Refinery Operations
Engineering Solutions, Maintenance, Reliability, Automation and Equipment

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Controlling Feedstock Contaminants in Diesel Hydrotreating Operations

Improving Unit Performance Requires Strategies for Avoiding Rapid Deactivation of Hydrotreating Catalyst Activity from Contaminants

Common "poisons" affecting hydrotreaters (**Table 1 on page 2**) were discussed in detail during a recent webinar presented by Dave Krenzke, Regional Manager of Hydrotreating Technical Services for Advanced Refining Technologies, LLC (ART).[1]

Higher feedstock volumes contaminated with catalyst poisons such as those listed in Table 1 are being processed in high complexity refining facilities. Many of these hydrocarbons are from sources recently introduced into the global crude market in significant quantities over the past five years. For example, Canadian Synbit and Dilbit crudes will come to make up a significant fraction of feedstocks to North American refineries. North American refiners and their technology partners are just now discovering the challenges encountered with upgrading these "cheap" crudes to ULSD specifications.

In other producing regions such as deep offshore Brazil, preliminary reports indicate that hydrocarbons from the Tepi oil field, which has been called the greatest oil discovery in the past 100 years, may be relatively high in nitrogen content. What has also been noticeable are the new challenges certain refining are facing with the "redistribution" of certain crudes. For example, the heavy Venezuelan crudes (e.g., Merey Crude: 16° API, 11.5 UOP K-factor, 2.7wt% S, 3600 ppm N, etc.) that U.S. Gulf Coast refiners began processing back in the 1980s are finding a new market in emerging refining regions such as India. To be sure, these new high-complexity facilities may nonetheless be unfamiliar with the be unfamiliar with these crudes.

To be sure, the contaminants found in these feeds can be particularly harmful to hydrotreating catalyst activity, such as with ULSD units. In anticipation of the challenges involved in processing these types of feedstocks, there has been a noticeable trend towards designing new diesel hydrotreating units at higher hydrogen partial pressures to compensate for catalyst activity loss from these poisons. Instead of operating at higher H_2 partial pressures, older units can be modified to meet Euro 4 or ULSD targets, for example, with higher catalyst volume and space velocity.

Contaminant Control

In general, silicone (Si) carryover from Si-based antifoam agents used in delayed coker operations will plug up catalyst porosity. Sodium (Na) and calcium (Ca) can originate from seawater exposure, poor desalting or caustic sources in the refinery. Arsenic (As) is becoming more of a common issue as more synthetic and crudes from Africa and Russia are processed. It is present at low levels throughout the whole boiling range for synthetic crudes, which is why arsenic traps may need to be employed.

Depending on the future cost of crudes, shale oil based hydrocarbons from Colorado that first drew interest in the 1980s are relatively low in sulfur may again become marketable in large quantities. However, they are high in As and Ni. Also, phosphorous (P) is becoming a problem

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Table 1. Feed contaminants commonly found in crudes.

Contaminant	Feed Guidelines	Common Source	Remedies
Si	< 1.0 wppm	Anti foam from delayed cokers	Guard catalysts
Na, Ca	< 0.5 wppm	Sea water; Caustic	Improved desalting; Guard catalysts; Don't send spent caustic to feed tanks or units
As	< 250 ppb	Crudes from W. Africa, Russia, Syncrudes	High Ni guard catalysts
Pb, P	< 0.5 wppm	Gasoline slop tanks, Imported feeds	Don't process feeds containing Pb or P
Ni + V	< 1.0 wppm total for Ni + V + Fe	Resid; Heavy feeds	Better feed distillation; Guard Catalysts; Bed grading
Fe	< 1.0 wppm total for Ni + V + Fe	Soluble: Corrosion; Insoluble: Unfiltered particulates	Inert guard material with high void space; Fe-traps (soluble); Top bed skimming
C7 insolubles MCR	< 100 wppm < 0.5 wt%	Resid; Heavy feeds	Better feed distillation; Guard catalysts; Bed grading

with some feeds. The presence of nickel (Ni) and vanadium (V) in heavier feeds has always been a significant concern to hydrotreating operations. Their presence may also mean entrainment is occurring.

These Ni + V contaminants are found in significant concentrations in deep- cut VGO streams (e.g., 1-2 ppm), which is why end- point control is really critical with heavy feedstocks. In hydrotreating operations, either one of these elements will behave like coke and plug up the catalyst. Si will also plug up catalyst pores. Although Fe in naphthenic crudes may not be as significant a problem as Ni + V poisoning of ULSD catalyst, it nonetheless is a corrosion precursor and leads to FeS formation. Soluble Fe generated from naphthenic or acidic based crudes lead to corrosive producst entering catalyst beds. ■

Editor's Note: Dr. David ("Dave") Krenzke is Regional Manager of Hydrotreating Technical Services for (ART) Advanced Refining Technologies, LLC in Richmond, California, USA (lkbj@chevron.com). ART is Grace Davison's joint venture with Chevron Products Company established to combine each organization's technology expertise, including fixed-bed, onstream catalyst replacement (OCR) and ebullating bed products. The joint venture offers a full line of distillate catalysts for processing ultra-low sulfur content gasoline and diesel fuel, including the SmART Catalyst System® and ApART™ catalyst system customized for individual refiners. The 45-minute "Troubleshooting Hydrotreating Unit Performance" webinar mentioned at the beginning of this discussion can be downloaded from the Advanced Refining Technologies section of the Grace website (www.grace.com/about/businesses/ART.aspx).

PROCESS OPERATIONS

Heavy Crude Processing Rebounding

How will the current supply and demand for Canadian heavy oil evolve over the next three years? In the near term, US Gulf Coast refiners face a profit crunch as Mexico is poised to reduce exports Maya crude by over 100,000 bpd going into 2012. In addition, geopolitics being what they are, is predicating significant uncertainty in the export of heavy Venezuelan crudes to US PADD III (i.e., Gulf Coast) refiners. What does this mean to a complex refiner's coking economics with "constrained" access to heavy crudes, regardless as to their source (flat-to-reduced shipments from Canada, Venezuela, Mexico, Ecuador, Brazil)?

Crude availability is only the beginning of the problems with crude security, the quality of the crudes that are being upgraded from Canada, Venezuela, and other areas are posing Cont. page 3

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some serious surprises. U.S. Gulf Coast oil refineries continue to face a profit crunch this summer as Mexico has reduced exports of the region's benchmark heavy crude just as regional demand for such grades rebounds.

Mexico remains the top heavy crude supplier to the Gulf Coast despite a five-year output slide. But it will cut shipments of Maya blend crude by at least 110,000 bpd once a long-delayed expansion of its Minatitlan refinery is completed.

The cutback will reduce exports of Maya to their lowest level in 15 years. The loss, equivalent to more than a tenth of the Maya exported in 2010 and about 5% of the overall Gulf Coast market, will almost certainly raise the relative cost of heavy crude and squeeze margins. The supply situation will tighten even more as demand for heavy crude in the Caribbean is expected to rebound with the restart of Valero's 235,000 bpd refinery in Aruba, a traditional Maya processor, and as refinery utilization in Mexico rebounds from 20-year lows. "Crude oil processing in Mexico has been low mainly due to poor fuel oil demand. As that clears up, runs will increase," said an official of Mexico's state oil monopoly Pemex.

Canadian heavy crude producers are already struggling with a glut of crude but cannot move it easily to the Gulf due to a shortage of pipeline capacity. So while some companies, notably Exxon Mobil Corp., have been able to take advantage of proprietary pipelines to access some cheap Canadian barrels, traders do not expect to be able to substantially increase Canadian supplies without resorting to very costly options like rail transport. ■

Kuwait Heavy Oil Upgrading Challenges

It is known that the global energy demand is increasing and this is putting pressure on the oil producing countries to increase their production capacities. For example, Kuwait oil production capacity is expected to reach 4.0 million bpd by the year 2020. In order for Kuwait to maintain its market share, not only the production capacity must increase but also heavy crude oil (API < 20) must be used as gap filler.

Kuwait is expected to produce 900,000 bpd of heavy oil by the year 2020. These current events are facing the oil industry in Kuwait with many decisions and technological challenges, including counteracting expected increased risk of corrosion and equipment failures during production and refining of heavy crude oil. The most damaging impurities are inorganic salts, organic chlorides, organic acids and sulfur compounds. ■

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

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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. ■

Hydrogen Recovery from Offgas

Demand for high purity hydrogen (H_2) in hydrotreating operations has led to increased pressure swing adsorption (PSA) capacity. Hydrogen recovery with PSA technology becomes favorable with offgases consisting of more than 40% hydrogen. Membrane-based technology instead of PSA technology may be preferable for lower hydrogen throughputs that don't require high H_2 purity.

Basically, the PSA process of purification uses an adsorbent in a fixed bed to adsorb offgas impurities at high pressure, which are then desorbed at relatively low pressure into an offgas stream. Thus an extremely pure hydrogen product with purities in excess of 99.9% can be achieved by this process. The various licensors of PSA technology have developed modular skid mounted units for fairly rapid implementation.

To mitigate operating cost, a large percentage of the molecular sieve adsorbent used in PSA-based H_2 purification is reused depending on the unit's operating history. Refiners and suppliers of PSA technology use certain criteria and testing procedures to determine if the adsorbent's activity is sufficient for reuse. However, many refiners opt to replace the entire molecular sieve adsorbent inventory as the cost of this material is relatively inexpensive.

According to several licensors of PSA technology, the primary vessels of these units can last over 20 years provided that the feed to the PSA remains free of water and other corrosive elements. As previously noted, due to their typical design configuration based on several fixed bed reactors arrange in series, PSA units lend themselves to modular skid mounted designs. For example, Linde, the world leader in PSA units, installed a PSA unit at a Canadian refinery capable of processing 21,200 Nm^3/hr of offgas, which coincides with recent increases in hydrotreating and/or hydrocracking capacity. ■

Applying Model Predictive Control

Many refiners have applied model predictive control (MPC) to major refinery units. Selective application of model predictive control (MPC) technology has been typically applied to linear refinery processes. The benefits come from determining and controlling the optimal properties and relative sizes of the various product streams. A study by Petrobras' Almeida et al discusses the application of MPC to moderately nonlinear processes.[1] The system used in this work is an industrial gasoline debutanizer column. In the debutanizer column, several nonlinearities are present in the advanced control level when the manipulated inputs are the reflux flow and the reboiler heat duty. In most cases the controlled outputs are the contents of C_5^+ (pentane and heavier hydrocarbons) in the LPG and the gasoline vapor pressure.. The Almeida approach considers several process models representing different operating conditions where linear models are identified. The results show that the multi-model predictive controller is capable of controlling the process in the entire operating window while the conventional MPC has a limited operating range.

According to a Pavilion Technologies blog provided by Michael Tay, Manager of Sales Engineering, he noted that MPC could move beyond the traditional linear applications and into more complex systems such as blend optimization. "These are highly non-linear in nature, which has led to mixed results when attempted with linear methods. There can be very large benefits in making blend quality control better by reducing blend give-away or by responding in real-time to blend component shifts as the blend component units shift in real-time," according to Tay.

Another complex application according to Tay is to control the CDU actively during crude switches. "These are also nonlinear and include challenging dynamics, but the value of success can be quite high," says Tay. ■

1. E. Almeida, Neto, M. A. Rodriguez and D. Odloak, "Robust Predictive Control of a Gasoline Debutanizer Column," Brazilian Journal of Chemical Engineering, Vol. 17, No.s 4-7, Sao Paulo.

INDUSTRY NEWS

FEED Projects Awarded for Saudia Aramco and PDVSA Refinery Projects

Foster Wheeler AG announced in early July that Foster Wheeler SOFCON, an unincorporated consortium between a subsidiary of Foster Wheeler's Engineering and Construction Group and A. Al-Saihati, A. Fattani & O. Al-Othman Consulting Engineering Co., (SOFCON), has been awarded a contract by Saudi Arabian Oil Company (Saudi Aramco) for the front-end engineering design (FEED) and project management services for the Clean Transportation Fuels Project at the Riyadh Refinery, Kingdom of Saudi Arabia. The objective of this project is to reduce sulfur content of gasoline and diesel produced by the refinery to 10 ppm, and to reduce the level of benzene in gasoline.

The company's FEED scope includes new isomerization, naphtha splitting and sulfur guard-bed units as well as the addition of new equipment, including a diesel hydrotreater reactor, in existing units. The FEED also includes the debottlenecking of the hydrocracker and gas concentration units, and replacement of crude and vacuum distillation tower internals. Other new facilities include two new tanks, a new pipe rack, instrument air compressor, condensate system, substation, process interface building and workshop. Main control and monitoring systems will also be upgraded, as will the laboratory facilities.

Foster Wheeler AG also announced July 5 that a subsidiary of its Global Engineering and Construction Group has been awarded a process design and FEED services contract by PDVSA for the new Batalla Santa Ines Refinery Phase I Hydroskimming section to be built in Barinas, Venezuela. Foster Wheeler's scope of work includes preparation of the basic engineering design package, FEED and early procurement assistance for the crude distillation unit, naphtha hydrotreater, continuous catalytic reformer and utilities and offsite facilities. The FEED is scheduled to be completed in the third quarter of 2011.

It was also announced on July 7 that a subsidiary of Foster Wheeler's Global Engineering and Construction Group has been awarded a contract by YPF.S.A. for the delayed coker heater in the new delayed coking unit at YPF's Complejo Industrial La Plata in Argentina. Foster Wheeler's scope of work includes engineering, equipment supply and supervision to construction and start-up. The fired heater is an integral part of the new coker, which uses Foster Wheeler's Selective Yield Delayed Coking (SYDEC℠) technology. Foster Wheeler is providing the detailed engineering, procurement services and assistance with construction and plant start-up for the new coker. The delayed coker heater for the new delayed coking unit is expected to be completed by June of 2012. ■

Kuwait May Tap Private Investors for $14.5 Billion Refinery

The *Bloomberg News Agency* reported on June 28 that Kuwait may seek private investors to help build its largest oil refinery after a government council revived the 4.0 billion-dinar ($14.5 billion) project, which stalled two years ago amid political opposition. The Supreme Petroleum Council, the emirate's highest decision-making body for oil policy, approved construction of the 615,000 bpd Al-Zour facility, Oil Minister Mohammad al-Busairy said in a telephone interview with a *Bloomberg* reporter in Kuwait City.

The council authorized the plan June 27, along with proposals to upgrade two of the country's three existing refineries so that they can produce cleaner-burning fuels, the minister said. Kuwait is trying to attract more private investment to help pay for costly industrial improvements and infrastructure as part of a 30.8 billion-dinar development strategy to boost energy output and modernize transport links. Kuwait suspended the project in March 2009 after opposition lawmakers said the leadership had circumvented the law in awarding contracts with foreign companies without going through the Central Tenders Committee.

In its first phase, the new plant would be able to process 300,000 bpd of products for the domestic market, according to al-Harami. The second phase, for 315,000 bpd, would replace output from Kuwait's oldest and smallest refinery at Shuaiba, which is planned for closure, and enable the country to be self-sufficient in refined products, the analyst said.

Once the Al-Zour facility is fully built, it should also have enough spare capacity to provide products for export, he said. Kuwait, which imports liquefied natural gas (LNG) to supply its power stations when demand peaks in the summer months, should be able to reduce its imports of LNG and eventually stop them, al-Harami said.

Kuwait is the fifth-biggest OPEC producer pumping 2.425 million bpd of oil in May, according to data compiled by Bloomberg. The country's current refining capacity is 930,000 bpd. The two refineries approved for clean-fuel upgrades, Mina Al-Ahmadi and Mina Abdulla, have respective output capacities of 460,000 and 270,000 bpd. The third, at Shuaiba, can process as much as 200,000 bpd. ■

U.S. Refining Capacity Up from Previous Year

Reuters news agency reported on June 29 that U.S. oil refining capacity increased by 152,000 bpd since the beginning of 2011 to the highest level in nearly three decades, but refining operations remain well below historical highs seen in the 1990s, based on data from the Energy Information Administration (EIA). There were 148 refineries operating in the U.S. at the beginning of 2011 with a capacity to produce 17.7 million bpd of petroleum products, up 0.9% from the previous year, the EIA said. The capacity increase is mostly due to the restart of PBF Energy's 182,200 bpd Delaware City, Delaware refinery that was purchased from Valero Energy in 2010. The refinery was idled this January, but the capacity was considered operable.

Exxon Mobil has the most U.S. refining capacity at nearly 1.855 million bpd. ConocoPhillips rose to second with 1.787 million bpd in capacity while Valero Energy fell to third with 1.682 million bpd in capacity, according to the agency. U.S. refineries were running at over 95% capacity in 1997 and 1998 to meet growing demand for petroleum products. Many refiners expanded to keep up with demand and refinery utilization still averaged above 90% through 2005, EIA said. The U.S. recession caused lower petroleum demand, pushing U.S. refining operations down to 83% of capacity in 2009. "While the refinery utilization rate increased to about 86% in 2010, it remains well below the levels seen from 1993 through 2005," the EIA said. ■

Alon USA CompletesVGO Hydrocracker Project

Alon USA Energy has recently completed the hydrocracker project at its Bakersfield, California refinery and the unit is now in operation..The facility is currently processing VGO produced by the company's other California refineries, producing on-spec product. Alon president and CEO Paul Eisman said the operation of the hydrocracker is the final step in the integration of the Bakersfield refinery with Alon's other California refineries. "The addition of the hydrocracker to our California refineries should result in significant improvement to our refining margins for those facilities," Eisman said. Alon is an independent refiner and marketer of petroleum products, operating primarily in the south central, southwestern and western regions of the U.S. ■

Fire adds to Russia's fuel shortage problems

A recent fire at Gazprom Neft's Moscow refinery will drop gasoline production by around 16% in June from a planned 200,000 tonnes, according to a Gazprom Neft statement.The production cuts could exacerbate Russia's fuel shortage as the country battles a gasoline deficit created by price caps and insufficient refining capacity. The Energy Ministry's data on refinery maintenance showed that Gazprom Neft recently shut a catalytic reformer with a capacity of 2,740 tonnes per day, a 4,300 tonne per day atmospheric unit and a hydrotreater, which processes some 5,500 tonnes of oil per day.

Traders said the company will be able to compensate for shortages in Moscow, the country's largest gasoline consumer, by receiving additional supplies from Gazprom Neft's Omsk and Yaroslavl refineries. It owns the Yaroslavl refinery together with TNK-BP, and Omsk could supply 30,000 tonnes, they said. ■

New Hydroprocessing Catalyst Manufacturing Plant

Axens and General Technology & Systems Company Ltd (GENTAS) announced July 5 that they have signed a Letter of Intent to build a world scale hydroprocessing catalyst production plant in Saudi Arabia. The plant will be designed to produce latest generation catalysts able to satisfy customer needs for clean fuels production that meet the most stringent environmental specifications. GENTAS is a member of the Shoaibi Group (www.shoaibigroup.com) undertaking joint ventures with its partner Saudi Trading and Research Company (STARC or www.starc.com.sa). ■

EDITORIALLY SPEAKING

Heavy Oil Processing Increasing in Spite of False Starts

Rene Gonzalez, Editor
Refinery Operations

According to a Reuters report issued on July 12, Canadian heavy oil prices have climbed against a backdrop of steady demand with the restart of refinery capacity that had been down for maintenance. According to the report, Western Canada Select (WCS) heavy blend for August delivery was discussed at $18-$19 a barrel under benchmark West Texas Intermediate crude (WTI), compared with around $20 under last week and nearly $23 under early in the month's trading window. However, many of the buyers at the current level were marketing shops and banks as opposed to refiners, a trader said.

Among restarts, Calgary, Alberta, Canada-based Husky Energy Inc. said in the second week of July that its 155,000 bpd Lima, Ohio, refinery was back at full rates after it took a crude distillation unit down for work in late June in order to carry out proactive maintenance as well as repairs on a crude unit furnace. A controlled shutdown of the crude unit furnace was initiated on June 27, following the discovery of a small leak in a radiant tube inside the unit. There were no environmental releases or safety issues associated with the event. According to a June 29 Husky Energy press release, "the overall pre-tax impact, including repair costs, is estimated as an opportunity cost of between $15 to $20 million, which considers the current market price environment. "Inventories there were 7.7 million barrels during the first week of July, compared with a near-capacity 10.2 million four weeks earlier," said Abudi Zein, senior vice president at Genscape (www.genscape.com).

Light synthetic crude from the Alberta oil sands was quoted at around $9.25 a barrel for August over WTI, compared with around $8.75 during the first week of July. The crude has held reasonably steady after Suncor Energy Inc. completed more than six weeks of planned maintenance on its Upgrader 2 last month. Recent information that is publicly available from Suncor noted that its year-to-date output has averaged 249,000 bpd, down from 289,000 bpd over the same span last year. Now that the Upgrader 2 project has been successfully completed, Suncor is still targeting average production of 280,000 bpd for 2011.

Canadian Natural Resources Ltd has said it expects to commission the four coker drums at its idled Horizon oil sands project in the first week of August and ramp up to full production over the following two to three weeks. The 110,000 bpd operation has been shut down since an early January explosion and fire at the upgrading plant.

On the other side of the world, crude oil production in China in June rose 1.6% from a year earlier to 17.15 million tonnes, the National Bureau of Statistics said on July 13. China is the world's second-largest oil consumer, which should come as no surprise to anyone. There is nonetheless a lot of speculation at the present time that Chinese oil companies and refiners may indeed become the biggest partner with Canadian bitumen upgraders, rather than U.S. Midwest and Gulf Coast refiners. The success of environmentalists and supportive politicians in blocking or delaying permits for heavy crude pipeline construction from Canada (to Midwest/U.S. Gulf Coast) reinforces these observations. Either or, the abundance of heavy crudes from Canada will find a market. ■

Calendar of Events

SEPTEMBER

22-23, *Russia & CIS Refining Technology Conference & Exhibition*, Euro Petroleum Consultants, Moscow, Russia, +44 (0) 20 7357 8394, www.europetro.com.

OCTOBER

9-12, *NPRA Q&A and Technology Forum,* San Antonio, Texas, +1 292 457 0480, www.npra.org.

NOVEMBER

Nov. 29 – Dec. 1, *ERTC 16th Annual Meeting*, Barcelona, Spain, +44 (0) 207 484 9700, conf@gtforum.com, www.gtforum.com.