Reduce FCC regenerator SOx and NOx Emissions

Achieve Cost Effective SOx Transfer Ability with Lower Rare-Earth Based Additive. In Addition, New Additive Reduces NOx Emissions by 80% at Reduced H₂ and/or Dry Gas Penalties

Two new recently developed SOx additives help refiners mitigate the rapid escalation in rare-earth (RE) based catalyst prices. These additives build upon the proven effectiveness of Grace’s Super DESOX® additive. Super DESOX® OCL additive is the first generation of low RE SOx additive. This additive has proven in commercial scale trial to be as effective as the Super DESOX® additive, resulting in on par pick-up factor efficiency as shown in Figure 1.

Additionally, a second generation of SOx additive with even lower RE has been developed, Super DESOX® MCD. Lab testing suggests it is possible with Super DESOX® MCD additive to attain a suitable and cost-effective balance between SOx transfer ability and additions. Super DESOX® MCD additive began multiple commercial trials in the second quarter of 2011.

NOx Reduction Additive

Unlike traditional FCC regenerator NOx reduction additives,

### Figure 1. Super DESOX OCL Additive --- Commercial Data.
the next generation GDNOX™ 1 NOx reduction additive utilizes a new technology platform that builds on the success of DENOX®, while allowing refiners the ability to achieve greater NOx reduction. And, unlike earlier generation NOx reduction additives, GDNOX™ 1 additive greatly mitigates H2 and/or dry gas penalties. GDNOX™ 1 additive is formulated to reduce exposure from inflation in RE pricing.

As extensive pilot plant testing shows in Figure 2, refiners have the ability to incrementally improve NOx reduction, by upwards to 80%, with increased GDNOX™ 1 additive dosing rates as shown in Table 1. To achieve targeted NOx reduction, the recommended dosing rate for GDNOX™ 1 additive typically ranges between 2.5 wt% and 7.5 wt% of catalyst inventory. The additive allows refiners to:

• Meet local/federal NOx regulations
• Meet EPA constraints without the cost of capital.
• Process feeds high in nitrogen with greater economic flexibility.
• Balance refinery-wide NOx emissions.
• Maintain FCC throughput.

Table 1. GDNOX™ 1 additive dosing rates can reduce FCC regenerator NOx emissions by 80%.

<table>
<thead>
<tr>
<th>GDNOX™ 1 Additive</th>
<th>Base Line NOx (ppm)</th>
<th>NOx after GDNOX™ 1 Additive (ppm)</th>
<th>Percentage (%) NOx Reduction</th>
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<tr>
<td>2.50%</td>
<td>292</td>
<td>139</td>
<td>50</td>
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<td>5.00%</td>
<td>287</td>
<td>110</td>
<td>60</td>
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</table>

![Figure 2. Pilot Plant Testing: NOx Reduction with Multiple GDNOX™ 1 Additive Additions.](image)

**The Author**

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**Effective Resid Processing with Low Rare Earth FCC Catalyst Technology**

It is well known that rare earth (RE) oxide improves faujasite zeolite stability by scavenging FCC feedstock metals and enhancing selectivity towards desired products. However, of concern to the refining industry is the substantial increase in RE-based catalyst prices. These escalating costs have accelerated development of RE-free FCC catalysts.

In this effort, a recently published paper by Sudhaker Jale and Ruizhong Hu at Grace Davison discusses the ResidUltra™ catalyst technology for cracking large molecules in resid feedstocks and delivering optimal coke selectivity. Historically, resid FCC catalyst with relatively high levels of RE have typically been employed to trap contaminant metals in the feed, thus protecting activity and
selectivity. For example, the IMPACT® resid catalyst developed by Grace in 2003 contained a proprietary Integral Vanadium Trap (IVT) technology and has demonstrated step-out improvements in coke selectivity and bottoms cracking in over 70 units worldwide.

Grace has now been actively pursuing development of RE-free and low RE catalysts for various feedstocks. Careful re-optimization of matrix functionalities for bottoms cracking and metals trapping has lead to development of the ResidUltra™ catalyst technology, which is currently in commercial trial at two locations. It’s RE content is about 40% relative to IMPACT® catalyst while still retaining the same activity and selectivity with all the benefits of Al-sol binding technology.

ResidUltra™ and IMPACT® catalyst samples from commercial production were deactivated via cyclic propylene steaming (CPS) at 1450 °F with 3,000 ppm vanadium and 2,000 ppm nickel tested side-by-side in the ACE over resid feedstock. Relative to IMPACT® catalyst, ResidUltra™ catalyst has:

- Similar catalytic activity
- Same hydrogen selectivity
- Slightly better coke selectivity
- Similar gasoline, LCO and bottoms yields
- Slightly higher octane number and LPG olefins yields.

Conversion effects for cat-to-oil ratio, coke, hydrogen and gasoline yields are plotted in Figures 1 and 2. In general, the performance of both of these catalysts can be considered equivalent even though ResidUltra™ has about 40% lower RE content. Nevertheless, the 40% reduction in RE content is an excellent economic incentive for refiners processing resid to switch to this novel catalyst technology.

Editor’s Note: This discussion was derived from a more detailed review of the ResidUltra™ technology discussed in the Spring 2011 issue of Catalagram (Issue #109, 2011, pp.s 24-26). “ResidUltra™: Low RE Catalyst Technology for Resid Processing Applications,” by Sudhakar J. and R. Hu. Additional information can be obtained by contacting the Dr. Sudhakar Jale, Senior Marketing Manager (sudhakar.jale@grace.com), and Dr. Ruizhong Hu, Manager of Research and Tech Support (ruizhong.hu@grace.com).

![Figure 1](image1.png)  
**Figure 1.** ResidUltra™ Catalyst has Slightly Higher C/O Ratio and Improved Coke Selectivity.

![Figure 2](image2.png)  
**Figure 2.** ResidUltra™ Catalyst Makes Slightly Less Hydrogen and Similar Gasoline Content.
Literature Cited

Asphaltene Precipitation and Fouling from Canadian Heavy Oils

A recently completed study by Hong et al concerning asphaltene precipitation and fouling from blends of Cold Lake and Athabasca heavy oil cuts and diluents of varying aromatics arrived at the following conclusions:1

When heavy oil cuts are blended with aliphatic diluents, asphaltenes are precipitated and heavy fouling occurs.

With diluents containing significant aromatic content, much less precipitation occurs and fouling is reduced. A resin-rich fraction extracted from the heavy oil reduced fouling at concentrations of ≥0.1%

Fouling rates increase moderately with surface temperature. For example, an increase of 25°C from 260 to 285°C resulted in a doubling of the initial fouling rate. With Cold Lake mixtures, deposits were of composition similar to suspended asphaltene solids, and with Athabasca blends were enriched in ash/clay and diluents constituents.

Solubility parameter values for the heavy oil–diluent blend components could be readily obtained from automated flocculation titrations, and stability of oil blends predicted by literature models.

Both the amount of asphaltenes precipitated in isothermal batch experiments, and the initial thermal fouling rate under fixed conditions can be related to the oil mixture solubility parameter, or to the more empirical colloidal instability index (CII).

Hydrocracking Study Now Available

Reportlinker.com announced in mid-April that a new market research report from GlobalData is available in its catalogue: “Refinery Hydrocracking Units: Global Market Analysis, Capacity Forecasts and Competitive Landscapte to 2015.” The report provides information on the global and regional refinery hydrocracking capacities and also highlights the key issues and trends in the global refinery hydrocracking market.

The research provides an in-depth analysis of the global refinery hydrocracking market, with focus on the refinery hydrocracking capacity growth by key companies and countries across various regions globally. The report also highlights the hydrocracking operations of some key refining companies globally. With more importance given to diesel-driven vehicles, the demand for diesel in the European market has increased. The increasing demand for diesel has forced the region to increase its hydrocracking capacity. The European region will see a capacity addition of 21.6 MMtpa for the period 2011-2015. The other regions of the world will see lesser additions than the capacity additions in the European region. Asia-Pacific will see a capacity addition of 17.5 MMtpa for the same period. The report provides detailed information and analysis of refinery hydrocracking markets by country and region. The report primarily focuses on:

The major trends and key issues which will impact the growth of the global refinery hydrocracking market during the period 2010-2015.

The refinery hydrocracking capacity of the top five countries, top five companies and top five refinery hydrocracking units in five global regions – Asia-Pacific, Europe, the Middle East and Africa, North America and South and Central America during the period 2000-2015. In each region, the hydrocracking markets of the key countries are analyzed further.

Capacity addition in global refinery hydrocracking capacity through expansion of existing hydrocracking units and planned completion of new refinery hydrocracking units during the period 2010-2015.

The top five companies in each regional hydrocracking market, their refinery hydrocracking capacity shares and their equity.
Yanbu Refinery Expanding with Saudi Aramco and Sinopec JV

Saudi Aramco and China Petrochemical Corporation (Sinopec) recently signed a memorandum of understanding (MOU) related to the ongoing development of the Red Sea Refining Company (RSRC), a world class, full-conversion refinery in Yanbu, on the west coast of Saudi Arabia. The MOU was signed by Khalid A. Al-Falih, President and CEO, Saudi Aramco, and Su Shulin, President, Sinopec. Saudi Aramco and Sinopec have agreed to initially subscribe to equity interests of 62.5% (Saudi Aramco) and 37.5% (Sinopec) in RSRC should they proceed to formally participate in a joint venture. Both companies bring commercial and technical knowledge and expertise to the joint venture while creating a strategic partnership to enhance trade of transportation fuels between a significant energy producer and a significant consumer.

In-Kingdom refinery projects such as the RSRC joint venture in Yanbu have the location advantage to effectively and efficiently supply both international and domestic markets. Development of this particular relationship with Sinopec in RSRC is a continuation of Saudi Aramco’s long-term strategy of making world-scale investments following a massive upstream program that increased the company’s crude oil production capacity to 12 million bpd. RSRC is one of a number of downstream projects where Saudi Aramco is demonstrating its commitment to meet future worldwide energy demand.

“The project is a further step by Sinopec to expand its international operation by developing its overseas refining and petrochemical business, and to sharpen its competitive edge. It will also help Sinopec gain access to more energy sources and secure China’s energy supply” said Su Shulin, President, Sinopec.

Axens and Shaw Selected to License Next Generation FCC Technology

It was announced in early April that Axens and Shaw have been selected to license the High Severity Fluidized Catalytic Cracking (HS-FCC) technology, which is designed to produce higher yields of propylene and other light valuable products. The HS-FCC technology has evolved during a 15-year development effort that combines the innovations of five separate entities.

During the first phase of development, JX Nippon Oil & Energy Corporation (JX) and Saudi Arabia’s King Fahd University of Petroleum and Minerals (KFUPM) formed a research venture, JX, who leads the technology developers, provided technical research and KFUPM provided the location for initial laboratory testing facilities.

During phase two, Saudi Aramco joined JX and KFUPM to continue developing the technology. The expanded team designed, built and operated a 30 bpd demonstration unit at Saudi Aramco’s Ras Tanura refinery.

JX embarked on the third phase of development including scaling-up of a demonstration unit to a 3000 bpd commercial demonstration unit, which is being built at JX’s refinery in Mizushima, Japan. Shaw and Axens provided engineering services for the unit, which is expected to be operational later in 2011. The HS-FCC design uses Shaw and Axens’ regeneration and catalyst transfer technology and expertise that stems from their 25-year FCC relationship. The two companies are recognized leaders in the FCC arena having licensed 50 grassroots and performed more than 200 revamp projects.

United Refining Company's Earnings Improved in 2Q2011

United Refining Company, a regional refiner and marketer of petroleum products in the U.S. announced in mid-April operating results for the second fiscal quarter and six month period ended February 28, 2011.

Adjusted earnings before interest, taxes, depreciation and amortization (EBITDA calculated on a FIFO basis before the LIFO inventory adjustment), for the three months ended February 28, 2011 increased $43.2 million to $28.5 million compared to a negative $14.6 million for the three months ended February 28, 2010. Adjusted EBITDA increased $45.4 million

Cont. page 6
for the six months ended February 28, 2011 to $31.2 million from a negative $14.3 million for the six months ended February 28, 2010.

Net sales for the three months ended February 28, 2011 and 2010 were $692.3 million and $594.7 million, respectively. This was an increase of $97.6 million or 16.4% over the prior year period. Retail petroleum sales volume and merchandise sales dollars both continued to increase on a comparable quarter basis resulting in 21 consecutive comparable quarter increases. Net sales for the six months ended February 28, 2011 and 2010 were $1,311.4 million and $1,215.7 million, respectively. This was an increase of $95.7 million or 7.9% over the prior year period.

United operates a 70,000 bpd refinery in Warren, Pennsylvania. In addition to its wholesale markets, the Company also operates 367 Kwik Fill®/Red Apple® and Country Fair® retail gasoline and convenience stores located primarily in western New York and western Pennsylvania.

Thailand Refinery Prepares to Meet Euro-4 Standards

Exxon Mobil Corp. plans to halt its Sriracha refinery in Thailand as it modifies units to reduce sulfur in fuels, according to two people with knowledge of the work and noted in a April 24 Bloomberg press release. The shutdown will start in September and last about five weeks, the people said, declining to be identified because the information hasn’t been made public.

The shutdown will enable work to be completed and enable the facility to produce low-sulfur fuels before Thailand’s switch to Euro-4 standards next year, which will limit allowable sulfur content in gasoline and diesel to 50 ppm or less.

Exxon Mobil said on July 29 that it began work on a clean-fuels project at the plant, with commissioning expected by the end of 2011. The company said on July 16 it would modify existing hydrotreating units to cut sulfur levels in gasoline and diesel to 50 ppm and build a facility to reduce benzene in gasoline to 1.0% to meet stricter fuel specifications that will take effect on Jan. 1, 2012.

Eni SpA Reports 1Q2011 Profit in Spite of Lost Libyan Production and Poor Refining Margins

Italy’s largest energy producer, Eni SpA said first-quarter 2011 profit rose 22% as higher oil prices offset lost production caused by violence in Libya, as reported in Bloomberg on April 27. However, refining margins are also likely to remain unprofitable in 2011, according to the statement. Refining output will probably decline this year particularly at the Venice refinery due to the halt in supply from Libya, the company said.

Corporate-wide adjusted net income climbed to 2.22 billion euros ($3.26 billion) from 1.82 billion euros a year earlier, the Rome-based company said April 26 in a statement. That surpassed the 2.09 billion-euro average estimate in a Bloomberg survey of 12 analysts. Net sales rose 16 percent to 28.8 billion euros.

“Eni delivered a solid set of financial results on the back of a favorable oil price environment,” Chief Executive Officer Paolo Scaroni said in the statement. “In spite of ongoing uncertainties regarding resumption of our activities in Libya, the profitability and growth outlook for our company has remained positive.”

Eni said since April the company has been producing 50,000 to 55,000 bpd oil equivalent in Libya for local electricity production, all coming from its Wafa facility. The loss in output is being partly compensated through ramped-up production in Egypt, Iraq and Italy, the company said. Eni also said it plans to start up new fields in Australia, Algeria and the U.S.

Valero Turns 1Q2011 Profit Despite Heavy Maintenance Schedule

Higher margins for diesel and jet fuel helped U.S. based Valero Energy reverse a loss in the first quarter of 2011 compared with the same period last year, the company said on April 26. The refiner earned a profit of $98 million, or 17 cents per share, compared with a loss in the first quarter of 2010 of $113 million, or 20 cents per share. Valero’s revenue in the quarter rose 42%, to $26.3 billion, compared with $18.5 billion a year ago.

Cont. page 7
“Clearly, the first quarter was a much better start to the year than last year,” Valero CEO Bill Klesse said. “Our refining system experienced strong margins and turned in solid results despite a heavy maintenance schedule and associated restart delays.” Klesse noted that refining margins for the entire industry were strong in the first quarter due to global fuel demand.

Exxon Mobil Continues to Expand Hydrotreating Capacity

Exxon is building a diesel hydrotreater at its Singapore refining complex, which will boost production of ULSD, according to a statement dating back to November 2010. The company also has inaugurated a hydrotreater at its refinery in Antwerp, Belgium, with annual output equivalent to the yearly consumption of two million diesel-powered cars. The unit has been operating since the end of January, Johan Scharpe, a company spokesman in Antwerp, said on April 8.

Canadian Crude Flow to U.S. Gulf Coast Refineries

Suncor Energy’s chief executive said earlier in April that he believes energy security will be the key to U.S. government’s decision on approval of the proposed Keystone XL pipeline to carry Canadian crude to the concentration of refineries on the U.S. Gulf Coast. "I think energy security will trump in regards to the Keystone XL pipeline," said Rick George, president and chief executive officer of Calgary-based Suncor Energy.

George said the crude that would travel down TransCanada Corp’s proposed Keystone XL pipeline would displace heavy crudes from Mexico, Venezuela and Saudi Arabia. "This is a very important source for the U.S.," he said.

Canada is already the largest exporter of crude to the United States, sending 2.5 million bpd of oil and oil products across the border in 2009, according to U.S. government data. The permit for Keystone XL is now facing opposition from environmentalists in both countries. The U.S. State Department is currently considering whether to issue a permit for the Keystone project.

Originally, the Cushing, Oklahoma-to-U.S. Gulf Coast leg of the pipeline was expected to be completed by 2013. U.S. refiners on the Gulf Coast are looking for the pipeline to move out some of the crude oil locked in storage at Cushing to their refineries.

Inventories of West Texas Intermediate, the U.S. crude benchmark, continue to rise in Cushing -- the delivery point of the NYMEX crude oil futures contract - pushing down the price due to lack of transportation options from the region to the large concentration of refineries on the U.S. Gulf Coast.

EDITORIALY SPEAKING

Profitability and Contradictions

It was only recently that the United States Energy Information Administration (EIA) forecasted that the retail price of regular-grade motor gasoline will average $3.86 per gallon during the summer 2011 driving season (the period between April 1 and September 30), up from $2.76 per gallon last summer. EIA forecasted the annual average regular retail gasoline price would increase from $2.78 per gallon in 2010 to $3.70 per gallon in 2011 and to $3.80 per gallon in 2012. It also noted that “current market prices of futures and options contracts for gasoline suggest a 33% probability that the national monthly average retail price for regular gasoline could exceed $4.00 per gallon during July 2011. It’s late April and we are already at $4.00 per gallon or higher in many areas of the country! Already, there are six states with retail gasoline prices higher than $5.00 per gallon.

Nonetheless, many refiners throughout the world are reporting margins improvements in the first quarter of 2011 as compared to this same time last year. In spite of rising oil prices, there is a growing demand for refined liquid products in the transportation sector. Other refined products, such as petrochemical feedstocks are also in demand.

Positive refinery margins will continue into 2011 provided that refined product prices do not lag behind feedstock prices. Unrest in the Middle East and geopolitical changes has shifted the flow of crude to the extent that assures a significant increase in production of discounted Canadian based bitumens and other heavy feedstocks in spite of the difficulties encountered with upgrading them to transportation fuels.

Many refiners processing higher percentages of these crudes are discovering that...
their crude unit just wasn’t designed for processing these feedstocks, even if the intention was to design the crude unit for these crudes (e.g., SAG-D)! With the wave of crude unit shutdowns and failures being quietly discussed in the industry, it’s back to the drawing board and requesting more money from management to re-design the crude/vacuum unit, especially the overheads. More than likely, desalting capacity needs to be increased, vacuum units need to be re-designed, etc. While plant engineers hold the designers’ hands to the fire for the their “mistakes,” refiners may need to adhere to the designer’s recommendations prescribed in the original scope.

Nonetheless, refiners everywhere seem to be committed to processing higher volumes of discounted crudes. For example, Turkish oil refiner Tupras, which is expanding its residuum upgrading capability, said this April that profit will rise this year if market conditions remained unchanged, with sales seen up 50% if oil remained at an average $120 per barrel.

"There is a high probability that profitability in 2011 will be higher than in 2010 if the market continues in this way," chief executive Yavuz Erkut told reporters on April 14. Tupras, owned by Turkey's largest conglomerate Koc Holding, made a 2010 net profit of 737 million Turkish lira ($490 million), on sales of 26.2 billion. The company expected borrowing for its residuum upgrading project (RUP), converting fuel oil into diesel and petrol, to be around $2 billion and the deal would become clear by the start of August 2011.

Refinery profitability in general has improved in many regions. This is validated in part by higher refinery runs. For example, Russian oil refining runs were up by 2.4% compared with the same month last year, Russian Energy Ministry data showed. Russian refineries processed 5.10 million bpd in February, up from 5.09 million bpd in January. In February 2010, Russian oil plants processing averaged 4.98 million bpd.

Elsewhere, Brazilian oil company Petrobras reported that sales of refined product in the last quarter of 2010 were 24% higher than those in the corresponding three months of 2009. Energy giant BP said in mid-April that first-quarter net profits leapt 17% to $7.124 billion as oil prices surged, one year after being hit by the US oil disaster. China's Sinopec said on April 24, that its 2010 net profit rose nearly 14% on higher oil prices and strong domestic demand for refined oil and chemical products. Asia's largest refiner reported a net profit of 71.8 billion yuan ($11 billion), up from 63.15 billion yuan in 2009, the company said in a statement to the Hong Kong Stock Exchange. Beijing-based Sinopec attributed its "good financial results" to China's rapid growth, robust demand and "the increase in the price of crude oil, oil products and petrochemical products." India's largest private sector firm, Reliance Industries, reported in mid-April its biggest-ever profits, but the rise lagged behind expectations due to lower-than-expected refining margins growth. The energy giant said net profit rose 14.1% to 53.76 billion rupees ($1.2 billion) for the three months ended March, from 47.10 billion rupees a year ago. Reliance's gross refining margins (GRMs) rose 22% to $9.2 a barrel for the quarter, against analysts' expectations of over $10 a barrel. It has been reported among industry circles that Reliance has a keen interest in processing higher volumes of heavy crudes as higher volumes of Venezuelan crudes are being diverted from traditional U.S. upgrading facilities to the Reliance Jamnagar mega-refinery. Hopefully, there will be no surprises at the crude unit or further downstream when running higher percentages of these crudes (let’s say 23% by total feedstock volume) for extended periods.
CALENDAR OF EVENTS

MAY


JUNE


OCTOBER


NOVEMBER

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