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FCC Catalyst Age Distribution Impacts Unit Performance

Grace Davison has Developed Sink/Float Method to Track Ecat Performance and Optimize Addition/Withrawal of Purchased Ecat and Fresh Catalyst

The FCC unit is one of the most dynamic and complex processes in a refinery. The reactor-regeneration configuration and the tons of catalyst flowing per minute means the unit can quickly become unstable, requiring immediate operator interaction. To better manage FCC catalyst inventory and mitigate the cost of adding fresh catalyst, it would benefit the refinery operator to know the age distribution of the catalyst in circulation.

For this reason, FCC experts at Grace Davison have developed the "Sink/Float" method for distinguishing the separation and percentage of FCC Ecat into fractions based on their respective densities. "Older" fractions tend to have higher density than "younger" Ecat fractions. By evaluating the characteristics and performance of the various age-distributed fractions of Ecat using the Sink/Float method, the health of an FCC unit's catalyst inventory (e.g., remaining activity, metals poisoning, etc.) can be determined and steps can be taken to improve operations.

Why Separate Ecat?

FCC Ecat generally displays a skeletal density between 2.4-2.8 g/ml. Ecat is mixed with varying concentrations of tetrabromoethane (TBE density = 2.96 g/ml) and tetrachloroethane (TCE = 1.58 g/ml). TBE:TCE ratios are adjusted until the desired split is achieved.

Due to continuous catalyst additions, the catalyst inventory has a broad age distribution. Recently

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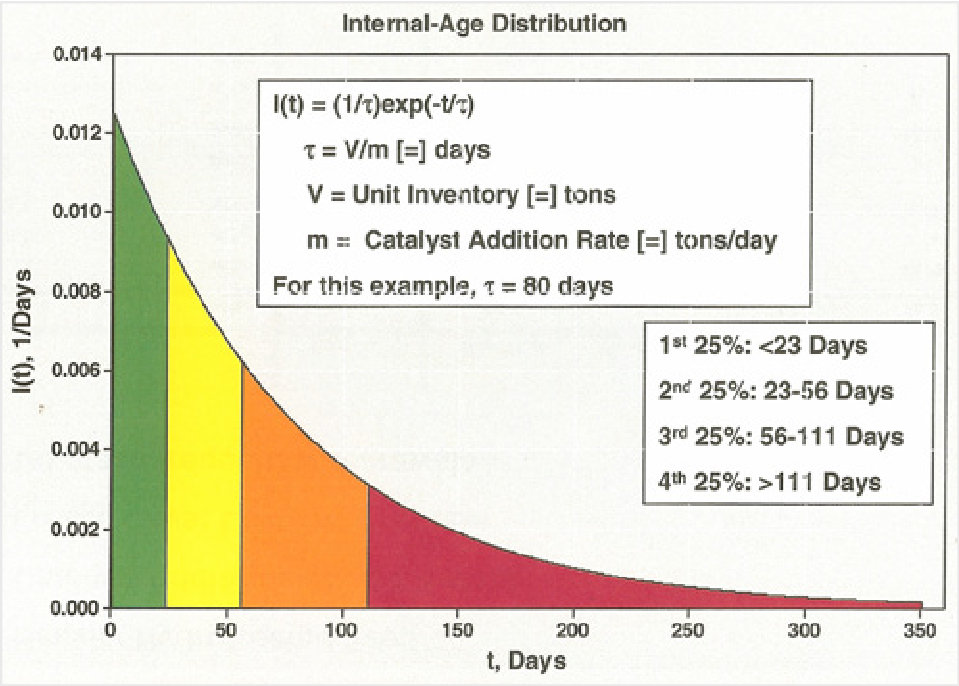

Figure 1. Determining length of time that catalyst is in the unit

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added catalyst will display relatively high activity and low metals. Older fractions may be in the unit for weeks or months and have high levels of metals and low activity. Understanding how equilibrium catalyst age distribution impacts catalyst performance can lead to unit improvement opportunities as shown in **Figure 1** (on page 1).

To demonstrate the importance of knowing the amount of time that a catalyst is circulating in a unit, several "real world" examples (e.g., heavily hydrotreated feeds) developed by Grace Davison experts show the frequency of Ecat turnover and catalyst addition rates. For example, due to the low delta coke displayed by the heavier fractions (higher density), high additions of an active catalyst are required for units with severely hydrotreated feeds.

Cyclone Problems

Another case demonstrates how the Sink/Float method helped predict an impending cyclone problem. In this example, a "standard" gas oil feed with an initial catalyst addition rate of about 0.28 lbs/bbl and 137 days that Ecat was in the unit before being withdrawn (τ = 137 days). However, a developing cyclone problem resulted in a τ value of only 79 days and a higher catalyst addition rate of about 0.48 lbs/bbl needed to match the losses.

At this point, the refinery operator could decide to stop withdrawing catalyst until the cyclone problem is resolved. The "challenged" cyclone is retaining the older, heavier and less active catalyst particles. So, the activity is lower than expected despite the elevated catalyst addition rate of 0.48 lbs/bbl.

An economical solution is this case may be to continue withdrawing catalyst and replace with purchased Ecat. This will lower overall Ecat activity but allow for the purge of older fractions. The use of purchased Ecat and fresh catalyst may also provide an economical way of maintaining catalyst withdrawals, keep unit inventory healthy and keep activity constant. ■

Editor's Note: More details on determining FCC catalyst age distribution with the Sink/Float method and employing this information to troubleshoot unit operations will be discussed in the Fall 2011 issue of the Grace Davison Refining Technologies *Catalagram* #110 (www.grace.com).

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PROCESS OPERATIONS

Improving Hydrocracker Quench Design

The hydrocracker reactor's (Figure 1) quench zone is an integral part of the reactor internals dictating stability of the hydrocracking catalytic reactions. The hydrocracking reactions occurring on the zeolitic catalyst has a high apparent activation energy, due to the interaction of nitrogen adsorption and cracking reactions.

In design, the maximum temperature rise per bed is usually limited at 20 to 25 °F for hydrocracking catalyst according to guidelines developed by control experts at H2Advance (www.h2advance.com). A good quench box design should limit the radial temperature spread for the bed inlet to less than 5 °F.

The function of a well designed quench box is to reduce the temperature spread for the stream coming from the bed above the quench box to attain minimal temperature spread to the bed below the quench box after the introduction of the quench stream.

Hydrocracker quench boxes that are in poor condition could result in higher than desirable radial temperature spread in the bed below the quench box. Hydrocracking technology suppliers such as Axens have developed quench boxes for optimal remixing of the effluents between beds. For example, Axen's emphasizes that its proprietary EquiFlow quench boxes are particularly useful when hot product from the previous bed is mixed with fresh, cooler hydrogen, providing the mixture with a uniform temperature before it makes contact with the subsequent bed.

The combination of the reactor internals revamp and an improved reactor control scheme enables a reliable operation for hydrocracker reactors. ■

Figure 1. Modern hydrocracker operations benefit from improved internals and reactor control schemes.

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Providing Real-Time Compositional Data in FCC Operations

Process gas chromatographs are increasingly being used to provide real-time compositional data in upgraded refinery process units, such as with FCC process control systems. The typical vacuum gas oil (VGO) feed to the FCC unit can also be supplemented by coker gas oil and other heavy petroleum streams such as from the deasphalter. In general, FCC optimization objectives include the ability to process a wider variety of feedstocks from thermal conversion units (e.g., coker gas oil) and catalytic conversion units (e.g., hydrotreated feeds).

Based on information available from Emerson Process Management Gas Chromatographs Division (www.emersonprocess.com), they have reported on opportunities that exist where process gas chromatographs can play a role in FCC unit optimization and performance, including:

- Monitoring the CO-to-CO_2 ratio in the flue gas leaving the top of the regenerator: This ratio is critical to regulating regenerator temperature since high temperatures damage the catalyst
- Monitoring main fractionators overhead vapors: This gas chromatograph application is typically used for two purposes. The first is to minimize the loss of naphtha/gasoline components in the overhead stream by keeping the C_5 concentration low. The second purpose is to monitor the C_4 and C_5 olefins generated in the reactor. These olefins are important feed components to other processes in the refinery such as the alkylation unit. ■

Avoiding Catalyst Reversal in FCC Operations

The FCC unit's reactor-regenerator configuration and the tons of catalyst flowing per minute can quickly lead to unstable operating conditions. With elevated temperatures and severe operating conditions, field instrument measurements are essential to understanding how the process is performing at any given moment. As the traditional heavy oil conversion unit in many refineries, the overall refinery suffers significant financial impact if the FCC unit experiences an unscheduled shutdown.

One main challenge for an FCC unit is to avoid a catalyst reversal in the reactor-regenerator section. Ensuring the differential pressure measurement is working properly is crucial, as the impulse lines for this application tend to plug. In addition, the main fractionator bottoms is severe requiring correct selection and installation of field instruments to ensure true measurements. In these circumstances the Rosemount's 3051S differential pressure transmitter with statistical process management has been put into service to detect line plugging and give adequate time to act before a reversal of catalyst incident occurs (www.rosemount-transmitter.com). ■

Crude and Product Blending Optimization

Princeps has launched two new applications for optimized refinery operations, both based on Paragon's optimization software AIMMS. OPTIMIX for multi-period blending enables the refinery operations manager to optimize product blending, enabling them to realize higher value out of the available components. OPTIMIX can perform multi-period blends over a planning horizon of several weeks.

It is a generic tool that can be easily configured to any refinery and bring instant value for money. Optimization can be done on component costs, quality specifications give-away or target recipes. The system can handle hot rundown components as well as tank components, including tanks in running-gauge operations. It also takes into account tank rotation and logistical constraints, which are unique features according to refinery specialists.

In addition, COMPASS for crude oil blending and scheduling enables the refinery operations manager to formulate crude oil blends, determine optimal cut-points and schedule crude transfers and crude runs in order to maximize the crude distillation units' throughput. COMPASS can handle several distillation units and takes into account all operational constraints such as feed and rundown capacity limitations, tankage capacity limitations, rundown quality requirements and all kinds of logistical constraints.

Both tools are typically used as companions to a simulation-based refinery scheduling system and are designed to be easily interfaced with such systems like Aspentech.

Princeps brings together engineers and experts specialized in industrial processes and applied mathematics for the development. ■

Refinery Emissions Monitoring Intensifies

In a recent posting on AnalyticExpert.com by by Michael Gaura, product manager at Emerson's Analytical Solutions, he noted that in late 2010, the U.S. Environmental Protection Agency (EPA) published new standards of performance in 40CFR60 subpart Ja that impact refinery emissions monitoring.

Historically, refineries were required to measure the hydrogen sulfide (H_2S) concentration in refinery fuel and flare gases. The new requirements mandate the measurement of H_2S and total reduced sulfur (TRS) – defined as H_2S, carbonyl sulfide (COS) and carbon disulfide (CS_2) – in flare gas streams and sulfur recovery unit (SRU) emissions. In Guara's blog post, he reviews some of the emissions monitoring changes and challenges that refineries are facing with these new requirements and how to meet them. ■

INDUSTRY NEWS

Heavy Maintenance in June Curtailed Chinese Refinery Processing

China's apparent oil demand in June was 36.92 million metric tons (mt), or an average of 9.01 million bpd, as a heavy maintenance program during the month curtailed consumption, according to Platts' analysis that is based on recent statistics released by the Chinese government.

June's demand of 36.92 million mt marked a slim rise of 0.5% from the same month a year ago. This year-on-year increase of 0.5% was drastically slower than year-on-year growth rates of between 8% and 15.8% recorded between January and May 2011, and June's oil demand at 9.01 million bpd was just marginally higher than the previous low of 8.95 million bpd in October 2010.

June's oil demand growth was the lowest in over two years as a number of Chinese refineries decided to shut their plants for repairs and maintenance last month because of lofty global crude oil prices, and output declined after an easing in a recent domestic diesel supply crunch," said Calvin Lee, senior writer, China, for Platts.

In June, Chinese refineries processed 35.56 million mt of crude oil, or an average of 8.69 million bpd, the lowest daily processing volume in nine months. In September 2010, the country had processed 34.91 million mt of crude oil, or an average of 8.53 million bpd. Analysts are expecting Chinese oil demand to rebound for the rest of 2011, especially in the fourth quarter.

"With the peak summer refinery turnaround period ending in August, crude runs will likely soon recover. Also, if history of the past two years is any indication, China's oil consumption could ramp up in the fourth quarter," said Lee. ■

Plans for New Ugandan Refinery Follows Recent Crude Discoveries

According to a July 21 report in the *Financial Times* of London, Uganda is planning to build only the second oil refinery in East Africa by 2015. Following the recent discovery of 2.5 billion barrels of oil, Uganda aims to develop a refinery in Hoima, according to Fred Kabagame Kaliisa, permanent secretary at the energy ministry.

The $2 billion plant should be able to produce an initial 20,000 bpd, rising to 200,000 over 30 years. At present, a refinery in the Kenyan port city of Mombasa is the only facility of its kind in East Africa, exporting fuel to Uganda, Rwanda and Burundi. But it only produces 32,000 bpd. Essar Group, the Indian company that owns 50% of the plant, has suggested plans to upgrade the 40 year-old facility to improve its efficiency and raise production.

It is clear that demand for oil products in East Africa will continue to rise and the Mombasa refinery is well placed to meet this demand," said Bimal Mukherjee, chief executive of Kenya Petroleum.

Following the discovery of reserves at Albertine Graben in 2006, government analysts estimate that Uganda will be able to support the production of over 100,000 bpd for the next 20 years, making the country the primary oil producer in East Africa. ■

Pakistani Refinery Increasing Capacity

Pakistan based *Business Recorder* publication recently reported that the Attock Oil Refinery (ARL) has planned to expand its existing crude oil refining capacity through a pre-flash unit and isomerization unit, which would cost $100 millions.

According to documents available with *Business Recorder*, the oldest oil refinery in the region is in the bidding process for expansion, up-gradation and diversification of its existing system due to ever-increasing demand of refining products in the country. The planned pre-flash unit would utilize additional 20,000-25,000 bpd of crude from TAL Block near (Kohat) projected within three-four years. The company is installing the pre-flash with distillation unit on a least-cost option, which would increase its capacity by 10,400 bpd. The existing capacity of ARL is 42,000 bpd, which would reach 53,000 bpd after the pre-flash unit installation.

ARL is seriously considering installation of an isomerization complex to upgrade its light strain run naphtha. A diesel hydrotreater unit has also been planned. Pakistan's current crude production is 65,000 to 67,000 bpd and total capacity of the refineries is 287,000 bpd or 12 million tons. ■

Azerbaijan Refineries Reduce Throughput

The Azerbaijan based publication known as News.Az recently reported that Azerbaijan's oil refineries refined 3.018m tonnes of oil in January-June, a fall of 115,000 tonnes compared to the same period in 2010. Azerbaijan has two oil refineries, the Heydar Aliyev Refinery and Azerneftyag, both of which are owned by the State Oil Company, SOCAR.

The two refineries refined 512,460 tonnes of oil in January, 418,540 tonnes in February, 575,930 tonnes in March, 532,830 tonnes in April, 513,760 tonnes in May and 464,920 tonnes in June. In 2010 as a whole, SOCAR supplied 6,220,000 tonnes of oil to both oil refineries. In 2009, the oil refineries received 6,035,000 tonnes of oil, 1,312 tonnes fewer than in 2008. ■

Indian Refiners Looking to Process more Saudi Arabian Crude

A *Reuters* sourced report from July 21 noted that Indian refiners have asked top exporter Saudi Arabia for more oil in August, sources said, as they fear Iran will halt supply of 400,000 bpd as Tehran escalates a seven-month long payment suspension triggered by US pressure. India's Bharat Petroleum, Hindustan Petroleum and Essar Oil have each asked for one million barrels extra for August, from Saudi Arabia, a source with knowledge of the matter said. ■

New Report on Iran Refining Industry

Research and Markets (www.researchandmarkets.com) has announced release of their study "The Future of Iran Oil Refining Market to 2015--- Forecasts and Insights into Iran Refining Markets, Companies and Refineries." This is a source of information and analysis on Iran refining industry for all industry professionals and strategists interested in the industry. It provides insights and forecasts of refinery capacities (atmospheric, coking, FCC, HCC), oil products production and consumption to 2015. Key refining strategies and operations of each of the major refining companies in the country are analyzed in detail. According to Research and Markets, the study identifies key investment areas in Iran refining market and also analyzes all the upcoming refineries in detail. ■

EDITORIALLY SPEAKING

Small Refineries at Higher Closure Risk

Rene Gonzalez, Editor
Refinery Operations

An article that appeared in the Brisbane Times on July 28, "The Future of Oil Refining in Australia Appears Clouded," bears a strong resemblance to similar refinery closures in Europe and North America. The article, published in the wake of Shell's decision to cease refinery operations at the Clyde refinery in Sydney, exemplifies how other resource-rich regions have also seen refinery closures over the past three years, including some US and Canadian refineries on the eastern seaboard, where terminal operations have nonetheless continued.

In the case of the Clyde refinery, the closure will cost 310 jobs at the refinery, although Shell said between 30 and 50 people would be required to continue working at the site once it had been transformed into a fuel-importing terminal. The growth of larger, cheaper refineries in developing Asian countries, such as India has factored into making the Clyde facility unviable but Shell executives stressed that Clyde's relatively small 75,000 bpd size was also a significant factor. Shell's larger Australian refinery at Geelong would be better able to withstand pressures from Asian and Middle Eastern refineries.

Of an additional concern to Australia's refining sector, Caltex has refused to commit publicly to the future of its Kurnell refinery in Sydney. Caltex has publicly stated that it was undertaking improvements to "maintain the viability" of the Kurnell facility. Mobil has also publicly stated that it has no plans to close its Altona facility.

It was also noted in the *Brisbane Time*s article that the security of Australia's fuel supply was not at risk. Just like in North America, the security of fuel supply in certain regions of North America (e.g., US East Coast) is not at risk as some oil companies close or sell off their refining assets, such as ConocoPhillps.

It is still too early to project how recent upstream developments and discovery of hydrocarbon rich zones of oil and gas in US, Canada, Poland, offshore Brazil and elsewhere will affect refiners in those respective regions. For now, economies of scale and process complexity compete as the most important factors relative to security of supply. To be sure, many of these "secure" supplies are nonetheless leveraged by the technical challenges that the industry is facing in bringing these hydrocarbons to upgrading facilities, such as the recently discovered Tepi oil field in Brazil's deep offshore.

However, it's no secret that new oil fields such as the Eagle Ford Shale formation is breathing new life into land-locked inland refineries in certain areas. For example, as discussed in a previous issue of *Refinery Operations*, the Valero refinery in Three Rivers, Texas is reportedly receiving 100% of its crude feedstock from the Eagle Ford Shale play. Nonetheless, even though this feedstock may have a 63 API gravity, it has been reported that higher-than-expected naphthenic acid generated from processing these feeds requires well planned corrosion control programs. ■