{eq}})}{(C_{a_{in}} - C_{a_{eq}}_{eq})}$$

and

$$\text{Conversion}_{eq} = 1 - \frac{(C_{a_{in}} - C_{a_{eq}})}{(C_{a_{in}} - C_{a_{eq}}_{eq}} = 1 - e^{-\frac{k \cdot 3600}{\text{GHSV}}$$

where: $k$ = first order activity catalyst, mol/sec
$C_{a_{in}}$ = inlet concentration of component A
$C_{a_{out}}$ = outlet concentration of component A
$C_{a_{eq}}$ = equilibrium concentration of component A, set by WABT and composition of outlet stream
GHSV = actual gas hourly space velocity.

Reactor outlet concentration will be the remainder of the inlet not converted plus equilibrium residual:

$$C_{a_{out}} = (C_{a_{in}} - C_{a_{eq}} \cdot (1-\text{Conversion eq}) + C_{a_{eq}}$$

The reactor space velocity expression is:

$$\text{actual gas volumetric flow (vol/hr)}$$
$$\text{GHSV} = \frac{\text{catalyst inventory (vol)}}{\text{1/hr}}$$

Reactor residence time is sometimes used as another expression of reactor loading, and it is related to GHSV:

$$t = \frac{1}{\text{ghsv}} \text{hr} \quad \text{or} \quad t = \frac{3600}{\text{ghsv}} \text{sec}$$

Conversion of components is dependent on space velocity and catalyst activity (see Figures 1 and 2). Equilibrium conversion compensates for the effects of concentration, composition and temperature. The resultant outlet concentration of components is determined by their inlet concentration, equilibrium and conversion.

The influence of space velocity on conversion is explicit in the first order reaction relationship. The quotient of activity divided by space velocity is proportional to the logarithm of conversion. Higher conversion is obtained with lower space velocity (greater catalyst volume) or higher catalyst activity. Higher gas rates, higher temperatures or lower pressures all increase
Comprimo® Sulfur Solutions

Gas Treating & Sulfur Technology
With more than 500 units built during the last 40 years, we are a global leader in the gas treating and sulfur recovery technology

Total Project Solutions
We are one of the world’s largest and most diverse providers of professional technical services. Our global network includes more than 200 offices in more than 25 countries
From our gas treating & sulfur technology centers of expertise in Leiden, The Netherlands and Calgary, Canada, we provide engineering, procurement and construction services to our clients around the world

Visit our webpage to learn more about all our products – www.jacobs.com/comprimo
actual GHSV for a given standard volumetric gas flow rate.

The influence of concentration is scalar on reactor outlet concentration; whereas higher concentration increases rate of disappearance and conversion remains constant, thus outlet increases in proportion to inlet concentration. If it is necessary to obtain a target outlet value for a given component, say to meet an environmental target, as an inlet concentration of that component becomes higher, a higher conversion is required.

The influence of tail gas compositional change is handled through the equilibrium value of CO or COS with their related reaction components and the equilibrium constant, Kp. The influence of temperature on equilibrium value for CO or COS is handled in the underlying equilibrium constant expression, which is a function of temperature.

The activity coefficient, k, represents catalyst activity. It must be determined experimentally, or may be determined for a specific operating plant from a plant test. Its relationship to temperature is represented by the Arrhenius relationship:

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

Where $A$ = activity coefficient

$E_a$ = activation energy exponent

$R$ = gas constant

$T$ = absolute temperature

An alternative expression is: $k = A \cdot T \cdot e^{-\frac{E_a}{RT}}$, but it is more complex to model and provides only slight improvement in correlation.

Parameters for the Arrhenius coefficients for COS hydrolysis were established from published data for alumina and fitted against plant data and experimental data on a SCOT catalyst. The CO function was fitted to SCOT catalyst data. This handles the important temperature dependency function for the activity and provides the basis for a model for reactor performance. The temperature dependency activity functions for CO and COS are generally proprietary to the respective catalyst manufacturers.

Chemical reaction equilibrium and kinetics are influenced by temperature as the following examples show.

The chart of experimental data in Figure 3 shows conversion decreasing as space velocity increases. This is entirely consistent with the first order reaction model. Note that in the reaction model, catalyst activity is a function of temperature, not space velocity. In Figure 3, the first order activity coefficient, k, is derived from values calculated from conversion and equilibrium and space velocity. The activities are almost constant for each temperature. The decline at low space velocity is attributed to low gas velocity in the reactor bed with diffusion limitations in mass transfer as the flow regime approaches a laminar state.

Temperature has a strong and direct influence on activity (see Figures 4 and 5). For COS, with an activity on the order of 1.5 to 2.5, an increase of factor 2 was observed for a 70°C increase. This relates to a 1% increase in activity for every degree Centigrade increase. A 1% improvement when compounded over 70 degrees is a doubling: $2 = (1.01)^{70}$.

Over the range 250-320°C, the k cosh catalyst activity for COS destruction doubles and equilibrium COS, for example, increases from 2 ppm to 15 ppm. Over the range 250-320°C, the k wgs catalyst activity for CO destruction increases 50%. Because the activity...
Optimize your plant for a safe, efficient start-up
Through our detailed engineering and expert field execution

When considering mechanical pre-commissioning and commissioning for your plant start-up – consider this.
Innovative engineering and service excellence results in greater quality. And THAT reduces costs. We’re an oil and gas services company committed to excellence. Everything we do in the field we engineer first to meet your specific needs.

Demand Professionals. Demand FourQuest Energy.

For a complete list of services, visit our website.

www.fourquest.com
youth – because the rate of activity decline increases:

• The equilibrium ‘back pressure’, which governs how low a concentration can possibly be achieved, is favoured by lower temperatures
• At low temperature, catalytic activity declines and conversion performance is dominated by kinetics; equilibrium does not matter very much since all equilibrium values are very low
• At conventional temperatures, catalyst kinetics are stronger, hence catalyst kinetic property is important, although equilibrium back pressure sets a lower boundary for performance
• At high temperatures, performance is set by equilibrium, if catalyst activity is fair and space velocity is reasonable.

Figure 6 shows the concentration of feed and product components through the reactor bed for Criterion C-534. This demonstrates the performance range for fresh catalyst in the conventional temperature range. Early bed effects are not measured, such as likely rise of COS concentration from early CS₂ conversion or the possibility of COS from sour shift with CO and H₂S. Note that conversion occurs for methyl mercaptan to methane. The bed is effectively ‘shortened’ by a loss of activity or an increase in space velocity. With a decrease in conversion outlet, the concentration moves away from equilibrium. Conversely, at higher temperatures, the catalyst has higher activity and reactions proceed faster. This is indicated by the shift in concentration profiles for a 20°C higher inlet temperature (see Figure 7).

The first order kinetic model provides a tool for quantification of design and evaluation of catalyst performance from operational data. This also is useful for forecasting performance for different conditions, such as increasing tail gas load (space velocity) or temperature. Activity and space velocity are paired, which means that, at constant catalyst activity, an increase in tail gas loading (space velocity) reduces conversion.

Figure 8 shows conversion with illustrative activity lines for start-of-

level is higher, the relative increase is a smaller percentage. Equilibrium CO for a standard feed example increases from 50 ppm to 250 ppm. Temperature can be increased to improve CO and COS destruction performance for a catalyst that has lost activity, but aging accelerates with increased temperature. This is usually an end-of-run tactic to extend a run to scheduled turnaround – not a fountain of
run, mid-run, and end-of-run conditions as a function of space velocity. If the condition of the catalyst is known, projections can be made about future performance capacity. A catalyst with good activity has the potential for a long cycle life and continued use, whereas a low activity catalyst probably needs replacement:

• In Figure 8, the relativity between SOR and EOR is half. This is illustrated at the 93% conversion level, with SOR achieving this conversion at 3000 GHSV and EOR achieving this conversion at 1500 GHSV.
• With respect to determining the state of the catalyst’s health, note that conversion of 93% can be achieved by a catalyst at all three health stages depicted, depending on space velocity (tail gas loading). Load matters because the same bed performance comes from a catalyst with good activity and plenty of life remaining, mid-life catalyst at GHSV = 2100 1/hr, or from a ready-for-replacement EOR catalyst loaded at GHSV = 1500 1/hr.
• Alternatively, at 2100 1/hr GHSV, conversion ranges from 87% to 98% depending on activity state.

Table 5 shows the first order activity coefficients needed to achieve the indicated conversion values at various space velocities. The required activity coefficients are a function of catalyst property and temperature. As the table shows, space velocity impacts unit performance, a higher space velocity requiring a proportionally higher activity for a given conversion. Lower space velocity may be achieved by adding more catalyst or lowering the gas rate at end-of-run.

This is a closing point on the issue of a combination impact of equilibrium and conversion. When CO conversion declines, be it from catalyst activity decline or space velocity increase, the outlet CO concentration rises; it is a sum of equilibrium residual plus unconverted material. This means that CO2 and CO are not in equilibrium, and the COS equilibrium coupled to those compounds will not be equal. The ultimate COS level is determined by parallel and sometimes competing pathways, such as hydrolysis and sour shift (hydrogenation). A higher than equilibrium CO level elevates the COS equilibrium as expressed via sour shift. The COS equilibrium value the system ‘feels’ will be between that expressed by hydrolysis with CO2 and sour shift from CO. Therefore, there is a knock-on effect on COS due to an elevated CO resulting from a weak conversion of CO. Thus, as goes CO, so goes COS.

Catalyst sulphiding

In order for a catalyst to realise its full capacity for activity, it is essential that the catalyst be properly loaded and activated. The TGU reactor catalyst, consisting of molybdenum and cobalt supported on an alumina substrate, is manufactured in a metal oxide form. Before the catalyst can be utilised in the TGU reactor, it must be made ‘active’ by converting the metal oxide sites to metal sulphide sites. Figure 9 depicts the sulphiding and reduction pathways. A sulphiding pretreatment step is required to activate the catalyst. During this step, the catalyst is heated in a controlled fashion to 600ºF (315ºC) in an H2 and H2S environment. The sulphiding
LEADERSHIP LIKE NO OTHER.

Learn from the industry experts. Attend the John Zink Institute.

Whether you’re looking to optimize your plant or maximize your career, our combustion and process courses will be invaluable to you. Learn from some of the world’s most recognized engineers and educators in the science of combustion. Courses offered year-round at our state-of-the-art facility or at your site.

For more information, contact us at johnzink.com/training-classes.
TGU catalyst deactivation mechanisms

Hydrothermal aging, the loss of a catalyst’s surface area and metals activity, caused by exposure to water vapour at normal TGU operating temperatures, is the primary deactivation mechanism in a stably operated TGU. In typical tail gas units, the decline in catalyst activity due to hydrothermal aging is gradual. TGU in service with air-blown Claus typically achieves eight years of catalyst life, and units have experienced as long as 12 to 14 years. Units in service with high-basis, oxygen-blown Claus may be expected to provide six to eight years’ life.

Misoperation can result in severe and rapid losses in catalyst activity. Primary TGU catalyst poisons are carbon and oxygen. Catalyst coking, primarily from poor burner operation, is one of the two common causes of catalyst poisoning. Catalyst activity is reduced by coke blocking access to and covering the active sites on the catalyst. Additionally, catalyst coking can cause high pressure drop across the catalyst by reducing the void fraction in the catalyst bed. Small quantities of oxygen over a period of time can deactivate the catalyst by blocking the active sites through a sulphation reaction. Larger quantities of oxygen that enter the TGU reactor can seriously damage the catalyst due to temperature excursions that can sinter the catalyst support. Exposure to hydrogen without H2S for extended periods of time at temperatures greater than 400°F (200°C) can result in reduction of catalyst to base metals.

Determining TGU catalyst health

TGU catalyst health can be determined in several ways. Indicators from which we can infer performance include:

- Temperature profile observed in the reactor bed
- Changes in conversion, indicated by increased incinerator emissions (SO2, maybe CO)
- Activity evaluation from reactor inlet and outlet stream composition, determination usually by unit testing and analytical evaluation results
- Measuring physical properties and/or activity testing for an actual catalyst sample.

The temperature profile in the reactor bed can yield a simple answer: if temperature rise has shifted into the mid and lower portion of the bed, the catalyst has poor activity and it is time to replace it. The incinerator has a likewise simple answer: if emissions are high but vent gas H2S level and the pit are normal, then likely the catalyst has poor activity and it is time to replace it. A catalyst assay activity test gives a definitive answer, but it is usually not available until the catalyst has already been removed from the reactor. The challenge is establishing activity for the not ‘obviously dead cases before replacement is under way.

Catalyst activity evaluation from unit performance testing is done when the unit is still running, so assessment is timely. However, the activity determined for the catalyst may be less certain, as is the need to replace it. Past practices that attempt to assess activity with online test data do not provide quantitative measures for catalyst activity, in part because many of them do not include tail gas loading.

Maximising service life from the catalyst and obtaining best tail gas unit performance means avoiding conditions that deactivate the catalyst. Conditions to avoid are excessive temperature (over 700°F), or a reducing atmosphere before sulphiding without H2S, exposure to oxygen, accumulation of soot or particulates, or exposure to heavy hydrocarbons or aromatics. High percentage water in tail gas (50%) accelerates hydrothermal aging and inhibits catalytic activity by occupying much of the catalytic surface.

The kinetic reaction model provides a measure of good quality, granular catalyst activity from compositional data provided by online performance test data. This approach explicitly includes tail gas loading and its impact on catalyst bed performance. Real performance can be discerned and, more importantly, future performance capability can be anticipated. A timely and appropriate catalyst change can be planned. A meaningful comparison can be made across time for tail gas reactor performance if all tests are conducted at the same temperature.

Temperature profile example

In TGU reactors with two or more levels of temperature indication (see Figure 10), the temperature
CRI Catalyst Company’s global resources in research and development (R&D), manufacturing, and surface and materials science establishes CRI as a desirable choice for custom catalyst development. CRI provides the tools to develop and progress your custom catalyst project from lab scale to full commercialization. Our customers are continuously striving to improve their production processes, provide better products, develop leading-edge technologies and maintain consistent operating results. In many cases, a key to achieving these goals is the development of custom catalyst products, designed specifically for individual customer applications/processes. CRI works with customers to create and/or identify specific catalysts to help achieve their program goals. It is all part of our commitment to delivering innovation.
an additional two to three years of cycle life, hopeful that she could report to management the turnaround planned for six months ahead could be postponed for at least another couple of years.

When more detailed temperature information was received, a plot showing the percentage contribution per reaction zone to the total reactor exotherm was generated (see Figure 12). This plot indicates that over the first 450 days of operation, activity in the top catalyst zone declined by approximately half. During this same period, the middle zone catalyst’s contribution to the total reaction exotherm doubled. Around day 950, the

DT = (Avg Top Temp – Reactor Tin) + (Avg Mid Temp – Avg Top Temp) + (Avg Btm Temp – Avg Mid Temp)

The second plot tracks the change in percentage contribution of the various reaction zones to the total reactor temperature differential throughout the cycle. It is calculated as follows:

Top Zone% = (Avg Top Temp – Reactor Tin) / DT

Middle Zone % = (Avg Mid Temp – Avg Top Temp) / DT

Bottom Zone% = (Avg Btm Temp – Avg Mid Temp) / DT

Figure 11 Total reaction exotherm, Customer 1

Criterion recommends that unit engineers or process specialists periodically record and plot the total temperature differential across the reactor as well as the percentage contribution to the total reaction exotherm by reactor catalyst zone – top, middle and bottom – from the beginning of the cycle. This technique is often helpful to determine effect on catalyst health after a unit upset or an unplanned shutdown.

Figure 12 DT contribution per reaction zone, Customer 1
WE’RE NOT EXAGGERATING. OUR BOILERS ARE SOMETHING TO BRAG ABOUT.

We custom design and custom build boilers to perform efficiently, safely and cleanly. Your RENTECH boiler will lower operating costs, reduce emissions, and provide faster start-up and cool-down. You’ll find satisfied customers on six continents with specialty boilers, HRSGs, wasteheat boilers and fired packaged watertube boilers from RENTECH. We’ve been designing and building boilers for people who know and care since 1996.

WWW.RENTECHBOILERS.COM
second zone starts to decline and the third zone contribution starts to increase. Figure 12, demonstrating the change in reaction exotherm distribution within the TGU reactor, provides a deeper level of discernment than Figure 11 which showed only the total reaction exotherm. A cursory examination of Figure 11 might have led to an incorrect determination of the TGU catalyst health. The majority of the reaction exotherm is generated from the hydrogenation of SO₂ and Sₓ and sometimes the water gas shift reaction of CO (CO heat release is dependent on the CO feed concentration to the TGU reactor). The hydrogenation of SO₂ and Sₓ proceeds to completion in a much faster manner than the slower hydrolysis reactions. By the time hydrolysis reactions have shifted lower into the catalyst bed, conversion of the slower hydrolysis reactions, particularly COS conversion, has typically undergone a step change reduction.

In a stably operated TGU, it is not an unreasonable expectation that the majority of the reaction exotherm remains in the upper portion of the TGU catalyst bed for the majority of the operating cycle. This is demonstrated in Figure 13.

The reaction exotherm shifting lower into the reaction bed is indicative of diminution of catalyst activity either through normal hydrothermal aging or a sudden operational upset. For example, a three-foot catalyst bed essentially becomes a two-foot catalyst bed. The upper portion of the catalyst bed no longer catalytically contributes to the reactions, resulting in effectively higher GHSV. Thus, a 2000 GHSV bed design becomes a 3000 GHSV bed and conversion is correspondingly lower.

Of the four indicators listed above, activity evaluation and measuring physical properties potentially provide the most conclusive information with regard to TGU catalyst health. Due to cost and/or difficulty, most TGU operators avoid both online sampling/analysis of the TGU reactor feed and outlet streams and collecting TGU catalyst samples for analysis in the midst of an operating cycle.

Periodically collecting and analysing hydrogenation reactor feed and effluent streams is also a useful way to gauge catalyst health. Collecting and analysing representative feed and outlet gases from the hydrogenation reactor can be quite challenging and is not often done by TGU operators. Companies such as Brimstone have the expertise to provide this service. The total cost associated for a maintenance shutdown for large tail gas units is often several times the cost of the TGU catalyst. Some TGU operators bring in a company like Brimstone several times during the TGU catalyst cycle life to benchmark TGU reactor performance. By employing this practice, an operator of a large TGU was able to gain confidence to extend a 10-year cycle length to 13 years and counting. In doing so, they have deferred several million dollars in catalyst and associated maintenance turnaround costs.

Analysis of catalyst samples is an effective gauge of the health of the TGU catalyst. The primary tests performed on the sampled catalyst include: surface area, carbon on catalyst, crush strength and, if the catalyst sample is collected and stored inertly, X-ray photoelectron spectroscopy (XPS). Comparing the results of the ‘used’ catalyst to fresh catalyst helps predict remaining
catalyst life/activity as well as providing clues to potential unit upsets or misoperation that may have occurred during the cycle.

Table 2 shows fresh and end-of-run (EOR) characteristics for Criterion C-534 conventional TGU catalyst.

An example of an application of XPS is shown in Figure 14. A customer with Criterion TGU catalyst, ex situ activated via Eurecat’s Totsucat G process, inertly loaded the fully activated catalyst. The customer put the bed under a nitrogen blanket for three weeks prior to starting the TGU. Upon introduction of SRU tail gas, the unit experienced SO2 breakthrough with the quench water pH dropping below 3. The H2 concentration in the reactor outlet gas stream was approximately 5 mol%. After making several operational adjustments, the TGU was shut down and it was decided that the catalyst would be replaced.

During the subsequent investigation, two events that might have impaired catalyst activity were identified. First, it was discovered that, at the midpoint between catalyst loading and start-up, readings from the thermocouples in the TGU reactor increased from ambient temperature to 250°F (120°C). Second, upon introduction of SRU tail gas, the in-line heater operation may not have been sub-stoichiometric. One or both of the events could have impaired catalyst activity by sulphation.

Spent catalyst samples collected during inert unloading of the TGU reactor were shipped to Criterion in air-tight sample containers for testing. The unit engineer also provided a retain sample of the Totsucat G processed catalyst loaded in the TGU reactor. Figure 14 shows the S 2p region. The location and intensity of the right peak for the fresh catalyst and west bottom samples indicate that these samples had significant amounts of sulphur present in the sulphide form. The location and intensity of the peaks for the east top, east middle, east bottom, west top, and west middle samples indicate that the sulphur is almost exclusively present in a sulphate form.

Figure 15 shows the oxide, sulphide and sulphate forms of Criterion C-534 TGU catalyst: the blue coloured material at the top is the oxide form; the black coloured material is the sulphide form; and the grey coloured material is the sulphate form. The customer mentioned that the appearance of the Totsucat G processed TGU catalyst loaded into the reactor was consistent with the sulphide form shown in Figure 15. The appearance of the catalyst that was unloaded from the reactor was consistent with the sulphide form shown in Figure 15. A photograph of the customer’s catalyst is shown in Figure 16.

Additionally, TGU catalyst samples can undergo activity testing versus ‘fresh’ catalyst in a TGU pilot plant. During TGU shutdowns, especially planned shutdowns, it is recommended to collect catalyst samples for analysis. Even if the first instance that catalyst samples may be caught is when the catalyst is being replaced, useful benchmarking information may be obtained.

Conclusions

Equilibrium and kinetic effects can
be summarised as follows:
• At low temperatures, performance is dominated by kinetics; equilibrium does not matter very much since all equilibrium values are very low.
• At conventional temperatures, kinetics is a stronger influence, and hence catalyst kinetic property is important, although equilibrium back pressure sets a lower boundary for performance.
• At high temperatures, performance is set by equilibrium if catalyst activity is fair and space velocity is reasonable.
• Catalyst performance is critical to achieving high sulphur recovery and the performance demanded by today’s environmental regulations.
• Conversion of sulphur species to H₂S in the reactor is affected by reactor performance and catalyst activity required.
• Conversion required is established by the inlet concentration of contaminants and environmental performance requirements.
• Space velocity (gas load) and catalyst inventory impact conversion.
• Temperature (absolute temperature) affects equilibrium back pressure and catalyst activity.
• COS is handicapped by high CO via sour gas shift, elevating outlet concentration.
• To cope with damaged catalyst, the temperature can be increased or the space velocity reduced.

Analysis of spent TGU catalyst can provide useful information on TGU operation and benchmarking

- Plotting TGU reactor temperature profiles can provide an indication of catalyst health while the TGU is in operation.
- Activity evaluation from analysis of reactor inlet and outlet stream composition can provide information to defer catalyst change-outs.
- Analysis of spent TGU catalyst can provide useful information on TGU operation and benchmarking.

Michael A Huffmaster is a process expert and consultant to industry for gas processing and treating, refining operation, CO₂ capture, and related research. His activities regarding sulphur recovery include amine treating, Claus, tail gas treating, and tail gas treating catalyst development, design and operation. He retired from Shell Oil in 2005 with 36 years of experience. He holds a bachelor of science degree in chemical engineering from Georgia Institute of Technology and is a registered professional engineer in Texas. Email: michael.huffmaster@att.net

Fernando Maldonado is the Business Development Manager – Gas Treating Catalysts for Criterion Catalysts and Technologies, located in Houston. He has global responsibility for Criterion’s gas treating catalyst business. Prior to joining Criterion Catalysts & Technologies in 2001, he held positions as a process design engineer, unit contact engineer, and an operations superintendent in two US Gulf Coast refineries. He holds a bachelor of science degree in chemical engineering from Texas A&M University. Email: Fernando.Maldonado@CRI-Criterion
maximize propylene

Refiners can tap into the huge potential of the FCC to maximize petrochemical yields by modifications to process conditions and the use of Johnson Matthey’s INTERCAT® ZSM-5 additives.

ZSM-5 chemistry is more than just cracking gasoline. When optimizing LPG olefins ZSM-5 plays many different roles. Light olefin oligomerization creates new gasoline olefins that can be cracked back down into LPG olefins in a dynamic ‘snakes and ladders’ type interaction. These insights have been applied in the additive for maximum propylene: SUPER Z EXCEED.

INTERCAT®

UK Tel +44 (0)1642 553601 Fax +44 (0)1642 522542
www.jmprotech.com

Johnson Matthey Process Technologies
Predicting future FCC operations via analytics

Data analysis enables a company to take advantage of patent information to unveil underlining development trends for formulating technology strategies for future markets

PATRICK J CHRISTENSEN, TOUSEEF HABIB, THOMAS B GARRETT and THOMAS W YEUNG
Hydrocarbon Publishing Company

American writer Mark Twain’s famous misquotation, “Reports of my death have been greatly exaggerated” may well be applied to the current status of refinery fluid catalytic cracking technology and certain gasoline-centric FCC units operated in parts of the world.

Declining gasoline demand caused by bioethanol mandates and improving vehicle fuel efficiency, poor fuel demand because of a weak European economy, rising shale/tight oil processing in the US resulting in growing production of gasoline and naphtha, and diminishing outlets for naphtha as more steam crackers source cheaper ethane and propane feedstock are the major reasons for concerns among refiners, technology holders, and catalyst producers. On the other hand, the FCC unit has been continuing to perform ‘miracles’ for refiners in light of increasingly stringent fuel standards, changing market conditions, and competing technologies. Its role has expanded from a gasoline machine to an olefins maker, a sulphur remover, a residue upgrader, and a ULSD feedstock contributor by maximising LCO output. Furthermore, it is lending itself to two additional roles – biofeeds user and refinery CO2 emissions reducer – to alleviate growing concerns over energy security and global warming.

So, the question is: what is the future of FCC operations? One way to predict is by looking at where technology companies have been investing in research and development, especially patent applications. This article analyses the patenting trends of FCC technology around the world during the years 2008 to 2013, reviews the significance of the data, and explains how the analytics can be used to predict the future business opportunities and challenges for refiners and technology developers alike.

Big data analytics
Analytics, which is a term referring to the search for and use of patterns in data, has been applied in a variety of industries to help businesses gain a competitive edge. Marketing agencies, sales companies, and even sports teams have turned to analytics.

In analysing refining technologies, FCC seems to be a good place to start, because it produces high volumes of fuels and petrochemical feedstocks. In addition, the FCC unit is considered to be the workhorse of the refinery.

Analytics has become a powerful management tool for refiners and vendors to establish a competitive edge

In the case of analysing patent data, the authors of a management handbook entitled Strategic and Competitive Analysis: Methods and Techniques for Analyzing Business Competition said, “Patent analysis is a unique management tool for addressing the strategic management of the firm’s technology and product or service development process. Translating patent data into competitive intelligence allows the firm to gauge its current competitiveness, to forecast technology trends, and to plan for potential competition based on new technologies.”

Analytics has become a powerful management tool for refiners and vendors to establish a competitive edge. A generalised combination of external and internal patent analysis can help companies assess their technology portfolios and directions in the context of the marketplace and enable them to strategically position their technologies, particularly at the time of changing crude slates and shift in product demand. Also, it is possible to identify areas that are not profitable and focus R&D investment elsewhere.

In analysing refining technologies, FCC seems to be a good place to start, because it produces high volumes of fuels and petrochemical feedstocks. In addition, the FCC unit is considered to be the workhorse of the refinery.

Trends and focus of FCC patent activities
According to Hydrocarbon Publishing’s database of patent literature for FCC there are 496 unique patents and patent applications with issue dates during the period 2008-2013. There are a number of different dates that can be associated with a given patent: filing date, issue date, priority date, and expiration date. The issue date denotes when the patent or patent application was published by the patent office.

Annual global patent counts
Figure 1 shows the annual global counts for FCC patents issued during the period 2008-2013. We see that this count dropped sharply
Regional differences

Figure 2 shows a regional breakdown of the global FCC patents issued from 2008-2013. The five regions shown provided 491 of the 496 FCC patents issued during the period. Four patents had insufficient information to establish their origins and one patent was from Russia. Based on this data, North American companies had 42% of the issued patents, and Asian companies were somewhat lower at 38%. European, South American, and Middle Eastern companies contributed 12%, 4%, and 3%, respectively.

Almost all of the Asian patents (169 out of 186) originated from Chinese or Japanese companies, while US companies provided 206 of the North American patents, the other two coming from Mexico. As for South America, 20 of the patents have Brazilian origin, with two coming from Colombia. The majority (36) of the European patents was issued to companies in the Netherlands, and almost all (15) of the Middle Eastern patents are from Saudi Arabia.

Company comparison

Globally, 67 companies received issued patents for FCC technologies during 2008-2013. Figure 3 shows the identities and the counts for those companies that received five or more patents. Twenty-three companies are in this group, and it is easily seen that two of these – UOP and Sinopec – readily stand out from the rest in terms of the number of patents awarded. Clearly, these two companies by themselves contribute heavily to the regional counts for North America and Asia that are shown in Figure 2. Also, their combined total of 171 patents is more than one-third of the global total of 496.

Specific applications

Figure 4 shows the number of global FCC patents with issue dates during 2008-2013 that are found in each of the 17 application categories. These cover almost all of the subjects to which FCC patents apply. It must be noted that a patent may fall into more than one of these categories.
Midstream Solutions with Industry-Leading Speed to Market

To win a race you need not only speed, but a timely start. Merichem Company has a proven track record of providing hydrocarbon treating solutions that meet the stringent timelines of our customers. Get your treating project off to a timely start by choosing Merichem Company as your technology licensor.

Merichem Company’s portfolio of midstream treating technologies includes our patented FIBER FILM® Contactor that offers a variety of caustic, amine and acid treating processes. Merichem also offers solutions for gas treating, including our patented LO-CAT® wet scrubbing, liquid redox system that converts H2S to innocuous, elemental sulfur. In addition to our large portfolio of licensed treating technologies, Merichem offers industry leading spent caustic management services that utilize Beneficial Reuse options to create a non-waste solution for your spent caustics. For fast, effective treating solutions, choose Merichem.

Think Fast...Think Merichem

Sweet Solutions® at the Speed of Your Business
Big changes
SOMETIMES START SMALL.

CATALYST SOLUTIONS THAT DELIVER VALUE:
CLARIANT CATALYSTS.
Our products are small, but they deliver big value. Use our high-performance catalysts to make more of what you want and less of what you don’t, all with less energy. We are ready for your big challenges.

WWW.CATALYSTS.CLARIANT.COM

what is precious to you?

Trust our long experience
from predecessor company
Süd-Chemie.
Consequently, the sum of the numbers shown at the tops of the columns in Figure 4 is greater than the actual number of patents that are represented. These categories can be sorted into five general groups. Where an application is placed in these groups is indicated by the number in parentheses at the end of the category name.

Group 1 concerns FCC product yields and qualities, and the four application categories here appear 207 times in the FCC patents issued during 2008-2013. The foremost category at 123 counts is that of light olefins yield. Please note that a small number of patents deal with producing aromatics (BTX) from non-conventional catalytic cracking processes, and these patents are included in the sections that cover light olefins yield. The three remaining categories in this group, which cover fuels, have a combined total of 105 counts, with gasoline reformulation making up almost half of them.

Group 2 covers energy and the environment. The three categories here show up 112 times in the 2008-2013 FCC patents. The leading focus for patents here has been SNOx emissions. This was a subject of 2008-2013 FCC patents almost four times as often as was greenhouse gas (GHG) emissions, and about twice as often as was energy management. Note that the SNOx application covers emissions of SOx, NOx, and particulate matter (PM).

Group 3 is for FCC alternative feed sources. There are only two categories here, and they appear 59 times in the patents for 2008-2013. The category of resid processing appears about one-fourth more often in the 2008-2013 FCC patents than does that of biofuels.

Group 4, catalysts and additives, includes patents in which formulations and preparation schemes for these materials are covered. Of course, most if not all of the patents that can be included here will fall into other groups as well. Together, additives and catalyst formulation/preparation are cited as applications 172 times in the 2008-2013 FCC patents.

Finally, Group 5, FCC operations, contains categories for FCC process stages and control. The process control application is made up of advanced process control, monitoring, and simulation/modelling. Together, the six categories in this Group appear 155 times in the collection of FCC patents issued during 2008-2013.

**One can uncover competitors’ strategies and future technology deployment by looking at where a company is applying its patent efforts**

**Patent mining**

A total of 496 unique patents offers a good size for data analysis. There are many ways to delve into the materials and use different metrics to bring out the intrinsic values for the research works. For illustration purposes, the following describes three of several metrics (or so-called levels of mining) that have been explored.

The first metric explores technology competition. One can uncover competitors’ strategies and future technology deployment by looking at where a company is applying its patent efforts. Often, R&D fundings are allocated to experimental works that satisfy customers’ needs (for example, iron trap to reduce catalyst poisoning when processing shale/tight oil in the US), capitalise business potentials recognised by market development executives (such as increasing benzene yield in FCC product to anticipate benzene supply shortfall), and complete the company’s product portfolio (such as cracking biomass).

For example in the Group 1 applications, FCC product yields and qualities, 35 companies have patents with issue dates in 2008-2013. The 23 that have two or more patents are shown in Figure 5. UOP and Sinopec are dominant players with respectively 37 and 34 issued patents. They are followed by Petrobras (14), Grace (13), and ExxonMobil and Saudi Aramco (12). Despite FCC being considered a developed technology, vendors like Grace and UOP still find opportunities in innovation. The same can be said of refining companies such as Petrobras, Saudi
Aramco and Sinopec. These companies outperformed their peers in investing FCC R&D efforts in boosting product yield and quality, and data also show their strategic focus and direction in the future. (Note: the label IND in Figure 5 represents patents issued to independent inventors.) So, what does this mean to the competitors of Grace, ExxonMobil, Petrobras, Saudi Aramco, and Sinopec?

A second metric goes further into innovation concentration. The goal is to find out development trends and which companies are involved.

To go deeper into the analysis, Figure 6 shows for companies in Figure 5 the distribution of patent coverage over the four application categories in Group 1 – gasoline yield, reformulated gasoline, LCO yield and/or quality, and light olefin yield. The most popular category appears to be light olefins yield. It dominates as the subject in the patents issued to UOP, Sinopec, Petrobras, Saudi Aramco, KBR, and others. On the other hand, ExxonMobil, Albemarle, Eni, and Shell lean towards LCO yield and/or quality, and it is of some significance for Petrobras and Total.

Gasoline yield gets most of the patent attention at Petroleum Energy Center and JGC, both of which are Japanese organisations. Finally, reformulated gasoline is the major application category for Grace and PetroChina, but it is also a very important part of Sinopec’s portfolio of patents for Group 1 applications.

A third metric breaks down the applications into the specific technology areas or themes where patent coverage is being pursued. The purpose of the analysis here is twofold: providing an overview of technology innovations in individual applications; and identifying potential areas of patent infringement or collaboration opportunities. For illustration purposes, Table 1 summarises the technology themes that appear in the four applications from Group 1 Application – FCC product yields and qualities.

Who can benefit?

R&D analytics presents tremendous resources for refiners and vendors alike, particularly R&D scientists and engineers, commercial development executives, corporate strategic planners, purchasers of products and services, and technology licensees. The information generated can be translated into technology strategies for refiners better preparing for the future, and business opportunities for vendors to help their clients meet operational and financial goals.

For refiners, this could provide something of a deeper level of analysis beyond what will come from the licensing companies that is mostly driven from a marketing perspective. A broad knowledge of patent directions and activities helps refiners understand technology trends, availability, and details in order to make better decisions in selecting the right technologies for their operations.

As for technology licensors, this could be another way to track competition. For example, Company X is the leading commercial provider of dual riser FCC technology, but Company Y with no market position in the technol-
UOP Uniflex™ residue-upgrading technology yields 25% more clean fuel, turning “bottom of the barrel” into “top of the line.”

Get the most from every barrel. The UOP Uniflex Process can double the diesel yield of other residue-upgrading technologies, turning the “bottom of the barrel” into more black on your bottom line. The Uniflex Process is a high-conversion, commercially proven technology that processes low-quality residue streams like vacuum residue into high-quality distillate products — leading to refinery margin increases of up to 100%. Simply put, with the Uniflex Process from UOP, you’ll maximize production and profits from every barrel.

Looking for exclusive information on UOP Uniflex technology? Scan the code to register for the UOP Portal.

© 2014 Honeywell International, Inc. All rights reserved.
Table 1

<table>
<thead>
<tr>
<th>Application</th>
<th>Process</th>
<th>Technology theme</th>
<th>Patent assignees*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline yield</td>
<td>Catalysts</td>
<td>Dual riser or multiple reaction zones</td>
<td>KBR, Luoyang Huazhi Petroleum Engineering, Nippon Oil, PetroChina, China Univ. of Petroleum (CUP), Sinopec, UOP</td>
</tr>
<tr>
<td>Gasoline reformulation</td>
<td>Catalytic</td>
<td>Various innovations to improve octane, increase propylene and BTX yield, and reduce gasoline</td>
<td>CDTech, Indian Oil, KBR, Nippon Oil, PetroChina, Saudi Aramco, Sinopec, SK Energy, UOP</td>
</tr>
<tr>
<td></td>
<td>Catalyst</td>
<td>Reducing gasoline sulphur</td>
<td>CUP, ExxonMobil, Grace, Idemitsu Kosan, PECJ, Sinopec/RIPP</td>
</tr>
<tr>
<td>LCD yield and quality</td>
<td>Process</td>
<td>Multi-stage or multi-reactor process configurations</td>
<td>ExxonMobil, Petrobras, Stone &amp; Webster, Eni, Sinopec/RIPP</td>
</tr>
<tr>
<td>Light olefins yield</td>
<td>Process and hardware</td>
<td>Co-processing heavier olefins</td>
<td>IFP, Sinopec, UOP</td>
</tr>
<tr>
<td></td>
<td>Catalyst</td>
<td>Unconventional approaches to make olefins and BTX</td>
<td>Indian Oil, Petrobras, Saudi Aramco, Sinopec/RIPP, SK Innovation, UOP</td>
</tr>
<tr>
<td></td>
<td>Catalysts and additives</td>
<td>Modified ZSM-5 zeolite</td>
<td>CUP, Petrobras, Reliance Industries, Sinopec/RIPP, Total</td>
</tr>
</tbody>
</table>

*Partial list

Technology has been issued a number of patents in this area over the past several years. As part of competition analysis, one can correlate R&D work with commercial offerings and product developments to monitor and predict the readiness of Company Y to enter the market. Patent analytics on a global basis allows technology companies to focus on competitors located within the same regional market but also with an eye on external market competition.

Most importantly, R&D personnel can track research trends based on big data analytics, size up competition, and compare technology development direction. One can identify potential infringement either by external companies on his or her technology, or vice versa by evaluating similar developments being patented by other companies. On the other hand, there may be opportunities for potential collaborations if similar work is being done.

Finally, one can identify emerging trends to see where commercial practices line up with recent R&D undertakings. Furthermore, incorporating some recent market fundamentals in terms of fuel and petrochemical feedstock supply/demand trends and also future business opportunities could provide guidance to companies in formulating future strategies.

Analytics: prerequisite for gap analysis and SWOT analysis

The investments in R&D by refiners and vendors reflect the current refining business environment and companies’ views of the future. Technology developments are being driven by numerous factors. The first major factor is the need to satisfy changing market conditions, including declining demand for gasoline in developed nations and rising demand for diesel in developing nations. With increasing NGL and tight oil used in the US, supplies of propylene, butadiene, and BTX from steam crackers are expected to be in short supply. Global fuel oil demand is declining due to increasingly stringent sulphur specifications of bunker fuels.

The second major factor is mandated environmental legislation requirements such as Tier 3 gasoline standards in the US to lower gasoline sulphur from 30 ppm to 10 ppm nationwide and
tighter controls on emissions of NOx, SOx, PM, and perhaps GHGs. Also included here is minimising waste discharges.

The third major factor is the global crude supply. This ranges from opportunity crudes like Canadian oil sands bitumen, extra heavy oil from the Venezuelan Orinoco Belt, and high TAN crudes to light, sweet, and highly paraffinic tight oils. In general, technology suppliers seek to offer better performance in catalysts and process designs for FCC units to improve yield and selectivity, reduce energy usage, and increase reliability and safety. All of this is with the ultimate goal of achieving superior operational efficiency and economic benefits.

Some people have looked at spending for R&D as being similar to playing a slot machine in a casino. If you continued to put money into the machine, sooner or later some payout would occur, and one could try to increase the frequency by putting money into multiple machines. Throwing money blindly at a problem is not a wise strategy. Although R&D investment is risky, unlike gambling on slots the risk here can be managed. One way is to have a comprehensive view of recent patent activities and of the competitive landscape via analytics. Another is to identify the differences between what’s patented and what the industry needs or wants through a gap analysis. Both of these can help a company to undertake a SWOT (strengths, weaknesses, opportunities, and threats) analysis and then formulate a R&D strategy that allies with the company objectives in achieving financial goals and business sustainability in light of fast-changing environmental legislation, market dynamics, and global competition.

This article is an adapted excerpt of a report, Strategic Roles of Fluid Catalytic Cracking in Refinery Operations: Predictive Analytics and Gap Analysis to Identify Technology Challenges and Explore Future Business Opportunities, by Hydrocarbon Publishing Company.

Reference

Patrick J Christensen is Project Manager with a BS degree in chemical engineering from Drexel University.
Touseef Habib is Technology Analyst with a BS degree in chemical engineering from the University of Delaware.
Thomas B Garrett is Senior Consultant with a BS degree in chemistry from Carnegie Mellon University and a PhD degree in chemical physics from Lehigh University.
Thomas W Yeung is Principal and Managing Consultant He is a licensed professional engineer in New York State and holds a BS degree in chemical engineering from the University of Wisconsin-Madison, a MS degree in chemical engineering from the University of Connecticut-Storrs, and a MBA degree from New York University.

Email: info@hydrocarbonpublishing.com
CREATING ENGINEERING SOLUTIONS SINCE 1953
Predicting reactive heavy oil process operation

Characterisation of feed and product yields through component structures for better understanding and prediction of operations

GLEN A HAY, HERBERT LORIA and MARCO A SATYRO Virtual Materials Group, Inc
HIDEKI NAGATA Fuji Oil Company Ltd

To understand and optimise reactive heavy oil processes encountered in refineries there must be a strong knowledge of the product yields and their physical properties. Sometimes property predictions within models of the reacting material are important due to operational constraints. The coke induction point, or point at which solid coke begins to form in heavy hydrocarbon mixtures, is an example of the importance of property predictions since many unit designs need to take into account solid precipitation if it occurs. The simulation modelling application discussed in this article applies to the Eureka process where fluidisation of reactor materials and inhibiting the coke induction point is essential.2

When catalytic or thermal cracking simulation models are developed, enough physics must be encoded into the mathematical development to accommodate for the significant changes in both the normal boiling point of produced material and the associated molecular structures. Many different models for the reactive chemistry mechanisms required to model this class of processes have been proposed. These mechanisms include the use of hydrogen donor components, cyclic ring breaking, dehydrogenation of saturated rings, and cracking versus oligomerised propagation of small to large molecules, to name a few. The required basis for the development of a reliable simulation environment designed to handle the type of detail associated with chemical reaction mechanisms requires flexible component chemical structures to represent the products from different chemical reaction pathways. In order to capture this type of behaviour directly within the requirements of industrial process simulation software a new PIONA (n-Paraffin, Iso-paraffin, Olefin, Naphthene, and Aromatic) pure component basis environment was developed to both characterise the feedstocks and the resulting products’ estimated chemical make-up and yields.

The PIONA technique consists of using constant groups also known as slates of predefined compounds required to cover the carbon number ranges for feeds and products necessary for the modelling of different refinery reactors, such as the Eureka process thermal cracking vessels. The different combinations of these component slates and the compositions of the components within allows for the matching of the experimental distillation curve of a given feed and the calculation of its chemical characteristics, ranging from simple properties such as molecular weight and standard liquid density all the way to more complex physical properties such as heating values, liquid viscosities, and pour points. The key advantage in using this method is its ability to capture the essential chemistry of the feedstock and product mixtures and how the changing compositions upon reaction affect property calculations. The number of components used in the simulation is kept constant and consistency is enforced throughout the simulations.

The PIONA structure group classification was found to introduce an unacceptable property estimation error in studies when modelling feeds with an average carbon number higher than ten, where larger aromatic content was encountered. Further investigation showed that a single aromatic structure group was not enough to differentiate multi-paraffin branched aromatic components against those more reacted compounds that were stripped of straight carbon branches. Therefore, an extra chemical type defined as ‘dehydrated aromatic’ is included in the PIONA technique. From a molecular structure configuration, these dehydrated aromatics replace branched contributions to a base aromatic ring with additional dehydrated aromatic rings.

Heavy oil reaction models
Models using detailed specific reaction pathways are commonly found in the technical literature on thermal cracking or pyrolysis of lighter gases such as ethane or even naphtha feedstocks. This is possible because the overall number of pure component and radical species are still manageable within a simulation environment (typically less than 150 species), assuming good numerical techniques for the integration of the differential component material and energy balances are employed. Even then, many of these models have to be linearised to help achieve faster computational speeds. Once heavy residual oil feedstocks are introduced, a change in mathematical solution methods for the compo
reaction pathways are exothermic instead of endothermic. In that respect, average boiling point lumping used by these models is completely non-predictive and would need to be rebuilt for specific processes and eventually even specific plants and equipment.

The PIONA slate technique was applied in the commercial process simulator software VMGSim, to represent multiple hydrocarbon feedstocks in lighter and heavier cut ranges.3,9 The focus was on property calculations and characterisation of multiple feeds using mixtures based on the same basis component slate. The ability of this PIONA system to model reactive systems is best illustrated in Figure 2 when compared with the lumped, linearised systems. In these lumped models, the resulting temperature profiles calculated for the furnace tubes can also be roughly estimated due to the matched enthalpy of formation for each lumped component, assuming the chemical structure shifts stay consistent and that enthalpies of combustion are available. Significant error would be introduced in these models if hydrogenation versus dehydrogenation occurred since these reaction pathways are exothermic instead of endothermic. In that respect, average boiling point lumping used by these models is completely non-predictive and would need to be rebuilt for specific processes and eventually even specific plants and equipment.

The PIONA slate technique was applied in the commercial process simulator software VMGSim, to represent multiple hydrocarbon feedstocks in lighter and heavier cut ranges.3,9 The focus was on property calculations and characterisation of multiple feeds using mixtures based on the same basis component slate. The ability of this PIONA system to model reactive systems is best illustrated in Figure 2 when compared with the lumped, linearised systems. In Figure 2, the

---

**Figure 1** Basic lumped component heavy residue thermal cracking representation

---

**Figure 2** Example of lumped kinetic versus PIONA kinetic thermal cracking reactive pathways
Callidus Technologies, LLC is an established world leader in process burner, flare and thermal oxidizer technology.

We have earned that reputation by providing solutions that set new standards in performance and reliability. Our approach to combustion science continues to break new ground every day with innovative new products and solutions for the world’s most difficult combustion challenges. This commitment to technical excellence is driven by our focus to provide a custom designed solution for every project based on each customer’s specific requirements. One example is our flare gas recovery system, designed to achieve zero flaring, reducing process fuel costs while eliminating visible flame, odors and auxiliary flare utilities.

Having one of the largest installed bases of process burners, production flares and thermal oxidizers in refining and petrochemical facilities around the world. Callidus should be your choice for next generation combustion equipment and solutions for new construction or retrofit operations with installation capabilities anywhere in the world.

Callidus Technologies, LLC
A Honeywell Company

7130 South Lewis, Suite 335, Tulsa, OK 74136, call 1-918-496-7599 or visit our website www.callidus.com
2014 Honeywell International Inc. All rights reserved.
ability to model the transition between carbon number and molecular structure types caused by chemical reactions modelled through reaction pathways is explained as well as the overall heat of reaction effects.

Characterising process feedstocks and predicting product yields

The key step for the correct modelling of a thermal cracking process such as Eureka is the definition of a correct mixture of PIONA based components needed to characterise the feedstock. Laboratory analysis of hydrocarbon feed material is used to provide the necessary information to fit the model of material stream values against measured properties. The reacted product yields are similarly characterised. The reaction kinetics of the thermal cracking vessel at the desired operating conditions are then simulated and the resulting material product yield’s properties and flow rates would be compared to known data. At that point, the process is repeated until the adjustable model parameters are properly defined and the errors between model and experiment are minimised.

The experimental data was gathered through a bench scale batch distillation apparatus shown in Figure 3. This bench scale atmospheric thermal boiling/thermal cracking vessel was meant to help understand, characterise, and fine tune the feedstock PIONA composition to be used in the simulation before being used as a basis for the construction of a complete Eureka plant model. The study was done using a Peace River vacuum residue sample representing material from an atmospheric crude tower followed by a vacuum tower in the actual refinery.

The feed sample was introduced to the thermal cracking vessel with the help of a carrier gas and heated to a temperature of 430°C through electric heaters for approximately 45 minutes. An agitator was added within the vessel to minimise temperature gradients, which helped mimic stripping steam introduced to the full scale vessels and the corresponding agitation in actual operation.

Table 1 shows a comparison between the bench scale experiments and VMGSim simulations for Peace River bitumen feed and product. Figure 4 shows how these product cuts’ details would look when shown in a similar manner to the simple lumped model represented in Figure 1.

Pour point calculation considerations

The key physical property for the quantification of pitch yield from experimental data included the liquid density, atomic gross analysis, heating value, and pour point of the product. In this case, all properties were important for final pitch product specification, but the pour point is a key indicator to ensure proper fluidisation of the material in the reactor for trouble-free, continuous operation. Typical standard methods to estimate pour points such as ASTM D97 also accepted by the American Petroleum Institute (API), could not be used in a simulation environment due to their inherent limitations. For example, the ranges of the ASTM D97 method’s equation are limited to petroleum fractions of 140 to 800 g/gmol and 13 to 50 API gravities and fell short in dealing with ranges of pitch products with molecular weights in the thousands of g/gmol and negative API gravities.

A more rigorous and flexible approach to handle the pour point calculation in the model was devised using viscosity as a correlating parameter. A value of 164 000 cP (164 Pa-s) was selected,
after discussions with heavy oil experimentalists, as a rough equivalent to a pour point based on the observed behaviour of heavy oils and bitumen at ambient temperature. From that reference point a temperature could be found at which the model’s pitch viscosity matched and became the estimated pour point temperature. In order to use this type of solution, it would then become important to accurately predict the viscosity of the heavy oil mixtures, also a challenging problem when dealing with heavy hydrocarbon feedstocks.

The viscosity prediction method chosen in the model for the feed and light to heavy product yields was the expanded fluid viscosity model (VMG-EF). The general principle of this model is that as a fluid expands there are greater distances between molecules and fluidity (inverse of viscosity) of the mixtures increases. The fluidity is assumed to be an exponential function of the expansion of the fluid from a near-solid state. An additional benefit of this method was that binary interaction parameters that model non-idealities due to different molecular sizes and chemical types could be incorporated into the PIONA component slate and characterisation procedure. At the end, the final model was tuned to within a few degrees centigrade to the experimental pour point temperatures together with some actual plant conditions. These results and other resulting feed and product comparisons of kinematic viscosity are shown in Figure 5.

The Advanced Peng-Robinson property package from VMGSim® (VMG-APR) and API correlations (VMG-API) were also used to predict viscosities and are shown in Figure 5. As expected, a correlation like the API based on lighter hydrocarbon mixture data matched experimental data very well for lighter products, but was inadequate when applied to heavier cuts.

**Application to Eureka process operation**

Complete process simulation models were developed once the experimental model’s property predictions and reaction kinetics.
were fine-tuned and validated against the available experimental data. Some of the key points centre on the coke formation trending in the preheating units (not discussed in this article) and operational optimisation like recycle ratio of reacted heavy feed to fresh feed. Figure 6 shows a general Eureka process setup and some of the resulting product yield trends of different bottom recycle oil ratios tested in the model. With the product properties and reacting material pour points being calculated for any point in the operation plant a good overall understanding of new feedstocks outside of previous running conditions was reached.

Conclusions
Characterisation of a heavy feedstock used in the Eureka reactive heavy oil thermal process was presented based on the use of an extended PIONA and carbon number component slate. This PIONA style simulation model basis was also used for tracking and estimation of hydrocarbon mixture thermodynamic properties before, after, and during reaction. Although solution times were not as fast as with conventional lumped kinetic models (minutes compared to seconds), this model showed flexibility in its more rigorous approach for process situations where structural shifts across different boiling point ranges could occur.

It was also shown that estimation of focal properties within a PIONA basis simulation, such as the pour point temperature used to monitor the fluidisation inside the vessel, could be estimated with a specially developed empirical correlation, more adequate to heavy feedstocks than available published methods. Estimation methods for properties like viscosity at different temperatures was reviewed with comparisons between the API method and a full range expanded fluid method. The latter allowed for proper temperature dependent viscosity trending when compared with measurements taken from reacted product cut samples.

The model successfully predicted shifts in component representation of feed to reacted products using a PIONA driven reactive kinetic pathway. This more generalised approach still contained all key reaction pathways allowing for the appropriate overall reactive shift to product mixtures in the model, which was further confirmed with resulting accuracy of property prediction comparisons and overall heat of reaction balances. Since the mixture properties calculated were directly tied to the component types and carbon numbers contributions in the model
there was accuracy shown in comparisons across a wide range of boiling point temperature product cuts. One could imagine catalyst driven reaction pathways also being potentially modelled using PIONA basis with the reaction kinetic rates properly altered to compensate for catalysed pathways.

VMGSim is a mark of Virtual Materials Group, Inc.

Acknowledgement
The authors are grateful to Fuji Oil Corporation Ltd and Virtual Materials Group, Inc. for the permission to publish this work. The authors would also like to thank Dr Yarranton and Mr Schoeggl at the University of Calgary for information provided regarding laboratory pour point measurements.

References

Glen Hay is Vice President of Business Development with Virtual Materials Group Inc., Alberta, Calgary, Canada. His experience is focused on reactors, heat transfer units, and overall plant modelling and optimisation. He holds a bachelor’s degree in chemical engineering from the University of Calgary and a master’s in advanced process control.

Herbert Loria is a Process Simulation Software Developer with Virtual Materials Group Inc. He specialises in the development of physical property packages, estimation methods for heavy oil physical properties, oil characterisation schemes and upstream applications for VMGSim. He holds a PhD in chemical engineering from the University of Calgary.

Marco Satyro is a Senior Fellow with Virtual Materials Group Inc. He is one of VMG’s founders and helped design the property package system VMGThermo. He graduated from the Polytechnic School of the University of Sao Paulo as a chemical engineer and holds a PhD from the University of Calgary.

Hideki Nagata is Manager of the Operations Management Group at Fuji Oil Company Ltd, Chiba, Japan. He holds a bachelor’s degree in chemical engineering from the University of Kagoshima and a master’s in reaction engineering.
No other hydrogen company supplies so much.

Air Products is the world’s leading supplier of hydrogen. We provide over 3,000,000 Nm³/hour — more than any other company. We own and operate more than 80 hydrogen plants around the world, and we have unparalleled operating knowledge and experience.

As the market leader, we would like to share this know-how to help you make the most of your assets. Helping you to improve productivity, lower operating costs and increase return on investment — that’s our commitment to refiners everywhere. To learn more, call +1-610-706-6890 or visit our website, airproducts.com/H2alliance.

tell me more
airproducts.com/H2alliance
Integrated hydrogen management

Redesigning an existing hydrogen system leads to an integrated, reliable and flexible supply

SAŠA POLOVINA, DANIJELA HARMINA and ANA GRANIC ŠARAC
INA Rijeka refinery

Hydrogen has become one of the most important refining energy media and its efficient use is of the highest priority. Therefore, refineries are forced to exploit their existing hydrogen sources to the maximum and continually increase their hydrogen sources.

This article describes the integration of two hydrogen systems at INA Rijeka refinery: one system linked to a catalytic reforming unit as a source of hydrogen and the other linked to a hydrogen generation unit based on steam reforming. The integration of these two hydrogen systems involves three different purities of hydrogen-rich gas. Hydrogen-rich gas produced by catalytic reforming is used in the refinery processes naphtha hydro-treating (NHT), isomerisation, kerosene hydrotreating (KHT1) and gasoil hydrotreating (GHT2). The hydrocracking unit’s requirement for make-up gas of high purity in large amounts relies on the hydrogen generation unit. The two sources of hydrogen and two systems of purification for hydrogen-rich gas give rise to three purity levels for hydrogen-rich gas:

• Gas from the catalytic reforming unit of 73-75 vol% purity, depending on the catalyst cycle stage (start-of-run or end-of-run)
• Gas after absorption with a hydrogen content of 83-85 vol%  
• Gas after purification in the pressure swing absorption (PSA) unit, with a hydrogen content of 99.99 vol%.

The current situation
Make-up hydrogen for the hydrocracking unit comes from the hydrogen generation unit which uses natural gas as feed. Make-up hydrogen for isomerisation, NHT, KHT1 and GHT2 comes from catalytic reforming.

In order to integrate these two hydrogen systems, and to achieve better utilisation of the produced hydrogen, the systems are connected via two pipelines with two manual valves. One pipeline supplies hydrogen produced in catalytic reforming (after obligatory purification in the PSA unit) as make-up for the hydrocracking plant; the other pipeline supplies hydrogen from the hydrogen generation unit as make-up for the isomerisation, NHT, KHT1 and GHT2 plants.

Shut-off for both pipelines relies on ordinary manual valves. Problems in the operation of one plant can lead to shutdowns of other plants connected to this integrated hydrogen system.

The hydrogen system in the catalytic reforming plant starts with the high pressure (HP) separator where hydrogen-rich gas is separated from unstabilised gasoline. The amount of hydrogen-rich gas produced depends on feed composition and process conditions in the reactor section. The purity of the produced gas depends on the pressure and temperature at the HP separator and on ambient conditions, especially temperature.

After physical separation, hydrogen-rich gas enters the suction vessel of the booster compressors where it achieves the required pressure and is distributed to the consumers.

A PSA unit is located between the HP separator and the booster compressors. This is used for purifying the reformer’s hydrogen-rich gas. Pressures at the HP separator, at the inlet of the PSA unit, and at the suction line of the booster compressors are regulated with the same pressure controller.

In addition to pressure control of these positions, the control valve has a safety role. In case of problems in the catalytic reforming process, fast depressurisation of the HP section in the refinery fuel gas system would be crucial.

This type of pressure control has significant disadvantages. Fine-level flow control of hydrogen-rich gas discharges to the fuel system cannot be implemented. At 1% valve opening, the flow rate reaches around 2000 Nm³/h. If the process is operated in a mode in which the regulator valve is opened or closed, large amounts of hydrogen are discharged to the refinery fuel system.

Booster compressors are the main part of the hydrogen system since they maintain the pressure required for normal operation of hydrogen consumers and high pressure...
absorption. Hydrogen at two different levels of purity is fed to the suction side of the compressors. If the PSA unit is operating, hydrogen purity is 99.99%; if not, hydrogen-rich gas is fed from the reforming HP separator.

After cooling and passing through the knockout drum, one part of the hydrogen-rich gas is distributed to the isomerisation and NHT plants and the rest goes through the absorption column. After purification, hydrogen-rich gas goes to the KHT and GHT units at a purity of 83-85%.

Make-up gas for the hydrocracking unit must be at 99.99% purity, which means that it can only come from the PSA unit.

Since two separate hydrogen systems are connected by a manual valve, this solution carries significant risks to the normal operation of both hydrogen systems. The risk is much higher for operation of the hydrocracker; in the event of a PSA shutdown, the connection between these hydrogen systems must be closed immediately, so the hydrocracker is without substantial amounts of make-up hydrogen. In order to compensate for the reduced volume of make-up gas, the hydrogen generating unit must significantly raise its capacity. Thus, sudden loss of the required amount of make-up hydrogen may lead to shutdown of the hydrocracker.

If operational problems in the hydrocracker lead to a shutdown of the PSA unit, problems in the old hydrogen system are less challenging. At the shutdown of the PSA unit a bypass is automatically opened to ensure the necessary quantity of gas for compressor operation. In this way, continuous supply of make-up hydrogen is ensured to all consumers connected to the pressure side of the compressor. By increasing the flow to the absorption column, a higher level of make-up hydrogen purity can be ensured. To ensure continuous hydrogen supply to all consumers, integration of two separated hydrogen systems is vital. The existing scheme of the hydrogen system in Rijeka refinery is shown in Figure 1.

Reconstruction of the existing hydrogen system

High pressure absorption and operation with one PSA unit

After separation in the reforming HP separator, hydrogen-rich gas goes to the suction vessel of the booster compressors. Pressure in the HP section, as well as in the PSA unit and the suction vessel of the compressors, is maintained by a pressure controller (PC).

In order to achieve the best possible pressure regulation, and to increase hydrogen utilisation and minimise discharge into the fuel gas system, an additional smaller control valve should be installed that would work in a split range configuration with the specified PC. This new, smaller PC would discharge in the normal operational range (at valve opening of 30-40%) around 100-150 Nm³/h hydrogen.
FULL RANGE:
Rod load up to 1'500 kN / 335'000 lbs
Power up to 31'000 kW / 42'100 hp

YOU GET MORE THAN JUST A PROCESS GAS COMPRESSOR
Lubricated up to 1’000 bara, non-lubricated up to 300 bara

FOR HIGHEST AVAILABILITY: We recommend our own designed, in-house engineered compressor valves and key compressor components

DESIGNED FOR EASY MAINTENANCE
We are the competent partner with the full range of services worldwide

→ www.recip.com/api618

YOUR BENEFIT:
LOWEST LIFE CYCLE COSTS

API 618

RELIABLE SWISS QUALITY

Compressors for a Lifetime™
Actions speak louder than words
High pressure CO₂ gas compression

MAN Diesel & Turbo has unique compression solutions in its portfolio for the complete range of CO₂, N₂, propylene and vapour related applications, with single machines or complete train solutions. Others talk about CO₂ compression. We have the credentials! Over 200 RG Gas compressor units are in operation or on order. We are world’s number one in CO₂ high pressure applications, thanks to sophisticated testing facilities and proven track records in the field. With an RG Gas compressor from MAN Diesel & Turbo you will gain an exceptionally flexible and optimized solution to maintain your business economic. Find out more at www.mandieselturbo.com

Engineering the Future – since 1758.
MAN Diesel & Turbo
Rich gas into the fuel gas system, which is a significant flow decrease compared to regulation by the previous PC. The current PC operates at a valve opening of 1–2%, discharging about 2000 Nm$^3$/h of hydrogen-rich gas to the fuel gas system. This old valve is usually closed, which means that when the valve is opened, in half an hour 1000 Nm$^3$ of hydrogen-rich gas is discharged. At 80% valve opening of the new PC, the old PC would take over regulation to ensure operational safety in the plant.

After the suction vessel, the booster compressors raise the pressure to the required 32 bar. Hydrogen-rich gas goes through the water cooler and knockout drum to the absorption column. Stabilised gasoline from the bottom of the debutaniser column of the reforming plant is used as absorbent. To achieve better absorption, the temperature of the absorbent is kept as low as possible. Therefore, stabilised gasoline from the bottom of the debutaniser column is first cooled in air and water coolers.

In order to supply make-up gas with a higher hydrogen content to all consumers, the pipeline for supplying the isomerisation and NHT units should be moved after the absorption column (see Figures 1 and 3). Thus all consumers in the old part of the refinery have a supply of make-up gas of sufficient quantity and quality. Once the needs of consumers of make-up gas are satisfied, the full volume of the excess hydrogen-rich gas could be sent to the PSA at the hydrogen generation unit. To further protect this PSA, any large amounts of liquid need to be removed by integration of an additional water cooler and knockout drum before the PSA (see Figure 3).

Hydrogen-rich gas purified in the absorption column has a similar chemical composition as gas from the HP section of the hydrocracker. This means that gas from the absorption column could go to the hydrogen generation unit’s PSA unit. This kind of operation would eliminate the need for two PSA units. Both plants would benefit from this solution; a tail gas compressor would be eliminated from reforming’s PSA unit, and consumption of expensive feed (natural gas) at the hydrogen generation unit would decrease.

In order to increase overall utilisation of hydrogen and to reduce consumption of feed for hydrogen production, online analysis of the hydrogen-rich streams, and reuse of these streams in refinery processes, should be implemented. Thus the integrated hydrogen system could be further improved. Cascade mode for hydrogen streams could be applied (see Figure 2).

The basis of this system is that each plant has its own direct line of make-up hydrogen. Off-gases from the HP sections of the isomerisation and NHT plants, containing a minimum 86 vol% hydrogen (see Table 1) also can be used as make-up gas for other plants. The limiting factor for this kind of usage is the

![Figure 2 Cascade use of make-up hydrogen](image)

Figure 2 Cascade use of make-up hydrogen

![Composition of high pressure off-gases at hydrogen consuming plants](image)

Table 1

<table>
<thead>
<tr>
<th>HP gas, vol%</th>
<th>HDS section of Isomerisation</th>
<th>NHT</th>
<th>HDS1</th>
<th>HDS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>86.24</td>
<td>91.1</td>
<td>86.43</td>
<td>74.5</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>2</td>
<td>1.3</td>
<td>1.4</td>
<td>2.32</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.5</td>
<td>0.25</td>
<td>0.7</td>
<td>0.14</td>
</tr>
<tr>
<td>i-C$_4$H$_10$</td>
<td>0.2</td>
<td>0.05</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>n-C$_4$H$_10$</td>
<td>0.23</td>
<td>0</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>n-C$_5$H$_12$</td>
<td>0.8</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>C$_7$H$_8$</td>
<td>0.4</td>
<td>0.15</td>
<td>0.8</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1 Composition of high pressure off-gases at hydrogen consuming plants
Maximize Reliability, Availability & Profitability with Ariel API 618 Process Compressors

With more than 19,000 possible frame and cylinder configurations for API 618 process service, Ariel compressors can be designed and built to maximize your unique process operation. Ariel has been producing durable, low-maintenance reciprocating compressors since 1966 and API 618 compressors since 1999. Ariel offers high quality compressors that ensure long continuous run-times.

Visit www.arielcorp.com to find an Ariel Process distributor in your region.

To learn more about Ariel Compressors, please visit www.arielcorp.com
connection to the PSA unit it is necessary to re-regulate it in order to keep the hydrogen yield at 85% and avoid any release of new hydrogen to the fuel gas system. In this way consumption of natural gas for hydrogen production can be reduced by an amount equivalent to the recovered hydrogen. Additionally, by reducing hydrogen generation capacity, significant savings can be delivered by the operation of only one PSA unit (that is, the operating costs of the other unit and of the tail gas compressor) because total tail gas from this PSA unit is used up in the steam reforming furnaces. It is important to emphasise that these two systems are connected in such a way that hydrogen from the hydrogen generation plant goes to the suction vessel of the booster compressors (see Figure 1), which means that pure hydrogen can be distributed to other plants in the refinery, even if the reforming plant.

Purity at 84 vol% hydrogen is enough for the operation of the GHT2 unit at maximum capacity. This off-gas contains high amounts of hydrogen so it is desirable to use it in some way. One possibility is to send it, after amine washing, to the inlet vessel of reforming’s PSA unit for purification and reuse. Compositions of these off-gases are shown in Table 1. Figure 2 illustrates cascade use of make-up hydrogen.

The hydrogen generation unit’s PSA unit works at a pressure of 22.4 bar so all hydrogen-rich gas streams at higher pressures can be directed to this unit. In this solution there is no cascade mode of operation and all off-gases from HP sections can be directed to the hydrogen generation unit’s PSA unit.

Pressure at this PSA unit is controlled electronically (see Figure 3) by a pressure controller located at its outlet. However, with a new connection to the PSA unit it is necessary to re-regulate it in order to keep the hydrogen yield at 85% and avoid any release of new hydrogen to the fuel gas system.

In this way consumption of natural gas for hydrogen production can be reduced by an amount equivalent to the recovered hydrogen. Additionally, by reducing hydrogen generation capacity, significant savings can be delivered by the operation of only one PSA unit (that is, the operating costs of the other unit and of the tail gas compressor) because total tail gas from this PSA unit is used up in the steam reforming furnaces. It is important to emphasise that these two systems are connected in such a way that hydrogen from the hydrogen generation plant goes to the suction vessel of the booster compressors (see Figure 1), which means that pure hydrogen can be distributed to other plants in the refinery, even if the reforming plant.

**Figure 3** Hydrogen system, absorber and hydrogen generation’s PSA unit in operation

![Hydrogen system, absorber and hydrogen generation’s PSA unit in operation](Image)
and absorption column. Hydrogen generation’s PSA unit operation of the refinery with is not in service. In such a way that all control valves are adjusted in a way that maintains pressure in the HP sections are working so that minimal amounts of hydrogen are discharged to the fuel gas system. (Purge of the system should be avoided in any event.)

In this operational mode, a pressure of 30.5-31 bar at the suction side of the booster compressor is sufficient to meet the needs of all hydrogen consumers. From the suction side of the booster compressor through the line, hydrogen is distributed to the consumers (see Figure 1). Because of higher utilisation of the produced hydrogen, all hydrogen-rich streams can be connected to the input of the PSA unit. Given the required pressure, streams from all HP sections of the refining process can be connected. However, the return of hydrogen-rich streams to the PSA unit can cause big problems for the PSA compressor; while the PSA unit produces ‘pure’ hydrogen, the returning flows from the HP sections have 95-96 vol% hydrogen content. Table 2 shows the composition of returning gas from the HP sections of the plants if the make-up gas is pure hydrogen.

Catalytic reforming’s PSA unit is designed for purification of gas with 73-75 vol% hydrogen content; the cycles of the PSA unit are also adapted for gas of this composition. However, since the PSA cycles are adjusted to purification of hydrogen-rich gas from catalytic reforming, some of the new returning hydrogen will end up in the tail gas and will be lost in the refinery fuel gas system. In addition, an increase in hydrogen content in the tail gas will reduce its molecular weight; this will apply an additional burden to the compressor and the entire tail gas system. Therefore, before deciding on further utilisation of these streams, the supplier of the PSA unit must be consulted, in order to readjust the cycles so that gas with higher hydrogen content can be purified and to ensure normal operation of the tail gas compressor.

As with the previous mode, these two new integrated hydrogen systems are connected and, if necessary, it is possible to open the valve for supply from hydrogen generation to the suction side of the booster compressor and satisfy demand for hydrogen from one of the plants, without increasing the capacity of reforming (see Figure 1). In this case, the valve on the make-up hydrogen line between the absorber and hydrocracker is closed.

Hydrogen recovery can be achieved, as in the previous case, with cascade connections between the plants. Cascade mode has an even greater significance than in the previous operational mode. As the make-up gas is pure hydrogen, for operation at average plant capacity much smaller amounts of hydrogen are needed. For example, processing 16-18 t/h of light gasoline at the HDS section of the isomerisation plant requires around 1200 Nm3/h of 73-75 vol% make-up hydrogen (once through reactor). This quantity is sufficient for processing about 58 t/h of heavy naphtha at the NHT plant, and the off-gas from this plant is sufficient for processing 22 t/h of feedstock in the hydrodesulphurisation unit.
THINK GERMAN, ACT LOCAL.

LOOKING FOR A RECIP PACKAGE AS UNIQUE AS YOUR SPECIFICATIONS?

WE ARE NOT JUST A PACKAGER, WE ARE YOUR ENGINEERING EXPERTS.

As the compressor OEM, our packages are engineered and customized to meet your specs. Our reciprocating compressors are specially designed in a wide range of sizes and configurations while operating up to 1,200 rpm across all types of gases. Also, 3D compressor package models are reviewed with you to ensure the best design for optimal operation and maintenance.

NEUMAN & ESSER USA, Inc.
Located in Katy, Texas
www.neuman-esser.com

Contact me for North America:
Roy Jacobs
Sales Manager for Upstream & Midstream
jacobsr@neuman-esser.com
Direct Phone: +1 713-554-9643

NEA GROUP Headquarters in Germany
In this way, 1200-1300 Nm³/h of hydrogen is sufficient for the operation of three plants. For no cascade connection between the plants, a much greater amount of hydrogen must be used. For example, at the capacities mentioned, the required hydrogen streams are 1200 Nm³/h for the isomerisation plant, 900 Nm³/h for NHT and 900 Nm³/h for KHT1, indicating a 1800 Nm³/h increase in hydrogen demand. This amount of hydrogen could be used in the hydrocracker and so further reduce consumption of natural gas in hydrogen generation. Figure 4 shows operation with two PSA units.

Directing reforming's hydrogen-rich gas to hydrogen generation’s PSA unit

Full utilisation of hydrogen-rich gas can be achieved by direct connection between reforming and hydrogen generation in two ways. The first is to send gas from reforming as feed to hydrogen generation (with a pre-reforming section). Considering that this gas has a high hydrogen content, it would place an unnecessary burden on hydrogen generation’s steam reforming reactor and lead to unnecessary energy consumption.

The second, better solution regarding energy consumption is to direct reforming’s hydrogen-rich gas to hydrogen generation’s PSA unit. To achieve this, pressure must be raised at reforming’s HP separator to a value that will provide smooth transport to the PSA unit. The composition of this gas is similar to that of gas from the HP section of the hydrocracker. Since hydrogen from hydrocracking off-gas is usually recovered at hydrogen generation’s PSA unit, there should be no problem purifying reforming’s hydrogen-rich gas at the specified PSA unit. Because gas from reforming contains some C₃, C₄ and C₅ hydrocarbons, for a PSA unit’s protection and in order to remove any large amounts of liquids, it is necessary to install an additional water cooler and knockout drum.

After purification, the produced pure hydrogen goes into two main streams, one stream to the hydrocracker and the second to the suction vessel of the booster compressors. Subsequently, after reaching the required pressure pure hydrogen is distributed to all consumers. Flow of hydrogen to the compressor suction vessel is controlled by a flow controller which ensures that the compressors always distribute exactly the amount of hydrogen necessary for normal plant operation. (The exact amount of hydrogen is considered to be the quantity of hydrogen that provides the necessary make-up for all consuming units.) The pressure controller that maintains pressure at the inlet of the booster compressor must be minimally opened.
In this way, an integrated hydrogen system is created, which ensures the supply to consumers of hydrogen of maximum purity, reduces consumption of natural gas for production of hydrogen at hydrogen generation and minimises hydrogen content in the fuel gas system. This mode of operation also ensures highly reliable and stable operation of this hydrogen system. The operation is shown in Figure 5.

However, there are restrictions. There is a point at which it is not possible to send additional hydrogen-rich gas from the catalytic reformer to hydrogen generation’s PSA because the PSA tail gas has too high a fuel value and the steam furnace reformer temperature cannot be regulated since no make-up natural gas is needed. The primary fuel for the steam reformer furnace is tail gas from hydrogen generation’s PSA unit, and temperature regulation is maintained by the addition of a secondary fuel, natural gas. Around 25% of the steam reformer duty is maintained through make-up natural gas. This value is related to the plant without addition of gas from the hydrocracker.

To illustrate this, the hydrogen generation capacity in Rijeka is 76 000 Nm³/h, with a standard yield from the PSA of 85%; hence the reformer gas flow would be about 120 700 Nm³/h. The overall reformer duty would be 100 million Kcal/h and the PSA tail gas would give 82 million Kcal/h. So we need a further 18 million Kcal/h which would require the consumption of around 2140 Nm³/h of natural gas.

The plant is designed to accept 5000 Nm³/h of hydrocracker off-gas, (composition around 83% H₂, 11% CH₄, 6% CO₂). In this case, the quantity of reformed gas drops to about 115 000 Nm³/h, which is about 95% capacity. If we assume that the furnace duty reduces linearly with the reformer load, the furnace duty drops to 95 million Kcal/h.

Figure 5 Directing reforming's hydrogen-rich gas to hydrogen generation's PSA unit
would be sent to either the refinery fuel gas system or to another gas consumer.

Conclusions
By reconstructing the existing hydrogen system, an integrated, reliable and flexible hydrogen system would be created. This new system would ensure the most favourable refinery operation.

With the described configuration of the system, the refinery could significantly reduce the consumption of natural gas for hydrogen generation.

Application of the cascade operational mode could solve two major refinery problems. It would reduce hydrogen content in the fuel gas system resulting in significant savings. If total hydrogen (taking 1600 Nm$^3$/h of 99.99% $H_2$) that can be saved by using the cascade operational mode is directed to the hydrocracking plant, the refinery can save up to €1 million per year, because the volume of natural gas used as feed for hydrogen generation is reduced.

By integrating the two systems of hydrogen purification (absorber and PSA), sufficient amounts of hydrogen of appropriate purity for the hydrogen consuming plants would be ensured. Loss of hydrogen by absorption purification is not significant.

Operation of a single PSA unit (in hydrogen generation) could provide significant energy savings because the other PSA unit (reforming) with the associated tail gas compressor would be in standby condition.

The biggest investment would be the construction of a pre-reformer at the hydrogen generation unit, but the benefits of this investment are huge. As total hydrogen ends up at hydrogen generation’s PSA unit, release of hydrogen-rich gas to the fuel system would be eliminated, and thereby the hydrogen content of refinery fuel gas would be reduced. Only hydrogen from low pressure sections would be present in the fuel gas system.

As hydrogen consumers receive pure hydrogen from hydrogen generation’s PSA unit, consumption...
of hydrogen in all secondary plants would be reduced. Also, tail gas from HGU’s PSA unit now contains C3-C4 hydrocarbon fractions from reforming’s hydrogen-rich gas, and has a higher calorific value which means that less make-up natural gas is needed for steam reforming furnace operation. The cost of reconstruction of the existing system is negligible compared to benefits of the described integrated refinery hydrogen system.

Further reading

Saša Polovina is an Area Manager in INA’s Rijeka refinery, Croatia, and is responsible for several processing plants as a technologist. He holds a MSc in chemical engineering and technology from the University of Zagreb.

Danijela Harmina is a Production Engineer at Area 2 of Rijeka refinery, which includes catalytic reforming, isomerisation, Merox units, a reformate splitter, a kerosene sweetening unit and a PSA unit. She graduated from the Faculty of Chemical Engineering and Technology at the University of Zagreb.

Ana Granic Šarac is a Process Engineer providing technical support for processing plants at Rijeka refinery including catalytic reforming, hydrogen management and purification, isomerisation, LPG/gasoline Merox and gasoline hydrotreating. She joined INA as a participant of the Growww programme and graduated as a chemical engineer from the University of Zagreb.
Innovation

High performance SUPERFRAC™ trays for difficult separations

8-pass SUPERFRAC™ high performance tray for 10 m column

Highest combined CAPACITY and EFFICIENCY single-pass cross-flow tray tested at FRI.

The SUPERFRAC™ tray has been industry validated for more than 25 years in new tower designs and revamping of existing trays. Suitable for all tray operating regimes, the SUPERFRAC™ tray provides:

• Increased capacity AND efficiency when revamping conventional trays
• Cross-flow enhancement and optimized flow distribution that promotes high tray efficiency for superfractionator applications
• Complete access for maintenance inspections without needing to remove the trays

Koch-Glitsch

United States (316) 828-5110 | Canada (905) 852-3381 | Italy +39 039 6386010 | Singapore +65-6831-6500

For a complete list of our offices, visit our Web site.

www.koch-glitsch.com

“K” KOCH-GLITSCH and SUPERFRAC are trademarks of Koch-Glitsch, LP and are registered in the USA and various other countries. YOU CAN RELY ON US is a trademark of Koch-Glitsch, LP. SUPERFRAC™ technology is protected by patents in the USA and various other countries; other patents pending.
Structured packing in a CO₂ absorber

Solvent regeneration is the biggest energy consumer in an amine treating unit but efforts to minimise energy consumption should be made cautiously

RALPH WEILAND and NATHAN HATCHER
Optimized Gas Treating, Inc.

Structured packing in deep CO₂ removal applications such as LNG production can offer significant advantages, including higher throughput, over other internals. Piperazine promoted MDEA is the most common choice of solvent for this application. However, tight designs, as typically specified in offshore situations, can make such units hard to operate. This article presents a case study in which absorber performance seemed to be disproportionately affected by the reboiler duty of the amine regenerator.

Liquefying natural gas enables it to be transported economically over immense distances to end users remote from the gas source. Shale gas is a large resource for natural gas liquids (NGLs), but it is also the source of enormous amounts of gas. The so-called shale gas revolution is what is in large part responsible for driving the construction of new LNG plants and specialised shipping.

Most shale gas is sweet in that it contains little or only nuisance amounts of hydrogen sulphide and other sulphur compounds. However, significant concentrations of CO₂ are normal. Before gas can enter liquefaction, CO₂ must be removed to less than 50 ppmv (and sometimes even lower), referred to as deep CO₂ removal.

To get to 50 ppmv CO₂ in a column of reasonable physical height it is necessary to speed up the absorption process. This is done using a few weight percent piperazine (typically 3-9 wt%). The rate constant for the piperazine-CO₂ reaction has the extraordinarily high value of 50 000 L.gmol⁻¹.s⁻¹ even at room temperature, making this amine an obvious choice as a CO₂ absorption rate promoter. All major solvent vendors offer at least one or two formulations of piperazine with MDEA for deep CO₂ removal applications, and some include such solvents as part of a licensed process.

Case study
The study is of an LNG related CO₂ removal unit using piperazine promoted MDEA in which the absorber contains structured packing and the regenerator is trayed. The packing specific (dry physical) area is nominally 250 m²/m³.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw gas</td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>Pressure, barg</td>
</tr>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>CO₂, mol%</td>
</tr>
<tr>
<td>Methane, mol%</td>
</tr>
<tr>
<td>C₂⁺, mol%</td>
</tr>
</tbody>
</table>

Before gas can enter liquefaction, CO₂ must be removed to less than 50 ppmv, referred to as deep CO₂ removal.

Lower heat of absorption than primary and secondary amines. This translates into lower solvent regeneration energy consumption; however, the down side is that MDEA by itself is unsuited to deep CO₂ removal. The CO₂ absorption rate is too slow and the phase equilibrium with CO₂ is often unfavourable.

www.eptq.com
On the other hand, the CO₂ concentration in equilibrium with the lean solvent climbs continually and steadily throughout the loading range (as it should). Below the transition point at 0.033 mole loading, the CO₂ leak closely follows the lowest achievable level consistent with a given lean solvent. Because treating very closely tracks CO₂ equilibrium over the lean solvent, it can be said that treating in this region is thoroughly lean end pinched. As will soon become evident, this term means that the CO₂ concentration in the treated gas is determined entirely by the solvent lean loading. Nevertheless, the transition itself is abrupt. The reason is subtle but revealing.

**Figure 2** shows a series of absorber gas-phase temperature profiles for several solvent lean loading values. The curves at the low loading end are what one might expect for CO₂ absorption by a fast reacting solvent such as piperazine promoted MDEA; the curves at the high loading end, however, are not. The observation that the peak temperature at the bulge increases with increasing loading provides the first clue to an explanation. There are at least two reasons the bulge temperature itself increases with loading: heat capacity decreases as loading goes up – that is, the same heat release results in higher temperature; and the heat of absorption itself increases with temperature and this exacerbates the effect.

Somewhere between a lean loading of 0.032 and 0.033 mol/mol, a bulge temperature is reached at which the partial pressure of CO₂ in the treated gas right at the bulge is equal to the partial pressure in equilibrium with the solvent there. In other words, at the transition loading, the driving force for absorption becomes zero. At a lean loading only slightly above this point the zero driving force explodes across most of the upper part of the column until the cold lean solvent draws the temperature down near the top of the packing and absorption resumes. The curves represented by the solid lines all correspond to lean-end pinch conditions. The dashed curves are important ones. This exercise uncovered a rather surprising sensitivity. It also demonstrated the importance of simulating the entire treating plant, not just the absorber or regenerator as isolated pieces of equipment, and of validating data before an optimisation study is started.

The first simulation run was based on what was thought to be good process information regarding compositions, flows, thermal duties, and so on. A thermal imaging scan of the absorber was also available, taken on the same day the process information was recorded on the plant’s DCS. The big surprise was that the simulated peak temperature in the absorber was found to be 40°C hotter than the thermal scan indicated, and the simulated bulge temperature covered most of the tower’s packed height. The simulated temperature profile could not have been further away from the thermally imaged one! But the main red flag was that the simulated solvent lean loading was nearly 0.07 moles CO₂ per mole of total amine. This is a ridiculously high value obtained by simulating the entire plant (less than 0.01–0.02 is more normal for a well maintained solvent). These observations indicated that bad data had likely been input into the simulation. However, the broad temperature bulge made it worthwhile first to isolate the absorber to assess the sensitivity to lean loading.

**Figure 1** shows that the residual CO₂ in the treated gas (blue line in the figure) steadily climbs with increasing lean loading, but it suddenly escalates explosively as the loading passes 0.033 mol/mol.
INNOVATIVE SOLUTIONS FOR THE HYDROCARBON PROCESSING INDUSTRY

Bilfinger’s engineering department constantly works to offer the best and innovative solutions to the Hydrocarbon Processing Industry:

JOHNSON SCREENS® SHAPED SUPPORT GRID (SSG)
designed to be installed into the bottom head of hydroprocessing or gas dehydration vessels, allowing better liquid and gas flow, bed utilization, distribution and an overall more efficient process than traditional flat surface grid assemblies. Patented design.

JOHNSON SCREENS® INLET DIFFUSER BASKET
designed to control velocities of gas or liquid distribution over media, providing improved performance over traditional plate disc type distributor designs as well as even distribution and minimal scouring at the top of the bed. Patented design.

BILFINGER WATER TECHNOLOGIES
www.water.bilfinger.com

Australia - Asia Pacific
Phone +61 7 3867 5555
Fax +61 7 3285 2788
asiapacific.water@bilfinger.com

France
Phone +33 5 4902 1600
Fax +33 5 4902 1616
france.water@bilfinger.com

North & South America
Phone +1 651 636 3900
Fax +1 651 638 3171
usa.water@bilfinger.com
all bulge pinched, meaning that along the flat part of these curves there is essentially no driving force for CO\textsubscript{2} transfer in either direction. As the bulge spreads further across the column at higher lean loadings, less and less gas is absorbed and this causes the peak temperature to decrease slowly.

Lean-end and bulge pinches can be more easily understood from plots of composition across the absorber. Figure 3 shows equilibrium (dashed lines) and actual (solid lines) mole fractions of CO\textsubscript{2} in the gas for the 0.032 and 0.035 lean loading cases. At the lower of the two loadings, below the transition loading, only the bottom section of the absorber has a concentration difference driving force for absorption. In the top section (the lean solvent end) the driving force is zero; hence, the operation is termed lean-end pinched. At the higher loading in the bulge pinched region, fully the middle three quarters of the column has no driving force. The driving force is pinched exactly along the temperature bulge. Consequently, here the column operation is called bulge pinched.

Gas treating engineers are often surprised to learn that systems using piperazine promoted MDEA in LNG production, and other deep CO\textsubscript{2} removal applications such as ammonia and hydrogen production, can undergo a sudden behavioural change near the transition point where the operation goes from a normal lean-end pinched condition to a bulge pinched state. Indeed, the existence of a bulge pinch is a new concept to many engineers who are otherwise well versed in acid gas removal.

However, piperazine as a promoter for MDEA has come into general patent-free use only relatively recently, so exposure to the details of this technology has been limited. In addition, mass transfer rate-based simulation is really the only way to identify such behaviour, and rate based simulation is a relatively new technology, albeit a very powerful one.

It may be worth noting that, in this instance, the 50 ppmv CO\textsubscript{2} target can be met with a lean loading of around 0.03 mol/mol. This is an unusually high value for piperazine-MDEA solvents. However, because it would require only very low energy inputs, it might be tempting to operate there. Unfortunately, the absorber could prove to be quite difficult to control in that part of the loading range. To keep away from a hard-to-control region of the operating map, one is forced to use higher reboiler energy inputs and to strip to quite a bit lower loadings, resulting in far better than the 50 ppmv CO\textsubscript{2} specification.

**Regeneration**

The two main parameters that are used to control solvent loading are the solvent flow rate and the reboiler duty. Solvent flow is normally used to limit the rich loading so that, for example, corrosion rates remain reasonably low. It is not usually used to control lean loading. Instead, lean loading control is done by manipulating the flow rate or temperature of the steam or hot oil entering the reboiler. As Figure 4 shows, lean loading is fairly responsive to duty at low reboiler energy inputs although the solvent becomes gradually harder to strip if only because piperazine holds CO\textsubscript{2} more tenaciously than MDEA does. A reflux ratio of 0.7 (right side scale) is clearly insufficient to reach a lean loading consistent with the treating specification. The specification can be readily met at a reflux ratio of 0.8 or higher, and reflux ratios in the range of 0.8–0.9 are normal for piperazine promoted MDEA solvents in deep CO\textsubscript{2} removal applications.
Conclusion
The possibility of a bulge pinch is a fact of life when piperazine promoted MDEA solvents are used for deep CO₂ removal in LNG, ammonia, and hydrogen production. A bulge pinch starts to form at the temperature bulge when the CO₂ concentration in the gas being treated reaches a value equal to the equilibrium value at the bulge. At that juncture, further absorption is not possible. Absorbing just a minuscule amount more CO₂ in the immediate vicinity of the bulge raises the temperature there to the bulge value too. Thus the bulge spreads. Perhaps the surprise is how rapidly the bulge can spread with seemingly minuscule increases in lean solvent CO₂ loading.
Solvent regeneration is the biggest energy consumer in an amine treating unit. Efforts to minimise energy consumption, however, should be made cautiously. Non-rate based simulation is oblivious to bulge pinches, so reboiler energy reduction efforts should be made with the aid of a real mass transfer rate based simulation tool, such as the ProTreat simulator. This will ensure that absorber operation is kept well away from the bulge pinched region and that the unit will function as intended.

The possibility of a bulge pinch is a fact of life when piperazine promoted MDEA solvents are used for deep CO₂ removal

Ralph H Weiland is a co-founder of Optimized Gas Treating with offices in Clarita, OK, Houston, TX and Buda, TX. He holds BASc, MASc and PhD degrees in chemical engineering from the University of Toronto.
Email: ralph.weiland@ogtrt.com

Nathan A Hatcher joined Optimized Gas Treating, Buda, Texas, as Vice-President, Technology Development, in 2009. He holds a BS in chemical engineering from the University of Kansas and is currently a member of the Amine Best Practices Group.
Email: nate.hatcher@ogtrt.com
When it comes to forming, handling and moving sulphur; no one company has more hands on experience than Enersul. We offer our own ground breaking proprietary technologies, developed in house though decades of operational experience and pioneering Research and Development. We market and operate the most complete array of new and innovative sulphur technologies and services for any capacity, in any climate. Contact us today and find out how Enersul is your solution For Everything Sulphur.

enersul@enersul.com

7210 Blackfoot Trail SE Calgary, Canada T2H 1M5 | +1 403 253 5969 | enersul@enersul.com | enersul.com
Reflux in a gas dehydration plant

Gas dehydration by adsorbent processes may lead to the damaging regeneration reflux phenomenon during adsorbent regeneration

SAJAD MIRIAN and HOSSEIN ANISI Nitel Pars Co (Fateh Group) XUANG YU Hengye Chemical Co SEPEHR SADIGHI Research Institute of Petroleum Industry

Dehydration of natural gas entails the removal of water that is associated with natural gases in vapour form. The natural gas industry has recognised that dehydration is necessary to ensure smooth operation of gas transmission lines. This pretreatment prevents the formation of gas hydrates and reduces corrosion. The three major methods of dehydration are direct cooling, adsorption and absorption. Adsorption-based processes for separation of multi-component gaseous mixtures are becoming increasingly popular. The new generation of synthetic and more selective adsorbents developed in recent years has enabled adsorption-based technology to compete successfully with traditional gas separation techniques.

Any adsorption-based separation process requires two essential steps: adsorption during which one or more components are preferentially adsorbed/separated; and regeneration during which these components are removed from the adsorbent bed. The adsorbent is repeatedly used in cycles by carrying out these two steps. When a regeneration step is carried out through reduction of the total pressure, the process is called pressure swing adsorption (PSA). Temperature swing adsorption (TSA) is another technique used for regenerating a bed of adsorbent that is loaded with the targeted impurity gas. This technology began commercially in the 1960s and continues today for drying continuous air and natural gas as well as other purification applications such as carbon dioxide stripping from air. TSA exploits the capacity of certain adsorbent materials, such as activated alumina, silica gel and zeolites, to adsorb gases at moderate temperatures (40°C, 100°F) and later release them when the temperature rises above 120°C (250°F).

Natural gas treating units using molecular sieves and TSA technology are usually optimised by manipulating both the adsorption and the regeneration time. By reducing the adsorption time, both the vessel size and the amount of adsorbent used are reduced. Therefore, the total cycle time is usually designed such that at the end of the adsorption a short time is available for appropriate regeneration of the adsorbent. Hence, the inlet section of the adsorption bed is faced immediately with a high temperature from the start of the regeneration without any heating ramp. Heating up the adsorber without using a heating ramp causes a strong temperature difference in the bed. So, at the bottom, the molecular sieve is very hot and desorbs the adsorbed water while the top layers are still at adsorption (low) temperature. Therefore, water desorbed in the bottom layer condenses in the top layer. This phenomenon is called refluxing or retro-condensation. A schematic diagram of an adsorber with regeneration refluxing is shown in Figure 1. To prevent this catastrophic phenomenon, a good molecular sieve formulation (binder and zeolite) or improvement in the regeneration condition is inevitably required.

In this article, modelling of the regeneration reflux phenomenon during regeneration is performed and the effects of it on the adsorption process are reviewed. Recommendations to prevent this phenomenon in a commercial scale dehydration unit (as a case study) are presented.

Process description

The purpose of a natural gas dehydration package is to reduce the water content of the natural gas to avoid freezing and hydrate formation in the pipeline. In order to utilise natural gas for urban consumption, the water dew point should be reduced to below -10°C, accomplished by using a molecular sieve adsorption unit which adsorbs water from the inlet gas.
To perform such a process, water saturated natural gas from the upstream unit is sent to the molecular sieve dehydration plant where the gas stream passes through a separator to retain any free water carry-over from the upstream facilities. It is then routed to the molecular sieve dryers. A dehydration package consists of four dryers loaded with a special type of molecular sieve 4A; at any time three dryers are in adsorption and one in regeneration. The feed stream is split into three identical streams, each of which passes downward through one of the beds that are in adsorption mode (see Figure 2).

Dry gas streams leaving the adsorption beds are joined and passed through a filter to retain any solid particles coming from the dryers. Finally, dry and filtered gas is sent to the municipal gas station via a transmission pipeline.

Each adsorption cycle takes eight hours. After that, the dryer is switched to regeneration mode for removing the residual water. At once, that bed which has completed the regeneration step is replaced. During the regeneration process, a regenerative gas stream is passed through a heater where it is heated to approximately 270°C. This hot gas passes upwards through the offline saturated dryer heating the molecular sieves. As the sieves are heated up, adsorbed water begins to desorb and is carried away by the hot gas. The operating conditions of the target adsorption and regeneration processes and specifications of their feeds are shown in Table 1 and Table 2, respectively.

Mathematical modelling of regeneration
A computational fluid dynamic modelling technique was used to model the momentum, content and mass transfer of fluid through porous media, and also to investigate the refluxing phenomenon in the regeneration process studied. To solve these set of equations, commercial software (Comsol Multiphysics Ver. 4.2) was employed that utilises the finite element method to discretise partial differential equations to ordinary differential equations and finally solve them. The following assumptions are considered during the mathematical procedure:

- To reduce computation time, 2D axisymmetric mode is assumed
- The gaseous phase is an ideal gas
- Entrance and exit effects are negligible
- There is no slip condition near the dryer wall.

Governing equations
Mathematical modelling of the target regeneration process is obtained by coupling a set of general equations (including continuity, momentum, energy and mass balances), and particular equations such as physical properties, adsorption and desorption isotherms and equation of state as follows:

Continuity equation:
\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = Q_{\text{m}} \]

Momentum equation:
\[ \frac{\partial}{\partial t} \left( \rho \frac{\mathbf{u}}{\epsilon_p} \right) + \nabla \cdot \left( \rho \mathbf{u} \mathbf{u} \right) = \nabla \cdot \left( -P \mathbf{I} + \frac{\mu}{\epsilon_p} \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^\text{T} \right) \right) - \frac{2\mu}{3\epsilon_p} \left( \nabla \cdot \mathbf{u} \right) T + \frac{\mu}{K_b} \mathbf{u} \cdot \nabla \mathbf{u} + Q_{\text{m}} \mathbf{u} + F \]

Energy equation:
\[ (\rho C_p)_{\text{u}} \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T = \nabla \cdot (k_b \nabla T) + Q \]

Feed and regeneration gas compositions

<table>
<thead>
<tr>
<th>Components</th>
<th>Adsorption</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, wt%</td>
<td>72.95</td>
<td>73.1</td>
</tr>
<tr>
<td>Ethane, wt%</td>
<td>8.13</td>
<td>8.14</td>
</tr>
<tr>
<td>Propane, wt%</td>
<td>4.11</td>
<td>4.11</td>
</tr>
<tr>
<td>i-Butane, wt%</td>
<td>1.22</td>
<td>1.22</td>
</tr>
<tr>
<td>n-Butane, wt%</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td>n-Pentane, wt%</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>n-Hexane, wt%</td>
<td>0.140</td>
<td>0.141</td>
</tr>
<tr>
<td>n-Heptane, wt%</td>
<td>1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>n-Octane, wt%</td>
<td>0.1897</td>
<td>0.19</td>
</tr>
<tr>
<td>n-Nonane, wt%</td>
<td>0.1622</td>
<td>0.1625</td>
</tr>
<tr>
<td>n-Pentane, wt%</td>
<td>0.0337</td>
<td>0.0338</td>
</tr>
<tr>
<td>CO₂, wt%</td>
<td>3.79</td>
<td>3.8</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>4.57</td>
<td>4.58</td>
</tr>
<tr>
<td>H₂O, wt%</td>
<td>0.1573</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption temperature, °C</td>
<td>47</td>
</tr>
<tr>
<td>Adsorption pressure, kPa</td>
<td>9101</td>
</tr>
<tr>
<td>Adsorption mass flow, kg/h</td>
<td>2.409e+05</td>
</tr>
<tr>
<td>Regeneration temperature, °C</td>
<td>270</td>
</tr>
<tr>
<td>Regeneration pressure, kPa</td>
<td>7929</td>
</tr>
<tr>
<td>Regeneration mass flow, kg/h</td>
<td>4.751e+04</td>
</tr>
</tbody>
</table>

Table 2
Introduction

Cartridge trays, also known as package trays, are generally used for tower diameters in the range from 12” (300mm) up to 36” (900mm). For tower diameters below 36”, the installation of segmental trays is difficult and packing is often preferable over trays. Ultimately, the decision on what technology to use comes down to process requirements and economics.

As can be seen below, the design and construction of cartridge trays is unique and a bit complex. Cartridge trays typically consist of one or more bundles of 6 to 10 trays stacked together and connected with several tie rods running through the bundle. This can be a challenge; the trays must be assembled with near perfect alignment to ensure trouble-free installation. The resistance of the tray seal rings increases the force required to install and remove the tray bundles so proper design and correct dimensions are critical. Alternatively, Sulzer also offers Slit Trays™ for smaller column diameters. These trays are installed individually to help minimize installation issues.

Design Considerations

The mechanical design of the cartridge trays should also be stronger than segmented trays since as they will be transported in assembled condition. The tray thickness should be increased (e.g. 12ga or 2.5mm when referring to stainless steel) to maintain rigidity and ensure a tight fit. Stronger tie-rods and Schedule 80 spacer pipes should be specified as well. Since the gaskets are more prone to distortion, it is preferable to install them after the trays arrive on site. The selection of gasket material should be based on temperature and service. Metal gaskets of a suitable material are often preferred for their mechanical durability.

Important Tips

During installation, the orientation of the trays with respect to nozzles should be fixed prior to the bundle insertion as it will be more difficult to rotate afterwards. Also, access around the outside of the column must be properly allocated during the design process to ensure that there is no external interference with the bundle during insertion or removal.

Standard pipe sizes are typically used for columns with cartridge trays. Care must be taken during construction not to compromise the diameter and roundness of the column to ensure that the tray bundles will pass through the without interference.

The Sulzer Applications Group

Sulzer has over 150 years of in-house operating and design experience in process applications. We understand your process and your economic drivers. Sulzer has the know-how and the technology to design internals with reliable, high performance.

Sulzer Chemtech, USA, Inc.
8505 E. North Belt Drive | Humble, TX 77396
Phone: (281) 604-4100 | Fax: (281) 540-2777
TowerTech.CTUS@sulzer.com
www.sulzer.com

Legal Notice: The information contained in this publication is believed to be accurate and reliable, but is not to be construed as implying any warranty or guarantee of performance. Sulzer Chemtech waives any liability and indemnity for effects resulting from its application.
Results and discussions

Figure 3 shows the temperature distribution of the adsorption bed at an early stage in the regeneration process. As is apparent in this figure, a high regeneration gas temperature (without enough ramp-up) leads to a large temperature gradient along the bed, and creates reflux at the early stages of the regeneration cycle.

At these operating conditions, due to the high pressure of the regeneration gas, high moisture concentration and a large temperature gradient are inevitable. For the design case, the licensor charged a molecular sieve with enough strength against reflux which could work more than four years without any malfunction. But for the next loading, a regular molecular sieve, manufactured by another company, could not withstand those conditions. It was observed that, only three months from the start of run, the loaded molecular sieve was ruined due to the reflux phenomenon. It also increased the pressure drop of the dryers. Therefore, it can be concluded that the molecular sieve, especially the binder and additives, should be made of appropriate raw materials to be capable of resisting the reflux phenomenon and preventing operational malfunctions.

As Figure 3 shows, for our case study liquid water moved downward until it encountered the heating zone. At this point, boiling water created a reflux which ground the molecular sieve into a powder. Since certain components of the binder were somewhat soluble in boiling water, the molecular sieve subsequently became a wet cake (mud) which was then baked by the rising hot gas. These soluble components could ion exchange with the zeolite and/or combine with anions in water to form solid salts (Na$_2$CO$_3$, CaCO$_3$, MgCO$_3$, NaNO$_3$, and so on). These solid salts could then paste the remaining pellets or beads together to form a solid mass. This solid mass, formed in an annulus shape with a centre opening of less than one foot, did not allow gas to pass through, and consequently reduced the effective diameter of the bed (see Figure 1).

Therefore, boiling water destroyed the molecular sieve such that the severity of the operating conditions should be greatly reduced to extend the replacement period of the adsorbent. The regeneration reflux showed some undesirable effects on the adsorption process which can be summarised as follows:

- Molecular sieve particle break-up
- Increasing pressure drop
- Gas channelling
- Premature water breakthrough which all lead to poor adsorber performance.

A high regeneration gas temperature (without enough ramp-up) leads to a large temperature gradient along the bed

<table>
<thead>
<tr>
<th>Recommendations and consequences to prevent reflux phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recommendation</td>
</tr>
<tr>
<td>1 Decreasing the regeneration gas pressure</td>
</tr>
<tr>
<td>2 Regeneration gas temperature ramp-up</td>
</tr>
<tr>
<td>3 Layer of activated alumina at the top of the bed</td>
</tr>
<tr>
<td>4 Change the heating gas flow direction from the top to the bottom of the bed</td>
</tr>
<tr>
<td>5 Try to reduce the heat loss through the top of the bed by adding extra insulation and even installing a steam tracer</td>
</tr>
<tr>
<td>6 Reverse all flows</td>
</tr>
<tr>
<td>7 Using a special molecular sieve</td>
</tr>
</tbody>
</table>

| Table 3 |

---

78 PTQ Q4 2014 www.eptq.com

10/09/2014 13:49
binder materials in water.

• Choosing an inappropriate flow direction in adsorption and regeneration.

Recommendations and consequences

The recommendations proposed in Table 3 can decrease the reflux phenomena which are reviewed in brief for the target gas dehydration unit.

According to recommendation 7 in Table 3, a special molecular sieve 4A (with high resistance against reflux phenomena), manufactured by Shanghai Hengye Chemical Co., was loaded into the target dryers about one year ago. To date, the dehydration unit has shown a good performance and no malfunction has been observed.

Acknowledgment

We would like to express our great appreciation to Mr F Noorbakhsh and Mr M A Fatemi for their valuable and constructive suggestions during the planning and development of this research work. We would also like to thank Nitel Pars Company, a subsidiary of Fateh Group, for technical assistance and financial support.

Further reading


Sajad Mirian is a Project Manager in the Adsorbents Department of Nitel Pars Co., Tehran, Iran. He holds a MSc in chemical engineering. Email: ms002@nitelpars.com.

Hossein Anisi is an Adsorbent Expert in the Adsorbents Department of Nitel Pars Co. He holds a BSc in chemical engineering. Email: ms003@nitelpars.com

Xiang Yu is an Application Engineer of Hengye Chemical Co., Shanghai, China. He holds a BSc in chemical engineering. Email: hyns@foxmail.com

Sepehr Sadighi is Assistant Professor with the Catalysis Research Division of Research Institute of Petroleum Industry (RIPI), Tehran, Iran. He holds a PhD in chemical engineering. Email: Sadighis@ripi.ir
EMPOWERING PROCESS SIMULATION

As a process engineer you need innovative tools to see your vision come to life.

VMGSim™ is a comprehensive steady state and dynamic process simulator that provides flexibility and control to help design new processes and improve your existing plant’s efficiency and bottom line.

Our PIONA molecular structure based oil characterization system allows high fidelity modelling of light to heavy hydrocarbons from the gathering system to refinery products and distribution.

Improve the past. Optimize the present. Design the future.

VISIT

to find out more.

U.S. • Canada • Japan • Europe • Australasia • Egypt • China • Middle East • Brazil
Override control of fuel gas

When natural gas was to be added to a refinery’s fuel gas system, detailed dynamic simulation of the new system ensured stable operation and a shorter start-up period

RAINER SCHEURING  Cologne University of Applied Sciences
ALBRECHT MINGES and SIMON GRIESBAUM  MIRO Mineraloelraffinerie Oberhein
MICHAEL BRODKORB  Honeywell Process Solutions

MiRO oil refinery in Germany has expanded its fuel gas system using natural gas as an additional energy source. The new natural gas system, which includes a complex override control structure, had to be integrated in the historically evolved fuel gas system outside of a shutdown. Therefore, a detailed dynamic simulation study (DSS) of the new and integrated overall fuel gas system was carried out using UniSim Design. The objectives of the DSS include ensuring stable and safe operation of the new system as well as shortening the start-up time.

This article gives an overview of the project and shows initial results after successful start-up of the new fuel gas system.

Refinery and natural gas import project
MiRO (Mineraloelraffinerie Oberhein) is one of the largest oil refineries in Germany. The refinery is located in Karlsruhe and consists of two sites which are interconnected in multiple ways (feeds, products and utilities). In the past, the fuel gas system of the refinery was based on liquefied petroleum gas (LPG) and fuel oil as the external make-up energy source. Price changes have made natural gas financially attractive as an additional energy source, and thus MiRO decided to include natural gas as an alternative make-up gas.

A simplified structure of the new integrated fuel gas system with the energy sources – refinery off-gas, FCC gas, coker gas, LPG and natural gas – is shown in Figure 1.

Price changes have made natural gas financially attractive as an additional energy source

In order to meet the varying requirements of the refinery, MiRO has developed a complex override control structure. In addition, piping and control of the new natural gas system had to be integrated in the historically evolved fuel gas system outside of a shutdown. Therefore a dynamic simulation study of the overall fuel gas system was carried out with the following main objectives:

• Ensuring the integrated fuel gas system is stable in all operating conditions and transition phases
• Ensuring there are no oscillations or other dynamic problems
• Testing the control configuration and pre-tuning the controllers prior to installation
• Ensuring additional control objectives (min/max flow rates, and so on) are met
• Testing that transitions from LPG to natural gas and back, as primary fuel, are easy to handle
• Safe commissioning
• Reducing commissioning time.

Dynamic simulation of fuel gas system
Dynamic Process Simulators such as Honeywell UniSim Design, Invensys Dynsym, or AspenTech Aspen Hysys Dynamics are based on first principle process modelling engines that allow realistic modelling of the transient behaviour of processes typically found in the oil, gas and chemical industries. In order to create a process model, the user selects readily available components and thermodynamic packages to define physical properties and phase equilibria for the system and then creates a flowsheet by adding and linking generic unit operation models (pipes, vessels, pumps, distillation columns, for instance) and control equipment (valves, PIDs, and so on). The resulting model can be initialised to a specific initial condition and run through different predefined scenarios as part of a dynamic simulation study.

Dynamic simulation studies are a standard tool in the process indus-
Override control is a control strategy where one manipulated variable is adjusted by two or more controlled variables, which are not selected at risk of integral windup, therefore an anti-windup strategy is required. One option is external reset feedback, which prevents windup and ensures that the outputs of all controllers are equal. Figure 3 shows a possible realisation of an over-ride controller with two controllers (C1 and C2), two controlled variables (PV1 and PV2), a low selector, external reset feedback (ERF), and one manipulated variable (OP).

The override control system of MiRO’s fuel gas system is far more complex and has to manage:
- A large number of controlled variables and controllers
- An elaborate structure
- Various requirements (safety limits, optimal operating point, and so on).

As an example, a part of the override control scheme is shown in Figure 4.

Simulation analysis of many scenarios
In order to ensure that the objectives shown above are fulfilled, extensive simulation analyses of a wide range of realistic scenarios were performed. For instance, in the case of a sudden shutdown of a 100 MW fired heater at five minutes simulation time the fuel gas system pressure stayed in the stipulated range as shown in Figure 5. The red curve represents the pressure.
At Spirax Sarco we help our customers to reduce emissions and improve energy efficiency.

We are the first for steam solutions in the oil and petrochemical industry:

• 38 Operating Companies across 6 continents
• A global network of over 5,000 steam experts
• 9 manufacturing sites worldwide
• 34 customer training centres across the globe

For more information visit www.spiraxsarco.com/opc
The blue curve shows the active OP, which directly controls the valve connected to HGP 260 P4 in Figure 4.

Because many PID controllers are involved, which may interact and cause oscillations, PID parameter tuning was a central point of the simulation analysis.

As a result of the investigations, a number of issues were adjusted such as:
- Pressure limits for flare gas relief
- Valve sizing
- Control parameters.

On the whole, simulation analysis has verified that the design of the fuel gas system, including the natural gas system, and the complex override control system is fully functional and error free.

**Commissioning of natural gas system**

In December 2013, the natural gas system was integrated into the existing fuel gas system. Standard control engineering tasks, such as linearisation of non-linear valve curves, were pursued where necessary. The control parameters which had been designed in the simulation study provided good starting points for detailed parameter tuning.

**Figure 4** Part of override control scheme of MiRO refinery

**Figure 5** Trend of fuel gas system pressure in the case of a 100 MW oven shutdown

Pressure set point is 8.5 bar(g), and the pressure rises up to 9.1 bar(g). The blue curve shows the active OP, which directly controls the valve connected to HGP 260 P4 in Figure 4.
tuning. In many cases, the control parameters of the dynamic simulation could be used without any changes.

As a result of the careful preparation, commissioning went smoothly without any significant problems. It is noteworthy to emphasise the short period of time that was required for commissioning and startup of the expanded fuel gas system.

**Conclusion**

MiRO refinery had to expand its fuel gas system for the usage of natural gas as an additional alternative energy source. A new natural gas system, which includes a complex override control structure, was integrated into the historically evolved fuel gas system outside of a shutdown. In order to ensure safe and stable operation of the new system, as well as a smooth startup, a dynamic simulation study of the fuel gas system was carried out using UniSim Design. The simulation study helped to develop a fully functional and error free system. As a consequence, commissioning and startup of the expanded fuel gas system went smoothly without any significant problems.

UniSim Design is a mark of Honeywell Inc.

**References**


Rainer Scheuring is Professor of Automation Technology and Control Theory at Cologne University of Applied Sciences. He holds a master’s in technical cybernetics and a PhD from Stuttgart University, Germany. Email: rainer.scheuring@fh-koeln.de

Albrecht Minges is a Senior Process Control Engineer in the department for process automation at the MiRO-Refinery in Karlsruhe, Germany. He holds a BS degree in process engineering from University of Applied Sciences, Mannheim. Email: Minges@miro-ka.de

Simon Griesbaum is a Process Control Engineer in the department for process automation at the MiRO-Refinery in Karlsruhe, Germany. He holds a master’s in chemical engineering from University of Applied Sciences, Mannheim. Email: griesbaum@miro-ka.de

Michael Brodkorb is Software Sales Support Leader EMEA at Honeywell Process Solutions in Tarragona, Spain. He has a degree in chemical engineering from University of Dortmund, Germany, and a PhD from Bradford University, UK. Email: michael.brodkorb@honeywell.com
There’s more than one way to skin the CAT!

Oryx GTL slurry phase distillate (SPD) raw wax catalyst slurry is the system where Everlasting Valves are installed. This unique valve was designed nearly 100 years ago for blowing down steam locomotive boiler solids. The U.S. Department of Energy in development of the clean coal technologies selected this valve as state of the art valve for dry solids and slurries.

A major licensor of refining processes now specifies the Everlasting rotating disc metal seated valve for Fluid Catalyst Crackers handling fresh catalyst and for hot CAT withdrawal. It is also listed in the “Best Practices” of a world class petroleum refiner for continuous catalyst reforming. A preeminent catalyst additive supplier has standardized on this valve concept for all their chemical injection units.

Spent catalyst recyclers use them on their vacuum truck load out systems. The flat rotating disc renews the sealing surfaces each time the valve is cycled. No other valve is similar, with vacuum through 10,000 psig (689b) and temperatures to 1500F (815C). See more specifications on the reverse side.

Whether it’s fresh, spent, dry or slurry use the Everlasting Rotating Disc Valve and see your CAT valve problems disappear. There are many ways of skinning the CAT, but one best valve for catalyst slurries.

Call us today at 1-908-769-0700 or visit our website at (www.everlastingvalveusa.com)
‘Snakes and ladders’ for maximising propylene

Changes in process conditions in tandem with ZSM-5 additives widen the potential for petrochemicals production from the FCC unit

BART DE GRAAF, MEHDI ALLAHERVI, MARTIN EVANS and PAUL DIDDAMS

Johnson Matthey Process Technologies

The modern day equivalent of turning lead into gold is upgrading oil into petrochemicals. Whereas in some parts of the world fluid catalytic cracking (FCC) units are being shut down because of poor economics, new units are still being built in growth regions like Asia and the Middle East. These new FCC units are typically designed as petrochemical FCC units, in particular to produce propylene, often from heavy residual feedstocks. Nowadays, margins for standard FCC units producing mainly transportation fuels are small or even negative, however not so for petrochemical FCC units.

Demand for petrochemicals is increasing, especially in Asia where there is a shortfall in mixed xylenes and propylene production. Mixed xylenes exports from the US account for 800 000 t/y or 25% of the Asian market’s consumption.1 Propylene is a key chemical for plastics such as polypropylene, acrylonitrile, propylene oxide derivatives, and so on. Global demand for propylene in 2000 was 25.1 million t/y, increasing to 42.3 million t/y in 2011 and is expected to grow to an estimated 62.4 million t/y by 2020. This growth is largely driven by increasing demand in Asia Pacific (to 62% of global demand), the Middle East and Africa.2 Growth in these regions outpaces that in North America. Future growth in the European market is expected to be very limited because of the Eurozone crisis.

There is a clear growing demand for petrochemicals, and the FCC unit is well positioned to meet it. Worldwide, 60% of the propylene is supplied by steam crackers, 30% by FCC and 10% by propylene on-demand units. To boost propylene yield in the FCC unit, typically ZSM-5 additives are used. The widely assumed model of how ZSM-5 additives work, that is commonly used, is simple: ZSM-5 cracks olefins out of the gasoline. This article shows this model to be incorrect. ZSM-5 does not just crack gasoline range olefins, it produces these too via oligomerisation. ZSM-5 acts both as a ‘snake’ and ‘ladder’, as in the board game, for olefins in the FCC unit. The interaction between hydrogen transfer (see Figure 1) and ‘snakes and ladders’ for olefins determines gasoline composition in the FCC unit. With this new model, gasoline compositions when using ZSM-5 can be explained and the ‘gasoline cracking’ model is left wanting.

Maximum propylene chemistry

Many reaction pathways play an important role when cracking a vacuum gas oil (VGO) or residue feedstocks into products over an FCC catalyst. The primary step is ‘cracking’, that is catalytically breaking carbon-carbon bonds (also known as beta scission). In this reaction, individual molecules react with acid sites on the catalyst forming carbenium ion intermediates that are readily able to crack. Cracking results in olefin formation via a) cracking large paraffins, b) ring opening of naphthenes, c) dealkylation of aromatic side-chains, and d) the subsequent cracking of the olefins formed in a) to c):

a) Paraffin cracking: large paraffin → Olefin + Smaller paraffin
b) Ring opening: Naphthene (ring) → Olefin + Aromatic

c) Dealkylation: Alkylaromatic → Olefin + Aromatic
d) Olefin cracking: Large olefin → Smaller olefin + Smaller olefin

Concurren reactions include thermal cracking, hydrogen transfer, dehydrogenation, cyclisation, trans-alkylation, oligomerisation and polymerisation. Thermal cracking and dehydrogenation are the primary sources of dry gas (C1-C2 and H2), and polymerisation produces coke. These reactions do not significantly

Figure 1) and ‘snakes and ladders’ for olefins determines gasoline composition in the FCC unit. With this new model, gasoline compositions when using ZSM-5 can be explained and the ‘gasoline cracking’ model is left wanting.

Maximum propylene chemistry

Many reaction pathways play an important role when cracking a vacuum gas oil (VGO) or residue feedstocks into products over an FCC catalyst. The primary step is ‘cracking’, that is catalytically breaking carbon-carbon bonds (also known as beta scission). In this reaction, individual molecules react with acid sites on the catalyst forming carbenium ion intermediates that are readily able to crack. Cracking results in olefin formation via a) cracking large paraffins, b) ring opening of naphthenes, c) dealkylation of aromatic side-chains, and d) the subsequent cracking of the olefins formed in a) to c):

a) Paraffin cracking: large paraffin → Olefin + Smaller paraffin
b) Ring opening: Naphthene (ring) → Olefin + Aromatic
c) Dealkylation: Alkylaromatic → Olefin + Aromatic
d) Olefin cracking: Large olefin → Smaller olefin + Smaller olefin

Concurren reactions include thermal cracking, hydrogen transfer, dehydrogenation, cyclisation, trans-alkylation, oligomerisation and polymerisation. Thermal cracking and dehydrogenation are the primary sources of dry gas (C1-C2 and H2), and polymerisation produces coke. These reactions do not significantly

Figure 1) and ‘snakes and ladders’ for olefins determines gasoline composition in the FCC unit. With this new model, gasoline compositions when using ZSM-5 can be explained and the ‘gasoline cracking’ model is left wanting.

Maximum propylene chemistry

Many reaction pathways play an important role when cracking a vacuum gas oil (VGO) or residue feedstocks into products over an FCC catalyst. The primary step is ‘cracking’, that is catalytically breaking carbon-carbon bonds (also known as beta scission). In this reaction, individual molecules react with acid sites on the catalyst forming carbenium ion intermediates that are readily able to crack. Cracking results in olefin formation via a) cracking large paraffins, b) ring opening of naphthenes, c) dealkylation of aromatic side-chains, and d) the subsequent cracking of the olefins formed in a) to c):

a) Paraffin cracking: large paraffin → Olefin + Smaller paraffin
b) Ring opening: Naphthene (ring) → Olefin + Aromatic
c) Dealkylation: Alkylaromatic → Olefin + Aromatic
d) Olefin cracking: Large olefin → Smaller olefin + Smaller olefin

Concurren reactions include thermal cracking, hydrogen transfer, dehydrogenation, cyclisation, trans-alkylation, oligomerisation and polymerisation. Thermal cracking and dehydrogenation are the primary sources of dry gas (C1-C2 and H2), and polymerisation produces coke. These reactions do not significantly
directly contribute to the creation of propylene (or other light olefins), but may have an indirect contribution via their impact on FCC unit constraints.

Propylene yields from the FCC unit are improved by increasing operation severity, conversion, and through the use of ZSM-5 zeolite containing additives. The higher the conversion the higher the propylene yield will be, especially when in the naphtha overcracking region (typically overcracking begins at 70-75 wt% conversion depending on feed properties). Operating parameters are modified in such a way that beta scission is maximised relative to thermal cracking, dehydrogenation, hydrogen transfer and polymerisation. Various process licensors have developed technologies for this purpose. Typically, the following process parameters are optimised to maximise conversion within unit constraints:

- Increased cracking temperature
- Increased catalyst circulation/catalyst to oil ratio
- Increased Ecatal activity
- Increased fresh catalyst make-up rate – hydro-treating for example.

Other parameters that significantly help to increase propylene selectivity are:

- Minimise hydrocarbon partial pressure. Reducing hydrocarbon partial pressure via dilution with riser steam shifts the reaction equilibrium towards light olefins by reducing light olefin oligomerisation (recombination) and hydrogen transfer reactions.
- Reduce hydrogen transfer reactions. These have the undesired effect of saturating light olefins to paraffins. This can be done by:
  - Reducing contact time: advanced riser termination systems provide rapid catalyst/oil disengagement which decreases hydrogen transfer.
  - Reducing backmixing: minimising catalyst slip in the riser reduces hydrogen transfer.
  - Reducing fresh catalyst: rare earth (RE) on ultrastable-Y (USY) zeolite is of particular importance in reducing hydrogen transfer. By reducing hydrogen transfer reactions, the gasoline becomes more olefinic and more readily crackable. Gasoline olefins are the prime source for LPG olefins. A catalyst with minimum rare earth helps to maximise propylene selectivity.

- Naphtha recycle - to crack every potential propylene precursor out of the gasoline
- Use a ZSM-5 additive.

All of these parameters help to maximise the propylene yield, but by far the greatest variable for increasing propylene yield is the use of ZSM-5 additives. ZSM-5 additives selectively crack gasoline range molecules into LPG olefins (C_3 and C_4), with highest selectivity for propylene – typically 50-60 wt% of the incremental LPG is propylene.

Maximum propylene FCC units employ high levels of ZSM-5 additives, often 10% or more in the circulating inventory. Some concern has been expressed that at extremely high inventory levels the ZSM-5 additive can cause dilution of base catalyst activity. However, dilution effects are rarely observed in practice because: target Ecatal activity is maintained by adjusting the fresh catalyst make-up rate – if slightly higher addition rates are required they effectively lower the ‘age’ of the inventory; and ZSM-5 additives do not significantly contribute to delta-coked (about 20-30% of the delta coke of the base catalyst), so as long as the FCC unit has some capacity to increase catalytic circulation rate ZSM-5 additives will not negatively affect conversion.

ZSM-5 additives are designed not to make coke; lowering delta-coked reduces regenerator temperature. The FCC unit responds to maintain the heat balance by increasing catalyst circulation to sustain the reactor temperature and restore conversion to the additive free level. For maximum propylene, resid applications the delta-coke reduction by ZSM-5 additives is a considerable benefit as it allows for either a higher conversion or for introducing a heavier feed.

**Effects on gasoline composition**

ZSM-5 additives crack gasoline into LPG, mainly propylene. However, introduction of ZSM-5 additives into the FCC unit also changes the gasoline composition substantially.

There is a great deal of literature discussing whether ZSM-5 additives increase the aromatics content in FCC gasoline – specifically, whether any increases in aromatics in gasoline are simply due to concentration effects, or whether ZSM-5 can produce aromatic components as well. Various conclusions are reported, including all permutations: gasoline aromatics may either increase, decrease, or stay the same depending on the study. This discussion on whether or not FCC gasoline range aromatics are formed under FCC conditions is remarkable considering that there are many industrial applications in which light olefins are used as feed, or appear as intermediates, in the formation of aromatics. The first of these olefin-to-aromatics processes became commercial in 1935. These processes make it clear that propylene will react to form aromatics over ZSM-5 at both high and low pressure. However, the majority of the studies mentioned previously indicate that ZSM-5 does not significantly increase the yield of gasoline range aromatics under FCC conditions – or ZSM-5 may even reduce gasoline aromatics slightly. This article seeks to resolve this issue by studying in more detail various reaction mechanisms and the effect of ZSM-5 on gasoline composition.

**Pilot plant study**

An ACE pilot plant study was conducted to establish effects of ZSM-5 additives on light olefin yields and gasoline composition. For this purpose, an FCC equilibrium catalyst (Ecatal) with a rare earth level of 1.2 wt% was selected. The relatively low rare earth level was chosen to avoid excessive hydrogen transfer reactions, which is important when maximising propylene selectivity. This catalyst was blended with various levels of equilibrated SuperZ Excel, a leading, commercially available ZSM-5 additive. ZSM-5 is more stable under laboratory deactivation
BIG ENOUGH TO EXECUTE.  
SMALL ENOUGH TO CARE.

GLOBAL CAPABILITIES

- Utility Flares
- Air-Assist Flares
- Steam-Assist Flares
- Flame Ring Low BTU Flares
- Vapor Combustors
- CEB® Ultra-Low Emissions Burners
- Service and Rentals
- Vapor Recovery Systems

Creating a Cleaner Planet:  
Gas and Vapor Technology & Services

www.aereon.com  |  sales@aereon.com
Profitable hydrocracking starts here

And ends here

PGM Recovery and Refining

For seven decades we’ve helped feedstock processors enhance profits with responsive—and responsible—refining and recovery of PGMs from spent processing catalysts. Tell us what we can do for you at sabinmetal.com

Profitable hydrocracking and hydrocarbon processing starts and ends with Sabin Metal worldwide.

Platinum • Palladium • Rhodium • Ruthenium • Rhenium • Gold • Silver

Processing facilities and technical service offices around the world
conditions than the REUSY containing FCC base catalyst. Because ZSM-5 zeolite has a higher silica alumina ratio (SAR) and smaller micropores than REUSY it requires a more severe deactivation. Deactivation conditions recommended for ZSM-5 additives are 815°C for 20 hours in 100% steam, a protocol that would be overly destructive for the zeolite-Y present in regular FCC base catalysts.

The study was carried out at 1060°F (570°C) to mimic petrochemical FCC operating conditions (equivalent to a riser outlet temperature of about 550°C) using a VGO feed. In a parallel study, a full range gasoline was used as feedstock and cracked at 1015°F (546°C) using the same catalyst/additive mixtures.

**ZSM-5 additive effect on LPG**

ZSM-5 additives selectively convert gasoline range components into LPG range olefins and have no significant effect on coke, slurry or LCO yields. Under extreme conditions, an increase in dry gas is observed, where ZSM-5 can produce small amounts of ethylene.

The observed LPG components boosted by ZSM-5 usage are propylene, mixed butylenes and isobutane. However, the ZSM-5 additive itself selectively produces light olefins: propylene and butylenes. It does not directly produce a significant amount of isobutane. The observed increase in isobutane is due to secondary conversion of isobutylene on the base catalyst via hydrogen transfer. The rate of hydrogen transfer is much higher for iso-olefins compared with n-olefins so there is minimal ‘loss’ of propylene and n-butylenes to propane and n-butane respectively via this mechanism. Higher rare earth on base catalyst leads to a greater conversion of isobutylene to isobutane, whereas lower rare earth leads to greater preservation of isobutylene (the ratio of isobutane to isobutylene may be used as a hydrogen transfer index in Ecact monitoring).

ZSM-5 is also known as an oligomerisation catalyst for light olefins. Propylene has been shown to be oligomerised over ZSM-5 (and other acid catalysts) to form gasoline range olefins. In the FCC these oligomers can then re-crack, forming more propylene and butylene. This has been termed the ‘snakes and ladders’ effect, and has the result of dynamically redistributing the olefins formed in the FCC from ethylene to very large olefins. The final composition depends on several variables, including ZSM-5 concentration, pressure and residence time. In this way olefins in the FCC unit play snakes and ladders, with a double role for ZSM-5 as both snake and ladder.

Overall, ZSM-5 additives substantially increase the propylene yield in the FCC (see Figure 2). Increasing the amount of ZSM-5 additive boosts the propylene yield significantly; however the effect on butylene yields is not as pronounced. The incremental effect of ZSM-5 additives on butylene yields strongly decreases when ZSM-5 concentration reaches very high levels. Increasing the ZSM-5 additive concentration from 25% to 50% in inventory continues to boost the propylene yield, whereas for butylenes no further increase was observed.

**ZSM-5 effects on gasoline composition**

In addition to cracking gasoline range molecules into light olefins, ZSM-5 isomerises gasoline range n-olefins into iso-olefins of the same carbon number: these too are subject to hydrogen transfer on the base catalyst where they are readily converted into iso-paraffins. Since
iso-olefins and iso-paraffins have higher octane numbers than their straight chain counterparts the gasoline octane improves partly due to this isomerisation effect.

Reduction in gasoline yield is an indication of ZSM-5 additive cracking activity. Gasoline is a mixture of paraffins, olefins, naphthenes and aromatics. Under FCC conditions, gasoline range olefins crack very readily on ZSM-5 additives. Naphthenes and paraffins are thought to crack under higher severity conditions, but aromatic rings do not crack. The observed decrease in gasoline volume therefore results in an increase in concentration of the least crackable parts of the gasoline, gasoline aromatics (see Figure 3). Gasoline aromatic cores (the C₆, aromatic rings) cannot be cracked so, as expected, they are preserved in the final cracked gasoline. However, C₆ and higher gasoline range aromatics contain substantial paraffinic side-chains which can be cracked. Therefore, although gasoline range aromatic cores cannot be cracked, the aromatic compounds can be dealkylated. This results in a reduction in the aromatic compound content, at the same time as an increase in the concentration of aromatic cores in gasoline.

To further study this effect, the carbon atoms in gasoline range aromatic compounds were calculated as aromatic cores and paraffinic side-chains for cases with and without high levels of ZSM-5 additive. As an example for toluene, xylenes and so on, only the aromatic core is counted as aromatic, while side-chains are counted as paraffinic carbon atoms. In this way toluene (CH₃-C₆H₅) has six aromatic carbons and one paraffinic carbon atom. Figure 4 shows that the change in aromatic core yield is small when adding ZSM-5 additives. The change however, appears to be negative (see Table 1). How can gasoline aromatic cores disappear when using ZSM-5 additives?

When cracking gasoline over Ecat with and without 25% ZSM-5 additive the gasoline composition changes (see Table 2). Most obvious and expected are the substantial decreases in olefins and naphthenes, more remarkable was the reduction in paraffins. This effect is even more pronounced when VGO is cracked over an Ecat/ZSM-5 additive blend (see Table 1). Whereas Ecat barely affects gasoline range paraffins, ZSM-5 additives with stronger acid sites were able to convert a sizable fraction of gasoline range paraffins. In the case of Ecat (without ZSM-5 additive) the observed reduction in paraffins was mostly via dealkylation of side-chains from naphthenes and aromatics. ZSM-5 additives showed a small effect of steric hindrance, hence a slightly lower amount of dealkylation was observed. It is interesting to note that in this data the reduction in paraffins was as large as that seen in naphthenes. This study also showed that the distribution of gasoline range aromatics changed: there was a decrease in heavier gasoline aromatics (C₉₋₁₀ aromatics) and an increase in light gasoline aromatics (C₆₋₇) – consistent with dealkylation (see Figure 5).

When cracking gasoline using ZSM-5 additive, the distribution of gasoline aromatic species shifted towards smaller aromatics (fewer or smaller alkyl groups attached) in a similar way to that observed when cracking VGO. However, in gasoline cracking the total aromatic cores increased, whereas in the VGO cracking case total gasoline aromatic cores decreased slightly when ZSM-5 was present. In gasoline cracking, aromatic cores were retained and additional aromatic cores were formed. In VGO cracking this mechanism also applies,

### Table 1

| Composition of gasoline components when cracking VGO over Ecat and Ecat + 25% ZSM-5 additive at 68% conversion. All components reported on a wt% feed basis |
|-----------------|-----------------|-----------------|
|                  | Ecat (no ZSM-5) | Ecat + 25% ZSM-5 |
| Paraffins, %     | 15.9            | 11.2            |
| Aromatics, %     | 13.4            | 12.3            |
| Napthenes, %     | 3.3             | 2.8             |
| Olefins, %       | 9.9             | 7.4             |
| Total gasoline, %| 42.5            | 33.7            |

### Table 2

| Composition of gasoline components as feed, and when cracking over Ecat and Ecat + 25% ZSM-5 additive. All components reported on a wt% feed basis |
|-----------------|-----------------|-----------------|
|                  | Gasoline feed   | Ecat (no ZSM-5) | Ecat + 25% ZSM-5 |
| Paraffins, %     | 34.9            | 32.4            | 28.7            |
| Aromatics, %     | 21.5            | 22.7            | 23.2            |
| Napthenes, %     | 11.6            | 6.3             | 6.4             |
| Olefins, %       | 31.5            | 14.1            | 11.0            |
| Total gasoline, %| 99.5            | 75.5            | 69.3            |

Figure 4 Ecat and Ecat with 25% ZSM-5 additive both readily crack olefins and naphthenes. ZSM-5 cracks more paraffins, and makes slightly more aromatics. Both Ecat and ZSM-5 dealkylate naphthenes and aromatics (SC Alkyls)

Table 2

www.epro.com
Reducing costs and waste, while increasing process uptime is not only stressful, it’s critical to operating a profitable refinery today. GE can help boost your plant’s efficiency by identifying profit-robbing problems, applying the most cost-effective treatments, as well as monitoring and maintaining the results. Keep your refinery operating safely and reliably, while lowering maintenance and energy costs with GE’s integrated solutions; encompassing water and process chemicals, equipment, and services.

GE’s offerings include:

• Comprehensive water and process chemical solutions
• Real-time remote monitoring and diagnostics
• Expert technical assistance for integrated solutions throughout your refinery

Let us help you manage the stress and uncertainty of today’s refining challenges . . . and deliver operational calm.
EXPERT INSIGHTS. RELIABLE SOLUTIONS. SUPERIOR PRODUCTS.

A PROVEN TEMPERATURE MANAGEMENT PARTNER

TRUSTED PRODUCTS

With over 100 years of experience, Chromalox knows that a true temperature management expert offers more than breakthrough products. In addition to a heat trace product line that includes cables and controls for a variety of tasks, we deliver industry-leading expertise and a team of solutions specialists. Talk to us today and see how Chromalox can develop an elegant solution for your most demanding pipe and tank process temperature maintenance, freeze protection, long pipe line heating, foundation heating, or snow and ice melting applications.

INDUSTRY EXPERTISE

RISK REDUCTION

COST CONTROL

Please contact Chromalox to discuss your needs with a heating specialist today!

www.chromalox.com | sales@chromalox.com

US Direct +01 412.967.3880 | US & Canada 800.443.2640 | UK +44 (0) 208 665 8900
but competes with cracking of aromatic precursors into light olefins. When cracking VGO, the decrease in paraffins with ZSM-5 additive present was more pronounced than the shift in olefins. Clearly, ZSM-5 additives do not just interact with final gasoline product. ZSM-5 is an active component in shaping the composition of the gasoline range components via cracking, aromatisation and oligomerisation (see Figure 6).

Gasoline chemistry over ZSM-5 additives and base catalyst involves an intricate web of reactions. Hydrogen transfer over the base catalyst converts gasoline (and LCO) range naphthenes into aromatics. Cyclisation reactions of higher carbon number (C₅+) olefins leads to naphthene formation, which can subsequently form aromatics via hydrogen transfer. In addition, higher carbon number naphthenes can be cracked open to form olefins, which can subsequently be cracked into light olefins. Light olefins can also oligomerise to form higher carbon number olefins which can either re-crack or subsequently form aromatics in ZSM-5 additives. (Light) olefins should therefore be seen as reactive intermediates shaping the gasoline and LPG composition, rather than terminal products in the FCC unit.

**Conclusion**

There is huge scope for maximising petrochemical yields in the FCC unit. Both process conditions and catalyst selectivities can be optimised to make this happen. Higher severity FCC conditions and use of ZSM-5 additives (ideally with low rare earth base catalysts) favour light olefin production. ZSM-5 additives are involved in many reactions in the gasoline phase. In addition to the well-known cracking and oligomerisation reactions, ZSM-5 can promote the creation of new aromatic species via oligomerisation and subsequent aromatisation. All of these reactions appear to be in dynamic balance under standard FCC conditions. Changing reactor conditions can help to push this to either side, creating more or less aromatics, improving or limiting propylene yields.

*Also known as “Chutes and Ladders” in the US. Super Z Excel is a trademark of Intercat JM.*

**References**

9. en.wikipedia.org/wiki/Snakes_and_Ladders

**Bart de Graaf** is FCC R&D Director with Johnson Matthey. Prior to joining the former Intercat business in Savannah he joined Johnson Matthey in the UK working on biofeedstock conversion processes. He holds a MSc in chemical engineering and a PhD in heterogeneous catalysis and chemical processes.

**Mehdi Allahverdi** is FCC Applications Manager with Johnson Matthey, Savannah, Georgia, US, where he works on catalyst evaluation and development. He holds a PhD in materials science and engineering from McGill University, Canada.

**Martin Evans** is Vice President of Engineering Technical Services with Intercat, responsible for providing technical assistance on the use of FCC catalyst additives and for the design and development of catalyst addition systems technology. He holds a BSc in chemical engineering from the University of Wales.

**Paul Diddams** is Vice President for FCC Additives with Johnson Matthey’s Refiners Division, with over 25 years’ experience in refining and catalysis, mainly in fluid catalytic cracking. He holds a BSc in chemistry from the University of Newcastle-upon-Tyne, UK, and a PhD in physical chemistry from the University of Cambridge, UK.
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.

Obviously, the main disadvantage of the ideal stage approach is just that—the use of ideal stages to model real trays or packing depths. However, 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 on a tray 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 enhancement factor 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, both the ideal stage and mass transfer approach 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. Although significant operating experience provides reasonable efficiency estimates for most processes, the empiricism in scaling up from ideal to real stages or ideal stages to real bed lengths can be a disadvantage when accurate overall efficiencies or HETP’s are unavailable.

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, as both require thermodynamic data to model equilibrium—for the tray composition in the ideal stage approach and for the interface composition in the mass transfer approach. Many of these mass transfer parameters are of limited accuracy but also may be of limited sensitivity in some systems. Both techniques are useful tools in process simulation.

For more information about this study, see the full article at [www.bre.com/support/technical-articles.aspx](http://www.bre.com/support/technical-articles.aspx).
Troubleshooting a $C_3$ splitter tower

Part 1: evaluation

Distillation trays are prone to channelling and multi-pass maldistribution in large diameter towers. Multichordal gamma scanning is key for solving such problems

HENRY Z KISTER Fluor
BRIAN CLANCY-JUNDT and RANDY MILLER PetroLogistics

The PetroLogistics giant $C_3$ splitter (see Figures 1 and 2) is a heat-pumped, 28ft (8.5m) internal diameter tower operating at 105 psig at the top. The tower contains four-pass, equal-bubbling-area fixed valve trays with mod-arc downcomers (MOAD) on the outside panels. Open area on the trays was 15% of the active area.

The tower started up in October 2010 and had experienced operational difficulties during its initial eight-month run. Tray efficiency appeared to be very low, about 40-50%, compared to a typical 80-90% tray efficiency experienced with conventional trays in a $C_3$ splitter. Due to the low tray efficiency it could not produce on-spec polymer grade propylene. The separation did not improve (if anything, it had become worse) upon turndown. Initial gamma scans through the centre tray panels indicated flooding.

PetroLogistics, Fluor (which was not involved in the tower design), and the tray supplier formed a task force to conduct a troubleshooting investigation to determine the root cause of the poor performance and to propose and engineer a fix. The strategy was to conduct a field investigation combining PetroLogistics’ expertise in operating the $C_3$ splitter, Fluor’s expertise in distillation design and troubleshooting, and the tray supplier’s expertise in tray design and modification. Tracerco was later brought in to provide diagnostic expertise in anticipation of extensive use of gamma scanning in identifying the root cause.

The troubleshooting investigation combined hydraulic analysis and detailed multi-pass distribution calculations with the specialised technique of multichordal gamma scanning with quantitative analysis. The hydraulic analysis and multi-pass calculations did not identify a reason for the low tray efficiencies, but confirmed that the trays are prone to channelling and maldistribution due to their large open areas. The gamma scans showed a maldistributed pattern on the trays, with high L/V ratios on the inside panels and low L/V ratios on the outside panels. The scans showed vapour cross flow channelling (VCFC) on the outside panels. Flooding was observed on the inside panels well below the
This is not a checkerwall. This is not a choke ring.
This is a VectorWall™ and it will change the way you look at your reaction furnace.
With unmatched mechanical stability, the VectorWall™ will increase your furnace capacity and eliminate ammonia carryover, saving your company millions of dollars.

Jeffrey J. Bolebruch  
Senior Market Manager

Our VectorWall™ is saving SRU reaction furnace operators millions of dollars

For more information check out our new video at petrochemical.blaschceramics.com

Or contact us: 1.518.436.1263  
vectorwall@blaschceramics.com
calculated flood point. The scans pointed at a combination of VCFC and multi-pass maldistribution as the root cause.

The investigation identified the high open slot area (15% of the active area) of the fixed valves to be the prime factor inducing the channelling and maldistribution. A likely initiator of the multi-pass maldistribution was liquid preferentially flowing to the inside panels from the false downcomers distributing the flashing reflux to the top tray’s panels. This preferential flow is believed to have occurred through the gap at which the reflux pipes entered the false downcomers. Another likely initiator was channelled vapour blowing liquid from the outside to inside panels across the off-centre downcomers. The high ratios of flow path length to tray spacing (2.4 to 3.7), high weir loads, and integral trusses projecting a significant depth (4in) into the vapour space were other conditions that promoted the channelling.

A short plant outage due to a problem elsewhere provided the opportunity for a quick fix. The key modification was blanking about a quarter of the valves on each tray to reduce the tray open slot areas from 15% to 11%. The gaps at the reflux pipe entry to the false downcomers were sealed and the false downcomer heights were raised to ensure good reflux split to the top tray panels. Anti-jump baffles were added across the centre and off-centre downcomers to prevent the possibility of channelled vapour from blowing liquid from the outside to the inside panels, towards the middle. Some downcomer blocks were installed to improve liquid distribution. The modified tower achieved tray efficiencies comparable to those obtained in well-operated, smaller diameter, low pressure C3 splitters.

To the best of our knowledge, this is the very first time that field measurements demonstrated interaction between VCFC and inside-to-outside-pass maldistribution. A lesson learnt is that this interaction must be considered when designing and operating large diameter towers. Finally, the investigation highlights that excessive open areas render trays prone to channelling and maldistribution, especially in large diameter towers containing multi-pass trays.

The hydraulic evaluation at initial operating conditions

Figure 2 is a simplified process sketch of the C3 splitter tower and its auxiliaries. Data for typical initial operation were collected at the highest rates at which operation was stable, about 20-30% below design. There is uncertainty about the reflux flow rate due to a metering error that plagued the reflux meter. The propylene product contained 3.4% propane (by mole) compared to the design 0.5%. The propylene content of the bottom stream was a little higher than design. The tower temperatures and pressures were similar to design.

There was a question of whether the trays in the tower were flooding or not. A typical pressure drop for good operation is normally about 0.1 psi per tray, while pressure drops exceeding about 0.2 psi per tray indicate flooding. For the C3 splitter, the pressure drop per tray at operating conditions was about 0.09 psi per tray, which argues against flood. In contrast, the gamma scans concluded that many of the trays were flooded. There was a need to reconcile the two conflicting observations.

To determine whether the tower was flooded, a plot of the measured tower pressure drop against the tower internal vapour traffic was prepared (see Figure 3). The internal vapour traffic is approximately the sum of the reflux and product meters. A point of inflection in such a curve indicates the vapour load at which liquid begins to accumulate in the tower, and is a good indicator of flood.
In Figure 3, the upper curve is for the entire tower, the lower curve is for the trays between the propylene side draw and the feed. Both curves show a point of inflection at vapour traffic just below 2000 mph, or a total tower pressure drop of 13.5-14 psi. This suggests that the initial operating loads in the tower were right at incipient flooding.

While some flooding could have started earlier, the significant accumulation of liquid started above these loads.

With the loads at which flooding initiated in the tower shown to be well below the design loads, it was concluded that the flooding was premature.

A simulation was prepared based on the operating conditions on 31 December 2010. Vapour and liquid loadings from that simulation provided the basis for hydraulic calculations. Table 1 shows the results of these hydraulic calculations. The values in Table 1 were calculated by Fluor. The Fluor values were more conservative than the tray supplier’s, but even Fluor’s calculations do not indicate proximity to any flood limits. This analysis verified the conclusion that the flood observed in the tower was premature.

The pressure drop values in Table 1 do not include the vapour static heads, while the tower pressure measurement does. The static vapour head is about 2.5 psi, or 0.015 psi per tray. Subtracting the static pressure drop from the total tower pressure drop of 13.5–14 psi gives 11-11.5 psi per tray of dynamic pressure drop, or about 0.068-0.072 psi per tray. This is in good agreement with the Fluor calculation.

Overall, the main issues identified in the tower were low tray efficiencies and premature flooding.

Possible theories
Several theories were advanced for the low efficiency and premature flooding. The task force performed a preliminary review of the theories to guide the field tests required to narrow in on the root cause. The following alternative theories were proposed.

Multi-pass trays maldistribution
The non-symmetry of multi-pass trays makes them prone to maldistribution. In four-pass trays, the inside panels are non-symmetrical to the outside panels. For good performance, the L/V ratio needs to be the same for the inside and outside panels. Maldistribution among the panels of multi-pass trays is a common source of tray efficiency loss. Lockett and Billingham show that the efficiency loss depends on the degree of L/V unevenness, as well as the proximity of the pinch.

Variations in the L/V ratio from pass to pass also adversely affect tray capacity. Regions where maldistribution increases the vapour or liquid loads are pushed closer to flooding, while other regions where the loads are reduced have surplus capacity.

Bolles defined the distribution ratio \( \phi \) as the ratio of the maximum pass L/V to the minimum pass L/V, and recommended keeping this distribution ratio below 1.2 to ascertain good tray efficiency. Summers tightened Bolles’s criterion to 1.1. Summers’s stricter criterion also keeps the loss of capacity due to maldistribution minimal.

To address this theory, we applied the Kister et al. and the Summers’ multi-pass maldistribution models. These models are among the most advanced and most reliable in the industry. The Kister et al method gave a distribution ratio of 1.09 while the Summers method gave a distribution ratio of 1.02, so both were in good agreement, giving distribution ratios below the stringent value of 1.1 maximum. There were...
some concerns that, with MOADs, it would be difficult to adequately model the outlet weir length, flow path length, and hydraulic gradient. We therefore re-ran the models with several variations. All showed that the distribution ratios for trays in this tower were robust to changes in these parameters and remained small. There was nothing in the calculations that would explain the observed large drop in tray efficiency and severe premature flooding.

**Pros:** Large maldistribution would explain the efficiency loss and premature flooding.

**Cons:** Hydraulic calculations showed low distribution ratios. The calculations verified that, by itself, this theory cannot explain the observations.

The theory of pass maldistribution was regarded as unlikely, but it may be combined with other theories.

Channelling combined with multi-pass maldistribution.

The large open slot areas (15% of the active areas), provided as part of the original design to keep pressure drop low for the heat pump system, can render trays prone to various forms of channelling such as vapour cross flow channelling (VCFC) at the high liquid loadings. High ratios of flow path length to tray spacing (2.4 to 3.7), high weir loads (7-9 gpm/inch of outlet weir) and integral trusses projecting a significant depth (4 inch) into the vapour space are conditions that when they come together with high open areas lead to VCFC.

VCFC is not the only form of channelling previously experienced on distillation trays. There are reports of other forms of channelling, such as due to excessive forward push (reverse vapour cross flow channelling, RVCFC) or due to vapour maldistribution. One thing they have in common is that they were only experienced at large tray open areas, high ratios of flow path lengths to tray spacing, and high liquid loads – conditions that apply also for the current trays.

In multi-pass trays, channelling is likely to interact with the split of vapour and liquid between the passes, generating or aggravating inside-to-outside-pass maldistribution. The large open slot area is also conducive to maldistribution between passes in multi-pass trays.³,⁴

**Pros:** This theory explains the premature flooding. The theory also agrees with the observation of efficiency loss without apparent flooding below 13.5-14 psi pressure drop. This theory explains the inability to operate at lower loads.

**Cons:** No experiences have been previously reported of interaction between tray channelling and multi-pass maldistribution. This theory leaves unanswered questions regarding the nature of the channelling and its propagation, and these needed to be investigated in the test programme.

This became by far the leading theory, even though at this point the details were not understood.

**Downcomer unsealing**

Downcomer unsealing was argued to be caused by vapour entering the off-centre and centre downcomers via large gaps where the supports go through the downcomers. This theory can combine with channelling on the trays.

**Pros:** This theory explains the premature flooding. The theory also agrees with the observation of efficiency loss without apparent flooding below 13.5-14 psi pressure drop. This theory explains the inability to operate at lower loads.

**Cons:** No experiences have been previously reported of interaction between tray channelling and multi-pass maldistribution. This theory leaves unanswered questions regarding the nature of the channelling and its propagation, and these needed to be investigated in the test programme.

This became by far the leading theory, even though at this point the details were not understood.
premature flooding and low efficiencies.

**Cons:** Hydraulic calculations showed that to lose the downcomer seal it would take a gap about one square foot in area, so if the gaps were properly welded this is unlikely. The trays were thoroughly inspected, and no gaps were seen, let alone gaps of this magnitude. This theory was therefore regarded as highly unlikely.

**Excessive hydraulic loads and poor metering**

Excessive reflux and boil-up rates due to incorrect metering can overload and flood the trays, giving low efficiencies.

**Pros:** Metering problems have caused poor operation in many towers, and there is such a case reported for a C₃ splitter.¹ In the current tower, the reflux flow was measured by an annubar meter with no independent check. There is a meter on the heat pump compressed gas, but that meter was not working.

This theory explains the premature flood and low efficiencies.

**Cons:** The annubar was checked and rechecked several times. While the compressed gas meter was working, a check found the annubar measurement to be within 1% of the value inferred from the compressed gas meter. During a crash shutdown the gas meter was fixed, and again verified the reflux measurement. Also, the annubar needed to be out by quite a factor to explain the observed poor performance. This theory does not explain the inability to operate at lower rates and the poor operation below flood.

This theory was therefore regarded as highly unlikely.

**Foaming**

Foaming is known to induce premature flood.

**Pros:** This explains the premature flood. Also, some of the gamma scan reports mentioned the possibility of foaming.

**Cons:** We are not aware of any foaming cases in C₃ splitters. Our survey of tower failures reported in the literature⁴ does not include a single case of foaming in a C₃ splitter. This theory does not explain the poor efficiencies at low rates and below flood. The tower feed does not appear to contain foaming components in significant concentration.

This theory was therefore regarded as highly unlikely.

**Damage**

Damage may possibly induce premature flood.

**Pros:** This explains the premature flood. Although uncommon, tray damage incidents may occur in heat-pumped C₃ splitters. The heat pump starts up at near full rates, which renders the tower start-up bumpy. At start-up, base liquid level is sometimes raised above the reboiler return inlet in anticipa-

**The theory of pass maldistribution was regarded as unlikely, but it may be combined with other theories**

The gamma scans show a consistent phenomenon throughout the tower. This pattern may be consistent with unbolted manways throughout the tower. Just a few unbolted manways are unlikely to
produce the scanning pattern observed.
The unbolted manways theory was therefore regarded as unlikely.

Likely theory
In summary, the channelling/maldistribution theory towered high above the others. However, the nature of the channelling and/or maldistribution remained poorly defined.
Part 2 of this article will describe the application of the specialised technique of multichordal gamma scanning with quantitative analysis7 to validate this theory, closely define and map the channelling and maldistribution patterns, and lead to the correct solution.

References
8 Kister H Z, Is the hydraulic gradient on sieve and valve trays negligible?, Topical Conference on Distillation, the AIChE Meeting, Houston, TX, April 2012.

Henry Z Kister is a Fluor Corp. Senior Fellow and Director of Fractionation Technology. He is the author of three books, 100 articles and has taught the IChemE-sponsored “Practical Distillation Technology” course more than 400 times. He holds BE and ME degrees from the University of NSW in Australia, is a Fellow of IChemE and AIChE, a Member of the NAE.
Email: henry.kister@fluor.com.

Brian Clancy-Jundt currently works in one of the largest propane dehydrogenation plants in the world with PetroLogistics and has had direct engineering oversight over all aspects of an olefins plant. He graduated from Texas Tech University with a BS in chemical engineering.

Randy Miller served as Vice President, Engineering for Petrologistics (2007-2014), instrumental in the design and development of the facility since the commencement of front end engineering design. He has worked in the petrochemical industry for over 20 years and holds a BS in chemical engineering from Texas A&M University, an MBA from University of Houston at Clear Lake, and is a Registered Engineer in Texas.

Predict Corrosion Rates
TRAYS FOR EVERY PROCESS

For gas processing, refining and a wide range of process applications. AMACS offers a wide selection of alloys, sizes and configurations to meet any mass transfer requirement. As a leader in the research and design of trays and tower internals, AMACS can design to your specifications or improve your process with our latest technologies.

- Valve (numerous options)
- Sieve or perforated
- Bubble cap
- Cartridge trays
- Dual Flow
- Gallery Distributor Tray

For all your process internal requirements make one stop- AMACS.
Overcoming tight emulsion problems

A refiner’s trials of a membrane coalescence mechanism were scaled up to plant level and delivered significant product recovery from tight aqueous emulsions

HERNANDO SALGADO Cartagena Refinery, Ecopetrol
LUIS MARÍÑO Ramgus S. A. – Pall Corp.
ROSÁNGELA PACHECO Barrancabermeja Refinery, Ecopetrol

One of the most challenging problems in refining and petrochemical processes is the separation of liquid emulsions and dispersions, which are often formed during the purification of products, especially when intimate contact between hydrocarbon and aqueous phases is involved. This is the case in the treatment of hydrocarbon fuels such as fuel gas, LPG, naphtha or jet fuel, when amines and caustic solutions and water are used to remove or wash contaminants such as H₂S, CO₂, mercaptans or naphthenic acids.

In many cases, these liquid solutions or solvents can be entrained by the main hydrocarbon product, forming tight emulsions and dispersions which are difficult to separate and are often discarded as effluents to the wastewater treatment unit. On the other hand, entrainment of these liquid solvents could potentially affect product specifications or cause operational upsets in downstream processes.

Nevertheless, emulsions and dispersions can be separated by coalescence, taking advantage of the interfacial tension between hydrocarbon and aqueous phases. In the coalescence process, two drops of a single phase and identical composition make contact with each other, forming a single bigger drop and in this way minimising their specific surface (surface per volume unit).

There are different types of coalescing media, from fibre glass of moderate performance through to special polymer membranes which can provide high performance in separating tight emulsions such as those with some content of surfactant compounds.

Tight emulsions

In many refining and petrochemical processes, formed emulsions are very stable due to the presence of small quantities of surfactant compounds which can be additives in regular use such as corrosion inhibitors or anti-foaming and anti-fouling additives, as well as contaminants such as naphthenic acids and sulphur compounds.

The tightness of an emulsion can be measured in terms of its interfacial tension, which is the free energy in the contact zone of two immiscible liquid phases. Interfacial tension is a consequence of the superficial tension of both liquid phases, and can be expressed in units of force per distance, generally in d/cm.

The presence of surfactants leads to the formation of micelles (of hydrocarbon in an aqueous phase) or inverse micelles (of an aqueous phase in a hydrocarbon), depending on the concentration of each phase, either the continuous or the disperse phase. The internal energy of an emulsion increases proportionally with surface and interfacial tension; therefore, the lower the interfacial tension is, the lower the free energy. Consequently, the emulsion is tighter, leading to the formation of smaller drops which are more difficult to separate.

The high coalescence and separation performance of polymer membranes makes them suitable for separate tight emulsions, which cannot be treated by using conventional coalescing materials and equipment.

Membrane coalescence mechanism

Membranes for coalescence are polymer fibres which vary in diameter sizes and surface treatments, depending on the application. The linked structure of the fibres forms very fine pores which allow droplets in the range 0.2-50 µm to be collected and transformed into a dispersion of bigger drops of 500-5000 µm diameter. However,
While pre-filtration is arranged in a separate vessel, coalescence and separation occur in the same piece of equipment, although they can be carried out in separated compartments. A typical process arrangement is shown in Figure 4.

Even though separation is not a formal step in the coalescence mechanism, it is required to achieve the main goal of coalescence, which is the separation of the two liquid phases involved in the emulsion. The selection of the proper type of arrangement of the coalescer-separator depends on the particular application, requiring (or not) an additional membrane cartridge to assure the separation of phases, as in the vertical arrangement.

The vertical arrangement is generally used to separate an aqueous contaminant dispersed in a hydrocarbon continuous phase with interfacial tension as low as 3 d/cm and a small difference in density between the phases. In such applications, the separation membrane is made of a hydrophobic material to retain the aqueous phase in a different compartment and to allow the hydrocarbon to flow through downstream in order to facilitate and assure the separation process.

The horizontal arrangement (see Figure 3) is generally used to separate hydrocarbons from a continuous aqueous phase with a greater difference in density. In this case, after coalescence is carried out, the separation of phases is achieved by settling the aqueous phase.

It should be taken into account that the processes described above correspond to general rules; however, lab or pilot testing is recommended in order to determine the appropriate membrane material to be used, as well as key performance parameters such as separation efficiency and flux through the membrane, which is helpful in designing an industrial facility.

Overcoming tight emulsion problems in a jet fuel treatment unit
A jet fuel treatment unit has a main goal of removing acidic compounds due to the small pore size of the fibres’ structure, particulate matter must be removed from the fluid before it is processed through the membrane.

The membrane coalescence mechanism is defined by the following steps (see Figures 1 and 2):
1. Removal of particulate matter in the pre-filter
2. Adsorption of droplets on the membrane fibres
3. Movement of droplets to membrane fibre intersections due to entraining by process flow
4. Coalescence of two tiny droplets to form a bigger one when a second droplet reaches the same fibre intersection
5. Release of bigger drops from the fibre intersections due to accumulation of drops and entrainment by process flow
6. Repetition of steps 2-5 with progressively bigger drops and larger pores in the fibre structure.

Membrane coalescence on the industrial scale
According to the mechanism discussed above, membrane coalescence is generally designed on an industrial scale with the following processing arrangement: pre-filtration, coalescence and separation. Generally, pre-filtration occurs in a vessel with filtration cartridges, with a mesh size depending on the amount and size of particles previously measured or estimated. The purpose of this step is to remove the solid particles which could increase emulsion stability and at the same time to protect the membrane’s functionality by preventing clogging of pores.
which are present in the jet fuel produced mainly in crude distillation units, for instance hydrogen sulphide (H₂S), naphthenic acids and mercaptans. In general, jet fuel treatment consists of a caustic washing (5% NaOH solution) to neutralise acidic compounds, followed by a water washing where the traces of caustic, previously entrained by the hydrocarbon stream, are removed. Thereafter, traces of water and surfactants are removed by adsorption on salt and clay beds respectively.

During the caustic and water washing steps, stable emulsions are generated due to intimate contact between hydrocarbon and caustic as well as between hydrocarbon and water. In order to assure a safe thickness in the emulsion layer, and in this way avoid excessive water entrainment in the salt/clay filters, the formed emulsions need to be discarded to an effluent treatment system, such as a wastewater treatment unit. The general flow scheme of the process is shown in Figure 4.

According to field observations and separation tests performed in an actual jet fuel treatment unit, the drained emulsions from both washing vessels (caustic and water) have about 50 vol% of each phase (hydrocarbon and aqueous). In the case studied, a flow of 4 gal/min was measured from each vessel; 4 gal/min of hydrocarbon (equivalent to 137 b/d) were being discarded to the wastewater system, negatively affecting the performance of the unit due to a high content of hydrocarbon and caustic in the wastewater.

In order to overcome this situation, a further separation step was proposed to recover hydrocarbon from the drained emulsions; and in this way enhance the wastewater system’s performance, while a valuable hydrocarbon stream could be recovered, improving the profitability of the refinery but at the same time its environmental performance and sustainability.

**Pilot test**

Following a rigorous selection procedure covering the alternatives, separation techniques such as gravity settling or coalescence with conventional materials were discarded, while membrane coalescence was the selected option due to the better results obtained from lab and pilot tests using the actual process fluid. The pilot test for demonstrating the membrane’s performance was carried out in an experimental set-up (see Figure 5), using the most challenging emulsion available to treat the jet-caustic emulsion.

The experimental set-up was connected to the caustic washing vessel to treat the actual process fluid, using a commercial fibreglass Pall DFT Classic pre-filtration module and a fluoropolymer Pall PhaseSep membrane module. The main goal of the pilot test was to prove the concept in a challenging environment and to calculate the separation efficiency and flux as
main process parameters for further scaling up.

As Figure 5 shows, the emulsion was fed to the pre-filter and thereafter to the membrane module, which is installed in the left-hand compartment of the coalescer; finally, the phases were separated in the right-hand compartment of the coalescer, where the recovered jet fuel flowed upwards and the aqueous phase settled downwards, as a result of their difference in density.

During the pilot test, the membrane module was tested at different flow (flux) values of emulsion, while the quality of separated hydrocarbon (aqueous phase content) was monitored in order to have an idea of the separation efficiency. On the other hand, taking into account that the test was carried out for four weeks, it was possible to test the mechanical and chemical resistance of the membrane material to the actual process conditions. The main results obtained from the test can be seen in Figure 6.

**Implementing the solution on the industrial scale**

Based on the results shown in Figure 6, with a flux lower than 3.5 gal/ft²·min it is possible to treat an aqueous phase content near to saturation (200-250 ppm of water in jet fuel), proving that the membrane coalescence technique is a feasible alternative for separating tight hydrocarbon-aqueous emulsions. Therefore, a flux of 3.5 gal/ft²·min of jet fuel was taken as a calculation basis to size the required equipment to treat 8 gal/min of emulsion at 52 vol% hydrocarbon and 48 vol% caustic solution (5°Bé). This led to a coalescer with a 40 inch (3.3 ft) long membrane module, in a vessel of 0.75 ft diameter and 6.5 ft long.

A process scheme of the current arrangement can be seen in Figure 7, where the pre-filter and the membrane coalescer vessel are integrated in a typical process scheme mounted in a single skid. In this case, a horizontal coalescer was selected due to the amount of aqueous phase present in the emulsion (48 vol%), as well as an estimated interfacial tension of about 0.5-1.0 d/cm.

Further analysis of the recovered jet fuel from the coalescence skid showed that the water content varied between 200 and 250 ppmwt, corresponding to water saturation of the hydrocarbon, indicating acceptable water and caustic entraining in the recovered jet fuel. Thus a performance similar to that obtained during the pilot test was observed in the industrial scale equipment, with potential recovery of 140 b/d of jet fuel and contributing to a better environment performance and sustainability of the refinery.

The ‘clear and bright’ appearance of recovered jet fuel on visual inspection confirmed its good quality for further processing in salt and clay filters (for the jet fuel product pool), or directly as a diluent for fuel oil blending, or in other uses.
comparison of the appearance of recovered jet fuel and the original emulsion can be seen in Figure 8.

Although the specific application described in this study is still of a relatively small size, it has demonstrated the suitability of membrane coalescence to separate tight emulsions, as well as its straightforward and safe scaling up after a few pilot or lab tests. It should be noted that other successful tests were conducted for different applications, such as amine-hydrocarbon separation and sour water-hydrocarbon separation, demonstrating again the suitability of membrane coalescence for multiple applications within the refining industry.

Conclusions

Membrane coalescence was demonstrated to be a successful technology for separating tight emulsions, contributing to more profitable and more sustainable operation of a refinery.

Pilot and lab tests results are easily and safely scalable to industrial applications, with a high reproducibility of process parameters and performance. On the other hand, these tests are helpful in selecting the right materials for both pre-filteration and membrane modules.

The content of the aqueous phase in recovered hydrocarbon is close to its saturation value, indicating high separation performance.

The authors would like to acknowledge Ernesto Gómez and Leonardo Sánchez from the Crude Distillation Department of Barrancabermeja Refinery, for the logistic and operational support which allowed to carry out the work described in this article.

Further reading


Hernando Salgado is Senior Process Engineer at Ecopetrol’s Barrancabermeja refinery and is a specialist in crude distillation and fuels treatment (naphtha and jet fuel). She holds a degree in chemical engineering from the National University of Colombia, Medellín.
Leading-Edge Technologies for On-Purpose Olefins

Medium and long-term forecasts expect to see a continuing growth in demand for on-purpose olefin production technologies (e.g. propylene, butylenes) such as dehydrogenation of light paraffins. Thanks to our advanced, proven Uhde dehydrogenation technologies, STAR process® and STAR catalyst®, we can supply, from a single source, complete, optimized process routes to propylene and butylene derivatives, e.g. Polypropylene, Propylene Oxide, ETBE and other high-value products.

Liquid hourly space velocity of 6 resulting in less catalyst and lower reactor volume
Available with and without oxydehydrogenation

Engineering Excellence

ThyssenKrupp Industrial Solutions

www.thyssenkrupp-industrial-solutions.com
Refiners require FCC catalyst technology that delivers the right selectivity at the right time. In a world where fuel demand is satisfied through a careful balance of free trade, weather events or refinery upsets could trigger price volatility in product markets. The ability to respond quickly to capture short-term market opportunities is critical. Amid declining gasoline demand in mature regions, refiners need to enhance distillate production. Grace’s premium bottoms cracking family, the Midas catalyst series, can be used to enhance FCC process flexibility and capture incremental profit as opportunity arises. These catalysts crack deep into the bottom of the barrel, enhancing total distillate and liquid yield, and have been demonstrated in over 120 refineries that vary broadly in feed composition and operating modes. The flexibility that the catalysts provide, used neat or as a component in a Genesis catalyst system, can enhance the yield value by $0.40-1.00/bbl of FCC feed.1

Midas is a moderate zeolite to matrix ratio FCC catalyst that has been successfully applied in half of North America’s FCC unit capacity as well as refineries in other parts of the world. Its success is driven by the fact that it effectively cracks all feed types: heavy resids, severely hydrotreated light feeds, and shale oil-derived feed streams, via the three-step bottoms cracking mechanism discovered by Zhao.2 The relatively large molecules at the bottom of the barrel that need to be converted must first be cracked by the catalysts’ matrix acidity. With molecular sizes of 10-30 Å, the hydrocarbons are too large to fit into the zeolite pores, which are typically below 7.5 Å. It is important that the catalyst have the proper pore size distribution to enable large feed molecules to enter, crack into lighter products, and diffuse out before being over-cracked to coke and gas. For free diffusion of resid molecules (>1000°F) to occur, the catalyst pore diameter needs to be 10-20x the size of the molecule, or 100-600 Å. The desired pore volume should be in the large mesopore region 100-600 Å. The benefit of mesoporosity for bottoms cracking is well understood.5 However, not all the measured pore volume is created equal. Catalysts with similar total pore volume measurements can vary widely in pore size distribution. Midas is designed to have high mesoporosity in the 100-600 Å range, typically twice as high as competitive offerings (see Table 1). Optimal porosity is required for effective kinetic conversion of

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total (cc/g)</th>
<th>Micropores (Å)</th>
<th>Mesopores (Å)</th>
<th>Macropores (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midas</td>
<td>0.389</td>
<td>0.092</td>
<td>0.206</td>
<td>0.091</td>
</tr>
<tr>
<td>Midas</td>
<td>0.412</td>
<td>0.092</td>
<td>0.232</td>
<td>0.071</td>
</tr>
<tr>
<td>Cat 1</td>
<td>0.386</td>
<td>0.116</td>
<td>0.102</td>
<td>0.168</td>
</tr>
<tr>
<td>Cat 2</td>
<td>0.413</td>
<td>0.092</td>
<td>0.089</td>
<td>0.232</td>
</tr>
</tbody>
</table>

Table 1 Higher mesoporosity of Midas promotes bottoms conversion

Resid streams present the greatest challenge in terms of deep bottoms conversion. The dynamic molecular dimensions of paraffins and aromatic species vary, based on carbon number and molecular configuration. Paraffins species present in the 700-1000°F boiling point fraction of FCC feed are typically in the nC14 to nC34 range for normal paraffins. The dynamic molecular size of these compounds is 12-20 angstroms (Å). The heavy resid fraction also contains an abundance of aromatic molecules (C14 to C60) in the 700-1000°F boiling range. The range of molecular size for aromatics is 12-25 Å. Even aromatic carbon molecules up to 60 carbon number are still less than 30Å in molecular size.

Porphyrins are organic, cyclic macromolecules that consist of a ring of nine or more atoms. Porphyrins are aromatic species often present in resid fractions and characterised by a central gap that can bond to a metal atom, such as nickel, vanadium, or iron. If a porphyrin is complexed with vanadium, it is termed a vanadyl porphyrin. The size of these metallic complexes also varies with carbon number, but is in the same dimensional range as typical resid hydrocarbons: 10-30Å.2

The relatively large molecules at the bottom of the barrel that need to be converted must first be cracked by the catalysts’ matrix acidity. With molecular sizes of 10-30 Å, the hydrocarbons are too large to fit into the zeolite pores, which are typically below 7.5 Å. It is important that the catalyst have the proper pore size distribution to enable large feed molecules to enter, crack into lighter products, and diffuse out before being over-cracked to coke and gas. For free diffusion of resid molecules (>1000°F) to occur, the catalyst pore diameter needs to be 10-20x the size of the molecule, or 100-600 Å. The desired pore volume should be in the large mesopore region 100-600 Å. The benefit of mesoporosity for bottoms cracking is well understood.5 However, not all the measured pore volume is created equal. Catalysts with similar total pore volume measurements can vary widely in pore size distribution. Midas is designed to have high mesoporosity in the 100-600 Å range, typically twice as high as competitive offerings (see Table 1). Optimal porosity is required for effective kinetic conversion of

---

www.eptq.com

Catalyst designed with advanced zeolite stabilisation technology provides selective conversion of heavy FCC feed molecules

YEE-YOUNG CHER, ROSANN SCHILLER and JEFF KOEBEL
Grace Catalysts Technologies

Figure 1 Pore volume comparison of commercial Ecats

Figure 1

Commercial examples of Midas’s high mesoporosity, as measured by Hg porosimetry of Ecat, are shown in Figure 1. Note that Hg intrusion measures the porosity greater than 36 Å, therefore the result specifies the porosity associated with the catalyst matrix only; N₂ adsorption or desorption must be used to capture zeolite porosity. Grace’s in-house manufacturing and quality monitoring of the specialty alumina used in Midas provides control over the resulting porosity. It is generally accepted that micropores (<100 Å diameter), though effective for cracking, lead to poor coke and gas selectivity as a result of poor diffusivity and over-cracking. Some competitive benchmarks with high surface area and activity are also high in matrix microporosity, resulting in wet gas compressor limitations that suppress feed rate and ultimately profitability. In contrast, Midas catalyst has the lowest amount of small pores and the highest amount of large mesopores. Optimal porosity guarantees gas selectivity and coke-selective bottoms conversion. High pore volume also serves to enhance the fluidisation characteristics. Several units have observed substantial improvement in the Ecat fluidisation factor following a reformulation to Midas or Genesis.¹

The proprietary matrix in Midas can withstand the most severe applications, particularly those challenged by high levels of contaminant iron and calcium. High alumina content in FCC catalyst is known to reduce the degradation of the catalyst surface due to iron and/or calcium poisoning.² Optimum distribution of mesoporosity also plays a role in maintaining performance, because diffusion to the active sites remains unhindered despite the high contaminant metals. Midas has been successful in maintaining bottoms conversion in units with some of the highest levels of contaminant iron on Ecat in the industry.

A good bottoms cracking catalyst requires high matrix surface area (MSA). However the activity of a high matrix catalyst needs to be balanced with an appropriate level of zeolite without compromising attrition characteristics. Additionally, an appropriate rare earth exchange level on the zeolite is critical to ensure optimal coke selectivity. An optimum exists in the relationship between zeolite unit cell size (UCS) and coke selectivity.² Too often, high matrix catalysts also have a high UCS, meaning they are over-exchanged with rare earth. Low zeolite input formulations with high rare earth exchange (albeit low total rare earth on catalyst) will retain a higher percentage of the fresh zeolite surface area in a severe regenerator, but the penalty for this over-exchanged zeolite is poor coke selectivity. The rare earth exchange in Midas catalysts is optimised to result in a formulation that lies in the so-called ‘sweet’ spot or between 24.28-24.32 Å for Ecat UCS to deliver the best coke selectivity. The right distribution of mesoporosity coupled with optimal activity and UCS gives the catalyst the coke selectivity edge in commercial cracking.

Commercial experience

Midas’s design features have led to high performance in many commercial examples. The first example comes from Refinery A that has an FCC unit processing a mix of VGO and light resid. The feed is moderately high in metals with good cracking characteristics. The base catalyst was a competitive high MSA catalyst with high rare earth exchange. The unit suffered from a dry gas constraint, especially in the summer. When the refiner switched to Midas, a 5-10% drop in total dry gas yield at equivalent riser temperature and metals loadings was observed; this allowed the refiner to maintain maximum feed rate throughout summer. The better coke selectivity also manifested itself in lower bottoms yield by 15%.

At Refinery B, the FCC unit was processing light resid using a high matrix, high UCS catalyst. While rare earth levels on the zeolite were high, the catalyst itself had low total rare earth because zeolite input was very low. In spite of the high rare earth exchange and resulting UCS, the unit was constrained on total wet gas and bottoms yield. There wasn’t enough zeolite present to complete the second stage of the bottoms cracking mechanism.² Zeolite is critical to reduce the size of the hydrocarbon via dealkylation. Insufficient zeolites cause coke precursors to condense on the catalyst surface and become coke before they can be converted into transportation fuels. Poor coke selectivity translates into subpar bottoms conversion.

Introduction of Midas provided a reduction in bottoms make on the...
End-to-End Combustion and Environmental Solutions Are Just the Beginning.

Experience a breath of fresh air.
From our ultra low-NOx products to our ultraknowledgeable people, every ZEECO® burner, flare, incinerator, and flare gas recovery system is backed by a Zeeco team dedicated to you and your project. From site evaluation and product design to manufacturing, testing, installation, commissioning, and unparalleled aftermarket parts and service, we deliver end-to-end answers to the industry’s biggest challenges.

Onshore or offshore. Upstream, midstream, or downstream.
Zeeco engineers innovative combustion solutions to keep operators in compliance, people safe, and plants running smoothly — and we deliver them on time and on budget.

Global experience. Local expertise.

ZEECO Ultra-Low NOx GLSF Free-Jet Burner

Experience the Power of Zeeco.

Burners • Flares • Thermal Oxidisers • Vapour Control
Aftermarket: Parts, Service & Engineered Solutions

Explore our global locations at zeeco.com
more feed was converted into gasoline and distillate, rather than LPG and coke.

At Refinery C, the FCC unit processes resid feedstock high in iron (Fe) and calcium (Ca). Over time, the unit suffered from classic symptoms of iron poisoning. As iron nodules built on the surface, Ecat activity, unit conversion and bottoms cracking all began to suffer. A switch to Midas provided higher activity and improved coke selectivity, delivering deeper bottoms conversion. Eventually the feed became heavier and more contaminated. The catalyst never lost its selectivity edge over the competitive high MSA base formulation, even after increases of 25-60% in Ecat Fe and Ca. The high mesoporosity is particularly effective in preventing a loss in cracking activity often seen during periods of high metals loadings. Fe and Ca can form eutectics that serve to essentially melt over the catalyst surface, blocking pores and suppressing conversion. The high mesoporosity of Midas ensures that high diffusivity is maintained. It is the preferred catalyst technology for FCC units processing high Fe feedstocks. The selectivity benefits realised at Refinery C are shown in Figure 2.

Refinery D routinely processes heavy resid in the FCC unit. Similar to the other examples, the objectives were to reduce dry gas and improve the yields of liquid fuels (gasoline and distillate), without compromis-
CHANGE YOUR MIND ON FOULING REMOVAL

ARE THESE IMAGES FAMILIAR TO YOU? FORGET ABOUT THEM!

Patented ITW Online Cleaning can remove any type of fouling from equipment, including the polymers, without the need to open or enter hazardous process equipment.

An entire Process Unit can be cleaned by utilizing ITW Online Cleaning in as little as 24 hours on an oil-to-oil basis. Online Cleaning can be applied at any time during the run of the Unit, in order to solve the problems when they start appearing, rather than when they are no longer sustainable. This will in turn avoid throughput reduction, giveaway and energy loss, associated with fouling. The application of ITW Online Cleaning will be therefore driven by performance recovery and Opex improvement, rather than the economics for placing a turnaround.

ITW Online Cleaning can be applied to all Refinery/Petrochemical/Gas Field/Oil Field production Units, as well as storage tanks, and is the only technology which has an immediate Return On Investment (ROI).

Regular application of ITW Online Cleaning will target an increased run length under clean conditions, with a far higher ROI.

For Turnaround applications, ITW Online Cleaning can eliminate/dramatically reduce the need for mechanical cleaning, thereby reducing downtime and improve operational HS&E. In a Turnaround application, an additional ROI increase can be targeted by applying ITW Improved Degassing/Decontamination to achieve quick and effective safe entry conditions. Our patented chemistry does not create any emulsion and fluids can be easily handled by Waste Water Treatment Plant.

EVALUATE ITW ONLINE CLEANING AND ITW IMPROVED DEGASSING/DECONTAMINATION TODAY TO IMPROVE YOUR PLANT'S PROFITABILITY!

For more informations contact: ITW S.r.l.- C.da S.Cusumano - 96011 Augusta - Italy
Tel. +39 (0931) 766011
E-mail: info@itwtechnologies.com
www.itwtechnologies.com

Join ITW Team worldwide and send your Curriculum Vitae to: jobs@itwtechnologies.com

New hiring Professionals Worldwide
ing feed rate. A switch to Midas catalyst met the objectives despite deteriorating feed quality coming to the FCC. Over time, the feedstock became heavier, contained more concarbon, and had higher metals loadings. Lower dense bed temperatures minimise thermal cracking, reducing dry gas yield. Slurry yield was held constant (see Figure 3).

The primary operating objective of the FCC unit at refinery E is to maximise LCO yield. Reformulating to a high matrix catalyst from the starting low matrix catalyst presented a challenge for this refinery. A wholesale change in the catalyst formulation was deemed to be risky. Grace introduced Midas to the FCC unit in a step-wise fashion. Initially, Midas was blended with the refiner’s base high zeolite catalyst (also a Grace catalyst) in a 50/50 ratio. The FCC unit realised a reduction in slurry yield of 12% (see Figure 4). Refinery E later increased the amount of Midas to 100% of the fresh catalyst requirement. Again, a step-change improvement in slurry yield was observed, and the incremental conversion was maintained as distillate as desired. Higher distillate yield (+15%) was observed over a wide range of conversion levels with Midas over the original base catalyst.

**Maximum matrix surface area**

Midas Gold is the latest innovation in this catalyst family, and is designed to provide maximum matrix surface area allowing refiners to further upgrade the bottom of the barrel while minimising coke. These catalysts feature Grace’s Low Coke Matrix (LCM) technology, which renders nickel inactive for dehydrogenation reactions. The coke selectivity advantage of Midas Gold delivers a 15% reduction in bottoms yield over prior formulations. Multiple commercial applications are under way.

**Conclusion**

Midas is Grace’s premium high matrix bottoms cracking catalyst family. It is designed to possess the key characteristics necessary for selective conversion of heavy FCC feed molecules. These characteristics
are controlled during proprietary manufacturing processes of specialty aluminas, zeolites and ultimately the whole catalyst itself. The net result is:

- Maximum matrix mesoporosity to minimise coke and gas formation and maximise bottoms upgrading
- Ideal pore size diameters to preserve free diffusion in and out of the catalyst, even in the face of metals contamination
- Optimised rare earth exchange to deliver best-in-industry coke selectivity
- Balanced zeolite-to-matrix activity to maximise product value from the FCC

Midas contains the highest mesoporosity in the desired range of 100-600 Å and the most optimal UCS in the market, providing a clear selectivity advantage over competitive catalysts. Several distinct grades are available, suitable for a wide range of feed and operating objectives. The catalyst's in-unit fluidisation properties are a solution for FCCs with fluidisation or circulation difficulties. Applied neat or in a Genesis catalyst system, Midas provides the option of running difficult or opportunity feedstocks to the FCC without suffering from poor coke and gas selectivity. Finally, the catalyst provides the flexibility to fine-tune the yield of the individual product streams to exploit short- or long-term economic opportunities.

In summary, the catalyst should be considered by any refiner seeking:

- Deeper bottoms cracking
- Enhanced bottoms conversion against an air blower constraint
- Ability to process high Fe and Ca feedstocks, such as Bakken and Eagle Ford
- Incremental fuels yield, for instance LCO, or gasoline and distillate maximisation
- Relief against a wet gas compressor constraint when cracking resid
- Capability to process opportunity crudes
- Improved catalyst fluidisation characteristics
- Flexibility to capture the value of opportunity crudes
- Ability to shift between gasoline and distillate modes of operation
- Rapid catalytic response to capture short-term economic opportunities.

References

1. Schiller R K, Grace Davison’s GENESIS catalyst systems provide refiners with flexibility to capture economic opportunities, Catalagram 107, 2010.

Yee-Young Cher is Regional Technical Service and Business Manager for Grace Catalysts Technologies, based in Singapore. Rosann Schiller is Marketing Director for Grace Catalysts Technologies, based in Columbia, MD, USA. She holds an MSE in chemical engineering. Jeff Koebel is National Technical Sales Manager for Grace Catalysts Technologies, working with customers in the eastern US.
Advanced Solutions for the World’s Toughest Energy Challenges

KEY TECHNOLOGIES:

MSDW™
Premium Lubricants

FLEXICOKING™
Resid Upgrading

MTG
Methanol to Gasoline

MIDW™
Premium Diesel

FLEXSORB®
Acid Gas Clean Up

ExxonMobil — Global Leader in Fuels and Lubes Process Technologies

Enabled by Proprietary Catalysts and Solvents

ExxonMobil Technologies are applied across our corporation and by licensees worldwide in a growing list of process industry applications. Leverage our vast experience and ongoing commitment to continuously improve our industry-leading technologies.

www.exxonmobil.com/tsl
Preventing emissions in coke removal

A closed, automated coke removal system aims for gains in environmental, economic and safety performance

ARTUR KRUEGER, BERND LANKERS and JOSEF WADLE
TriPlan AG

Conventional delayed coker units feature open pit/pad coke handling methods, utilising a range of mechanical equipment including bucket cranes, front loaders, offsite crushers, dusty loading facilities and blackened railroad shunting or truck loading areas.

In contrast, the Closed Coke Slurry System (CCSS) developed by TriPlan in Germany offers the operator a modern process that is completely enclosed. It is environmentally friendly by eliminating coke dust emissions, and it also provides effective water management by cleaning and recycling the water used in the coke quenching and cutting process.

The CCSS has completely automated operations, the plant components are designed and fabricated with a view to high reliability, resulting in significantly enhanced overall plant reliability. The safety aspects attained in this design find a high acceptance level by the operators as well as the workforce. Streamlined operations result in reduced cycle times for coke drum unloading and dewatering, providing an interesting pay-back to the operator.

In the hydrocarbon processing industry, the conversion processes, from crude to clean products, are continuous. Residues from atmospheric or vacuum units are converted by a number of different processes into added-value products, to obtain maximum benefit from the bottom of the barrel. One of these conversion methods is the delayed coker unit (DCU). The product obtained from this unit is commonly known as petroleum coke which serves as the feed for a number of different applications.

Unlike the other processing units in the refining business, delayed coking is a discontinuous batch operation. Full coker drums are opened on a regular basis for unloading. Challenges come from the process itself, the metallurgy of the equipment, and safety, health and environmental issues in view of the high degree of mechanical handling steps that are typical for a traditional pit/pad system. Consequently, field operators face more manual work in an uncomfortable, and sometimes risky, work environment that is not known in other refinery units. Staffing figures for operators, maintenance staff and additional housekeeping contractors are traditionally high and result in a substantially increased workload.

These cost elements are considered unavoidable and are tolerated by operating companies. However, coker outages due to breakdown and repair of mechanical equipment mean loss of coke production capacity, and clean product uplift value deteriorates dramatically, eating into the unit’s revenue stream.

Traditional processing in coke drums

The process step from liquid coker feed to the solid coke formed in the coke drum is independent, whether it involves the established pit/pad design or CCSS technology for handling the coke after cutting.

The feed is heated to commence cracking, ultimately to extinction to carbon due to the long residence time in a drum. Once a drum is filled up, the feed stream is switched to the next empty drum and so on. Therefore a delayed coker consists at least of two, sometimes of four or even six drums.

After switching, the full drum is isolated from the rest of the unit for further processing. With injection of steam into the coke bed, light hydrocarbons are stripped out, then the bed is hardened and cooled. Further cooling is achieved through repeating quenching (filling and emptying) with water. Once the bed temperature falls below 100°C, the drum top and bottom flanges are manually opened (more recently, remote operated slide valves are commercially available to replace the risky flange operation).

Coke removal takes place with a high pressure cutting water circuit at 250-300 bar. First, a vertical hole is drilled into the coke bed with a downward water jet nozzle. This is followed by the cutting operation in which a horizontal water jet slices top down to ream out the drum up to the wall until the drum is empty. The resulting coke chunks are flushed through the drilled hole.

Open coke handling is a burden on the environment

Delayed coker operators with a pit/pad system have made efforts, together with mechanical equipment suppliers, to improve the mechanical steps in the process, in particular with installation of top and bottom unheading equipment. Unit on-time capacity has been increased, contributing to the unit’s
cash flow. At the same time, environmental concerns have been addressed, as well as the creation of a healthier workplace.

In the traditional pit/pad process, coke handling from the outlet of the coke drum after cutting, to loading onto trucks/railcars, happens in open space. The free stacking of hot coke during the cutting operation and storage of the coke from one coke drum (typically 1000 t/d) result in a highly visible steam plume for several hours. During this time, the coke stack cools down and drains excess free water to the ground or into a receiving maze, usually uncovered. It is known from investigative reports that the steam contains coke fines and aerosols, and also aromatics and other polycyclic hydrocarbons.

US federal and state regulations, and European Community directives on environmental issues in the hydrocarbon processing industry, call for a critical review of all possible sources of air emissions and ground pollution, such as the mechanical equipment mentioned above, including black water laden with coke dust and fines, throughout all stages of coke handling and storage.

Technical solutions to alleviate these problems, for example the enclosure of coke piles, water/oil spraying, are all aimed at fighting the problems at the back end rather than at the source. They are costly but can still be insufficient.

Closed coke slurry technology

In Europe, coker operators have to demonstrate that their current practice is in accordance with best available control technique (BACT). This is where TriPlan CCSS technology comes into play. It is a completely enclosed system, avoiding the mechanical, environmental and health drawbacks which are inherent in conventional pit/pad systems.

In all coke handling steps, from the discharge point at the bottom of the coke drum to the coke to loading onto trucks/railcars, the coke handling from the outlet of the coke drum after cutting, to storage. The primary advantage is the avoidance of black water laden with coke dust and fines, throughout all stages of coke handling and storage.

In Europe, coker operators have to demonstrate that their current practice is in accordance with best available control technique (BACT). This is where TriPlan CCSS technology comes into play. It is a completely enclosed system, avoiding the mechanical, environmental and health drawbacks which are inherent in conventional pit/pad systems.

In all coke handling steps, from the discharge point at the bottom of the coke drum to the coke to load-out, the water circuits are designed for re-use of contaminated water in the process after clean-up, and the effective separation and removal of coke fines. These steps have been streamlined at all stages of the process, making it no different from any other typical process unit in the refinery. This is achieved by pumping the coke slurry stream in a fluid state. With consistent improvement of metallurgies in the equipment that forms part of the CCSS, the process is robust and stable.

An installation has been operating for more than six years without interruption for repair or maintenance work in service in a refinery in Germany. The instrumentation in this process permits a fully controlled operation and allows the console operator to view the status of the process at any time.

In summary, the technology gives the delayed coker operator an operationally enhanced process, with ecological as well as economic advantages. Figure 1 illustrates the principle of the technology.

Mastering corrosion and abrasion in hot, wet and harsh service were the prevailing challenges in the course of developing the CCS process. These challenges were compounded by the fact that some equipment has to be totally newly designed and constructed to suit the special purpose.

To pump solids like coke, a reduction in grain size by crushing is required prior to entering the pump. The crusher is located immediately beneath the coke drum. A remotely operated telescopic chute connects the crusher and drum bottom flange prior to the boring/cutting operation. A slurry pipe routes the mix of crushed coke and water into the pit.

Crusher torque, materials, essential construction details like teeth pattern, roll diameter, pull-in and swallow capability are designed to cope with large chunks and peak loads, often simultaneously. All of these parameters are aimed to meet specific requirements for achieving maximum run length.

Likewise, the construction and
At AltairStrickland, obsessing over the tiniest details is an enormous part of who we are—and a huge advantage for our clients. Our fanatical focus on pre-planning to reduce project schedule helps ensure a safer, more cost-effective turnaround every time. When a million pounds of steel is hoisted from a million-dollar crane, that’s not the time for costly surprises. That’s why we use AutoCAD® 3D surveys, even plywood to build full scale models to explore virtually every conceivable “what-if” scenario. Over the top? Maybe—but we believe your next FCCU revamp or turnaround deserves it.

How can we obsess for you?
emcor_info@emcor.net  866.890.7794  altairstrickland.com

CRITICAL PROJECT EXECUTION FOR THE REFINERY AND PETROCHEMICAL INDUSTRIES
materials of the slurry pump enable stable and reliable transport of abrasive slurry at lowest net positive suction head (NPSH) requirements.

An important objective is system availability to handle various coke loads and stream conditions – from water-only up to avalanche-style coke bed break down – which is convincingly solved in the design of crusher and pump together with its sensible drive concepts. In addition, a stable transport water rate is provided to maintain pumpable slurry at all times.

Another issue is the use of the coarse coke in the dewatering bin as a filtration bed for fines-laden black water. Selective operational steps provide an absolutely clear water run-off with shorter residence times, to be collected in a tank and re-used as quench and cutting water for the next cycle. The well known abrasion effects in expensive multi-stage cutting water pumps are basically history.

The technological and economical advantages of the system include:

Reduction in cycle time
The CCSS system permits a reduction of the total cycle time of up to four hours (see Table 1).

Capacity gain
Shorter cycles allow the operator to process more feed, which also results in increased production of clean products, depending on downstream capacity for light products. A production gain of 400 tonnes of coke can be achieved. Another aspect is the avoidance of unit downtime due to repair and unscheduled maintenance. Feedback from existing delayed coker units indicates an average loss of 5% of the optimum yearly production schedule due to damage or wear and tear in the mechanical equipment which amounts to approximately 400 hours’ outage each year.

Reliability
The equipment in the CCSS system is robust and reliable due to its design and to metallurgy selection for each and every component. The unit operates without trouble between two regular scheduled coker turnovers. In the refinery reference unit mentioned earlier, a record of 99.9% unit availability was achieved over a period of six years.

Capital cost (capex)
In a grassroots/greenfield project for a delayed coker, the design of the CCSS downstream equipment can be planned and executed at incremental capital cost. In the example of a two-drum unit with a capacity for each drum of 1000 t/d of coke, a payback time of about 1.5 years can be achieved. However, the design varies between individual delayed coker units and a careful study is required.

Operating cost (opex)
An average loss of 3% of the optimum yearly production schedule due to damage or wear and tear to mechanical equipment, resulting in approximately 400 h/y outage, costs €300 000-500 000 per annum.

However, the yearly loss of light products, depending on their market value, in the range of €10 million per hour of cycle time, is significant in comparison. Environmental issues are alleviated through the completely enclosed process, offering an advantage also when renewal of existing permits or permitting of new units is required.

Conclusion
The CCSS technology is a convincing solution when a new coker unit is planned. A mix of gains that are economical, ecological, technical, and safety-orientated comes into play. Investment decisions will consider operational benefits, in addition to pure capex considerations, when new coker units are being planned. Furthermore, increasing awareness of environmental issues by permitting authorities in many countries would also provide strong support for the technology described here.

Artur Krueger is the Houston, Texas-based Senior Account Executive with TriPlan AG, Germany, consulting to operators and engineering firms on coker projects worldwide. He holds a master’s degree in business from Columbia University, New York and a betriebswirtschaft graduate business degree from Wirtschafts-Akademie, Bremen, Germany. Email: artur.krueger@gmail.com

Bernd Lankers is a Project Manager with engineering company TriPlan in Germany. He has over 40 years of refinery and petrochemical experience, including several major overseas project assignments. He holds a BS degree in chemical engineering and economics from the University of Applied Science at Bingen/Germany.

Josef Wadle is a Senior Consultant with engineering company TriPlan in Germany. He has over 42 years of broad refinery background with various project assignments as lead mechanical engineer. He holds a BS degree in process automation/ control and chemical engineering from the University of Applied Science at Mannheim/ Germany. He is also a certified welding and metallurgical engineer.
What you can do

with a touch of blue.

You can...

Improve your refinery profitability by maximizing the production of clean transportation fuels with our leading residue upgrading technologies.
Deliver the best in refinery hydrogen production while reducing your operating costs with our unique Terrace Wall™ reformer design.
Enhance the efficiency of your overall sulfur recovery to achieve peak operating and environmental performance with our SRU technology.

And these are just the technology options. There is so much more you can do with a touch of blue. Visit www.fwc.com.
Who monitors the most reciprocating compressors?

When you look at the numbers, it all adds up to PROGNOST Systems:

- Largest installed base of online diagnostic systems on reciprocating compressors
- The world’s top refiners and HPI producers trust PROGNOST® systems
- Over 20 years of experience in monitoring reciprocating machinery

PROGNOST has one focus – reciprocating machinery. Our dedication ensures that your system remains best-in-class.

reply@prognost.com  www.prognost.com
Troubleshooting steam ejectors

Some causes and practical solutions concerning problems with refinery steam vacuum ejectors

NORMAN LIEBERMAN
Process Improvement Engineering

The majority of vacuum ejectors in refinery services do not perform as per their design. Steam vacuum ejectors, or jets, are widely used in both condensing steam turbine surface condensers used to generate power and drive large compressors. Also, steam jets are employed in vacuum towers which are used to produce paving asphalt and lubrication oils.

Poor performance of a steam turbine surface condenser will typically increase the energy requirements to generate electricity by 10%. Poor performance of a steam jet in a refinery may cost the refiner $20,000 (US) per day in reduced gas oil recovery from visbreaker bottoms or from delayed coker feed. Degraded vacuum may preclude meeting the viscosity and flash point specification for the production of paving grade road asphalt or industrial fuel oil.

Many refiners are able to sustain a reasonable vacuum during the winter, but find that their vacuum breaks and their steam ejectors start to make a surging or hunting sound when summer arrives.

The problems that give rise to these malfunctions number in the hundreds. A book on this subject\(^1\) has been rightly criticised for omitting half of the common causes for vacuum system malfunctions. The following tabulation is far from complete, and only represents the most common malfunctions seen most recently.

**Erosion of steam nozzle threads**

The steam nozzle (see Figure 1) is typically machined from 316 (L) stainless steel. It is not generally subject to damage to its threads. The major problem is that the stainless nozzle screws into the carbon steel ejector backing plate. The female threads of the backing plate corrode-erode, apparently due to galvanic corrosion and/or erosion due to wet motive steam. The motive steam then partly by-passes the steam nozzle and blows into the mixing chamber. The moisture in the steam acts like an electrolyte. Superheated steam would reduce this galvanic corrosion problem.

Another common cause of steam nozzles becoming loose because of erosion of their threads is because the nozzles were never installed properly. Either the threads were dirty or the nozzle was not screwed in tightly. This reportedly happens when the steam nozzles are replaced in the field. However, we have noted this problem on original ejectors too, with no history of nozzle removal. Whatever the cause, a small amount of leakage around the threads will escalate due to steam erosion. So, if steam nozzles are removed for inspection, clean off all the threads and reinstall the nozzles tightly using Teflon tape.

If you notice an improvement in vacuum by reducing the motive steam pressure by 20% below the design motive steam pressure, eroded threads may be the problem. We have temporarily fixed this failure with lots of Teflon tape. Why do the ejector manufacturers not use a stainless steel backing plate, and weld the steam nozzle to the ejector and avoid this problem? Actually, several refiners do follow this useful practice.

**Plugging of steam nozzles**

We have written about this subject and published photos of partly plugged steam nozzles extracted from a steam turbine surface condenser.\(^2\) The problem here is silicates and other hardness deposits in the motive steam supply. This is such a consequence of poor level control in upstream waste heat steam boilers. This is such a...
common problem that the manufacturers typically provide a small, screwed, clean-out plug in the backing plate of the ejector (see Figure 1). As most vacuum systems have two or three parallel sets of jets, one could isolate one jet and easily clean out the silicages while still on-stream.

Incidentally, if one steam ejector with a relatively clean nozzle is operating in parallel with a jet with a fouled nozzle, the good jet will extract motive steam out of the fouled ejector and greatly degrade the efficiency and capacity of the clean ejector.

**Distance between steam nozzle and diffuser throat set wrong**

The distance between the steam nozzle and the inlet to the diffuser (see Figure 1) is adjustable. There are spacers that are installed between the ejector backing plate and the steam nozzle that are used to make this adjustment which is supposed to be done in the factory. This adjustment is, at least partly, a function of the motive steam pressure. On several troubleshooting projects, the author, having failed to correct the ejector malfunction, was told by the vendor that the steam nozzle position had been incorrectly set in the factory for the current motive steam pressure and temperature.

**Moisture content of steam**

The variable that provides the energy to compress the gas to the ejector is the kinetic energy of the motive steam. This kinetic energy is not derived from the motive steam pressure but from the motive steam’s enthalpy or heat content. If the steam is wet, the moisture flashes to steam in the steam nozzle. The resulting conversion of the sensible heat of the steam to latent heat of evaporation of the entrained water reduces the speed or velocity of the steam entering the diffuser. In one recent case, wrapping 25 ft of a two-inch steam supply line with loose insulation improved the vacuum from 54 to 49 mm Hg.

On the other hand, highly superheated steam is also marginally bad for the ejector’s performance. Hence, steam condensate is injected through a ‘desuperheating station’. However, it is not uncommon for the temperature controller to be set a few degrees below the saturation temperature of the motive steam. The author has seen this done at two refineries recently. The effect, of course, is to inject uncontrolled water into the motive steam. Auto-refrigeration of the exterior of the converging section of the ejector will be observed. Also, there will be erosion of the carbon steel threads where the stainless steel steam nozzle screws into the ejector body as a consequence of the water in the steam. In one refinery, correcting this problem improved vacuum from 28 to 15 mm Hg.

**Air leaks that cause nitrogen in the off-gas to exceed 10-20%**

The easy way to find significant air leaks is to look for moisture condensing on the ejector’s body, barometric drain legs, or flanges. Air, as it is drawn into the diffuser or flange, expands and auto-refrigerates. In areas of high humidity, atmospheric moisture will condense out on the exterior of chilled metal surfaces. The quite common solution for on-stream repair is duct tape. This is a permanent and inexpensive repair technique. Air leaks in a seal leg will cause poor drainage through the affected leg and condensate back-up.

High concentrations of CO₂ as opposed to oxygen, in the vacuum tower off-gas is an indication of an air leak in the line connecting the fired heater to the vacuum tower – obviously a potentially dangerous situation which requires careful inspection of the heater’s ‘transfer line’. Imagine what may (and has) happened if the vacuum is suddenly lost and the pressure in the transfer line goes positive. Several catastrophic fires have resulted.

**Condenser pass partition baffle leakage**

The heat transfer coefficient (U value) of a surface condenser, vacuum tower pre-condenser, or an ejector after-condenser should be about 110–130 BTU/hr/ft²/°F. However, only too often the observed U value is only 30–40. This would superficially indicate fouling. Yet, frequently, both the shell side and the tube side of the condenser are found to be quite clean. The problem is not fouling or really even a low U value, but the cooling water leaking internally inside the condenser channel head (see Figure 2). If the closure or clearance between the channel head pass partition baffle and the channel head tube-sheet is not tight (and there is no way to pressure check this closure), water will leak from the inlet side of the channel head, directly to the outlet side. If there is sand in the cooling water, the leakage rate will gradually increase due to the scouring action of the sand.

![Figure 2 A leak at the pass partition baffle gives a false impression of fouling](image-url)
Superficially, the problem seems to be a large delta T between the cooling water outlet and the condenser vapour outlet temperature, hence the small calculated U value. In reality, the U value is normal. It is just that a large percentage of the cooling water supply is by-passing the condenser’s tubes.

One can identify this sort of malfunction by comparing the calculated water side pressure drop, to the observed delta P. To prevent this problem, use of a silicon sealer along the edge of the channel head, pass partition baffle and the channel head tube sheet is recommended.

**Defective seal strips**
The shell side seal strips are intended to keep hot vapours in the inlet to a condenser from blowing out directly to the vapour outlet (see Figure 3) and by-passing the air baffle. This malfunction is indicated by the condenser vapour outlet being 20-40°F hotter than the liquid outlet. The reason for the defective seal strips is that the seal strips are too short, damaged on installation, or made of the wrong materials. In one installation observed recently in Mexico, the refinery vacuum tower’s first stage condenser’s seal strips were made out of brass. As the vacuum tower overhead vapour contains NH₃, HCN, HCl, H₂S, CO₂, and H₂O, brass is not the correct metallurgy. The destroyed seal strips were replaced with 316 (L) stainless steel, which did not help either as they were not installed wide enough to contact the interior of the shell. It is best to extend the seal strips by ⅛ inch beyond on the condenser shell’s inner diameter.

**Fouled final condenser in a steam turbine surface condenser**
Quite often, the final condenser, which is the last component of the small two-stage ejector system used on all such condensers, fouls on the steam side. The correct solution to this very common malfunction is not to clean but to discard the final condenser and vent the second stage condenser vapour effluent directly to the atmosphere. Why then are surface condensers which are serving condensing steam turbines equipped with a final condenser in the first place? The answer is that there is no answer, other than historical precedent.

**Steam turbine surface condenser loss of vacuum**
The two-stage ejector system that provides the vacuum to a steam turbine surface condenser is connected to the two-stage condenser (see Figure 4). The very small condenser shell (typically 12-18 inches in diameter) has an internal segregation baffle that divides the shell into two unequal compartments. Failure of this segregation baffle is common and allows the discharge of the second stage condenser to leak back into the suction to the second stage ejector. An extremely large loss in vacuum in the steam turbine surface condenser results. This quite common failure has reduced a very large steam turbine horsepower output by almost 10%. The solution to this problem is to simply vent the discharge from the second stage ejector directly to the atmosphere. As noted earlier, the second stage condenser serves no function. The author has by-passed this component of the standard condensing steam turbine many times and has never observed any detrimental effect. That is, simply vent the discharge of the second stage ejector directly to the atmosphere.

**Condensate back-up in condenser**
This common problem is also indicated by the condenser vapour outlet being hotter than the liquid drain line. Once the liquid backs up inside the condenser shell and covers the bottom edge of the air baffle (see Figure 4), there will be a step change reduction in vacuum, as liquid is drawn up into the inlet of the downstream ejector. Factors observed in the past few years that cause condensate back-up are:
- Drain line plugged with wax
- Flange leak on drain (barometric seal leg) line, that draws air into the seal leg
- Corrosion of drain line inside seal drum, above the seal drum’s liquid level
- Seal drum flooded due to faulty level control
- Sludge in seal drum above the bottom level of the internal drain

![Figure 3 Broken seal strips permit internal vapour by-pass around baffle](image-url)
ual performance characteristics. Its performance does not often conform to expectations, but more frequently to the minimum performance that one is willing to tolerate.

Refrigerated cooling water
Some refiners employ emergency rental package cooling water refrigeration units during the summer months. These packaged units will reduce the cooling water temperature to the condenser by typically 20°F. On many if not most units, this reduction in the cooling water temperature will have a dramatic effect on improved vacuum. A packaged chilled water system can be put into service quickly. Naturally, this is a relatively expensive option compared to operating the existing system properly. Still, the refiner sometimes is forced to adopt such expedients, particularly when producing paving grade asphalt during summer operations.

Determining non-condensible flow rates without a flow meter
The main concern when troubleshooting an ejector system is to determine if the vacuum system is working on its vendor performance curve. If there is no flow meter, a series of actions can be followed to obtain the non-condensible load to the ejectors:

- Obtain an off-gas sample from the seal drum. Check for N₂ content. Assume N₂ content is 5% for illustration purposes
- Through a small (¼-¾ inch) screwed fitting, located at the suction of the first or second stage ejector, allow air to be drawn into the ejector system
- Wait five minutes and obtain a second off-gas sample from the seal drum. Check for N₂. Assume the N₂ content is now 25%
- Assume that the air velocity through the screwed fitting is 1100 ft/s, the sonic velocity consistent with critical flow
- Calculate the volume flow of N₂ (78% of air), based on the open area of the screwed fitting, and the 1100 ft/s air velocity
- Calculate the density of air at the current ambient conditions (about 0.075 lb/ft³)

<table>
<thead>
<tr>
<th>Component</th>
<th>No air admitted, Mol%</th>
<th>Air added through ½ inch nipple, Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>7.8</td>
<td>2.9</td>
</tr>
<tr>
<td>O₂</td>
<td>1.5</td>
<td>11.1</td>
</tr>
<tr>
<td>N₂</td>
<td>5.8</td>
<td>43.8</td>
</tr>
<tr>
<td>C₁</td>
<td>18.2</td>
<td>6.4</td>
</tr>
<tr>
<td>CO</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>C₂</td>
<td>13.2</td>
<td>4.9</td>
</tr>
<tr>
<td>H₂S</td>
<td>9.9</td>
<td>3.7</td>
</tr>
<tr>
<td>C₃</td>
<td>14.2</td>
<td>6.5</td>
</tr>
<tr>
<td>C₄</td>
<td>15.1</td>
<td>7.9</td>
</tr>
<tr>
<td>C₅+</td>
<td>11.7</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Table 1

Figure 4 Steam turbine surface condenser ejector system failure

Figure 4 Steam turbine surface condenser ejector system failure
- Multiply the volume of air by its density, to obtain pounds of air flow per second.
- As the N₂ content has increased by 20% (25-30%), you may assume that the air flow calculated above is about 20% of the non-condensible gas flow. Therefore, multiply the pounds of air per second calculated above by approximately four.
- If the molecular weight of the cracked gas is different from the molecular weight of air, multiply the pounds of flow by the ratio of the molecular weight of the non-condensible gas, divided by the molecular weight of air (29). See Table 1 for an actual set of test results from a low sulphur refinery vacuum tower.

If using air as a calibration gas is unacceptable, argon or helium may be employed, but this is a time consuming option. But take care to select a screwed fitting size that will not greatly impact the vacuum tower operating pressure. Also, the seal drum off-gas contains 10-40% H₂S. The fatal concentration of H₂S is 0.1%. Fresh air equipment when obtaining these samples is advisable.

Conclusions
The examples cited here are a tiny segment of the vast number of problems that beset steam ejector and surface condenser performance. There is always an understandable temptation to consult the equipment vendor for advice and guidance, when trying to troubleshoot steam ejector performance problems. Typically, this does not help. Only field investigation, experience, careful measurements and experimentation appear to offer any hope of a successful outcome. The ejectors should and will perform on the manufacturer’s performance curves. The main ingredient needed to achieve this result is the dedication and the determination of the field troubleshooter.

References
1 Troubleshooting Vacuum Systems, Wiley Publications.
3 Lines J R, Understanding ejector systems necessary to troubleshoot vacuum distillation, Graham Corp. Technology Bulletin, Batavia, NY, US.
5 Applied process design for chemical & petrochemical plants, Ejector & Vacuum Systems, 218-222.

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 since 1983 to over 18 000 engineers and experienced plant operators. The first of his eight books, Troubleshooting Process Operations, has been continuously in print for 35 years. He previously worked for Amoco Oil in Whiting, Indiana and Texas City, through 1980, and until 1983 was Refinery Manager for the Good Hope refinery in Louisiana. He graduated from Cooper Union in New York City in 1964.
Email: norm@lieberman-eng.com

Others simply sell you a product – we offer a solution.

Best Valves since 1867

OHL Gutermuth

Specialized in high pressure low/high temperature
Customized Valve Design „MADE IN GERMANY”

Helmershäuser Straße 9-12 - 63674 Altenstadt / Germany
Phone +49 6047.8006-0 · Telefax +49 6047.8006-29
www.ohl-gutermuth.de · E-Mail: og@ohl-gutermuth.de

PTQ Q4 2014 129
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.
Asphalt quality prediction and control

With knowledge of heavy vacuum gasoil cut-point and asphalt density, asphalt quality can be inferred

ZAK FRIEDMAN
Petrocontrol

Much has been written about crude column product separation by advanced process control (APC) but very little about vacuum column APC. Why? Vacuum distillation unit separation is important, especially in asphalt mode, when vacuum pitch is sold as a premium product, and controlling asphalt quality is high on the list of economic priorities. One guess is that such APC applications have not been reported because of inability to infer asphalt qualities, and without such inference vacuum column APC would not be effective. Recently, Petrocontrol had the opportunity to set up asphalt quality inferential models at two refineries; this article describes the inferential techniques and shares the inferential performance data.

Both refineries are located in North America. Refinery A is a land-locked refinery and throughput is limited by asphalt sales. The product grades vary from shingles to road asphalts. Refinery B runs mostly road asphalt by blocks and only from certain crudes. In summer, asphalt is the most lucrative product.

Asphalt quality is typically measured by dynamic shear rheometer (DSR) apparatus, where the number reported as $G^*/\sin(\delta)$ is a measure of viscosity at a given temperature. Our DSR inference relies on the knowledge that asphalt viscosity correlates with average boiling point and density. The average asphalt boiling point is estimated from column measurements, but for density we need the aid of a density analyser. Without online density measurement, DSR inference is not plausible.

Refinery A had installed a density meter and developed asphalt DSR inference several years ago but the model was less than perfect. It would predict adequately for a few days, and then suddenly would have to be biased substantially, even when the crude had not changed. That had caught us by surprise. What was going on? Operation has not changed much but the lab test is suddenly showing a different value. Upon studying the DSR test we realised it is carried out at several defined temperatures of 46, 52, 58, 64 or 70°C, the specific test temperature being a part of the asphalt grade specifications. During asphalt runs the schedulers switch grades often; carried out at different temperatures, the lab test would yield different results. The operator, not being aware of the change of DSR test temperature, views the sudden lab–inference discrepancy as a sign of problematic inference and turns off the APC.

The vacuum column configuration

Figure 1 shows a typical vacuum column configuration. Reduced crude feed comes from the atmospheric crude column through a furnace and into the flash zone. There are two distillate products: light vacuum gasoil (LVGO) and heavy vacuum gasoil (HVGO). LVGO is diesel range material, going into the diesel pool. HVGO is FCC or hydrocracker feedstock. There is a possibility to also draw vacuum wax, though normally wax is circulated back to the furnace to improve the separation. As is common in vacuum column designs, the draws are from total...
Occasionally bias the density reading and/or DSR correlation.

The GCC inferential package

Generalised cut-point calculations (GCC) is a well established inferential package for wide cut fractionators such as the crude and vacuum distillation units. GCC uses column measurements to first identify the true boiling point curve for the feed, and then it estimates product cut-points. Being a first principles based model, GCC has performed better than other methods, and has in addition the ability to infer cut-points during crude switches. Several GCC related papers have been published, and it is not the object of this article to cover additional GCC sites beyond saying that HVGO cut-point is predicted well. That is important for the asphalt inference because HVGO back end cut-point is identical to asphalt front end cut-point.

Figure 3 shows a one-year trend of HVGO 98% point inference model (HVG98_M) against lab tests (HVG98_L). HVGO 98% is predicted from HVGO cut-point, and the high fidelity of this prediction indicates that the HVGO cut-point is well estimated. That trend is for refinery A. We cannot show the equivalent refinery B trend because refinery B does not test the HVGO distillation curve.

Is the front end asphalt cut-point good enough for this inference? Viscosity is, after all, a function of asphalt average boiling point. In calculating asphalt average boiling point our model assumes the asphalt effective back end cut-point to be 800ºC. Given that asphalt effective endpoint is indeed around 800ºC the magnitude of crude to crude inferential variation is fairly small.

DSR modelling

There is a way to consider DSR lab tests carried out not only at one temperature in isolation but also at other test temperatures. Given the sensitivity of viscosity to temperature, there is a certain temperature called TE, such that if the DSR test were to be carried out at TE the test result would have a value of precisely 1.00 KPA. The DSR-
Mega air separation units for the world’s largest gas-to-liquids (GTL) project in Qatar.

Qatar Shell GTL Ltd., a member of the Royal Dutch Shell Group, and Qatar Petroleum count on Linde Engineering’s expertise for Pearl GTL in Qatar.

In 2006, Linde was awarded with the turnkey contract to build eight large air separation plants for the Pearl GTL plant in Ras Laffan Industrial City, Qatar. When Pearl GTL – the world’s largest GTL facility – went on stream in 2011, Qatar became the “global GTL capital”.

The eight air separation plants produce 860,000 cubic metres of oxygen per hour, which are used to convert 140,000 barrels of natural gas into liquid hydrocarbons. As such, Pearl GTL is the largest integrated complex of its kind in the world.

With this project, Linde demonstrates once again that it is responding to the challenge of producing cleaner fuels and energy to meet increasing worldwide demand. Furthermore, the company confirms its leading position as a technology provider and EPC contractor.

Linde AG
Engineering Division, Dr.-Carl-von-Linde-Strasse 6-14, 82049 Pullach, Germany
Phone +49.89.7445-0, Fax +49.89.7445-4908, info@linde-le.com, www.linde-engineering.com
temperature model we are using is:

\[
\ln\left(\frac{G}{\sin(\delta)}_{\text{test}}\right) = B \times \left(\frac{1}{T_{\text{test}}} - \frac{1}{T_{\text{ref}}}\right)
\]

(1)

Where \(T_{\text{ref}}\) is the test temperature in °K and \(\frac{G}{\sin(\delta)}_{\text{test}}\) is the DSR outcome of that test.

With knowledge of coefficient \(B\), Equation 1 permits calculation of \(T_{\text{ref}}\) from a DSR test result at any temperature. Refinery A tests the same asphalt sample at different temperatures and for a given test sample the TEs calculated from test results at different temperatures should be identical. Thus, even if the viscosity-temperature relationship is not precisely known the many lab tests at different temperatures give us the opportunity to calibrate the temperature influence.

Figure 4 tests this concept, covering 20 days of TE calculations. The lab tested samples at 46 (TE46_L), 52 (TE52_L), 58 (TE58_L) and 64°C (TE64_L). The reported DSR results are very different at each temperature because viscosity is quite sensitive to temperature, but the calculated TE values coincide within half a degree. The fifth green square lab value in Figure 4 (DSR_L) is a laboratory calculation of TE based on interpolation among the several test results. Finally, the blue trend of Figure 4 is a TE inference as a function of VGO cut-point and asphalt density readings. While not perfect, this inference tracks the lab well and can reliably be used for control.

**DSR inferential performance**

Figure 5 illustrates refinery A’s inferential model performance over the same 20 days compared to lab data at 58°C test temperature. The blue line and orange squares of Figure 5 are trends of DSR inference and DSR lab test, both at 58°C. The blue line inputs are shown in brown and green. Brown is the asphalt density measurement after temperature correction to 15°C. Green is the HVGO cut-point inferred by GCC (right scale), °C. API and cut-point often trend as a mirror image, where the gravity changes as a result of cut-point change, but the mirror image is not perfect because gravity can also change with crude type, and refinery A continuously changes the crude mix.

**Figure 6** shows a typical refinery B five-day trend. Referring to the right hand scale, the orange diamonds are DSR test temperatures, the red triangles are temperature TE, calculated from the lab DSR test result data, whereas the heavy purple line is our TE inference. On the left hand scale, green squares are DSR test results, and finally the blue line is our DSR inference as calculated from our TE model and lab test temperature.

**DSR control performance at refinery B**

The complexity of refinery B’s multi-variable predictive controller (MVPC) is beyond the scope of this article. Suffice to say that there are many product quality inferences, as well as many constraints, and the MVPC manipulates both the atmospheric crude column and vacuum column together. Changes in the crude column affect asphalt quality and to achieve the desired DSR both atmospheric gasoil (AGO) and HVGO draw must be manipulated. AGO is the lowest draw of the atmospheric column and changes of AGO affect vacuum column feed and asphalt quality. Figure 7 shows a five-day trend illustrating how DSR control is accomplished. During these five days, several grade switches took place. DSR inference is shown in green, which compares well against lab DSR test results in red diamonds. Upon grade switches, both the inference and lab result jump, not because of any process change but simply because of the change in test temperature. The TE value itself actually does not change until column conditions change.
Anyway, upon that inference jump the APC controller reacts quickly, changing the main manipulated variable: AGO draw (orange) and HVGO hot reflux (blue), bringing DSR to target. Vacuum diesel draw is shown in magenta. It often moves as a mirror image of AGO, but that mirror image is not perfect, indicating that other changes have occurred, for example crude quality drift due to a non-uniform crude tank.

Conclusions
We have demonstrated that with knowledge of HVGO cut-point and asphalt density one can infer asphalt DSR. In our case, HVGO cut-point is a GCC inference whereas the density is measured by an on-stream analyser. Our inferential procedure involves the following steps:
1. Obtain an inferential estimate of HVGO cut-point, a GCC model calculation
2. Obtain a current asphalt density reading and asphalt analyser temperature
3. Correct the analyser density reading to 60°F
4. Estimate TE, the temperature at which asphalt DSR would be precisely 1.00 KPA
5. Obtain the lab DSR test temperature appropriate for the asphalt grade
6. Use equation 1 to convert TE into \( G^*/\sin(\delta) \) at the test temperature.

While this procedure is not trivial we have shown that good inferential precision is achievable.

Further, we have integrated the DSR inference into a large MVPC, manipulating both the crude and vacuum columns. In addition to controlling all distillate properties at targets, subject to equipment constraints, we have also achieved effective control of asphalt DSR. Asphalt is one of the most profitable refinery products and its precise quality control has a high value.

References
5 Schuler M G, Kesler M G, Friedman Y Z, Refinery uses column data to infer and control asphalt DSR. In our case, HVGO cut-point is a GCC calculation whereas the density is measured by an on-stream analyser. Our inferential procedure involves the following steps:
7 Friedman, Y Z, Control of crude fractionator product qualities during feedstock changes by use of a simplified heat balance, American Control Conference, 1985.

Y Zak Friedman is Principal Consultant with Petrocontrol, based in New York City.
Email: zak@petrocontrol.com
ERTC 19th Annual Meeting
Lisbon • 18 – 20 November 2014
gtforum.com/ertc-annual-meeting

Average attendees: 500

Attendee company type
*Average attendees: 500

- Academic
- Refiner
- EPC
- Supplier

Attendee job function

- Product & Technology Sales & Marketing: 57%
- Engineering: 29%
- Other: 9%
- Project Management: 5%

Attendee seniority

- Head/Manager: 56%
- Director: 16%
- Board/C-Level: 11%
- General Manager: 5%
- Other: 12%

Geographical region

- Europe: 61%
- UK: 13%
- Americas: 12%
- Middle East/Africa: 8%
- Asia: 4%
- Russia/CIS: 2%

Still the best conference to get a good overview of new technologies, contact international experts and renew friendships

Senior Advisor, OMV

For many years ERTC has been the best event in Europe, where you can be informed about the latest developments in the oil industry, meet interesting people and make contact with service providers

General Technical Manager, Hellenic Petroleum

All the major companies within the industry have sent representatives to ERTC including: Bapco • BP • CEPSA • Chevron • Engen • ENI • Essar • ExxonMobil • Galp Energia • Grupa Lotos • GS Caltex • Gunvor • INA • MOL • Murco • Neste • OMV • Petrobras • Petroineos • Phillips66 • Reliance • Rompetrol • Rosneft • Repsol • Saudi Aramco • Shell • Sinopec • Sibur • Total • Topras ...to name just a few.

To find out more and to book your place visit gtforum.com/ertc-annual-meeting
Oman Oil Refineries and Petroleum Industries Company (Orpic) approached Zeolyst Specialty Catalysts (ZSC)* for assistance in enhancing the performance of its transalkylation unit. ZSC simulated the transalkylation process in a pilot plant test unit running Orpic feed and found that switching to ZSC’s ATA-21 catalyst would help with further process optimisation.

The transalkylation process involves transferring an alkyl group from one organic compound to another and enables operators to upgrade low-value streams (including heavy aromatics C₉₊ and toluene) to high-value feedstocks for paraxylene and benzene.

Transforming low-value feedstocks into valuable products is a major goal of the petrochemical industry. Plant operators aim to maximise the production and purity of the desired products while reducing their overall costs.

In most industrial catalytic processes, catalyst performance optimisation is a critical focus area. The study facilitated the decision to perform an early catalyst changeout justified by the improved performance when using ATA-21 catalyst. Orpic planned a catalyst changeout for the end of Q1 2013.

The main driver for catalyst replacement was to improve Orpic’s economic benefit significantly by using the latest technology for transalkylation, the company said. The challenge was to select a catalyst that would improve productivity and help to debottleneck a specific unit. Orpic chose ZSC’s ATA-21 catalyst on the basis of a techno-commercial evaluation of the proposed yields and the projected improvements of various catalysts (see Figure 1).

ATA-21 is the latest in the ATA (advanced transalkylation) range of high-performance transalkylation catalysts developed and commercialised as a result of the partnership between ZSC, South Korea’s SK Innovation and Shell Technology Centre Amsterdam in the Netherlands. These transalkylation catalysts exhibit high activity and efficiency for the treatment of heavy feedstocks.

Shell Global Solutions worked closely with the Orpic operations team to help meet Sohar’s goals and says that it was confident that ATA-21 would meet the challenge at Sohar based on continual optimisation and confirmation of pilot plant performance. The catalyst delivers very low aromatics loss and reduced hydrogen requirements, and offers high benzene purity. Low hydrogen requirements help to reduce utility or investment costs, and the catalyst’s high stability means that

---

**Figure 1** Transalkylation upgrade project: plant operation with original catalyst

- Catalyst X produces non-aromatics in C₆-C₇ boiling range.
- Due to non-aromatics make, benzene purity is off-specification.
- 1.5kbd of benzene with impurities has to be drawn to aromatic extraction unit to maintain benzene final product purity.
- Aromatic extraction unit utilisation is limited.
- Reformer and crude distillation unit rate is limited.

---

**Figure 2** Transalkylation upgrade project: plant operation with ATA catalyst

- Catalyst ATA formulation produces low non-aromatics in C₆-C₇ range.
- Benzene purity is improved.
- Side draw in stabiliser is reduced to zero.
- Improved aromatic extraction unit utilisation.
- Debottleneck reformer and crude distillation unit.
a typical cycle can run from four to eight years, depending on the operating conditions.

Orpic placed the commercial order for ATA-21 in December 2012; catalyst delivery to the Oman site was slated for February 2013. Manufacturing and delivering 60 tonnes of novel catalyst technology within such a tight schedule was a technical and logistical challenge, but the collaboration of Shell Technology Centre Amsterdam, ZSC and SK Innovation enabled quick delivery of the first commercial catalyst samples to Amsterdam for catalyst evaluation and qualification.

This was ZSC’s first user of ATA-21 catalyst and its first transalkylation customer in the Middle East, so there was no room for error. When the catalyst was ready for shipment, extra measures were taken to meet the start-up schedule. Logistics were put in place to ensure that the catalyst would be on-site for installation and a successful start-up.

Selecting the ZSC catalyst and having it delivered to site on time enabled Orpic to replace the old catalyst as planned to gain the benefits associated with the new catalyst at the earliest opportunity, says the Oman company.

There is often a stabilisation period following the introduction of a new transalkylation catalyst system. Typically, the high activity of the catalyst results in side reactions and affects the high benzene purity target. For the first 12 hours at Sohar, process adjustments were implemented to achieve the high benzene purity requirement with the inclusion of a stabiliser side stream. Unlike some other catalysts on the market, within a few days, the performance of ZSC’s ATA-21 catalyst stabilised and the operator was able to shut down the stabiliser side stream. In addition, the operating temperature was 80–90°C lower than that achieved with the historical catalyst charge. This start-of-run temperature reduction with ATA-21 helped to improve the energy efficiency of the aromatics unit further (see Figures 1 and 2).

During the first few weeks of operation, ZSC received regular updates from Sohar. Two weeks into the production cycle, the plant operators reported that they were pleased with the performance.

The ZSC catalyst helped to increase conversion and yields of selected products (paraxylene and benzene) and reduced by-products such as heavy aromatics and low-cost blend material (see Figure 3). The quality of the benzene being produced improved substantially; which, in turn, resulted in debottlenecking of the extraction unit.

Furthermore, the cost of olefin treatment came down because the products from the new catalyst system contain less unsaturated materials. After a few months of operation following the introduction of the new catalyst, Orpic says that it could safely conclude that the performance of the Orpic aromatics complex had shown a marked improvement and enabled the company to achieve new production records for benzene.

For more information: Richard.mauer@shell.com

**Upgraded control for amine and sour water acid gases**

In 2008 Jacobs introduced its Advanced Burner Control Plus (ABC+) for SRUs fed with amine acid gas (AAG). This upgraded control system is based on the existing ABC system that has proven its value in decades of operation in sulphur recovery units worldwide. Whereas ABC leans heavily on feedback from the tail gas analyser in case of acid gas composition changes, the ABC+ system adds a feed gas analyser to anticipate changes in AAG composition. The readings from the AAG analyser are used by the ABC+ PLC to calculate the air to AAG ratio as well as the AAG mole weight. In a client’s DCS these online variables are used to significantly improve the feed forward control response of ABC, thus forming ABC+. Jacobs has taken the next step by including sour water acid gas (SWAG) control into ABC+.

SWAG mainly differs from AAG because it contains a significant amount of ammonia. Furthermore the hydrogen sulphide as well as the carbon dioxide content is much lower and the water content is much higher than in AAG. Last but not least, the hydrocarbon content is often higher; it contains more hydrocarbon species which tend to fluctuate more than in amine acid gas. Ammonia can be rapidly measured by the combined UV/IR optical cell that is part of the ABC+ feed forward analyser. Furthermore, the SWAG analyser can be set up to also measure already familiar
species from the AAG analyser. Apart from SWAG being different in composition compared to AAG, the data received by the ABC+ PLC is processed in the same way. In this way, the SWAG feed forward control response can be significantly improved, providing the same analytically driven control concept as already available for AAG.

ABC+ has been shown to provide SRU control robustness, enabling processing of varying quality sour gas from refineries as well as gas fields. It is suited to handling feeds that vary in flow rate, pressure, temperature and composition. Often these variations result from upstream operating complexities. By offering an effective feed forward control, the problems of increased SO₂ emissions, potential production losses and regulator non-compliance can be avoided. Considering sour gas composition changes, the usually strong dependence of ABC+ on the tail gas analyser is relieved somewhat since the focus now shifts more towards the feed gas analysers.

The first ABC+ system was installed at Keyera Simonette gas plant in Canada in 2008 and this set-up has been running successfully ever since. Thanks to the ABC+ system, the number of upsets as well as the quantity of flared acid gas was significantly reduced. Shortly after start-up, Keyera, then still belonging to Suncor, reported an increase in capacity of about 10% which directly increased revenues.

Since then, an improved ABC+ hardware concept has been developed together with partner Analytical Solutions and Products (ASaP, Amsterdam). The first improved system, AAG ABC+, has been running successfully since early 2012 at Valero Pembroke refinery in Wales, UK. At the same refinery, SWAG ABC+ has been started up in July 2013 and, after some extra commissioning attendance, also runs satisfactorily. This was merely due to some tuning in the analytical set-up of the SWAG analyser, which could be done online. Some aspects during the start of the project had to be assumed, which could later be rectified with the aid of the vendor during actual operation.

After experience at Valero Pembroke, very similar AAG and SWAG ABC+ systems have been started up in 2014 at Esso Augusta (Italy) as well as CPC Talin (Taiwan), while a similar project at Takreer (UAE) is halfway in this process. All locations report stable operation leading to good unit performances.

In the case of the CPC Talin installation, low SO₂ emission from the SRU is secured by application of a tail gas scrubber. The primary benefit of the ABC+ control in this case is the prevention of bypass operations and trips, also when the feed gas composition and/or quantity changes in AAG and/or SWAG. Because of this, the use of caustic in the scrubber can be kept low, which translates into lower operating costs and a smaller bleed stream.

For more information: Jenny.deWolf-Rikkers@jacobs.com

---

When you have a job to do, you’re not thinking about your flashlight’s engineer or the design, functionality or keen ingenuity that offers a premium product for the GREATEST VALUE.

In fact, you don’t have to think about your flashlight at all. Because it’s a STREAMLIGHT.
Online cleaning and decontamination of a crude unit

A refinery wanted to validate ITW’s Online Cleaning and Improved Degassing/Decontamination technologies to use them strategically for future turnarounds/slowdowns and during the run.

Online Cleaning was carried out on the entire crude distillation unit (CDU, which has two preheat trains) and took 24 hours. Subsequent to that, as the refiner wanted to further recover downtime (and reduce steam-out requirements), ITW applied its Improved Degassing/Decontamination technology, which took 24 hours. By manways opening, the following results had been achieved: 
- LEL = 0% 
- HC = 0 ppm 
- H2S = 0 ppm 
- benzene = 0 ppm 
- ammonia = 0 ppm 
- pyrophorics = nil.

Moreover, for the first time in the unit’s history, there was no need for columns wetting as pyrophorics were completely eliminated. All of the maintenance operations were conducted under dry conditions.

Visual inspection of the bundles confirmed the results of Online Cleaning. The refinery decided therefore not to extract some bundles during turnaround, but to check their performance at unit start-up.

At CDU start-up, the results of Online Cleaning were comparable to mechanical cleaning. The outlet temperatures of the trains were the same and the fouling factor of the H.E. cleaned with ITW were comparable to the mechanically cleaned ones. The results of Online Cleaning technology exceeded the refiner’s expectations, says ITW.

No waste was generated. All of the washing fluids were sent to a slop oil tank and fully reprocessed at unit start-up, with no problems at all during reprocessing.

For improved degassing/decontamination, the condensate was routed directly to the oily sewage. Again, no problems were recorded at the API separator/wastewater treatment plant.

Given the successful application, the refinery will consider ITW Technologies applications as follows:
- Avoid CDU slowdown to clean the preheat trains
- Regular application on the visbreaker to increase run length
- Rescheduling of future downtime during turnarounds by taking into consideration both the reduced time for safe entry and the reduced need for cleaning exchangers.

ITW technology can be used to clean storage tanks on a closed-loop basis, with no operator entry.

For more information: mferrara@itwtechnologies.com

Alternative to stick-built sulphur plants

Prosernat, acting both as process licensor of a portfolio of sulphur recovery technologies (AdvaSulph for sulphur recoveries up to 99.9%+) and as specialist of modular treatment units, has delivered modular sulphur units which meet a variety of project constraints. In general, the project execution scheme where the same company carries out simultaneously the process design and the modular fabrication and delivery offers significant cost/delay savings compared to a traditional execution scheme where basic design/FEED is followed by EPC tendering with subsequent stick-built fabrication. The modular design and supply scheme also helps to solve specific site constraints such as congested areas, ongoing operations, lack of manpower or harsh climates. The following two projects illustrate those benefits of modular supply for sulphur recovery units.

Prosernat delivered modular tail gas treatment to Ecopetrol’s Barrancabermeja refinery in Colombia for start-up in 2010. The design uses Prosernat’s proprietary process Clauspol designed to achieve 99.7% sulphur recovery downstream of a 110 t/d Claus unit. The unit comprises a tail gas absorber (delivered loose) and smaller process equipment items delivered totally skid mounted in order to meet the refinery’s plot space limitations and also to speed up the installation of the unit.

A modular gas sweetening and sulphur recovery unit delivered by Prosernat to Total EP’s Kharyaga site in Russia consists of two main units:
- A gas sweetening unit (GSU) to remove the H2S from associated gas, designed with AdvAmine MDEAmax, a proprietary selective MDEA process developed by Total and licensed by Prosernat
- A Claus unit with sulphur degassing (SRU) with a sulphur production capacity of about 16 t/d.

The Kharyaga project had to cope with two main constraints:

Figure 1 Modular gas sweetening and sulphur recovery units at Total EP’s Kharyaga site
• The field is located beyond the arctic circle and the severe climatic conditions do not favour site works
• Transportation from the nearest sea port to the site had to be made by road and train which limited the size and weight of each single transported element to 3400 mm width x 3460 mm height x 18 000 mm length and 37 tonnes weight.

In order to meet these constraints, both the GSU and the SRU were made of an assembly of several smaller skids, each single skid being designed to meet the limitations of transportation. The SRU is composed of 38 main equipment items installed in 11 skids, representing a total weight of 300 tonnes. The GSU is composed of 43 main equipment items installed in 12 skids representing a total weight of 330 tonnes.

The whole gas treating plant is composed of 23 skids and weighs 630 tonnes (see Figure 1).

Modular design is of course applicable to complete sulphur blocks. At the end of 2013 Axion Energy placed an order with Prosernat for its Campana refinary in Argentina to design and deliver a fully modularised sulphur plant comprising: complete amine fuel gases treatment system; double stage sour water stripper; Claus plant; tail gas treatment (with Prosernat’s licensed Sultimate process); and incinerator and sulphur degassing. This complete sulphur block is designed to produce 30 t/d with sulphur recovery of 99.9% and it will be made of 24 different skids, each weighing between 50 tonnes and 100 tonnes.

For more information: pweber@prosernat.com

Hydroprocessing internals upgrade

Chevron Lummus Global (CLG) worked with a private refiner to upgrade the reactor internals in a hydrocracking unit to improve the safety, operability and profitability for this unit. This refiner was perpetually struggling with high catalyst bed outlet temperature spreads, severe cold and hot spots, poor quench gas distribution, poor catalyt bed temperature control and low volume expansion. The quench gas distribution was so poor that lower bed hot spots could only be indirectly controlled by a combination of moves between the upper bed quench valves. This raised significant operating safety and emergency response concerns.

CLG reviewed the existing reactor internals design and performance and determined that the temperature control issues were due to inadequate mixing between cold quench gas and hot process gas, compounded by limited mixing and temperature equilibration between the gas and liquid phases. CLG also compared plant yields, chemical hydrogen consumption and volume expansion to pilot plant results for the same feed and catalyst system and determined that plant results were below expectation. Further, this performance gap was due to poor gas and liquid distribution to the catalyst beds resulting in severe gas and liquid channelling and overall low catalyst utilisation. The company

www.eptq.com
determined that the gas and liquid mixing and distribution issues could be resolved, and temperature control and volume expansion improved by replacing the reactor internals.

CLG proposed upgrading to its latest generation Isomix internals which are comprised of two primary process components: a sealed collector tray and central mixing device; and a distributor tray based on high efficiency flow nozzles, a new concept in multi-phase flow distribution.

Isomix internals have significant advantages over prior generations. For instance, the mixing box achieves intimate gas-liquid mixing, promotes heat transfer between the two phases, and provides stable performance over a broad range of gas and liquid flow rates. The distributor tray flow nozzle promote high catalyst utilisation by providing uniform gas-liquid distribution with high liquid dispersion and superior surface coverage. They also provide intimate mixing and heat transfer between gas and liquid phases which supplements mixing box performance. Flow nozzles are tolerant to distributor tray out of levelness and agitation of the liquid surface, so performance does not degrade if solids accumulate or tray segments warp over time.

This refiner has historically taken a conservative approach to the application of new technology. It was important that CLG could demonstrate prior experience with similar installations. Isomix internals were developed circa 2003, commercially proven in Chevron units from 2003-2008 and commercially proven in licensed units since 2008.

The unit performance post-upgrade to Isomix internals has exceeded expectations for this refiner. The benefits achieved are:

- Direct temperature control of all catalyst bed temperature sensing points (inlet and outlet), with no hot or cold spots even at high quench gas rates
- Excellent catalyst bed temperature profile control, with the ability to operate completely flat (equal average bed outlet temperatures), which is desired to maximise product selectivity and cycle length
- Reduced catalyst bed radial temperature spreads to 1°C maximum at the inlet and outlet of all beds, even at high catalyst bed axial temperature rise
- Increased volume expansion including a 6% increase in recoverable middle distillate (jet/diesel)
- Increased cycle length by 12 months, from three years to four years (estimated after three-plus years on-stream)

Figure 1 shows the catalyst bed inlet and outlet radial temperature spread over time for Bed 3. This bed has the highest axial temperature rise and quench gas flow rate, and showed the worst radial temperature spread and quench gas maldistribution prior to the upgrade. The improved performance is representative of all beds following similar installations. Control console data are shown in Figure 1. Point by point field surveys conducted at start of run confirmed that the actual radial temperature difference for this bed and all other beds was 1°C maximum spread at all levels.

For more information: BSRI@chevron.com

---

**The distributor tray flow nozzles promote high catalyst utilisation by providing uniform gas-liquid distribution**

Recent cooperation between Clariant and Siemens Fuel Gasification has resulted in a new sour gas shift (SGS) process and catalyst for coal to chemical applications, which present significant end user advantages in terms of cost, efficiency, safety, and feedstock flexibility.

One of the main challenges in SGS technology is to avoid temperature run-away along the reactors. This is especially true for dry feed gasification technologies with carbon monoxide (CO) concentrations of more than 60 vol% (dry) in the syngas. Traditionally, there are two techniques used to avoid this. The first is the addition of excess steam to raise the steam to gas ratio in the syngas. Traditionally, there are two techniques used to avoid this. The first is the addition of excess steam to raise the steam to gas ratio in the syngas. The second is partial condensation of water to lower the steam to gas ratio. In either method, adjusting the steam concentration in the gas reduces the equilibrium temperature of the shift reaction, thereby avoiding undesired and highly exothermic methanation as a side reaction.

The new SGS technology developed by Clariant and Siemens Fuel Gasification uses a completely different, more efficient approach to avoid temperature run-away reactions; the temperature is controlled by a
DigitalRefining.com is already the most extensive source of freely available information on all aspects of the refining, gas and petrochemical processing industries, providing a constantly growing database of technical articles, company literature, product brochures, videos, industry news, industry events and company information.

Visit DigitalRefining.com to see what content is relevant to you
catalyst. Based on Clariant’s ShiftMax 821 catalyst, the new technique enables a simple, once-through process, which requires no further adjustment of the exit gas from the gasifier for temperature control. The simplified layout also uses smaller and fewer reactors. Furthermore, the system offers greater feedstock flexibility due to its entrained flow Siemens Fuel Gasifier, which is able to produce syngas from a wide range of fuels, even for low ranks of coal.

The new technique can handle various steam to gas ratios as well as high carbon monoxide content in the gas. This results in improved availability and reliability in the whole process. Because of steam independent control of the exothermal reaction, the process is inherently safe.

Through optimisation and simplification of total plant concepts, the new SGS technology significantly decreases total capital cost for coal to chemical and IGCC (integrated gasification combined cycle) applications. Compared to conventional sour gas processing, the new solution reduces capital expenditure for the costs with up to 30% lower catalyst volume. Hence, it offers substantial financial benefits, particularly for large scale applications.

The ShiftMax 821 catalyst has undergone testing at Clariant’s R&D laboratories in Louisville, Kentucky, and its performance has been verified in a large scale coal to methanol unit. After three years of operation, the unit still demonstrates very high performance.

In addition to joint development of the new SGS technology, the agreement between the two companies appoints Clariant as the exclusive catalyst supplier for all Siemens gasification integrated SGS projects. The collaboration covers all global projects. However, commercialisation will focus on China – the region with the highest growth rate of coal to chemical projects. The partners’ first large scale plant is expected to go online in 2016.

For more information: HansGeorg.Anfang@clariant.com

Ceramic extends air distributor life

By switching from stainless steel to a ceramic construction based on refractory grade alumina bonded silicon carbide for its FCC air distributor nozzles, a refiner expects a significantly extended lifetime for the distributor nozzles in severe operating conditions.

Within a FCC unit, there are a number of different types of air/steam rings. In each of these there are small nozzles that distribute air over the grid, which creates the fluidised bed. These FCC air distributor nozzles are subjected to high temperature, high velocity, erosive environments. To function in this harsh environment, FCC air distributor nozzles have historically been fabricated from a variety of erosion-resistant metallic materials. While these materials are proven effective at reducing rates of erosion, by their nature, they do not perform well in sliding abrasion or at elevated temperatures. As such, they pale in comparison to most ceramic bodies. Ceramic materials are widely accepted and proven to be more resistant to erosion than metallic materials at acute angles of impingement. The characteristics that impart erosion resistance also tend to make these materials suited for nozzle applications that rely on consistent orifice diameters for performance and reliability.

In an FCC air grid, the nozzle diameters set the velocity of air exiting the nozzle. Designers engineer specific orifice diameters that minimise catalyst attrition while preventing catalyst from entering the nozzle. If the orifice in the nozzle erodes and becomes larger than designed, a scenario could develop where the pressure drop decreases, causing catalyst fines to re-enter the nozzle leading to accelerated wear and ultimately grid failure. Nozzle length is also a critical dimension in nozzle design, and it is set based on the nozzle diameter. It is important for the nozzle to be long enough to allow the air/steam passing through the restriction orifice to spread across the entire grid. If the tip of the nozzle erodes, this length is sacrificed and air distribution across the bed is diminished. This can ultimately lead to reduced catalyst recovery.

It is important that refineries step away from traditional metallic solutions and embrace ceramics

Over the years, many metallic and ceramic materials have been tried in grid nozzles, all with varying results. The life of these various materials has been quite inconsistent, from six months up to 20 years. As turnarounds grow further apart and the need to stay in operation becomes ever more vital, the median life of the grid nozzles must be extended. It is therefore important that refineries step away from traditional metallic solutions and embrace ceramics.

One such refiner did that recently. Based on 10+ years of life that a sister plant experienced with ceramic air grid nozzles, the refiner converted its current 304H stainless steel nozzles over to ceramic, in this case Blasch’s Altron.

Altron is a refractory grade alumina bonded silicon carbide that exhibits the wear resistance generally seen in fully dense technical ceramics, which can be subject to catastrophic failure from thermal shock due to sudden swings in temperature. This material can be cast into precise, intricate nozzle shapes that require no finish machining. Coupled with an engineered welded assembly, the ceramic/metal nozzle can be welded to the grid with ease. Thermal expansion allowance, sealing and tolerance control have all been thought out with each nozzle design. Once installed, the Altron material can take the full brunt of the erosive wear and high temperatures. Orifice diameters and nozzle length maintain their geometry throughout the life of the FCC campaign giving refiners the ability to hit their financial performance objectives.
NAVIGATE NEW TRENDS – ATTEND AFPM MEETINGS

The global energy landscape is rapidly changing. Growth in production is leading to changes in technology, planning and management at all levels. Gain a competitive advantage. Come to 2015 AFPM Meetings to hear about the latest developments impacting our industry.

**Annual Meeting**
San Antonio, TX
March 22 – 24

**International Petrochemical Conference**
San Antonio, TX
March 29 – 31

**Security Conference**
New Orleans, LA
April 13 – 15

**Labor Relations/ Human Resources Conference**
New Orleans, LA
April 16 – 17

**National Occupational & Process Safety Conference and Exhibition**
Austin, TX
May 12 – 13

**Reliability & Maintenance Conference and Exhibition**
Austin, TX
May 19 – 22

**Board of Directors Meeting**
(Paid registration only)
Park City, UT
September 20 – 22

**Q&A and Technology Forum**
New Orleans, LA
October 4 – 7

**Environmental Conference**
Salt Lake City, UT
October 18 – 20

**International Lubricants & Waxes Conference**
Houston, TX
November 12 – 13
Once installed, Blasch’s Altron FCC air distributor nozzles will far exceed the turnaround time on the cat cracker which will allow the reliability engineers to focus on other areas of the plant.

For more information: LGicewicz@blaschceramics.com

### Active steam trap management

An oil refinery in Texas was experiencing a high failure rate in its 4790-strong network of steam traps. The refiner was also experiencing water hammer problems caused by the accumulation of condensate and freezing sulphur lines, caused by flooding in the tracing system. Eventually, losses were so high that the plant management team called upon Spirax Sarco to help them reduce their costs.

A thorough steam trap audit carried out by our Spirax Sarco’s Energy Services Group revealed several problem areas:

- Improperly installed and leaking steam traps
- Incorrectly specified traps, unsuitable for their applications
- Freezing sulphur product caused by poor drainage of process condensate
- Water hammer
- Blowdown wastage (a potentially valuable source of recoverable heat)
- Steam turbine inefficiencies.

By replacing failed steam traps and putting in place a steam trap management programme, Spirax Sarco resolved most of the problems experienced by the customer, improving process efficiency and reducing energy losses.

According to the site operations manager, the audit programme has been in effect for several years and has resulted in significant steam savings. In addition, Spirax Sarco has carried out a detailed steam leak survey and an air/nitrogen leak survey, identifying additional annual savings of $160,000 and $460,000 respectively and has managed the steam trap population, leaving the customer to focus on the process.

Key benefits of the project include:

- Savings of almost $800,000 in the first year alone after implementing a steam trap audit programme. Within five years this figure had reached $4.7 million
- Resolved the problem of freezing sulphur lines by replacing incorrectly specified steam traps with versions more suitable for the application
- Identified potential annual savings of over $900,000, by recommending the replacement of the damaged boiler blowdown heat recovery system (which was dumping valuable, hot blowdown to the sewer) with a packaged heat recovery system
- Reduced the annual steam trap failure rate from 5.5% to 1.5% within five years
- Eliminated water hammer problems caused by a leaking high pressure steam trap by identifying missing or cold (malfunctioning) steam traps.

For more information: Greg.Ferkin@uk.spiraxsarco.com

---

### Optimised loading of naphtha hydrotreaters

A US refiner asked Criterion to help reduce the frequency of catalyst changeouts and reduce overall cost without sacrificing unit throughput on their two naphtha hydrotreating units (NHT). The unit cleans up coker naphtha feed for the reforming unit so the ability to stretch the catalyst cycle life beyond the current eight months per reactor has a direct impact on profitability. As the incumbent catalyst supplier for the unit, Criterion focused on quickly reviewing the operating data and current set-up.

Each hydrotreating unit has two single-bed reactors in series. The unit configuration provides the flexibility to change which reactor is in the lead position, leaving the alternate reactor as the lag. This flexibility also allows the unit to isolate a reactor while the other remains in service as needed. The primary method of deactivation for these reactors is silicon poisoning, which is very common in this service.

The loading profile prior to Criterion’s optimisation (see Figure 1) was to load each reactor in series with silica trap catalyst (MaxTrap [Si] in this case) followed by an active denitrification catalyst to balance activity with poison control, thus setting the cycle life. After about eight months, the lead reactor would be deactivated from poisoning. The operators would then exchange the lead-lag positions of the reactors to facilitate a reload of the spent reactor. Operation would continue in this manner until the reactor deactivated on poisoning cycling lead/lag reactor positions again, completing a full reload in a 16-month time frame. Although this scenario provided quality naphtha feed, the duration was such that the expense was not falling into the capital spend 100% of the time. Additionally, the operating scheme created a percentage of unit operation loss that categorised the unit out of the top quartile bracket.

Criterion evaluated several catalyst loading options and concluded that obtaining the maximum cycle life required the two reactors to be operated in series with...
Russia & CIS Oil & Gas Executive Summit

19 & 20 FEBRUARY 2015, DUBAI

Join the Top Executives
Shaping the Industry of this Key Region

Over 300 top oil & gas leaders, consultants, regulators, financiers, lawyers, licensors & solution providers.

Over 30 enlightening, inspiring presentations & engaging discussions on key issues like:

- Market Trends - Global & Regional Outlook
- Major Challenges facing Russian & CIS Refiners & Petrochemical Companies
- Regulations & their Industry Impact
- Long Term Strategic Planning in Volatile Market Environment
- Update on Large Scale Modernisation Plans - Major Current & Planned Projects
- Project Financing: Strategies to Access Capital
- Achieving Operational Excellence
- Improving Organisational Structure
- Leadership Strategies Discussions

The Executive Summit will be held in parallel with the 6th IGTC - International Gas Technology Conference 2015 at the same venue.

WWW.EUROPETRO.COM  |  MARKETING@EUROPETRO.COM  |  + 359 2 859 41 57
an optimised loading scheme to facilitate longer cycles and fewer changes. Configuration changes meant that the lead reactor had a primary function of poison control, leaving the lag reactor as the activity reactor for denitrification. Compared to the existing loading scheme, the new loading scheme provided substantially more poison control catalyst in the lead reactor. With the unit run length controlled by feed silicon poisoning, using Criterion’s MaxTrap[Si] catalyst extended the cycle life beyond 12 months. While the MaxTrap[Si] lead reactor is changed out, the configuration allows the lag reactor to remain in service. Once reloaded, the reactor repositions itself in the lead and operation continues.

In this new scenario, the lag reactor does not reach maximum capacity on Si poison for several lead cycles. The timing is synchronised to allow both reactors to be shut down in sequence and the lag reactor catalyst is changed along with the lead on the third or fourth change, depending on poison levels in the feed slate. When this occurs, the scheme provides again for uninterrupted operation while both reactors are reloaded. The lead reactor containing MaxTrap[Si] is unloaded first and reloaded as the lag reactor. This configuration consists of Criterion DN-140 followed by Criterion’s Ascent DN-3531 while the current lag reactor remains in service (see Figure 2). Once the lead reactor is reloaded, it is then switched into service while the lag reactor is reloaded as the lead reactor with MaxTrap[Si] catalyst. When loaded, this new lead reactor is put into service to restart the cycle scheme. This loading methodology ensures flow to the unit is not interrupted and product quality is not compromised.

Utilising the new loading scheme, the refiner benefits by achieving less frequent catalyst changeouts and lower fill costs. The lead reactor is expected to achieve a cycle length of 12 months, while the lag reactor is expected to achieve a cycle length of 36 months. The majority of the catalyst purchased and loaded is MaxTrap[Si] in the lead reactor, which has saved in fill
Valve control for reciprocating compressors

In a pilot study, Neumann-Esser (NEA) demonstrated that a fast-switching clearance pocket valve controlled by process gas is a highly efficient solution for reciprocating compressor mass flow adjustment. The company says that its Bluepocket design provides the opportunity to fit or even retrofit existing compressors relatively easily. The add-on system does not need any auxiliary hydraulic equipment, which is not allowed in some applications. It is also not necessary to measure intricately the crank position. In the pilot study, process gas was successfully used to control the valve’s switching points under all operating conditions. Feedback from early installations reflects significant energy savings.

Mass flow control using clearance pockets is one of the most energy effective means of adjusting compressor performance. Solutions using fixed clearance pockets are common in this context. However, these standard options enable only a stepwise mass flow control, whereby throttling the mass flow depends on the compressor stage pressure ratio. Clearance pockets are also used for stepless mass flow regulation using a

manually operated piston for setting the clearance pocket.

If this variable pocket solution is applied, it is possible to insert a mechanical drive and to connect it to a process management system. However, such an approach would be highly complex and could only be implemented with great effort, says NEA.

The new method uses pressure control to set the valve switching point. Pressure control enables the activation of the clearance pocket at lower or higher pressure. In both cases, the switching pressure of the clearance pocket valve is depending on the control chamber pressure or rather the control pressure.

Control pressure is the actuating variable for adjusting reciprocating compressor mass flow. Hence, control pressure must be adjusted in order to change the operational point. If the operational point is to be maintained, control pressure must be kept at a specified level. Adjustment or maintenance of control pressure is effortless with process gas as the control medium. The control chamber connects to the cylinder’s suction side or control side using solenoid valves, depending on whether control pressure is to be reduced, maintained or increased.

Standard approaches for a pressure monitoring system for the control chamber include pneumatic or solenoid valves, a pressure sensor and a control circuit. The clearance pocket valve is a novel development whose requirements are basically equivalent to those of normal compressor valves:

- Fast operation and short reaction time
- High operating life
- Low pressure loss for higher compressor efficiency
- Low additional fixed clearance for high volumetric efficiency at maximum compressor load.

These requirements are contradictory in part because short reaction
times and high durability require low valve lifts and, on the other hand, low pressure loss needs a large cross-sectional valve area. The answer to these requirements is a valve design which is very similar to the familiar poppet valves. Figure 1 shows the design of the new clearance pocket and these valves.

The compressor design must be adapted to the new conditions; rod loads, load reversals for the crossheads and so on must be rechecked. The static and dynamic stress distribution must be recalculated using the finite element method (FEM) and simulated.

To ensure the durability of the valve elements, their dynamics must be checked precisely. Here, low impact velocities are essential in order to ensure a long service life. Therefore, the permissible valve lift was determined by simulating valve dynamics. Since there are different operating points, the simulation of dynamics must be implemented under the respective conditions. The simulation displays that the higher the pressure fluctuation in the cylinder, the higher the impact velocity of the valve elements. Figure 2 shows a graph of the cylinder pressure over the crank angle at 100% load including pressure fluctuation. The valve's switching points which provide the highest impact speed occur when opening and closing the poppet valves. The valve elements consist of compressor valve materials which have been proven in time and time again, in particular for manufacturing poppet valves. The valve lift is designed in order to avoid exceeding the permissible impact velocity range, irrespective of the operating status.

For more information: martina.frenz@neuman-esser.de

Meeting gasoline sulphur regulations

In the mid-2000s, Japan committed to lower gasoline sulphur. As early adopters of more stringent gasoline quality regulations, Japanese refiners faced challenges similar to those that US refiners face today in meeting Tier 3. Since 2005, Japanese refiners have utilised Grace GSR products to maintain compliance, observing 35-40% reduction in the gasoline sulphur/feed sulphur ratios allowing them to meet the 10 ppm gasoline specifications.

The new Tier 3 ultra-low sulphur gasoline regulations have the potential to create further challenges for US refiners. Tier 3 regulations require the reduction of the average gasoline pool sulphur level to ≤10 ppm with an 80 ppm cap by January 2017, compared to the current limit of ≤30 ppm with an 80 ppm cap. Compliance will require adjustments to operating strategies and possible capital investment. With FCC gasoline making up approximately 36% of the gasoline pool, the average FCC gasoline will have to be controlled at or below 25 ppm. In-unit reduction of FCC gasoline sulphur with GSR technologies create a variety of opportunities and options for refiners to drive profitability while meeting the new Tier 3 gasoline requirements, says Grace.

These clean fuels solutions create economic advantages around feedstock and gasoline blending and asset optimisation, according to the developer. The refiner can adjust operating conditions in order to preserve octane, maximise throughput or extend pre-treatment and/or post-treatment hydrotreater life. Many refiners have utilised the technologies to create operating flexibility during hydrotreater outages and generate gasoline sulphur ABT credits to defer capital investment.

GSR technologies have been used in more than 100 FCC applications worldwide delivering 20-40% sulphur reduction in FCC naphtha in both full and partial burn operations. The additive technologies are used at a 10-25% loading in inventory, whereas the catalyst are a customised 100% drop-in replacement for a base catalyst. The longest continuous application is now 12 years.

For more information: julie.ellis@grace.com

Crude oil analysis by NMR

Online analysers based on nuclear magnetic resonance (NMR) technology enable accurate correlation with laboratory analyses, according to Modcon.

In order to reduce the cost of a crude oil blend, refineries are obliged to blend maximum quantities of low cost crude oils with sweet crudes. Incorporating heavy crudes has not only the benefit of reducing CDU feed costs but also increases the capacity of heavier distillates like gasoil.

Crude blending can be performed by in-tank blending or in-line blending. Especially in the case of in-line blending continuous measuring of the physical properties of the crude oil feeds provides a platform for directly mixing different crudes feeds, resulting in a blend which continuously conforms to the requested specification.

NMR process analysers have the advantage of being non-optical analysers and therefore applicable in transparent and opaque fluids alike. NMR analysers are molecule specific and they make it possible to distinguish qualitatively and quantitatively between the different chemical structures of the molecules.

Physical properties and NMR spectra are the outcome of the presence of different molecules in a crude blend. Correlating them enables a refiner to quantify the properties of crude oil: API Gravity, true boiling point yield, aromatic content, olefin content, pour point, water, total acid number, sulphur and other parameters.

High accuracy in the correlation between results obtained by NMR process analyser and in the laboratory characterises the new generation of NMR process analysers. NMR magnets are sensitive to temperature differences, hence early generations of NMR process analysers were sensitive to temperature differences due to the accumulation of excessive heat by electronics and heat conducting measuring probes. In the new generation of NMR process analysers, the overall design excludes any accumulation of heat in the magnet or in its surroundings by uncontrollable fluctuations, such as heat transformation by electronics, the magnet itself and
by the material, which is measured. This increases its stability to heat fluctuation by some eight degrees. This means that any required heating of the crude oil is possible, without affecting the analytical results, as long as a temperature deviation of ±10°C is maintained.

Taking into account the time required for laboratory analyses, the cost to perform crude oil assays, or the purchase and maintenance of SimDist justify the use of NMR process analysers for crude oil analysis and in CDU feed monitoring processes, it enables precise monitoring of the quality of blend production, or of the crude oil entering the CDU.

Thanks to Aspect imaging for their cooperation in NMR analysing crude oils.
For more information: ronnym@modcon-systems.com

Pilot ignition for zero flaring

With ever-increasing environmental regulations and a continued focus on safety by the oil and gas industry, the criticality of highly reliable and effective pilot gas ignition systems has never been more important, says Aereon. Failure of the ignition system can cause environmental excursions with resultant fines, reduction in production throughput, bad company publicity or, even worse, a safety issue that causes injury or death to the site workers.

Flare Industries, an Aereon company and supplier of flare systems, has over the last 30 years developed proprietary pilot ignition systems. One of these was developed for ‘zero flaring’ or for operators who cannot, or prefer not to, burn continuous pilot gas.

The Continuum Ignition System requires no pilot gas, instead utilising a slipstream of combustible waste gas which is ignited with a high voltage electric arc, creating the ‘pilot flame’ which then ignites the bulk of the waste gas like a conventional pilot. This arc usually occurs every 20 seconds for a two second duration (timing is adjustable), 24 hours per day, for continued waste gas combustion without the need for additional and sometimes costly continuous pilot gas. This helps not only reduce the extra emissions generated from the pilot gas, but also improves combustion integrity as the pilot routinely ignites any gas that is present in the flare system.

Flare Industries has added its Mechanical Retractable Package to the system. This allows the operator to move the pilot system from flare tip to ground level, for ground level access to the key system components when required. This can also save costs through the elimination of fixed ladders and platforms usually required with fixed pilot systems, according to Aereon. With an optional solar package, the ignition system can also be used in remote locations that do not have ready access to electrical utilities.

For more information: tlyons@aereon.com

Frankfurt am Main · 15 – 19 June 2015

ACHEMA 2015

➢ World Forum and Leading Show for the Process Industries
➢ 3,800 Exhibitors from 50 Countries
➢ 170,000 Attendees from 100 Countries

Be informed.
Be inspired.
Be there.

www.achema.de
<table>
<thead>
<tr>
<th>Company</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACHEMA 2015</td>
<td>151</td>
</tr>
<tr>
<td>Aereon</td>
<td>89</td>
</tr>
<tr>
<td>Aerzener</td>
<td>67</td>
</tr>
<tr>
<td>AFPM</td>
<td>145</td>
</tr>
<tr>
<td>Air Liquide</td>
<td>IFC</td>
</tr>
<tr>
<td>Air Products and Chemicals</td>
<td>54</td>
</tr>
<tr>
<td>Albemarle Catalysts Company</td>
<td>IBC</td>
</tr>
<tr>
<td>AMACS Process Tower Internals</td>
<td>104 &amp; 107</td>
</tr>
<tr>
<td>Ariel Corporation</td>
<td>60</td>
</tr>
<tr>
<td>Axens</td>
<td>OBC</td>
</tr>
<tr>
<td>BASF Corporation, Catalysts Division</td>
<td>11</td>
</tr>
<tr>
<td>Bilfinger Water Technologies</td>
<td>71</td>
</tr>
<tr>
<td>Blasch Precision Ceramics</td>
<td>98</td>
</tr>
<tr>
<td>Bryan Research &amp; Engineering</td>
<td>96</td>
</tr>
<tr>
<td>Burckhardt Compression</td>
<td>57</td>
</tr>
<tr>
<td>CB&amp;I</td>
<td>7</td>
</tr>
<tr>
<td>Chevron Lummus Global</td>
<td>9</td>
</tr>
<tr>
<td>Chromalox</td>
<td>94</td>
</tr>
<tr>
<td>Clariant</td>
<td>40</td>
</tr>
<tr>
<td>CRI Catalyst</td>
<td>30</td>
</tr>
<tr>
<td>Criterion Catalyst &amp; Technologies</td>
<td>4</td>
</tr>
<tr>
<td>Delta Valve</td>
<td>117</td>
</tr>
<tr>
<td>DigitalRefining.com</td>
<td>143</td>
</tr>
<tr>
<td>Emcor Industrial Services</td>
<td>121</td>
</tr>
<tr>
<td>Enersul</td>
<td>74</td>
</tr>
<tr>
<td>ERTC 19th Annual Meeting</td>
<td>136</td>
</tr>
<tr>
<td>EuroPetroleum</td>
<td>147</td>
</tr>
<tr>
<td>Everlasting Valve Company</td>
<td>86</td>
</tr>
<tr>
<td>ExxonMobil Research and Engineering Company</td>
<td>118</td>
</tr>
<tr>
<td>Foster Wheeler</td>
<td>123</td>
</tr>
<tr>
<td>Four Quest Energy</td>
<td>25</td>
</tr>
<tr>
<td>GE Water &amp; Process Technologies</td>
<td>93</td>
</tr>
<tr>
<td>Grabner Instruments</td>
<td>85</td>
</tr>
<tr>
<td>Grace Catalysts Technologies</td>
<td>17</td>
</tr>
<tr>
<td>Graphite Metallizing Corporation</td>
<td>101</td>
</tr>
</tbody>
</table>

For more information on these advertisers, go to [www.ptqenquiry.com](http://www.ptqenquiry.com)
Albemarle has extensive experience in designing catalyst systems to maximize volume swell. Commercial experiences validate the benefits of using Nebula® and STAX® to realize economic gain from ULSD hydrotreaters. Albemarle’s Nebula catalysts deliver the highest denitrogenation and hydrogenation activity of any base metal hydrotreating catalyst. When combined with our STAX technology to balance unit objectives with capabilities, hydrogen addition over the catalyst cycle can be optimized based on the limitations of the unit.

For more information on Albemarle catalysts for maximizing volume swell or the many products and services Albemarle provides, CALL (281) 480-4747 TODAY OR VISIT WWW.ALBEMARLE.COM
Stimulate the heart of your hydroprocessing unit

Impulse™, the catalyst technology that combines the stability you recognize with the activity you need

Single source ISO 9001 • ISO 14001 • OHSAS 18001

www.axens.net