REFINERY OPERATIONS

Engineering Solutions, Maintenance, Reliability, Automation and Equipment Relevant to Refinery Processing and Operations

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FEATURE: Grace Experts Discuss Solutions for Upgrading "Processed" Feedstocks to ULSD

Reports published over the past two years by Grace Davison authors have focused on challenges encountered when upgrading light cycle oil (LCO) and other opportunity feedstocks to diesel, particularly ultra low sulfur diesel (ULSD). This coincides with plans by numerous refiners who had planned on increasing hydrotreating complexity when distillate margins were high relative to gasoline margins.

In spite of today's less lucrative distillate margins (relative to 18 months ago), refiners are still going forward with plans to increase diesel production. For example, at the May 24 NPRA Maintenance and Reliability Conference, one independent refiner located along the Gulf Coast noted that they are planning to commission a new diesel hydrotreater early this summer with the intentions of being able to upgrade higher volumes of LCO to ULSD. This will be followed up with a major FCCU and alkylation unit turnaround in the first quarter of 2011 (1Q2011).

Going back to early 2009, A paper presented by Grace Davison's Brian Watkins and Chuck Olsen (AM-09-78) at the NPRA 2009 Annual Meeting focused on exploiting the use of LCO and other opportunity feedstocks towards ULSD production. This was followed up with a paper at the NPRA 2010 Annual Meeting that discussed maximizing the distillate pool via increased LCO hydroprocessing.[1,2]

Some of these opportunity feedstocks, having already been processed through conventional refinery processes, may pose unexpected challenges to refiners wishing to incorporate them into the distillate pool.

Some of these streams have proven to be significantly more difficult to process, underscoring the fact that it is important to understand the potential impacts of processing new feed streams in order to avoid unpleasant surprises.

The Watkins and Olsen authors point out how FCC LCO and coker diesels have long been used as feed components combined with a straight run (SR) feed source to produce ULSD products. The quality of the LCO varies with distillation range, and depends on the severity of the FCC feed pre-treatment as well as on the conditions in the FCC and FCC catalyst employed. A common element in LCO is a very high concentration of polynuclear aromatic (PNA) compounds relative to other feeds as shown in Table 1 that was previously published in the 2010 NPRA paper by Watkins, Krenzke and Olsen (AM-10-166).

The Watkins et al. paper from 2009 (AM-09-78) discusses how synthetic diesel material is often initially processed by either a coker or ebullating bed (EB) residue hydrocracking unit, and then processed through a hydrotreater or hydrotreater /hydrocracker combination. These hydrocracking units tend to operate at severe conditions in conjunction with high hydrogen partial pressures. At these conditions, removal of all the easy, less refractory sulfur is readily achieved, and the majority of the multi-ring aromatics are saturated. This leaves a product which is relatively low in sulfur and PNAs, and when added as feed to a ULSD unit gives rise to a surprisingly difficult feedstock to process.

The diesel products from an EB unit, a fixed-bed (FB) unit and the synthetic crude diesel provide very different sulfur distribution patterns compared to the SR feed and LCO shown in a detailed diesel feedstock analysis from the Watkins et al. AM-09-78 paper. It shows how almost all of the sulfur species in those feeds are multi-substituted dibenzothiopehenes, the so-called hard sulfur species (see Table 1 on page 2).

Watkins et al. point out how the species groupings from sulfur speciation using a GC-AED technique indicate little about what the actual molecular structure is since the basic technique separates out the sulfur based on boiling point distribution. The sulfur molecules left in these previously treated

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feeds have already been processed once in a high temperature, high pressure hydrotreating application. Those conditions easily remove the majority of sulfur molecules and leave only those sulfur species that are multi-ring, sterically hindered molecules and other aromatic nitrogen compounds.

It is these species that require a greater level of saturation or ring opening before the nitrogen or sulfur can be removed. It is likely for there to be very low concentrations of multiple ring, partially saturated compounds that need to be more fully saturated in order to remove the sulfur, and this is enough to make it more difficult to produce 10 ppm sulfur product from such feeds.

When considering the use of synthetic crudes, an understanding of the upstream processing is important. Watkins et al. point out that production of synthetic fuels involves a combination of several processes in order to accommodate downstream processing. These upstream processes include coking or an EB residue operation, followed by a hydrotreating or hydrocracking operation in order to produce a lighter grade material.

These products are then blended in with other heavier materials as a diluting or cutting stock and sent downstream as synthetic crude. The synthetic diesel used in this published work is taken from a product diesel cut from a synthetic VGO hydrocracker. Watkins et al. showed the activity difference between the straight-run (SR) and the blended SR/synthetic diesel, noting that at higher product sulfur, the two feedstock's respond fairly similar to each other.

Table 1: Cetane Number of Pure Compounds

	Compound	Formula	Cetane Number
Paraffins	n-Decane	$C_{10}H_{22}$	76
	n-Pentadecane	$C_{15}H_{32}$	95
	n-Hexadecane	$C_{16}H_{34}$	**100**
	n-Eicosane	$C_{20}H_{42}$	110
Isoparaffins	3-Ethyldecane	$C_{12}H_{26}$	48
	4,5-Diethyloctane	$C_{12}H_{26}$	20
	Heptamethylnonane	$C_{16}H_{34}$	15
	8-Propylpentadecane	$C_{18}H_{38}$	48
	7,8-Diethyltetradecane	$C_{18}H_{38}$	67
	9,10-Dimethyloctadecane	$C_{20}H_{42}$	59
Naphthenes	Decalin	$C_{10}H_{18}$	48
	3-Cyclohexylhexane	$C_{12}H_{24}$	36
	2-Methyl-3-cyclohexylnonane	$C_{16}H_{32}$	70
	2-Cyclohexyltetradecane	$C_{20}H_{40}$	57
Aromatics	1-Methylnaphthalene	$C_{11}H_{10}$	0
	n-Pentylbenzene	$C_{11}H_{16}$	8
	Biphenyl	$C_{12}H_{10}$	21
	1-Butylnaphthalene	$C_{14}H_{16}$	6
	n-Nonylbenzene	$C_{15}H_{24}$	50
	2-Octylnaphthalene	$C_{18}H_{24}$	18
	n-Tetradecylbenzene	$C_{20}H_{34}$	72

As the application becomes more demanding, the required reactor temperature increases dramatically for the synthetic diesel feed as compared to the SR feed. The blended feed requires more than 25°F higher temperature relative to the SR to achieve ULSD sulfur levels. No doubt, many refiners who planned on increasing ULSD production to meet future market requirements may encounter some unexpected processing challenges.

1. Watkins, Brian and Charles "Chuck" Olsen, "Distillate Pool Maximization by Exploiting the Use of Opportunity Feedstocks Such as LCO and Synthetic Crudes," Grace Davison, NPRA paper #AM-09-78.

2. Watkins, Brian, David Krenzke and Charles "Chuck" Olsen, "Distillate Pool Maximization by Additional LCO Hydroprocessing," Grace Davison, NPRA paper #AM-10-166. ■

Refining Technology

Changes in FCCU Operating Strategy

Many refiners are considering a "mid-course" change in FCCU operating strategy to compensate for reduction in refinery utilization rates. While some facilities are running at 100% utilization rates, utilization rates in regions such as North America and Europe are averaging less than 85%. Changes in plant operating strategies are therefore required to improve efficiency, primarily to the FCCU.

FCCUs that went through a major revamp and start-up during the 2006-2008 upcycle were designed to operate at maximum feed rate with a targeted four- or five-year turnaround (TAR). However, it was noted in a paper presented at the March 2010 NPRA Annual Meeting in Phoenix that it may be worthwhile to consider the advantages of an early shutdown (*AM-10-174: "FCC Opportunities at Lower

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Throughputs," Steve Gim, et al., The Shaw Group). In the Gim et al. paper, the economics of an early shutdown for implementation of technology modifications were evaluated, involving:

- Feed system
- Reactor design
- Riser termination technology
- Stripper design
- Regenerator design.

Some of the important points noted in this paper are that operating strategies for much of the world's 16 million b/d FCC capacity should consider adjusting to the higher reactor temperatures encountered at the top of the reactor riser (about 1000°F [538°C] or higher). In most cases, these higher reactor temperatures are encountered as higher resid volumes are being processed through many of these units at the same time that higher volumes of light olefins (e.g., propylene) production are being targeted.

* Shaw Group Authors (NPRA paper AM-10-174) : Steve Gim, CFA, Manager, Financial & Technology Valuation; Warren Letzsch, Senior Refining Consultant; Harvey McQuiston, FCC Program Manager: Chris Santner, Director, Catalytic Cracking Technology. ■

Hydrotreater Depressuring Systems

Depending on market conditions, refiners have run their hydrocracking unit in a variety of modes. For example, engineers at one facility report having run their hydrocracker in vacuum gas oil (VGO) cracking mode in some cycles, and in diesel/light cycle oil (LCO) treating mode in other cycles. Regardless, considering today's growing emphasis on safety and reliability, the issue of installing a reliable automatic and/or remote depressuring system is growing in importance.

It appears that hydrocrackers and most new hydrotreaters incorporate at the very least, remote manual depressuring systems. The higher pressure and more severe hydrocracking operations require the installation of an operational automatic and remote depressuring system to avoid runaway reactions. Other reasons for investing in depressuring systems is that depressuring the recycle loop can be an appropriate response to an external fire.

The ANSI/API Standard 521 suggests that "depressuring for the fire scenario should be considered for large equipment operating at a gauge pressure of … 250 psi … or higher." This is a reason that many relatively low pressure hydrotreating units are equipped with emergency depressuring systems.

Certain licensors of hydrotreating reactors do not design for automatic depressuring of hydrotreaters. For example, one licensor specifies that its designs be equipped with a manually activated depressuring system to lower the unit pressure to 50% of design pressure in 15 minutes. Installation of automatic and/or remote depressuring systems will be discussed in more detail in the *Refinery Operations* "Innovations in Hydrocracking & Hydrotreating Technology," to be published in November 2010. ■

Avoiding Visbreaker Shutdowns

Cleaning a visbreaker bottom circuit in two days is feasible provided that any mechanical cleaning requiring extraction of the heat exchanger bundles is reduced or eliminated. Online chemical cleaning of visbreaking units (VBUs) in less than 48 hours has been documented at several refinery facilities.

In one specific case, a VBU's vacuum section residue storage temperature (outlet of last exchanger leading to IGCC) increased to a level that was leading to an unscheduled shutdown, five months before the unit was scheduled for a turnaround. An unscheduled VBU shutdown would have impacted the entire refinery.

By applying technology from ITW S.r.l. (www.itw.it), the VBU preheat train was cleaned to recover 45°C on residue storage temperature and continue with the unit run until the scheduled refinery turnaround. The technology can also improve furnace inlet temperature (FIT) or debottleneck a unit during the run (e.g., to solve a delta P increase problem). ITW also reported it cleaned a 310 ton/hr VBU with 28 heat exchangers in 36 hours with no waste or emissions generated from cleaning operations.

During the steam-out phase of a unit shutdown, use of a patented chemical will significantly reduce steam-out time (half of the time or lower, as compared to the case with no chemical) and hence refinery downtime. At the same time this chemical will eliminate any noxious odor during steam-out as well as any pyrophoric iron problems. According to ITW's Dr. Marcello Ferarra, "the chemical does not create any emulsion and is biodegradable; therefore allowing condensates to be very easily handled in the refinery's waste water treatment plant."

"We have used this technology for cleaning/degassing/decontamination of CDU, VDU, FCCU, VBU, MEA, DEA , Merox, SWS, ethylene, butadiene, blowdown and fuel gas networks. For example, in a vacuum unit, the main fractionator has been cleaned/degassed/decontaminated in only two days, compared to four days for standard steam-out. The column was safely entered (LEL=0, benzene=0, H2S=0, ammonia=0) by maintenance personnel after only 2.5 days from ITW operations start-up, compared to 6 (six) for standard steam-out," added Ferarra. ■

Unit Automation

Wireless vibration transmitter helps increase plant reliability and safety

Emerson Process Management is helping plants increase reliability of essential rotating equipment with use of the CSI 9420 Machinery Health™ Vibration Transmitter.

This wireless vibration transmitter gives console operators information to avoid a process shutdown or potential safety incident. The predictive diagnostic capability also benefits maintenance personnel, letting them know when rotating equipment needs service.

As a component of Emerson's Smart Wireless solutions, the rugged industrial transmitter connects quickly, easily, and economically to any machine. Through the PlantWeb® digital plant architecture, the transmitter delivers vibration information over a highly reliable self-organizing wireless network for use by operations and maintenance personnel. Configuration, diagnostics, and alerts from the wireless vibration transmitter are available in AMS™ Suite predictive maintenance software. Vibration data is also available to data historians or any control system for trending and analysis with other process parameters. In addition to measuring overall vibration, the CSI 9420 Machinery Health transmitter includes PeakVue™ technology for advanced bearing diagnostics.

Users indicate they can cost-effectively apply this device on a wide range of equipment such as pumps, motors, fans, compressors and many other types of equipment. Benefits from deploying the wireless vibration transmitter go beyond equipment reliability.

Emerson's Smart Wireless solutions extend the PlantWeb architecture to deliver new information access and mobility for improved decision-making and plant performance. The Smart Wireless field solutions integrate smart monitoring instruments wirelessly in a self-organizing mesh network that delivers greater than 99.9 percent reliability by automatically adapting as devices are added or removed, or obstructions encountered. Smart Wireless products are supported and full compliance with the WirelessHART and IEC 62591 standards.

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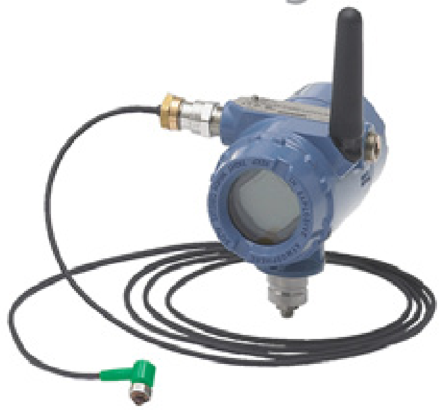

CSI 9420 Machinery Health Vibration Transmitter

Learn more click here.

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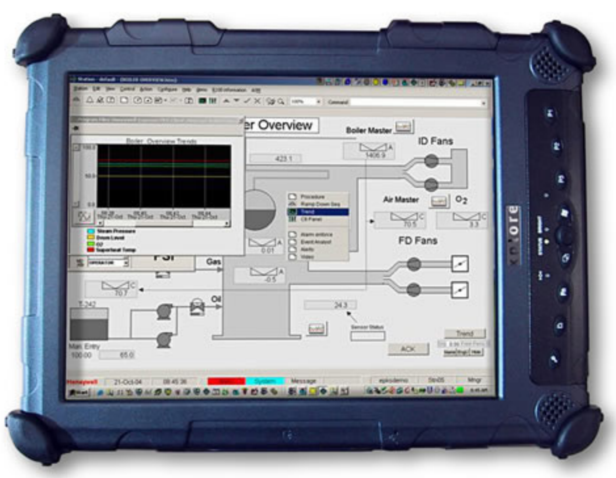
Improving Reliability and Process Efficiency beyond 2010

The recently concluded 2010 NPRA Maintenance & Reliability Conference shows a significant trend where equipment and service providers are increasing the level of automation expertise within their ranks. From suppliers of valves and actuators to suppliers of instrumentation and analytical services, taking a closer look at each of these types of businesses shows the extent to which they have increased their automation capabilities. Faster response times, the ability to keep everyone informed, optimized project efficiency, safer operations, cost control and seamless interfacing between individual unit operations and corporate decision-makers is what is accelerating this trend.

Upgrades to turnaround planning and scheduling software continue to roll out. In most cases, the contract between the licensor and petrochemical facility involves extended periods of training to capture the increasing range of digital reporting and archiving in an auditable framework required by the industry.

In many cases, a technology licensor will partner with an automation supplier that has a demonstrated capability for reducing costs and providing reliable and secure measurement and monitoring solutions for process units ranging from FCCUs and hydrotreaters, to visbreakers and delayed cokers. For example, earlier this year, GS Engineering & Construction, an international construction services company,



Sample screen capture of Experion® PKS automation solution

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Improving Continued

selected Honeywell and its Experion® Process Knowledge Solution (PKS) for a complete automation solution for Qatar Petroleum's Mesaieed refinery.

As the main engineering contractor for Qatar Petroleum, GS Engineering & Construction implemented Honeywell's Experion PKS control platform integrated with the Fail Safe Controller (FSC®) system, an advanced safety platform. According to information available from Honeywell, both GS Engineering & Construction and the refinery benefited from the following:

- Implemented an integrated control and safety system with zero technical issues
- Met and exceeded rigorous schedule and delivered on-spec production a month ahead of schedule
- Simplified project execution with a one-stop solution provider for integrated control and safety system Increased safety and process availability with a unified safety solution
- Improved production and profitability
- Improved access to HART related field data based on full integration into control system.

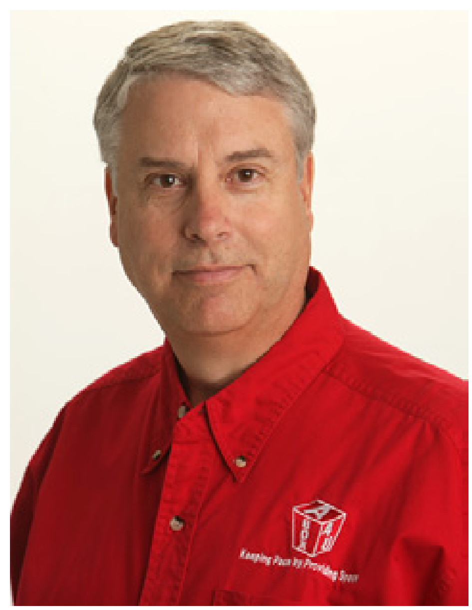
A detailed discussion on the success of this tri-lateral industry cooperation between the refiner, main engineering contractor and Honeywell is beyond the scope of this discussion and should be deferred to information sources such as www.theoptimizedplant.com for further detail.

Finally, one other important area that has emerged in 2010 has been the use of automated solutions to reduce energy consumption by up to 10% and help abate greenhouse gas emissions. These solutions include simulation tools, manufacturing execution systems, advanced process control (APC) applications and emissions monitoring as will be discussed in future issues of *Refinery Operations*. ■

Company Profile

Interview with an Industy Innovator

In an exclusive interview with Refinery Operations, Jeff M. Lange, who is the CEO of blast resistant module (BRM) manufacturer, A Box 4 U, emphasizes reliability and diversity for meeting today's rigorous safety standards in refinery operations:



Refinery Operations: *Considering the safety and reliability emphasis in today's refinery operations, how is A Box 4 U adjusting its product line for the refining industry (e.g., tool sheds, control rooms, etc.)?*

Lange: The petrochemical industry is certainly much more focused on safety & reliability than ever before. More and more regulations are required from us in order to work with our current and new clients. We not only have been adapting our product to stay out in front of those requirements but our procedures as well.

From the very first BRM unit that we built, we have been demanding about the unit being able to exceed the ratings that we stamp on the unit. Our philosophy is that we are saving lives and as the market leader in BRM's we want to set the standard for safety. This includes many things that require education of our clients to understand why our product is different in many ways than the portable office that they were used to in the past.

Regarding procedures, our staff is constantly putting new programs and procedures in place that make us ready when asked for such things by our clients. Some new products that we have developed recently are open multi-section units that provide the client with unlimited open space to meet whatever their needs are for larger size modules. We were the first to develop a specially designed tool crib that handles the flow of workers and product seamlessly.

Refinery Operations: *Can you point out any unique challenges that your company has encountered in the process industry?*

Lange: Ground space is often a limiting factor, so we developed our Quad Pod, which provides for stacking of any of our units to take up half as much physical ground space as conventional units. Extreme climates are often involved with the areas we serve. We have developed units to meet the needs of those environments. We always listen to our clients needs. We like to create exactly what they need to accomplish

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Interview Continued

their particular objectives and overcome the obstacles. That is especially true as we are replacing existing fixed facilities with our modular units that give the client the ability to move those facilities as their needs change in the future, without tearing down an expensive fixed facility and being able to reuse the units at another location.

Refinery Operations: *Some of the most important innovations involving BRMs have evolved from government and military specifications for "in-the-field" BRMs. How are these innovations benefiting the refining industry?*

Lange: As the only provider of BRM's to both the petrochemical industry and the military, we are constantly learning of new improvements and facilities that would improve the efficiency for both of those clients.

Determining solutions to the needs of each client help provide better service and product to our clients, which is a main effort of A Box 4 U.

Refinery Operations: *With mega-refinery projects coming on-line in developing countries like India and China, how do you see their requirements for BRMs evolving? Is your company positioned to be a player in these regions?*

Lange: A Box 4 U is certainly positioned to be a worldwide provider of BRMs. We have delivered many units to countries outside the US already and are in talks with many countries and clients around the world. Safety is not only a concern for the United States.

It is a growing concern for the world. Again, our ability to provide products to the safety and security markets around the world will benefit the refinery and petrochemical markets at the same time.

Refinery Operations: *What motivates you and your staff throughout your organization to provide high quality solutions for the industry?*

Lange: Our whole organization is excited by the fact that we are the market leader in an industry that is just getting started in many ways. We have many opportunities and are focusing on those that need our services first and more urgently.

Talking to new clients each week about how we can serve them in saving lives is very motivating to us, and we take our role extremely seriously. We always do the right thing. ■

Editorial Comments

Adhering to Maintenance Work Scope with Hydrotreating Equipment

Adhering to added hydrotreater unit maintenance work scopes that have been approved requires resources and diligence for tracking and reviewing to ensure that the equipment under scrutiny is inspected by operations personnel. This takes into account scheduled work and extra work that should be listed and checked off for proper line-up.

Concerns with hydrotreater safety and reliability are increasing as more units come on line and are operating across a wider range of operating parameters, including higher H2 partial pressures and higher temperatures towards end-of-run (EOR). For example, in one incident documented on an industry related website, www.h2incidents.org, it was emphasized that when closing valves in a hydrotreater unit shutdown, it should be ensured that they are closed completely (obviously). For this objective, bull plugs must be installed tight enough so that they will not loosen as a result of contraction/expansion occurring during hot and cold cycling and/or compressor vibration. When closing a valve, a valve wrench must be used to synch-up by using force to turn the valve handle a 1/4 turn. When installing a bull plug, a wrench must be used to ensure that the bull plug is tight.

Cognizance of these procedures must involve plant operations and health/safety personnel to develop an operational mechanical integrity checklist to ensure that all mechanical equipment components are addressed.

While no two gas oil hydrotreaters are alike, many of these procedures and checklists have evolved from experience with operating hydrotreaters against a wide envelope of operating conditions and process objectives (e.g., FCCU feed pretreatment, LCO upgrading to ULSD, etc.). For example, at one refinery, a hydrogen leak occurred from a one-inch gate valve on a makeup gas line in a gas oil hydrotreater.

When the leak was discovered, the gas oil hydrotreater unit shutdown procedures were immediately implemented and emergency response was requested. The gas oil hydrotreater unit was fully shut down after about 30 minutes. Shutdown consisted of sufficiently depressurizing the unit and adding nitrogen to allow safe closing of the leaking one-inch gate valve and installation of the associated missing bull plug.

During this event, the one-inch gate valve was found to be open roughly 10% with no bull plug in the valve, allowing the hydrogen to leak to the atmosphere.

The hydrotreater involved in this incident had been re-commissioned 18 months earlier after a company ownership change occurred and had undergone recent maintenance and testing prior to activation for operation. A post-event investigation determined the likely cause of the hydrogen leak was that the one-inch gate valve was not completely closed prior to the start of operation. The investigation

Rene Gonzalez, Editor, Refinery Operations

determined that a possible scenario for the loss of the valve bull plug was expansion and contraction during hot and cold cycling of the unit combined with vibration from a nearby reciprocal compressor over the 18 months since re-commissioning. ■

Editor's note: *Additional detailed information on hydrogen leaks in hydrotreaters and other hydroprocessing units can be found at www.h2incidents.org. The H2Incidents website is a database-driven website intended to facilitate the sharing of lessons learned and other relevant information gained from actual experiences using and working with hydrogen, such as in hydrotreaters, steam methane reformers (SMRs), etc.*

Calendar of Events

JUNE

13-17 Honeywell Users Group Americas Symposium, Phoenix, +1 800 822 7673, www.honeywellusersgroup.com.

21-24 Purvin & Gertz LPG Seminar, Singapore, +1 (713) 331 4000, www.purvingertz.com

23-25 ERTC Training Seminar, "Hydrogen Production by Steam Reforming," London, +44 (0)870 240 8859, www.gtforum.cocm.

27-30 AIChE Process Development Symposium, Lake Ozark, Missouri, +1 800 242 4363, www.aiche.org.

JULY

18-22 ASME Pressure Vessels and Piping, Bellevue, Washington, +1 800 843 2763, www.asme.org.

AUGUST

8-12 ASME International Heat Transfer Conference, Washington, DC, +1 800 843 2763, www.asme.org.

*24-25 NPRA Cat Cracking Conference, Houston, +1 202 457 0480, www.npra.org.

SEPTEMBER

22-24 Euro Petroleum Consultants Ltd 10th Russia & CIS Refining Technology Conference, +44 (0)20 7357 8394, www.europetro.com.

* *Refinery Operations* is sponsoring the 72-page special report, "**Innovations in Fluid Catalytic Cracking,**" to be published in advance of the August 24-25 NPRA Cat Cracking Conference in Houston. Please feel free to contact the editor for submission of articles at +1 713 449 5817 (editor@refineryoperations.com).

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Contact Us

Rene Gonzalez
Editor
Refinery Operations
PO Box 11283
Spring TX 77391
USA
editor@refineryoperations.com
Mobile: +1 713 449 5817
Office: +1 281 257 0582
Fax: +1 281 686 5846
www.refineryoperations.com