



Optimizing FCC Operations in a High Rare Earth Cost Market: Part I

Highlights of Recent Grace FCC Webinar Focusing on Unit Operation and Profitability when Reformulating FCC Catalyst to Lower Rare Earth

Higher feed volumes are processed through FCC units than ever before, at the same time that more challenging feedstocks have entered the market. The industry has responded with effective catalyst chemistry that has included adding higher quantities of rare earth (RE) to the zeolite. However, with the unprecedented inflation in RE costs, the onus is now on reformulating FCC catalysts to lower RE, while maintaining or exceeding the high levels of performance achieved by the latest catalyst systems.

In an FCC webinar earlier this summer, Grace Davison's David Hunt discussed zero and low RE catalyst alternatives and commercial updates, including a case study detailing catalyst's impact on operation and profitability at a refinery's FCC unit.

Future Role of Lower RE Catalysts

The role played by RE-based catalysts over the past 50 years cannot be disputed. More recently, constrained units have benefited from RE-based catalyst activity, which is effective in mitigating reduced residence time in FCC reactors. Nonetheless, recent RE price inflation compels refiners and their catalyst suppliers to seek other alternative to RE-based zeolites.

Briefly, 97% of the world's RE supply is from China. Since the beginning of 2011, RE prices have been highly inflated and there are limited short term options for supply of RE such as lanthanum (La). For example, lanthanum oxide (La₂O₃) was recently \$140,000/

metric ton on the Asian Metal Index, a 2700% increase in price over the course of a year! This is why the industry has demonstrated such a strong response to finding solutions to RE inflation.

Rare earth supplies are expected to remain in critically short supply until at least 2014, when mines in other parts of the world are fully developed. Lanthanum (atomic number: 57) is the lightest of the rare earths as shown on a typical Periodic Table of the Elements. Lanthanum has been the dominant RE metal engineered into FCC catalysts, followed by cerium (Ce), which has been used primarily in SO_x reduction additives as well as in some NO_x reduction additives.

Ensuring High Activity

Rare earth applications were developed in the 1960s and have provided unique functionalities to FCC operations by way of improved zeolite active site density, selectivity and hydrogen transfer, as well as to protect the zeolite from metals deactivation. Initially, RE-free catalysts were developed in the 1980s and 1990s to maximize FCC gasoline octane as lead was being phased out of the gasoline pool and alkylation capacity was not sufficient to provide octane requirements. Rare earth based catalysts provide high conversion for units that may be constrained by coke yields or catalyst circulation.

The aluminum (Al) atoms within the zeolite structure bring about a charge and balance for acid types on the zeolite. RE exchange increases zeolite active

acid site density and prevents dealumination. A catalyst designed with a high RE exchange for high gasoline selectivity will have more

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aluminum atoms (e.g., 16 Al atoms/unit cell; Si/Al = 12; UCS = 24.32 Å) than a catalyst with a low RE exchange for high LPG olefin selectivity (e.g., 7 Al atoms/unit cell; Si/Al = 27; UCS = 24.25 Å). The Al atoms are also slightly larger than the Si atoms. Adding RE to a zeolite surface therefore area increases unit cell size (UCS) due to higher acid site density. This increases feed conversion and activity at constant C/O ratio. Catalyst circulation limited units of course benefit from a very active catalyst.

Units that operate in the 24.30 to 24.34 UCS range produce lower coke per unit of conversion and gasoline. In addition, air blower constrained units operating within this 24.30 to 24.34 UCS range produce higher conversion and activity than (for example) units that are blower constrained, as compared to FCC units operating at a lower UCS. Gasoline octane (RON) and olefins decrease with increasing UCS, which was important in the late 1990s and early 2000s period when refiners had to meet olefins limits specified by the US EPA's Complex Model requirements.

Rare Earth Alternatives

A worldwide Ecat database covering the past decade shows an increasing use of RE from about 2.0 wt% in 2000 to almost 3.0 wt% in 2010. During that same time period, activity and UCS increased while Ecat zeolite surface area decreased. In 2011, the industry has actually seen its first decline in 20 years of RE content and UCS. Of course, the rapid increase in RE cost has predicated pulling the RE content out of FCC catalyst.



Refiners are beginning to see the benefits of low rare earth exchange catalyst formulations in their FCC units

Are we pulling too much RE out of the zeolite? This will be discussed further in Part II of the next issue of *Refinery Operations*, as reformulating catalysts to lower rare earth (RE) content have been commercialized, they have demonstrated their ability to prevent dealumination and meet product specifications, even in high sulfur and resid operations (e.g., 2000 ppm Va). ■

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PROCESS OPERATIONS

ISOCRACKING Technology Update

Chevron has established several licensing partnerships for its proprietary technology in Russia through Chevron Lummus Global (CLG), Chevron's joint venture with CBI/Lummus Technology.

Licensing Chevron's ISOCRACKING® catalyst, Kirishi Nefteorgsintez

(Surgutneftegaz) is building one of the world's largest ISOCRACKING™ units. The facility, expected to be commissioned in 2012, is designed with an annual processing capacity of 3.0 million metric tons of vacuum gas oil (VGO). It will enable production of

high-quality fuels for Russian and foreign markets and produce diesel fuel that complies with Euro 5 European emission standards.

The energy company Tatneft has licensed the ISOCRACKING technology for the Taneco

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Nizhnekamsk refinery, which is under construction. This refinery will manufacture high-quality diesel and jet fuel. Startup is expected by late 2011 or early 2012. The technology behind Chevron's ISODEWAXING catalyst was licensed to produce base oils at the same refinery. The base oils facilities are expected to start operation in 2013.

CLG has a sales contract with Rosneft's Tuapse refinery for a hydrocracker and diesel hydrotreater license. The contract also covers a future supply of catalysts for the Tuapse refinery. This refinery will produce jet and diesel fuels. Startup is planned for 2012. Hydrocrackers typically run at high temperature 650-800°F (345-425°C) and very high pressures of 1500-3000 psi (105-210 bar). Hydrocracker reactors contain multiple fixed beds of catalyst typically containing palladium, platinum, or nickel. These catalysts are poisoned by sulfur and organic nitrogen, so a high-severity HDS/HDN reactor pretreats feedstock prior to the hydrocracking reactors. Hydrocracker units may be configured in single stage or two-stage reactor systems that enable a higher conversion of gas oil into lower boiling point material.

Chevron also sells hydrotreating catalysts and technical support to refiners in Russia through Advanced Refining Technologies, a joint venture with Grace-Davison (www.grace.com).

Oman Refineries and Petrochemicals Company (ORPC) will use ISOCRACKING technology from CLG at the heart of its Sohar Refinery Expansion Project to boost margins and increase production.

As previously discussed in *Refinery Operations* (Vol. II, No. 8, May 4, 2011), the Sohar hydrocracking facility in Oman will process almost 74,000 bpd of VGO and light cycle oil (LCO). The investment will enable Sohar refinery to increase its naphtha production for its petrochemicals complex and produce high quality ULSD and kerosene. CLG's hydrocracking technology was selected by ORPC after a thorough analysis showed it offered the best overall economics by a well-proven process scheme.

Also, Saudi Arabian Oil Company (Saudi Aramco) recently signed a



Leon de Bruyn, Chevron Lummus Global Joint-Manager Director

hydrocracking unit license agreement with CLG for applying ISOCRACKING technology to the Jazan Refinery Project that is currently in the front-end engineering design (FEED) phase. The CLG licensed hydrocracker will be utilized to convert 106,000 bpd of VGO — from the new 400,000 bpd Jazan refinery — into high quality diesel fuel, meeting EURO V quality requirements. With this award, ISOCRACKING technology has been selected by Saudi Aramco for their newest refinery projects in the Kingdom.

CLG's Joint-Managing Director, Leon de Bruyn, stated that "Saudi Aramco is a world leader in applying the most advanced technologies to its export and domestic refineries, while demanding the safest and most efficient operations for all aspects of their projects. This continues a very strategic relationship for us and we look forward to providing a full range of support services to Saudi Aramco and the Jazan Project team."

CLG will provide an engineering package, including the hydrocracking reactors, proprietary ISOMIX® internals, ISOCRACKING® catalysts, follow-up technical support during the detailed engineering design, training prior to startup, and startup support during the commissioning of the new refinery. ■

Refinery Propylene Production

Propylene from off-gases produced in fluid catalytic cracking (FCC) units is primarily expanding in Asian refineries. In addition, a growing percentage of propylene is produced using on-purpose technologies such as propane dehydrogenation (PDH) and metathesis.

The primary source of propylene is from cracking naphtha and other liquids such as gas oil and condensates to produce ethylene. By altering the cracking severity and the feedstock slate, the propylene:ethylene ratio can vary from 0.4:1 to 0.75:1. Smaller amounts of propylene can be obtained from cracking propane and butane. The cracking of liquid feedstocks is carried out predominantly in Europe and Asia. However, recent gas discoveries in North America (e.g., Eagle Ford Shale) may predicate

increased production from C₂ through C₄s. Another source of propylene is from refineries where splitters recover the propylene from the off-gases produced by FCCs. However, refinery propylene needs to be purified for chemical and polymer use.

With propylene demand growing faster than ethylene, combined with the building of more ethane crackers (which produce no propylene) rather than naphtha crackers, on-purpose technologies are being employed increasingly to make propylene. The main on-purpose process used is PDH but it is only economically viable in cases where low-cost LPGs are available. Propane is converted to propylene at 500-700°C in a reactor containing a noble metal catalyst.

Refiners operating FCCUs that produce

high levels of propylene have seen different or excessive product contaminants when compared to a less severe operation. In certain refineries, this may impact gasoline or LPG treating units, as what has been previously discussed in NPRA Q&A transcripts. For example, Shaw has proprietary DCC [deep catalytic cracking] technology units with extensive operating data. As far as LPG treating, Shaw experts have not really seen any particular issues with gasoline or LPG treating units.

A typical FCC yield includes light olefins (ethylene, propylene, and butylenes) totaling 10-15

wt% on feed. FCC total light olefin yield can be increased to 25-30 wt% on feed with the proper selection of catalyst and operating conditions. ■

INDUSTRY NEWS

Shanghai Petrochemical Company Increases Refining Capacity in Spite of Financial Losses

Sinopec Shanghai Petrochemical Company Limited ("Shanghai Petrochemical" or the "Company") announced August 26 the unaudited operating results of the Company and its subsidiaries (the "Group") prepared under International Financial Reporting Standards ("IFRS") for the six months ended June 30, 2011 (the "Period").

According to IFRS, turnover of the Group for the Period amounted to RMB49,500.8 million, representing an increase of 37.01% over the previous year. Mr. Rong Guangdao, Chairman of Shanghai Petrochemical, said, "In the first half of 2011, the Chinese economy continued to maintain stable and relatively fast growth, while China's petrochemical industry continued to maintain a healthy and steady operation. However, international crude oil prices surged significantly and stayed at high

levels, and the profitability of the oil refining industry declined substantially, resulting in a turnaround from profits to losses. Coping with external market changes with a proactive approach, the Company continued to increase total physical production volume of products, and made every effort to push forward various tasks on production, operation, reform and development. During the Period, crude oil processing volume and outputs of gasoline, diesel, jet fuel, synthetic resin & plastics and other products reached record highs once again as compared to previous corresponding periods. The natural gas comprehensive utilization project reaped good economic benefits."

The fully completed Phase 5 Project of the Group continued to effectively produce its overall scale effect during the first half of 2011. As a result, total

volume of goods produced increased by 14.87% year-on-year. During the Period, the Group processed 5,678,300 tons of crude oil (including 131,400 tons of crude oil processed on a sub-contracting basis), an increase of 12.60% year-on-year. Outputs of gasoline, diesel and jet fuel were 510,300 tons, 2,055,700 tons and 402,500 tons respectively, representing increases of 10.24%, 33.49% and 5.78% year-on-year respectively. Outputs of ethylene and propylene were 492,100 tons and 258,700 tons respectively, representing decreases of 0.36% and 4.30% year-on-year respectively.

In the first half of 2011, international crude oil prices fell after a rise but in general tended to surge significantly and remained at high levels. The Group's average unit cost of crude oil processed was RMB4,937.91/ton in the first half of 2011, representing

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an increase of 25.57% year-on-year. The Group's total costs of crude oil processed during the Period increased substantially by 42.89% year-on-year to RMB27,390.2 million, accounting for 61.76% of the Group's cost of sales for the Period.

During the Period, the Group fully commenced the construction of the Phase 6 Project, with the refinery re-vamping and expansion project as the key project, of which the construction of the new 3,900,000 tons/year residual

oil hydrogenation plant, the new 3,500,000 tons/year catalytic cracking plant and the carbon fiber project with a capacity of 1,500 tons/year have already commenced. ■

Idemitsu's Chiba Refinery Increasing FCC Propylene Production

Japan's third largest oil refiner, Idemitsu Kosan Co., said on August 4 that it has completed a 16 billion yen (\$208 million) upgrade to the 45,000 bpd FCC unit at its Chiba refinery near Tokyo to raise output of high-value-added petrochemical products and gasoline reformat. The unit is currently in test production and will begin commercial production from around the

autumn, a company spokeswoman said. The upgrade improved the unit's operational efficiency to one of the best in the country, the spokeswoman added.

Propylene output capacity has been increased to 86,000 tonnes from 67,000 tonnes per year, while that of gasoline reformat has increased to 1.5 million kilolitres (about 26,000 bpd) a year from 1.3

million kl. The upgrade also raised the yield ratio of butene to 15.2% from 14.1%.

The company said the unit's propylene output can be raised to up to 210,000 tonnes in the future from 86,000 tonnes now if it conducts additional work on downstream units. ■

World's Largest Paraxylene Plant to be Built in South Korea

Japan's JX Nippon Oil & Energy Corp said in early August it and SK Innovation Co of South Korea would invest 1.35 trillion won (\$1.3 billion) to build the world's biggest paraxylene plant and a lubricant facility in South Korea.

The two firms will spend 1 trillion won on a 1 million tonnes per year paraxylene plant to start output in 2014 at SK's Ulsan complex in South Korea, and the remainder on a lubricant plant with a capacity to make 1.35 million kilolitres per year of lubricant base oil. SK also confirmed the investments. JX said it would provide feedstock for the

paraxylene plant from its refineries in [Japan](#).

The move follows a similar \$1 billion paraxylene project in South Korea by Japan's Cosmo Oil Co and Hyundai Oilbank and comes at a time when margins for paraxylene are expected to improve on the back of robust demand from [China](#) and other Asian nations. JX currently has the top market share in paraxylene output in Asia, and the venture will raise its output capacity by 500,000 tonnes to 3.12 million tonnes per year.

Faced with a structural decline in Japanese oil demand with population peaking and an accelerated shift

to more environment-friendly energy sources, Japanese oil refiners are looking abroad for expansion opportunities. For example, No.3-ranked Idemitsu Kosan had plans to make a final investment decision at the end of the summer on building Vietnam's second refinery. JX is also considering a similar refinery project in Vietnam. Japan's oil sales fell for the fourth straight month in June after the March earthquake and tsunami disrupted refinery operations and curbed economic activity. ■ (note: \$1US Dolar = 79.020 Japanese Yen).

Orpic Increasing Heavy Oil Processing

Oman Oil Refineries and Petroleum Industries or Orpic, owned by the government of the Sultanate of Oman, is expected to start production from its expanded refinery at Sohar, Oman, in 2015, technology provider UOP said in a statement in early August.

Orpic has selected UOP and Foster Wheeler technology to process heavy oil and expand fuel and petrochemical production. Both companies, in collaboration, will provide the technology license and basic engineering package for the expanded unit that will be able to

process 2.5 million mt/year of heavy crude.

Orpic will use the UOP/Foster Wheeler Solvent Deasphalting process to convert heavy crude to low-contaminant deasphalted oil, which will be used to produce LPG, gasoline, jet fuel, diesel and propylene. The

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SDA process produces a high-quality, low-contaminant deasphalted oil rich in paraffinic-type molecules that is used in fuel and petrochemical production.

Orpic owns four plants at Sohar and Muscat with a total production capacity of 222,000 bpd of products including naphtha, LPG, gasoil, gasoline, fuel

oil, jet oil, as well as 818,000 mt/year of paraxylene, 198,000 mt/year of benzene and 350,000 mt/year of polypropylene. ■

Qatargas Doubling Condensate Refinery Capacity

Paris-based Technip has won the contract to design a capacity-doubling expansion of Qatargas's Laffan condensate refinery, the Qatari state energy company said on August 25. Under the front-end

engineering and design (FEED) contract, Technip will design facilities to boost the refinery's capacity to 292,000 bpd from the current 146,000 bpd. The design contract is scheduled for completion

in the first quarter of next year and Qatargas expects to award the engineering, procurement and construction contract to build the facilities by the end of the third quarter of 2012. ■

PetroVietnam Dung Quat Refinery Restarted

Vietnam's 130,000 bpd Dung Quat refinery, which produced more than 3.3 million tons of oil products in the first seven months this year, restarted operations on August 30 following a shutdown for maintenance that ended earlier than expected, as reported in Vietnam-based Thanh Nien News.

State-owned oil and gas group

PetroVietnam shut down the facility on July 15 for scheduled maintenance, which was scheduled to last through mid-September. The plant is expected to be operating at full capacity within ten days, news website VnExpress reported, citing Nguyen Hoai Giang, Chief Executive of Binh Son Refining and Petrochemical Co, which operates

Dung Quat. He noted that the next maintenance is due in four years, when local technicians and experts are set to be capable of fixing problems themselves without depending on foreign expertise.

Petrovietnam plans to expand the annual capacity of the plant to ten million tons by 2017, from 6.5 million tons. ■

BP Whiting Refinery Delaying Startup of New Hydrotreater and Coker

An August 27 report from the Associated Press says BP has delayed the startup of part of its \$3.8 billion Whiting oil refinery expansion until mid-2013, citing the northwestern Indiana project's "many variables."

The upgrade will equip the complex

to become a top processor of high-sulfur crude taken from Canadian tar sands. The project, designed to deal with the higher level of impurities found in that crude, was expected to be completed and operating by late 2012.

BP spokesman Brad Etlin said some

components of the modernization at the complex about 20 miles southeast of Chicago will begin operating on the earlier schedule. But he said the startup of the project's new gas oil hydrotreater and coker will be delayed until mid-2013. ■

Murphy Oil Refinery Sold to Valero

Valero Energy Corp. based in San Antonio, Texas (USA) agreed August 31 to acquire Murphy Oil Corp.'s 135,000 bpd refinery at Meraux, Louisiana for about \$625 million. The deal includes \$325 million for the refinery and related

assets and \$300 million for the refinery's current inventory. Valero said it plans to close the deal in the fourth quarter. The refinery has a Mississippi River dock and is located about 40 miles from Valero's refinery in St. Charles Parish. The

deal also includes a product terminal, a 20% interest in the Collins Product Pipeline and terminal and a 3.2% interest in the Louisiana Offshore Oil Port. Valero currently has 15 refineries. ■

EDITORIALLY SPEAKING

Opportunity Crude Processing

If you are planning on staying in the refining business, then you should expect to process a wider range of feedstocks with poorly understood chemistry and processing challenges. This probably means upgrading a refinery's crude and desalting units to deal with corrosion and fouling precursors, as well as preparing primary conversion units, such as the hydrocracker to increase distillate and petrochemical products. However, some refiners are finding out the cost of upgrading opportunity crudes are higher than expected due to the unusual concentrations of troublesome compounds (e.g., mercury, arsenic, etc.).

Opportunity crude processing technology is available and is in a constant state of improvement by the technology licensors. Opportunity crudes generally have greater than 1.0 wt% sulfur and less than 26 API gravity, with a TAN greater than 1.0. We are nonetheless seeing some unexpected increases in the cost of dealing with the combinations of compounds in these feedstocks causing serious corrosion problems in crude/vacuum units, and fouling in FCC unit gas plant operations.

Some of the technology that refin-

ers have relied on to deal with these problems, including problems with "standard" crude slates, has increased significantly. For example, the costs of rare earth oxide materials used in FCC catalysts and additives have experienced about a 2700% increase in cost in less than 12 months, as discussed by Grace Davison's David Hunt in this issue's Feature article. For a perspective, if the rate of inflation on the rare earth element lanthanum (used in FCC catalysts) were applied to a \$2.00 cup of coffee, the new cost would be more than \$25.00.

Just as common, many refiners have to deal with upgrading desalting capacity and performance to avoid downstream operational problems such as corrosion, equipment fouling and catalyst poisoning.

There are other cost factors that should be considered outside of the refiner's direct control, such as the transportation and logistics with moving opportunity crudes to the refinery facility.

One of the most notable cases is the current controversy with the proposed construction of the Keystone Pipeline from Canada to the US Gulf Coast, which will provide high-complexity

Gulf Coast refiners a reliable supply of heavy Canadian crudes. However, politicians and pseudo-environmentalists

may halt the project in spite of the project's ability to provide the US with a secure supply of feedstock and jobs throughout the oil industry value chain.

So it comes as no surprise that some of the most profitable facilities are those fortunate to be able to process a "narrower range" of standard crudes over a prolonged period. For some refiners, such as export refiners that seem to process the widest variety of crudes, heavy oil upgrading programs are necessary and figured into operating costs, as they blend increasing percentages of opportunity crudes with standard crude slates.

If you can afford the cost, the upcoming 4th High TAN & Opportunity Crude (HTOC 2011: info@connection.org; +65 6338 4090) Conference in Singapore (September 15-16) will focus exclusively on the technology and economics associated with running opportunity crudes. ■



Rene Gonzalez, Editor
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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*, ational Petrochemical & Refiners Association (NPRA), San Antonio, Texas USA, +1 (202) 457 0480, www.npra.org.

11-13, *Central & Eastern European Refinery & Petrochemicals 14th Annual Meeting*, World Refining Association, Gdansk/SOPOT, Poland, +44 (0) 207 067 1818, www.wraconferences.com.

NOVEMBER

1-2, *Downstream Asia 2011*, The Energy Exchange, Singapore, www.theenergyexchange.co.uk.

7-10, *Sulphur 2011*, CRU, Houston, Texas USA, +44 (0) 20 7903 2300, www.sulphurconference.com.

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