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Engineering Solutions, Maintenance, Reliability, Automation and Equipment

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Zero/Low Rare Earth FCC Catalyst Technology Ready for Commercialization

New Formulations are Equally Effective on Hydrotreated Feedstocks and Resid Feedstocks

Shawn A. Abrams, Vice President and General Manager, Grace Davison Refining Technologies

Grace Davison announced earlier this summer the successful global commercialization of eight fluid catalytic cracking (FCC) catalysts and additives with zero or low rare earth (RE) content.

Shawn A. Abrams, Vice President and General Manager for Grace Davison Refining Technologies, said, "In order to relieve the cost pressure on customers while maintaining or improving product performance, Grace Davison Refining Technologies has responded quickly to the issues of rare earth price and availability by developing eight new zero/low rare earth catalysts and additives. Grace is investing capital at its manufacturing facilities to make these technologies available globally."

The REpLaCeR™ family includes five new catalysts for both hydrotreated and resid feed processing with zero and low RE content: REsolution™, REBEL™, REACTOR™, REMEDY™ and REduceR™ FCC catalysts. The REpLaCeR™ family of catalysts utilizes proprietary zeolites and state-of-the-art stabilization methods to deliver performance similar to current RE-based FCC technologies. For example, extensive R&D work to develop the REBEL RE-free high matrix catalyst system for FCC applications delivers the same activity and selectivity over resid feedstock as the well proven MIDAS®-100 catalyst (**Table 1**).

In addition, Grace has recently introduced ResidUltra™, a new catalyst with 40% less RE than benchmark resid catalysts. Finally, a series of low RE environmental additives is currently in commercial trials. These include Super DeSOX-OCI™

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Table 1. REBEL™ catalyst delivers the same activity and selectivity over resid feedstock as RE metal based catalysts.

ACE Yields at Constant Conversion (CPS-3 deactivation, 3000 ppm Ni + V)		
	REBEL™ Catalyst	MIDAS®-100
Cat-to-oil	5.8	5.5
Dry Gas, wt%	1.8	1.8
Propylene, wt%	3.5	3.5
Butylenes, wt%	5.2	5.4
Gasoline, wt%	46.6	46.8
Bottoms, wt%	9.6	9.5
Coke, wt%	4.2	4.3

In This Issue...

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and Super DeSOX-MCD™ sulfur transfer additives.

RE metals have always played an important role in FCC operations for stabilization of the Y zeolite component of FCC catalysts. However, recent export quota restrictions on RE metals from China has caused the prices of these RE-based catalysts to rapidly rise. China is the primary source of RE metals, which is why more cost effective RE-free catalyst have been highly sought after by many refiners. A more detailed discussion on the development of RE-free FCC catalysts is discussed in Vol. II, No. 3 of *Refinery Operations*: "The Development of Rare-Earth Free FCC Catalysts," by Colin Baillie and Rosann K. Schiller.[1] ■

1. Vol. II, No. 3 of *Refinery Operations* can be downloaded from the *Refinery Operations* website (www.refineryoperations.com) or contact Rosann Schiller at Grace (rosann.schiller@grace.com).

GRACE Davison
Advanced Refining Technologies

PROCESS OPERATIONS

Increasing Desalting Capacity

Refiners are increasing desalting capacity as two-stage desalting capacity is increasing with heavier crudes and blended feedstocks. For example, a refinery processing 100,000 bpd of crude receives roughly over 5.0 tons per day of salts and solids.

Management of this material in the refinery is critical due to its impact on corrosion of distillation columns, fouling of process equipment, as well as reduction of catalyst life. In addition to increased salt content removal capacity, the latest injector/mixer desalter technology provides more efficient utilization of wash water and chemicals, and improved crude-water separability.

It is generally understood that dehydration efficiency of a desalter is usually 95% in a single stage and up to 99% in a two-stage configuration. In addition, if the salt compounds (typically NaCl, $CaCl_2$ and $MgCl_2$) that are not removed from the oil, higher levels of HCl-related corrosion can be expected in downstream process operations when considering that higher severity conditions and temperatures are expected when upgrading low gravity crudes.

Desalting technology continues to improve in reliability and reduced energy consumption as the impact of organic acids and asphaltenes on downstream refinery operations needs to be minimized as will be discussed in further detail in the next issue of *Refinery Operations*. ■

Upgrading FCC LCO to Diesel Pool

Many refiners are still feeling the impact of ULSD regulations on the addition of FCC light cycle oil (LCO) to the diesel pool. LCO, with a cetane number averaging around 25, is much higher in sulfur level than straight-run (SR) diesel and contains up to four times the concentration of aromatics, making LCO significantly denser.

Addition of FCC LCO into the ULSD pool has required modification of distillate hydrotreating units for much higher severity operation. In addition, FCC feed hydrotreating or mild hydrocracking has been required with high sulfur feeds in order to shift a significant portion of FCC LCO into the USLD pool. Up to 50% of the FCC gasoline sulfur can be concentrated in the back end (> 425 °F) of the gasoline pool. Available methods for analyzing total gasoline sulfur include:

- ASTM D2622: A wavelength dispersive X-ray fluorescence technique capable of detecting sulfur levels greater than 10 ppm
- ASTM D5433**:** An oxidative combustion based technique using a UV fluorescence detector. This test is applicable in the wide range of 1 to 8000 ppm
- ASTM D4045**:** An oxidative combustion based technique using hydrogenolysis and rateometric colorimetry. Sulfur detection is in the range of 0.02 to 10 ppm.

■

Assessing Corrosivity of High TAN Crudes

Concerns over processing crudes with TAN numbers greater than 1.0 have lead to discussions of oil sands dil/synbit segregation from other heavy crude oils. However, this could potentially cause significant logistical midstream problems with pipeline and terminal systems charged with transporting segregated crudes to the refinery.

The Canadian Crude Quality Association (CCQTA) and producers in the oil sands play have been addressing this issue with a variety of ongoing projects. From a practical

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perspective, knowledge of a crude feedstock's potential corrosivity through currently available test methods has often been lengthy and expensive, and has led to inaccurate results.

To more accurately and quickly determine the corrosivity potential of opportunity crudes, Southwest Research Institute (SwRI) has developed radio tracer technology (RATT) to measure crude oil corrosivity.

According to information available from SwRI, test coupons are irradiated to develop suitable tracers for detection using on-line gamma ray spectroscopy. Corrosion is then measured by monitoring the buildup of radioactivity in a closed loop system as a function of time. Detection and measurement of corrosion is available in real time for heavy crudes and high TAN crudes at shorter test times of about four hours. The corrosion potential of these opportunity crudes can be indexed to the corrosion of known crudes through back-to-back testing or database reference, according to information available from SwRI (www.swri.org). ■

Ebullated Bed Hydroprocessing's Role in Bitumen Upgrading

The technical advantages for ebullated bed hydroprocessing in upgrading bitumen feedstocks versus thermal conversion processes, such as coking, include a less aromatic product. With the addition of hydrogen, there is a significant amount of sulfur and nitrogen reduction, along with the previously mentioned saturation of aromatic rings. Nevertheless, coking is the primary upgrading process of choice for the two largest bitumen upgraders (Suncor and Syncrude: about 1.0 million bpd of upgrading capacity). Other significant bitumen upgraders include Husky Oil and Shell.

Husky Oil processes over 55,000 bpd using ebullated bed hydroprocessing, followed by coking of the unconverted residue, whereas the Shell-led Scotford upgrader uses ebullated bed hydroprocessing alone for primary upgrading. All upgrading facilities require hydrotreating or hydrocracking to remove sulfur and nitrogen to levels normally handled in downstream refining facilities, such as with the refiners in the Midwest region of the US.

To be sure, upgrading facilities require significant sources of hydrogen, albeit through steam reforming plants or pipeline. As bitumen processing approaches more than 3.0 million bpd by 2015, what happens at the upgrading stage cannot ignore the downstream refineries, and their processes.

A key issue for bitumen and other SCO feedstocks are the challenges to improving distillate and gas oil quality. These problems are to some degree exacerbated by coking, where cracking in the absence of hydrogen promotes the formation of unusually high aromatic hydrocarbon species.

According to some experts familiar with processing bitumen feedstocks, this is not easily corrected in the conventional refinery processes, particularly when meeting ULSD specifications. This factor alone can limit the percentage of SCO in the typical refinery diet, which is why hydrocracking is expected to play a greater role in keeping SCO market values competitive with light crudes. In addition to producing high quality distillates and zero residue, hydrocrackers are inherently better able to handle the aromatics.

Recent interest in partial or field upgrading (for viscosity reduction and diluent savings) will also play an important role in upgrading bitumens. Many of these processes, such as deasphalting and visbreaking may play a larger role, especially where residue use for hydrogen and energy positively influences primary upgrading process selection. ■

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INDUSTRY NEWS

New Refinery in Central Vietnam

Vietnam National Petroleum also known as Petrolimex has unveiled plans to invest $4.4-$4.8 billion for constructing the Nam Van Phong complex, a new refinery in central Vietnam. The complex with a capacity of 200,000 bpd will be built in Nam Van Phong facility in Khanh Hoa province.

The main products produced from the refinery will include petrol, diesel, jet fuel, kerosene, LPG and other petrochemical products. Petrolimex issued an initial public offering in late July, seeking investors for construction of the complex.

The company is plannning to join hands with PetroChina to construct a 225 km pipeline connecting Chinese state oil giant's Qinzhou refinery in Guangxi province with Petrolimex's K130 terminal in Vietnam's Quang Ninh province. The primary objective is to construct the pipeline by 2014 with an initial annual capacity of 10 million tonnes to take Chinese refined products to Vietnam. ■

New Pemex Refinery in Final Engineering Stage

Mexico's state oil company Pemex announced that is in the final engineering stage for its planned $10 billion (estimated) 250,000 bpd Tula refinery in Hidalgo state, company COO Carlos Murrieta told a webcast on August 2.

Mexico's energy minister Georgina Kessel said in June that the tender process for refinery construction will not be completed until the first half of 2012. Pemex officials had previously announced that the process would be completed in early 2011.

"The refinery will be working in coordination with the existing Tula refinery, and in that sense it's critical that we finalize the overall optimization. We have all the resources for that," Murrieta said. The new Tula refinery project, which was announced in mid-April last year, was initially scheduled to be completed in 2015. Neither Pemex nor the government has yet discussed pushing back the startup date. ■

Petrobras Investing in Mexican Refining Infrastructure

Petroleo Brasileiro (Petrobras) has unveiled plans to invest $11billion in various oil exploration, production and refining projects in Mexico between 2011-2015. The company plans to make a majority of the investment in the petrochemical plants and refineries in Mexico's Gulf states.

Petrobras plans to buy the Etileno XXI project in Coatzacoalcos, a port in southern Veracruz and construct an ethylene processing plan for the project with capacity to produce 1 million tons of ethylene and its derivatives. The production from this plant will meet the deficit for ethylene products in Mexico. ■

Valero Completes Purchase of Chevron Pembroke Refinery

US-based Valero Energy has completed the purchase of Chevron's refinery in Pembroke, Wales, along with its marketing and logistics assets throughout the UK and Ireland. Valero has purchased the refinery for $730million, excluding working capital, and was funded from available cash.

The company said the Welsh unit is the largest and most complex refineries in Europe and has total capacity of 270,000 bpd. Valero now has 15 refineries, with a combined capacity of 2.9 million bpd of throughput. ■

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Earthquake Damaged Sendai Refinery Restart Planned for Late 2012

Japan-based JX Nippon Oil & Energy plans to resume operations at its refinery in Sendai at the end of 2012. The refinery with a capacity to produce 145,000 bpd was shut down due to the damages caused by the massive earthquake that hit Japan in March.

The refinery's shipping facilities also caught fire, causing extensive damage. The company is also planning to construct a 1MW solar facility on the site of the refinery to meet the energy needs of the plant.

JX will invest $640 million for the reconstruction of the plant including the 1MW solar plant, reports Reuters. The refinery is the last one to be restarted after the March earthquake, while the other two damaged refineries in Kashima, Negishi are back online. ■

Inland US Refiner Reports Strong Margins

Western Refining, Inc. reported on August 5 that net income of $100.1 million for the second quarter ending June 30, 2011, or $1.10 per basic share and $0.94 per diluted share, compared to second quarter 2010 net income of $14.4 million, or $0.16 per basic and diluted share. The improved results for the quarter were due to stronger refining margins, which were primarily the result of the continued price advantage of WTI crude oil as compared to Brent and other water-borne crude oils.

Jeff Stevens, Western's President and Chief Executive Officer, noted that total refinery throughput averaged approximately 153,000 bpd. “The strong refining margins for inland refineries processing WTI-priced crude oils contributed to our solid earnings in the quarter," said Stevens.

"The Company continues to see strength in the futures market for both distillate and gasoline Gulf Coast crack spreads. Therefore, we are taking the opportunity to lock in these unusually high margins on a portion of our future production by adding to our hedging positions. Capturing these spreads is an important component of our strategy to reduce debt and strengthen our balance sheet," added Stevens. ■

Extension of Construction Start Date Expected for Hyperion Refinery

The South Dakota (USA) state environmental board recently announced it is considering a Texas company’s request to extend the construction start deadline for a $10 billion oil refinery planned for southeastern South Dakota.

The state’s Board of Minerals and Environment previously approved an air quality permit for Hyperion Resources of Dallas in August 2009, but that permit required construction to begin by February 2011. The company now wants 18 months to start construction from the date a final permit is issued.

The proposed new Hyperion’s refinery north of Elk Point, South Dakota (USA) would process 400,000 bpd of Canadian tar sands crude oil each day into low-sulfur gasoline, diesel, jet fuel and LPG. It would be the first new U.S. oil refinery built since 1976. The project would include a gasification-based power plant to supply electricity for the refinery using solid petroleum coke feedstock. ■

Proposed Refinery in North Dakota Acquires Wastewater Discharge Permit

United States Senator John Hoeven said on August 4 that the Environmental Protection Agency (EPA) has approved a key permit for a proposed oil refinery on the Fort Berthold Indian Reservation in the state of North Dakota. Officials say the permit allows for the discharging of treated wastewater from the refining process.

The refinery would process oil from the Bakken Formation in western North Dakota. The 15,000 bpd Mandan, Hidatsa, Arikara (MHA) Nation Clean Fuels Refinery is expected to be one of the few oil refineries to be constructed in the United States in the last 30 years. ■

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Sunoco CEO Discusses Operating Options

Independent refiner Sunoco Inc. Chairman and Chief Executive Lynn Elsenhans said on August 4 that the Philadelphia, Pennsylvania based company "does not have a bullish outlook for refining," during a conference call to analysts to discuss second-quarter returns, in which the Sunoco's refining business lost $44 million. The loss was attributed to multiple equipment failures at its Philadelphia refinery that began in April and lasted into July.

In the short-term Elsenhans said the best option for Sunoco was to continue operating its Philadelphia and Marcus Hook, Pennsylvania, refineries. Since Elsenhans took over as chief executive in 2008, Sunoco has shut one refinery and sold two others. The company also recently spun off its metallurgical coke-producing subsidiary. ■

SAPREF Refinery Preparing for Scheduled Maintenance

South Africa's 180,000 bpd SAPREF in Durban will conduct a routine maintenance in August, the company said on August 5. According to a company spokesman, more details will become available in the month. SAPREF is jointly owned by BP Plc and Royal Dutch Shell. ■

EDITORIALLY SPEAKING

Timing Investments in an Oscillating Business Cycle

Rene Gonzalez, Editor
Refinery Operations

Operational strategies, safety and reliability programs are closely integrated with each other in a business climate where profitability cycles are narrowing while the duration of marginal cycles seem to be widening, even with the advent of more capable technology.

Technical innovations are nonetheless too expensive for some operators. While for others, the "timing" on their investment is off, such as with those who recently changed crude slates without fully taking into account crude characteristics that can lead to levels of corrosion that were not anticipated.

Other processors are well-positioned to invest in new innovations. For example, technology is what provides refiners with competitive flexibility against low demand for some products and relatively higher demand for other products. However, that flexibility is very dependent on the mechanical "availability" of the technology (new or old).

This is one important reason for the relatively long cycle lengths observed in implementation of some new processes and configurations, as uncertainty with regard to the mechanical reliability of the process may not provide the confidence level needed for capital investment. In some areas, such as compressor technology, where there have been significant improvements in turbocompressor performance, the challenge faced by many refiners is due to available capital.

In many cases, it is perceived that "older" technology is better understood and can therefore be more precisely targeted with mechanical reliability strategies that will ensure higher run lengths and less unplanned shutdowns.

This trust in more mature processes helps mitigate the magnitude of the required investment should a decision be made to invest in new technology. For example, a refinery may decide to go forward with a new hydrocracking unit while forgoing with building a new FCCU, which otherwise would seem to be a logical option in Asia and the Middle East for example, where demand for gasoline and petrochemical feedstocks continues to grow.

Interestingly, the onus on finding new ways to leverage mature technology in a down cycle may be one of the reasons that many specialized engineering consulting organizations, staffed by specialists who retired or were laid off from refining companies, are staying quite busy. They are helping certain refiners improve the performance and efficiency of existing assets, rather than building new capacity. For example, in Europe operating efficiency of the largest refineries has been improved to try and remain competitive with Middle Eastern and Indian refineries. However, recent plans to exploit new hydrocarbon resources, such as shale formations in Poland, could predicate capital investment in upgrading technology (e.g., visbreaking, coking, ebullated bed hydrocracking, etc.) for these new feedstocks.

In developing regions, technology licensors and suppliers pursuing large capital projects emphasize that they continue to offer process technology well

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in advance of market requirements and regulatory timetables.

In most cases, the processes that are performing up to expectations from a process development approach are based on collaboration, teamwork and shared benefit. This synergy no doubt fits well in an era where there is a greater need to "manage" processing streams down to the molecular level. ■

Calendar of Events

SEPTEMBER

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

OCTOBER

Oct. 9-12, NPRA Q&A and Technology Forum, San Antonio, Texas, National Petrochemical & Refiners Association (NPRA), +1 (202) 457 0480, www.npra.org.

Oct. 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

Nov. 8-10, Invensys North America OpsManage'11 Conference, Invensys Operations Management, Nashville, Tennessee, USA, opsmanage@invensys.com, www.iom.invensys.com.

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

Nov. 29 – Dec. 2, Refinery & Petrochemicals in Russia & the CIS Countries 15th Annual Roundtable, World Refining Association, Geneva, Switzerland, +44 (0) 207 067 1818, www.wraconferences.com.

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