Celebrating 100 years of operations at our Curtis Bay Works
Alcyon™ Catalyst: A New Star Emerges
Grace Davison introduces Alcyon™ catalyst, a revolutionary new FCC catalyst designed for maximum activity

Grace Davison Refining Technologies

Units that are circulation limited can’t take full advantage of improved feed quality. When the FCC catalyst is not active enough regenerator temperatures become too low and desired reactor temperatures can’t be achieved. Some refiners resort to burning torch oil or recycling slurry to provide additional delta coke which is often detrimental to the operation. Alcyon provides superior activity and stability while maintaining excellent coke and dry gas selectivity. Alcyon is Grace Davison’s latest invention proving once again. We don’t just make FCC catalysts, we make FCC catalysts for you. www.e-catalysts.com
Dear Refiners,

These are difficult times, highly unpredictable and full of uncertainties. The last two years, for example, have been unlike anything I have ever experienced since joining Grace Davison’s RT North American sales force in 1986. I believe that as 2010 comes to an end and 2011 begins, we must, more than ever, critically examine our actions to become better prepared for this coming year of uncertainties.

Everyone is conscious of price. Every day the papers and journals are replete with articles and editorials citing the recent governmental rulings and interpretations as they apply to our various businesses.

In addition to all the imposed controls, we at Grace Davison have observed our raw material escalate in the last two years at a higher rate than we have ever before seen. However, our fluid cracking catalysts remain one of the biggest bargains available to the refiner today. Grace Davison, as the industry leader, has been instrumental in advancing the catalytic side of FCC technology, while at the same time, routinely passing along to the refiner the fruits of our cost-savings programs. Our Alcyon™ catalyst is a perfect example of just such a saving.

Prices that are too low cannot produce the return on investment necessary to maintain efficient plants, provide the capital to meet pollution standards, conduct an aggressive research effort, continue the necessary and much appreciated services and, most importantly, guarantee the continued supply of consistent, high quality, premium catalysts the refining industry has come to expect from Grace Davison.

Healthy suppliers are a requisite for a healthy industry.

Whatever your FCC catalyst and additives requirements, you can feel confident that we at Grace Davison will continue delivering the quality and service we have been known for in our 68 years of serving the world’s refineries.

Sincerely,

Emery J. Udvari
Technical Sales Leader, North America
Grace Davison Refining Technologies
Alcyon™: New Catalyst Design for Maximum Activity and Conversion
By Rosann Schiller, Ann Benoit and Yuying Shu

Reducing Sulfur Oxide Emissions from the FCC Unit
By Renaud Kieffer, Maria Luisa Sargenti and Colin Baillie
Grace Davison Refining Technologies Europe

OlefinsUltra® HZ Technology Improves Propylene Yields
By Kristen Wagner and Denise Farmer

The Role of the Rare Earth Elements in Fluid Catalytic Cracking
By Rick Wormsbecher, Wu-Cheng Cheng, and Dieter Wallenstein

Answers to the 2010 NPRA Q&A FCC Questions
By Rosann Schiller, David Hunt and Stuart Kipnis

Low NOx FCC Promoter Optimization at CITGO Petroleum Corporation’s Lake Charles Refinery
By Kent Turner, CITGO Petroleum Corp.; David Hunt and Eric Griesinger, Grace Davison

From the Editor:

This issue reflects the refining industry’s current concern with the price and availability of rare earth. This crisis is addressed in our Guest Editorial on the opposite page, as well as in a technical article. Grace Davison remains committed to providing refiners with technology for tailored solutions, a broad product portfolio, strong, market-focused R&D, flexible manufacturing, and the industry-leading tech service you have come to expect from us.

On another note, Yuying Shu, co-author of the Alcyon™ catalyst article, has been honored by the Daily Record as one of 25 Maryland “Innovator of the Year” recipients. Yuying is recognized along with the rest of the Alcyon™ catalyst Team: Jeff DelMartin, Ruizhong Hu, Brent Machado, Rosann Schiller, Wilson Suarez and Rick Wormsbecher.

Finally, the front cover of this issue features our Curtis Bay plant, which celebrated its 100th anniversary of operation in September 2010. While our FCC plant is far newer than that, we join our fellow employees in marking this milestone.

Sincerely,
Joanne Deady
Vice-President, Global Marketing
Grace Davison Refining Technologies
Alcyon™: New Catalyst Design for Maximum Activity and Conversion

Introduction

Alcyon™ is a new ultra high activity catalyst from Grace Davison and represents a true breakthrough in catalyst technology. Refiners have turned toward hydrotreating FCC feedstocks to meet the requirements of increasingly stringent regulations for ultraclean fuels and tightening refinery emissions standards. Alcyon™ catalyst is specifically designed for the unique challenges faced by FCC units processing severely hydrotreated (HT) feeds, delivering the highest activity per unit surface area to achieve maximum conversion. Yet despite its high activity, Alcyon™ catalyst retains the right selectivity, enabling you to maximize yield within your refinery process constraints.

While the focus of this article is on HT applications, any FCCU requiring maximum activity, processing low Conradson Carbon feedstock, or routinely bumping up against constraints can benefit from the selectivity advantages of the Alcyon™ catalyst family. The flexibility exists to moderate the activity for a less extreme operation; the formula-
tion designated for the latter purpose is Alcyon™ G catalyst.

**Hydrotreated FCC Feedstock**

When a feedstock is improved via hydrotreating, it ironically presents unique challenges for fluid catalytic cracking (FCC) catalyst optimization. Because hydrotreated feedstocks contain a larger amount of crackable molecules, very high conversion catalysts are needed for optimum yields and heat balance constraints. Hydrotreating decreases the sulfur and nitrogen content and increases the hydrogen content of the feed. The hydrogen (H) content of the FCC feedstock typically ranges from 11.8 wt.% for aromatic feeds to about 13.5 wt.% for highly paraffinic feeds. For reference, the H-content of an n-paraffin, such as hexadecane, is 15 wt.%. As the H-content increases, the feedstock becomes easier to crack. In the FCCU, the hydrogen balance must be satisfied as does the heat balance. The extent of conversion to lighter products is limited by the amount of hydrogen in the feed. The hydrogen balance can be used to calculate the expected conversion level for a given feed H content.

The following example illustrates the effect of feed hydrogen on conversion. Typical vacuum gas oil (VGO) feed has a hydrogen content of 12.5%. The H content of the FCC products is known from the molecular structure and the molecular weight. The average H-content of the lighter cracked products (<430°F) varies with product selectivity but is typically about 14.5%; The FCC (<430°F) product contains more hydrogen than the feed because the molecules are smaller. The average H-content of the “unconverted” (>430°F) fraction (LCO + HCO) is dependent on the operation but is typically about 9.25 wt.%; and the H-content of the coke is about 6 wt.%. For a given coke yield of 5 wt.%, the hydrogen balance dictates that the conversion should be 70 wt.%. If the feed were hydrotreated to a hydrogen content of 13 wt.%, an operation with the same coke yield of 5 wt.%, would yield a much higher conversion level of 80 wt.%. In order to satisfy the hydrogen balance, conversion must rise when the feed H increases, or in other words the FCC must make more <430°F fraction.

This is indeed observed commercially. Table I lists properties of Alaskan North Slope VGO, before and after severe hydrotreating to remove 95% of the sulfur. After hydrotreating, feed nitrogen, Conradson Carbon and VABP decrease, while API gravity and K-Factor increase. The contaminant metals, primarily nickel and vanadium, may also be reduced. The H-content increases from 12 wt.% to 13 wt.%. When these two feeds are cracked in a pilot unit, the HT feed achieves higher conversion, gasoline, and LPG for a given coke yield while yielding lower dry gas and bottoms. But the HT feed requires both higher riser outlet temperature (ROT) and higher cat-to-oil ratio (C/O) to achieve the same coke yield as the base case.

Higher unit conversion means that more bonds must be broken in the riser. The molar expansion from the cracking reaction is a good measure for the average number of bonds broken in

### Table I

**Commercial Impact of Hydrotreating**

<table>
<thead>
<tr>
<th>Feed</th>
<th>ANS VGO</th>
<th>HT ANS VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘API</td>
<td>19.8</td>
<td>25.4</td>
</tr>
<tr>
<td>Sulfur, wt.%</td>
<td>1.2</td>
<td>0.06</td>
</tr>
<tr>
<td>Nitrogen, wt.%</td>
<td>0.17</td>
<td>0.08</td>
</tr>
<tr>
<td>Con. Carbon, wt.%</td>
<td>0.27</td>
<td>0.09</td>
</tr>
<tr>
<td>K Factor</td>
<td>11.7</td>
<td>12.0</td>
</tr>
<tr>
<td>H Content, wt.%</td>
<td>12.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Reactor T, °F</td>
<td>980</td>
<td>995</td>
</tr>
<tr>
<td>Feed T, °F</td>
<td>500</td>
<td>465</td>
</tr>
<tr>
<td>Regen T, °F</td>
<td>1378</td>
<td>1300</td>
</tr>
<tr>
<td>Cat/Oil, W/W</td>
<td>5.2</td>
<td>7</td>
</tr>
<tr>
<td>Air Rate</td>
<td>BASE</td>
<td>BASE</td>
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<tr>
<td>Conversion, vol.%</td>
<td>70.0</td>
<td>80.2</td>
</tr>
<tr>
<td>C2+, wt.%</td>
<td>3.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>4.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>
the reaction. A molar expansion of four implies that an average of three bonds are broken in the molecular weight reduction reactions from cracking. An estimate of the molar expansion can be calculated from the coke free conversion for different feedstocks and assumptions about the average molecular weight of the products.

The coke free conversion is the conversion where the coke is not included. In the example above, a 70 wt.% normal conversion is a 65 wt.% coke free conversion, with 5 wt.% coke. Figure 1 shows a plot of the calculated molar expansion versus coke free conversion for a HT-VGO and VGO. Because of the hydrogen balance requirements discussed above, the molar expansion increases.

It may appear that the increase is only slight and not significant. Molar expansion increases by only 0.6, yet as we saw in the commercial data (Table I), that translates into substantially higher conversion. When the feed hydrogen content rises, hydrogen in products must increase as well. As much as a 10% increase in conversion occurs when a VGO is hydrotreated for a seemingly small shift in molar expansion. The catalyst should also have the right selectivity to satisfy the hydrogen balance within unit constraints.

Increased molar expansion may result in a new constraint. At high conversion, more moles of product need to be compressed and the wet gas compressor may begin to limit the process.

In addition to the hydrogen balance, one must also consider delta coke. Delta coke is, simply put, the difference between carbon on spent catalyst after stripping and carbon on regenerated catalyst. Total coke yield is the delta coke times C/O and is the amount of coke burned in the regenerator. The burning of the total coke is responsible for fulfilling all the heat requirements, including the heat of reaction, in the FCC process. Total coke cannot change unless there is a change in the heat requirements. If the heat requirements are held constant, a change in delta coke will cause an opposing change in C/O to maintain the total coke yield constant.

There are four contributions to delta coke: feed carbon, contaminant coke, stripping coke and catalytic coke. The feed carbon coke is related to the Conradson Carbon level. Stripping or cat-to-oil coke results from the carry-over of occluded hydrocarbons after stripping. The feed carbon coke tends to be independent of the catalyst but stripping coke can be influenced by the physical properties of the catalyst. Contaminant coke results from the catalytic effect of metals in the feed and can be minimized with the use of metals traps or antimony. Lastly, catalytic coke is a function of conversion and is the intrinsic coke making tendency of the catalyst.

After feed is hydrotreated, the relative contributions to delta coke shift (Figure 2). Both feed carbon and contaminant coke are reduced dramatically. We can assume that the stripping coke remains constant. Therefore, the bulk of the coke requirement must be supplied by catalytic coke. If the catalyst is not active enough to drive up conversion, delta coke falls and
less coke is burned in the regenerator. That means C/O (circulation rate) must increase for a set ROT. At high circulation rates approaching the limits of unit design, the natural response is to turn down severity with either lower ROT or higher preheat which both lower conversion. The new operation is more prone to low regenerator temperatures due to the shift in the coke contributions after hydrotreating. The FCCU needs a high activity catalyst that supplies all of the delta coke because providing delta coke by burning torch oil or recycling slurry is detrimental to the operation. At low regenerator temperatures, it may be difficult to remain below the permitted CO limit.

**Grace Davison’s breakthrough FCC catalyst, Alcyon™**

Alcyon™ FCC catalyst was specifically developed by Grace Davison for applications that require maximum activity and conversion. Alcyon™ catalyst delivers increased activity yet preserves the coke selectivity benefits which is a paradigm shift in what the industry has come to expect from conventional FCC catalyst. Grace’s technology innovation in Alcyon™ catalyst is to improve conversion by enhancing the rate of cracking within the catalyst particle.

The rate of cracking is proportional to the number of active sites and the surface concentration of hydrocarbons. The conventional route to higher activity in FCC catalyst is to increase the number of active sites, either by increasing rare earth content or the zeolite concentration. Grace has discovered a way to increase the concentration of hydrocarbons within the particle. This fundamental research has resulted in a zeolite with a modified surface that has increased hydrocarbon adsorption capacity and hence a higher cracking rate. For the same number of active sites, Alcyon™ technology increases the surface area concentration of hydrocarbon, increasing the cracking rate per site and driving conversion.

The proprietary zeolite modification in Alcyon™ catalyst supplies the highest activity of any catalytic technology with a low surface area per kinetic conversion (SA/K). Low SA/K number is desired as excessive surface area required by traditional FCC catalyst technology carries
unstripped hydrocarbon product to the regenerator, causing yield loss and increasing coke with no benefit. Also, unstripped hydrocarbon product can burn very hot locally, degrading the catalyst.\textsuperscript{3}

An added benefit of Grace’s proprietary zeolite is superior activity retention that has been verified in field performance. Alcyon is particularly well suited for refiners looking to re-optimize unit operation to maximize profitability yet remain within operating limits. For any given coke yield, Alcyon\textsuperscript{TM} catalyst achieves higher conversion, maximizing total FCC barrels to the refinery gasoline pool.

**Performance Data**

Let’s consider a refinery that is processing VGO in its FCCU. The base case operation makes 2.5 wt.% coke per unit of feed and requires a C/O ratio of 5.5, which is well within the operating window. The FCCU then undergoes a significant change in operating philosophy. The VGO is now 100% hydrotreated. As previously discussed, the sources of delta coke shift, and in order to operate at the same coke make, a C/O of 8.2 is required (Figure 3) beyond the physical circulation limit of the FCC. As a result, the unit may need to reduce severity, recycle slurry or use torch oil in order to achieve heat balance, all which will minimize the yield benefit of the new feedstock.

When Alcyon\textsuperscript{TM} catalyst technology is applied, the coke requirement is satisfied with only a modest increase in C/O which is well within operational capabilities. Figure 3 shows the cat-to-oil ratio versus coke for the base
catalyst cracking the VGO and the HT-VGO feed, and Alcyon™ catalyst cracking the HT-VGO feed.

The base catalyst achieved higher conversion on the hydrotreated feed but needed very high C/O to do so. Alcyon™ catalyst on the other hand, can deliver the same conversion but at substantially lower C/O ratio; only slightly higher than the base case VGO operation (Figure 3). In a real world example, Alcyon™ catalyst has demonstrated superior stability and activity retention over the base catalyst technology (Figure 4). The refiner was able to increase equilibrium MAT by 2 wt.% conversion while maintaining the equilibrium coke factor. Alcyon™ catalyst enabled the refiner to maintain a comfortable heat balance without a sacrifice in coke selectivity, despite a drastic change in operating philosophy.

A second example demonstrates an interesting case where Alcyon™ catalyst technology is more coke selective than the incumbent catalyst, yet still delivers more delta coke to further drive conversion. This unit is currently using a competitive catalyst and is constrained by WGC capacity. However, they can not lower ROT and still meet the desired conversion targets. Figure 5 shows that the Alcyon™ catalyst is more coke selective than the base catalyst; that is, at constant conversion Alcyon™ catalyst makes lower coke. Alcyon™ catalyst is more active than the competitive base and produces the same coke at lower cat-to-oil, meaning that the delta coke is higher (Figure 5). Figure 6 shows that at constant coke, even at one number lower cat-to-oil, that is lower catalyst conversion.

**Figure 5**  
*Alcyon™ Catalyst is More Coke Selective and More Active*

**Figure 6**  
*The Selectivity of Alcyon™ Catalyst Delivers Higher Conversion Despite Lower C/O*
Alcyon™ catalyst has delivered higher activity and increased delta coke, which reduced C/O yet conversion improved. The expectation of reduced C/O is lower conversion and here we see the opposite with Alcyon™ catalyst. It’s a real paradigm shift and represents a true innovation in the field of FCC catalysis.

When the pilot study yields are modeled to simulate an actual heat, mass, and hydrogen balanced commercial operation, Alcyon™ catalyst delivers a clear advantage. Alcyon™ catalyst is more active and selective (Table II), achieving the targeted conversion at lower severity. Alcyon™ catalyst increases gasoline yield and reduces slurry. Despite increased conversion, Alcyon™ catalyst actually reduces the wet gas (scfb) by 5%, lifting the compressor constraint allowing for a re-optimization of operating conditions to maximize unit profitability.

Alcyon™ G: FCC Catalyst to Maximize Barrels in the Gasoline Pool

The examples presented thus far focus on severely hydrotreated feedstocks. But what if your operation isn’t quite as severe? What can Alcyon™ catalyst do for you? Because Alcyon™ catalyst is formulated on Grace’s proven alumina sol binding platform, the flexibility exists to moderate the activity for a less extreme operation; these catalysts are designated Alcyon™ G catalyst. At reduced activity, the coke selectivity advantage of Alcyon™ G catalyst is even more pronounced relative to the base catalyst. The improvement in coke selectivity directly translates into increased gasoline yield. Alcyon™ G catalyst also produces a more olefinic LPG stream, that can be used as alkylate feed (Figure 7). The increased yield is achieved at equivalent total LPG yield, which will not constrain downstream operations. The net result is an overall increase in total barrels going to the refinery gasoline pool.

Summary

When an FCC feedstock is hydrotreated, the quality improves as the H content increases. To satisfy the hydrogen balance, conversion must also increase. The FCCU needs a high activity catalyst that supplies enough selective activity to achieve higher conversion and the necessary delta coke. The heat balance should not be satisfied by burning torch oil or recycling slurry, as these are oftentimes detrimental to the operation. Higher conversion also means higher molar expansion, which may cause a limit at the wet gas compressor. The new catalyst should also have the right selectivity, to satisfy the hydrogen balance within unit constraints.

Alcyon™ catalyst is a breakthrough FCC catalyst technology suitable for any unit seeking to maximize activity or conversion. It can alleviate unit constraints such as circulation and compressor limits, and enable refiners to take full advantage of improved feedstock quality. In commercial

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Alcyon™ (relative to base case)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate</td>
<td>-</td>
</tr>
<tr>
<td>Cat Adds</td>
<td>-</td>
</tr>
<tr>
<td>Feed T (°F)</td>
<td>-</td>
</tr>
<tr>
<td>ROT T (°F)</td>
<td>-5.0</td>
</tr>
<tr>
<td>Regen T (°F)</td>
<td>+9.0</td>
</tr>
<tr>
<td>Circulation, tpm</td>
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</tr>
<tr>
<td>C/O Ratio</td>
<td>-0.4</td>
</tr>
<tr>
<td>Yields</td>
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<tr>
<td>Wet Gas, SCFB</td>
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<tr>
<td>Gasoline, lv.%</td>
<td>+2.0</td>
</tr>
<tr>
<td>LCO, lv.%</td>
<td>-</td>
</tr>
<tr>
<td>Slurry, lv.%</td>
<td>-0.3</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>-</td>
</tr>
<tr>
<td>Conversion, lv.%</td>
<td>+0.3</td>
</tr>
</tbody>
</table>
application, Alcyon™ catalyst has delivered the same benefits to a refiner who was challenged to maintain selectivity after a major process change. Alcyon™ G, a lower activity catalyst based on the same zeolite, can be utilized to increase the total barrels in the refinery gasoline pool via its controlled selectivity for gasoline and butylene.

Alcyon™ catalyst is the latest of 11 new products introduced since 2008 by Grace Davison Refining Technologies. Alcyon™ catalyst’s revolutionary technology and performance represents Grace’s continuing commitment to delivering to refiners a broad portfolio of FCC catalysts and additives, designed to meet current and future market needs, backed by industry-leading technical service and a highly flexible manufacturing system.

References

Reduction of Sulfur Oxide Emissions from the FCC Unit

Introduction

Although the amount of sulfur oxide (SOx) emitted from FCC units is relatively small, it still accounts for most of the SOx released from oil refineries. The major options for reducing SOx emissions from the FCCU include flue gas scrubbing (FGS), hydrodesulfurization (HDS) and the use of a SOx-reduction additive. FGS requires a high capital investment and the operating costs are high. In addition, discarding the spent treating compounds, such as lime, caustic soda, or other compounds can also be problematic. HDS requires the highest capital investment but will also provide improved yields as well as lower SOx emissions. Therefore, the use of SOx reduction additives is often the preferred route taken by refiners, as they require very little capital investment and are extremely effective in reducing SOx emissions.

Due to new, more stringent, local environmental legislations Refinery A located in Western Europe was confronted with the challenge of reducing SOx emissions from the FCC regenerator...
This is highlighted in Table III, which shows daily and yearly SOx bubble limits for the refinery before and after January 1, 2009.

Faced with the various options for tackling SOx reduction, the refinery chose the additive route and began using Super DESOX® additive in December 2008. The results of this trial will be discussed in this article.

**Super DESOX® Additive**

Super DESOX® additive was commercialised in 2003 and is based on a patented magnesium-alumina spinel structure, which has been successfully used by more than 70 refiners worldwide. To understand why this magnesium-alumina spinel structure works so well, it is necessary to examine the mechanism for the catalytic reduction of SOx emissions in the FCC unit. A schematic diagram of the oxidation and reduction reactions of sulfur compounds in the FCC unit is shown in Figure 8. In the regenerator, sulfur contained in the coke is oxidized to SO2 and SO3. Both of these sulfur oxides are absorbed on the SOx additive, where SO2 is further oxidized to SO3 in the presence of oxygen and an oxidation catalyst in the additive. In the regenerator the SO3 reacts with magnesium oxide in the alumina spinel and is converted to magnesium sulfate. Compared to free magnesium oxide, the spinel in Super DESOX® additive is extremely effective for this sul-

### Table III

**SOx Bubble Limits for the Refinery**

<table>
<thead>
<tr>
<th></th>
<th>Average SOx Bubble Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Daily (mg/Nm3)</td>
</tr>
<tr>
<td>Before 1st January 2009</td>
<td>1700</td>
</tr>
<tr>
<td>After 1st January 2009</td>
<td>1700</td>
</tr>
</tbody>
</table>

![Figure 8](image_url)

**Figure 8**

*Catalytic SOx Reduction Using Super DESOX® Additive*
fate formation and a stable sulfate is formed under regenerator conditions. In the reactor the magnesium sulfate is reduced by hydrogen to form magnesium sulfide. Super DESOX® additive plays an important role here, too, because the magnesium in the alumina spinel is less basic than free magnesium oxide, thereby making the sulfate easier to reduce. In addition, vanadium on the spinel structure further decreases the stability of the magnesium sulfate, especially under reducing conditions, and in the presence of steam. The magnesium sulfide is then hydrolysed to a magnesium oxide in the stripper which then returns to the regenerator to complete the catalytic cycle. Super DESOX® additive has the highest SOx reduction activity on the market and has been widely utilized in SOx reduction applications.

Establishing a Baseline for Uncontrolled SOx Emissions

A number of operating variables have been identified as having significant effects on the performance of SOx reduction additives.1-3 Some of these include the presence of combustion promoters, the ratio of catalyst circulation rate to unit catalyst inventory, unit temperatures, availability of oxygen in the regenerator, feed sulfur content and SOx concentration.

Various scientific studies have shown that the fraction of thiophenic sulfur in the feed has a direct impact on the coke sulfur content deposited on spent catalyst and thus, on SOx emissions. Therefore changes in uncontrolled SOx emissions can be accurately estimated by measuring thiophenes in feed. However, it is uncommon for refiners to be able to measure thiophenic feed content on a regular basis. It is therefore recommended to estimate uncontrolled SOx emissions by measuring feed sulfur or even better with slurry sulfur (the slurry being the most aromatic product of the FCCU).

Due to the various operating variables that can affect SOx additive performance, it is necessary to establish a baseline of uncontrolled SOx emissions to be able to calculate the true SOx reduction caused by the additive. This baseline is calculated by performing correlations for every relevant parameter based on pre-trial unit data. To establish a baseline for Refinery A, approximately three months of unit data was used.

We observed that in general parameters such as slurry density and slurry sulfur content correlated well with SOx emissions. However, due to a lack of slurry measurements, it was decided to use feed properties instead. In this respect, the main parameters turned out to be feed sulfur content (S.charge), vacuum residue throughput (RSV) and flue gas oxygen content, as shown in Figure 9. Using the excellent data from the refinery, the correlation in Figure 10 was established using the normalized SO2 values from the pre-trial period (from October 21, 2008 to January 12, 2009). The high value of R2 (86.9) signifies the extremely good correlation obtained.

As expected, it can be seen that increased feed sulfur plays a major role in the above correlation, i.e. SOx emissions increase with increasing feed sulfur. In addition, increased residue...
throughput can also be expected to increase SOx emissions, which is indeed observed in the correlation. The incorporation of more residue results in increased SOx emissions due to the more refractive nature of its sulfur-containing compounds that will thus end up more readily in the coke on catalyst. The other important variable in the correlation is flue gas oxygen content. Increasing oxygen promotes the oxidation of coke on spent catalyst and thus the oxidation of sulfur species to SOx.

**Trial of Super DESOX® Additive at Refinery A**

The Super DESOX® additive performance at Refinery A is estimated by comparing the measured SOx emissions with the predicted uncontrolled SOx emissions, of which the latter is based on the correlation in Figure 10. To reach the target of reducing SOx emissions by 30% Grace Davison recommended using Super DESOX® additive at 0.8 wt.%, with a prior period of base loading to accelerate the introduction of the additive in the inventory. However the refinery decided not to have a base-loading period and began using 0.8 wt.% of Super DESOX® additive directly. The additive pre-blended with fresh catalyst was delivered to Refinery A on January 12, 2009 and entered the unit around January 19th as seen from the subsequent and obvious drop in flue gas SOx emissions, shown in Figure 11.

*Flue gas SOx was measured as SO₂ by an online analyser, and the SO₂ values are normalized to 3% excess oxygen in flue gas.*

**Figure 10**
Correlation of SOx Emissions

$$SO_2^* = -44.2 + 1796 \times S\text{ feed (\%)} + 4.94 \times RSV (t/h) + 40.2 \times O_2 (\%)$$

$$S = 36.0330 \quad \text{R-Sq} = 87.9\% \quad \text{R-Sq(adj)} = 86.9\%$$

* Normalized to 3% excess flue gas oxygen

**Figure 11**
Flue Gas SO₂ Emissions Before and During Super DESOX® Additions*

*Northington* 2005

...
The effect of Super DESOX® additive was immediate with average SOx reductions of 23% observed within the period of January 19th to February 15th in which the additive was pre-blended at 0.8 wt.%. This can be effectively considered as a base-loading period during which a stationary concentration of additive is reached in the inventory. It was subsequently decided to reduce Super DESOX® additive pre-blending levels to 0.5 wt.% during February 16th to March 29th. The average SOx reduction performance during this period remained high at 25%. In the subsequent period between March 30th and June 30th, this refinery decided to increase Super DESOX® additive pre-blending levels to 1.5 wt.% to gain an idea of just how much SOx reduction could be achieved, and during this period the average reduction rate increased to 41%. Starting on September 28th, the refinery started pre-blending Super DESOX® additive at 1.8 wt.% due to increased feed and slurry sulfur levels, resulting in average SOx-reduction levels of 66%.

Figure 11 shows that SOx values measured over time were somewhat volatile. This is due to the variations in feed and slurry sulfur content during the trial period, which is reflected in the predicted uncontrolled SOx levels. As shown in Figure 12, feed sulfur varied between 0.31 and 0.52 wt.%, while slurry sulfur varied between 0.6 and 0.9 wt.%. In terms of retention levels of Super DESOX® additive the refinery acknowledged excellent performance. Indeed, Super DESOX® additive is recognized in the market for its retention properties.
During the period where Super DESOX® additive was added at 1.5 wt.% a serious inventory deactivation occurred due to increasing vanadium contamination of the Ecat, as shown in Figure 13. It is testament to the superior performance of Super DESOX® additive that even with the dramatically increased Ecat vanadium levels, and the subsequent drop in MAT activity, levels of SOx reduction were still achieved.

Conclusions

As a consequence of increasingly stringent local environmental regulations, Refinery A was forced to reduce SOx emissions by 30%, and Grace Davison recommended the use of Super DESOX® additive as the quickest and most cost-effective route to achieve this. Using the excellent data from the refinery a baseline for uncontrolled SOx emissions was established so that an accurate evaluation of the SOx-reducing performance of Super DESOX® additive could be evaluated. The trial of Super DESOX® additive was considered a complete success achieving the refineries objectives even with lower amounts of the additive than first predicted. Refinery A is now using Super DESOX® additive continuously as a simple, efficient and cost-effective solution to reduce flue gas SOx emissions.

References

Designed for maximum propylene production in high severity, high demand FCC units, OlefinsUltra® HZ additive is the latest development in ZSM-5 technology from Grace Davison. OlefinsUltra® HZ additive offers superior attrition resistance and the highest activity per pound of any ZSM-5 additive on the market. The novel, patented composition provides a combination of stability and selectivity required to maximize performance in an FCC unit.

Recently, a refiner who was limited by the wet gas compressor turned to Grace Davison for advice on how to further increase C₃⁺ production, yet stay within process limits. Laboratory ACE testing was conducted to predict the benefits of using Grace’s light olefins additives. The study revealed that OlefinsUltra® HZ additive gives the highest C₃⁺ yields at constant wet gas volume. Figure 14 clearly demonstrates the C₃⁺ advantage of OlefinsUltra® HZ additive over relatively lower activity ZSM-5 additives. OlefinsUltra® HZ additive allows a boost in revenue with incremental propylene yield, without further constraining the refinery operation.
Table IV below shows the normalized yield comparisons from the ACE study of different Grace Davison light olefins additives at constant conversion.

Grace Davison is the leading global supplier of high activity, high stability light olefins additives which include OlefinsMax®, OlefinsUltra® and OlefinsUltra® HZ brands from Grace Davison. These products are being used today in over 60 FCC units world-wide, providing value to the refiner in terms of incremental propylene, additional feed to the alkylation unit, and higher gasoline octane.

If you would like more information on Light Olefins Additives or any of our other FCC products, please contact your Grace sales representative.

Table IV
Yield Comparisons of Different Light Olefins Additives at 5 wt.% in Ecat

<table>
<thead>
<tr>
<th>72% Conversion</th>
<th>5% OlefinsMax®</th>
<th>5% OlefinsUltra®</th>
<th>5% OlefinsUltra® HZ</th>
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<tr>
<td>Dry Gas, wt.%</td>
<td>1.8</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>7.0</td>
<td>7.3</td>
<td>8.2</td>
</tr>
<tr>
<td>Total C₃’s, wt.%</td>
<td>8.0</td>
<td>8.4</td>
<td>9.4</td>
</tr>
<tr>
<td>Total C₄⁺’s, wt.%</td>
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<td>8.2</td>
<td>8.4</td>
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<td>Total C₅⁺’s, wt.%</td>
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<tr>
<td>LPG, wt.%</td>
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<td>LCO, wt.%</td>
<td>20.4</td>
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<tr>
<td>Bottoms, wt.%</td>
<td>7.2</td>
<td>7.3</td>
<td>7.3</td>
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<tr>
<td>Coke, wt.%</td>
<td>3.4</td>
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</tr>
<tr>
<td>RON</td>
<td>92.6</td>
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<tr>
<td>C₃ Olefinicity</td>
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<tr>
<td>C₄ Olefinicity</td>
<td>57.2%</td>
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</table>
Role of the Rare Earth Elements in Fluid Catalytic Cracking

Rare earth metals are a key component in fluid cracking catalyst, and are also used in small portions in almost every advanced industrial product. World wide demand for rare earths has increased due to consumer demand for lightweight, superminiaturized electronic components such as cell phones, iPods, and flat panel displays, as well as increased demand for ‘green’ technologies such as hybrid cars and wind turbines. So-called “rare earths” are actually more common than more familiar metals, but tend to be concentrated in hard to extract ore deposits. As a result, the world’s supply tends to come from only a few sources; China alone accounts for 95% of the world’s rare earth output. Recent export quota restrictions on rare earths from China have caused the price of these critical components to fluid catalytic cracking catalysts to rapidly rise. Because of these new market forces, we present a review here of the role of rare earths in fluid cracking catalysts.

The use of rare earth exchanged zeolites in cracking catalyst was described by Plank and Rosinski⁰, both of Socony Mobil Oil, in the
early 1960’s. They discovered that rare earth-containing zeolites were about 100 times more active than the traditional silica-alumina amorphous catalysts of the time. This invention was to have a profound effect on petroleum processing. Plank and Rosinski were inducted into the Inventor Hall of Fame in 1979.

Grace Davison fluid cracking catalysts are complicated mixtures of several components that are designed and tailored to meet the requirements of a particular FCC unit and feedstock. The rare earth elements perform two critical roles in the FCC catalyst. First, they control the activity, coke selectivity, and olefin selectivity of the zeolite portion of the catalyst. Second, in units that run high vanadium and consequently suffer from severe deactivation conditions, rare earths are used as vanadium traps, improving the coke selectivity even more and also improving the activity retention of the catalyst.

The zeolite component of the fluid cracking catalyst is responsible for most of the cracking activity. Since rare earths are used to control the activity and selectivity of the zeolite portion of the catalyst, a brief discussion of zeolites is warranted. Grace Davison catalysts use rare earth ultra stable Y type zeolite, or REUSY zeolite which was invented in the late 1960’s by McDaniel and Maher², both of W. R. Grace, and as the name implies is a very stable zeolite. A stick figure representation of the framework structure of Y type zeolite is shown in Figure 15. The structure is composed of a framework of tetrahedrally coordinated silicon or aluminum atoms by oxygen atoms that are shared between the tetrahedral sites. In Figure 15, the tetrahedral vertices represent silicon or aluminum atoms and the “sticks” connecting them represent oxygen atoms. The active sites of the zeolite are associated with the aluminum atoms, which are represented in Figure 15 by yellow dots, for clarity. As may be evident in Figure 15, zeolites are very high surface area materials, about 900 m²/g. For comparison, one heaping tablespoon of zeolite has the equivalent surface area of an American football field. Another useful visualization is to consider that if a hydrocarbon feed molecule “lays down” on the surface of the zeolite and it encounters an active site (yellow dot in Figure 15), it may undergo a cracking reaction. For the purposes of this discussion, we will use the expression “active site density” to mean “framework aluminum site density” to stress that the sites in the zeolite responsible for cracking are associated with the framework aluminum sites.

The active site density controls the activity of the zeolite portion of the catalyst. Careful chemical structural research work done in the 1960’s determined that the unit cell size (UCS) of the zeolite, as measured by x-ray diffraction, is proportional to aluminum site density, hence, the active site density in the zeolite. The unit cell dimension is an easy and attractive method to gauge the site density in the zeolite in equilibrium catalyst (Ecat). The higher the UCS, the higher the site density. For instance, a zeolite with UCS of 24.40 Å has a high site density of active sites, whereas a UCS of 24.30 Å would be considered moderate, and a UCS of 24.25 Å would correspond to low site density.
The role of zeolitic rare earth is to manipulate the in-use active site density of the zeolite as measured by the UCS. Zeolites used in cracking catalysts undergo reactions in the high temperature steam environment of the regenerator that destroy the active sites. As catalysts age in the FCC regenerator, the UCS is always dropping by a reaction called “dealumination” of the zeolite, where the active sites react with steam and become consumed irreversibly. (Using the visualization analogy from above, the yellow dots in Figure 15 are removed by the “dealumination” reaction.) The rare earth ions in the zeolite retard this deleterious reaction from occurring, and thereby retard the lowering of the UCS with catalyst age. This active site preservation is critical to the activity in the unit. Manipulation of the active site density of the catalysts with rare earth, renders a broad spectrum of catalyst activity and/or selectivity profiles available to refiners.

Table V shows that the UCS of a series of lab deactivated catalysts increases uniformly with rare earth content. This means that the zeolite active site density in the catalyst is increasing, and hence, the activity of the catalyst is also expected to increase. Table V also shows the conversion at constant catalyst-to-oil ratio for the same catalysts. Here again, the intrinsic activity of the catalyst increases with UCS, or rare earth content. In this way, the activity of the catalyst is controlled not only by the zeolite content, but also the rare earth level on the zeolite.

Site density not only controls the intrinsic activity, but also the selectivity, of the zeolite in the catalyst. High site density zeolite...
Lites have higher intrinsic activity but poorer coke selectivity and lower gasoline olefins (lower research octane number or RON), while lower site density zeolites have lower intrinsic activity with much improved coke selectivity and higher gasoline range olefins (higher RON). Work done by Rajagopalan and Peters \(^3\) at Grace Davison showed that zeolites with a site density corresponding to a UCS of about 24.30 Å had a “sweet spot” in the activity/gasoline yield versus coke selectivity trade-off. This is shown in Figures 16 and 17, which show the gasoline yield, coke yield, gasoline range olefins, and RON for a range of catalysts with different unit cell sizes. The catalysts were designed to have approximately the same activity, and the comparisons in Figures 16 and 17 are made at constant conversion, in order to compare the selectivity differences. As discussed, there is a maximum in gasoline and a minimum in coke selectivity for a UCS of 24.30 Å, while the gasoline olefins and RON decrease with increasing UCS. By operating at or near a UCS of 24.30 Å, a refiner can maximize yields and take advantage of the coke selectivity with maximum feedstock throughput. This discovery of the activity and coke selectivity benefits of REUSY was another transforming event in petroleum cracking, taking place in the mid 1980’s, which allowed refiners to dramatically increase FCC capacity and improve the overall production of gasoline. (See “The Quiet Revolution: REUSY”).

By far most refiners target the “sweet spot” of around 24.30 Å, as shown in Figure 18, which is the distribution of UCS’s of samples submitted to Grace Davison for Ecat analysis. No refiners operate below 24.24 Å, because the overall zeolite activity would be too low to maintain MAT activity. There are a few refiners operating with UCS in the 24.34 - 24.40 Å range; generally these refiners have a low olefin requirement on the product gasoline and therefore, must operate at a high UCS to control the olefins in gasoline. The rare earth level on the zeolite is a major control variable available to the refiner. While there are many factors which effect the zeolite UCS in the unit, rare earth on the zeolite in the most important, followed by catalyst addition rate. In the most general sense, increased catalyst additions will increase the UCS (decrease catalyst age), but it is not as strong a variable as rare earth. The regenerator
conditions, metals levels, catalyst loading limitations, etc. all play a role in controlling unit performance and catalyst additions.

Rare earths are also used in the catalyst as vanadium traps to reduce the deactivation caused by vanadium poisoning. Vanadium destroys the zeolite and increases production of coke and light gas. The precursor for vanadium poisoning is vanadic acid, which is volatile in the regenerator. As a result, vanadium in the regenerator is very mobile, and it quickly re-distributes itself to the youngest catalyst particles. Since vanadic acid is an acid, it promotes undesired side reactions that destroy the zeolite. It is advantageous to trap the vanadium into an inert form so that the deleterious side reactions are abated. The rare earths are “basic” oxides and can react with the vanadic acid trapping it and preventing reaction with the zeolite. Grace Davison’s IMPACT® and Nektor ULCC catalyst technologies employ integral rare earth oxide based vanadium traps. The integral rare earth trap technology (IVT-4) has proven to be the most effective technique for controlling vanadium poisoning. Figure 19 shows electron microprobe images of an Ecat that show a strong correlation of vanadium with rare earth. The resultant rare earth vanadates are very stable and inert under FCC conditions, greatly reducing zeolite deactivation and coke and gas production. The coke selectivity improvement due to the IVT-4 technology in IMPACT® catalyst is dramatic (Figure 20). Optimization of the catalyst UCS in combination with integral vanadium trapping make IMPACT® and Nektor ULCC catalysts the most coke selective catalyst technologies, especially appropriate for high metals operations.

Despite the tightening of supply, rare earth metals remain key components of the FCC catalyst and certain FCC additives, and there are no easy substitutes. Rare earth metals stabilize the zeolite and provide vanadium trapping functionality to those users processing resid. Rare earths are also used in some key FCC additives for pollution control. The recent price escalation is impacting FCC catalyst suppliers and their customers globally. Fortunately for the refining industry, the lighter rare earths that are expected to be relatively abundant in the future provide the best performance.

Grace Davison is committed to working with each customer to re-optimize his/her catalyst formulation with the goal of reducing
overall rare earth content of the catalyst while maintaining acceptable performance. Whatever your catalyst requirements, you can feel confident that we at Grace Davison have the capabilities to continue the reputation for quality and service that we have established in our 68 years of serving the world’s refineries.

References

1. There are several patents, see for example Plank, C. and E. Rosinski, “Catalytic Hydrocarbon Conversion with a Crystalline Zeolite Catalyst. 1964: US3140253 (A)”.
2. There are several patents, see for example Maher, P.K. and V. McDaniel, “Z-14US and Method of Preparation Thereof. 1966 : US3293192”.

The Quiet Revolution: REUSY

The introduction of rare earth zeolite catalysts over silica alumina based catalysts in the 1960’s had a profound effect on the profitability and operation of the FCCU. Venuto and Habib’s book “Fluid Catalytic Cracking with Zeolite Catalysts,” published in 1979, documents this upheaval. On page one they write, “The importance of catalytic cracking is undisputable…. and the economic impact of zeolite catalysts on catalytic cracking is tremendous.” The process of conversion to rare earth zeolite catalysts was swift, taking only seven years from invention in 1962 to 90% of the US FCC units by 1969. At that time, the “savings to refiners alone” was estimated to be $250,000,000.

While the game-change caused by the use of zeolite catalysts in the 1960’s is undisputed, a second, quieter technological breakthrough occurred in the 1980’s. This advance was the introduction of REUSY catalysts by Grace Davison (see adjoining article). Invented in the early 1960’s, the full benefits of REUSY were not realized until Rajagopalan and Peters discovered that catalysts equilibrated with a unit.
cell size of 24.30 Å resulted in optimal gasoline yield at minimum coke. This discovery was to have a profound effect on the FCC in a unique and more subtle way.

Since 1980 the total FCC feed barrels processed per day in the US has grown, while simultaneously there has been a steady drop in the number of units (Figure 21). Essentially, less steel in the ground is processing more feed. A more careful inspection shows that the rate of capacity growth was fastest in the late 1980’s and early 1990’s, corresponding to the switch to REUSY catalysts. A steady growth in capacity has continued, while the number of FCC units in the US declines.

FCC units operate in heat balance, meaning that all the heat required to vaporize the feed and provide the endothermic heat of reaction is supplied by the burning of coke. An FCC unit will always adjust itself to remain in heat balance by producing enough coke to satisfy the energy requirements. If all the operating conditions remain constant, the effect of a more coke selective catalyst (one that makes less coke per unit conversion) is to circulate more catalyst to satisfy the energy requirements. As circulation rate increases, the consequence of improved coke selectivity is higher conversion for a fixed feed rate without sacrificing conversion.

However, the refiner can capture the value of improved catalyst coke selectivity another way, and that is by increasing the feed rate without sacrificing conversion. More feed can be processed for a given set of conditions because the coke yield per unit feed of the new catalyst is lower. In summary, the benefits of improved coke selectivity are either increased conversion, or increased capacity, or both.

Since the introduction of REUSY catalysts, Grace Davison continues to provide technological advances aimed at improving the overall coke selectivity. Particular emphasis has been in the areas of resid processing and decreased coke produced by contaminant metals. In the early 1990’s, Grace Davison introduced matrix technologies for decreasing the coking tendency from nickel. Later in the 1990’s Grace commercialized integral rare earth based, vanadium traps, employed in catalysts such as IMPACT™ and Nektor ULCC brands. Iron resistant catalyst platforms, such as MIDAS® catalyst, were brought to market in 2003. With an active R&D program focused on innovation, the market can continue to expect further advancements in catalyst coke selectivity from Grace Davison.
85. What is the typical range that you employ for iron content on FCC equilibrium catalyst? What methods are available to determine how iron is accumulated on the catalyst surface? How does the distribution of iron on the catalyst surface impact the FCC operation, yield structure and emissions?

David Hunt
Grace Davison, Houston, TX

Grace receives Ecat samples for most of the FCC units operating worldwide. The figure at right shows the distribution of average equilibrium catalyst Fe levels for 2010 for all FCC units that have provided Ecat samples to Grace. Mean Fe levels are 0.57 wt.% and the highest Fe level in one unit is 1.36 wt.%.

Iron can be detrimental to the unit in many ways including bottoms conversion, catalyst circulation stability and SOx emissions.

Yaluris showed using an Electron Probe Micro-Analysis (EMPA) technique that iron from organic iron sources is primarily a catalyst surface contaminant. Yaluris also used scanning electron microscopy and optical microscopy techniques to confirm Fe is a surface contaminant. The figure on page 27 is an EMPA image of an FCC catalyst particle cross section. Warmer colors on the surface of the particle confirm that Fe and CaO are primarily surface contaminants.

Yaluris discussed how Fe contamination can lead to pore closure and nodule formation.

The presence of Na and CaO can act as fluxing agents, aggravating the effect of Fe. The figure on page 27 shows decant oil or main fractionator bottoms yield vs. Ecat Fe plus CaO levels. Decant oil increases at the higher contaminant levels due to the damaged catalyst pore structure.

**Question 85**

**Ecat Fe Distribution, wt.%**

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.56639</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.24000</td>
</tr>
<tr>
<td>1st Quartile</td>
<td>0.45750</td>
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<tr>
<td>Median</td>
<td>0.54000</td>
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<tr>
<td>3rd Quartile</td>
<td>0.62000</td>
</tr>
<tr>
<td>Maximum</td>
<td>1.36000</td>
</tr>
</tbody>
</table>

95% Confidence Intervals

**Mean**

- 0.50 - 0.52
- 0.54 - 0.56
- 0.58

**Median**

- 0.50 - 0.52
- 0.54 - 0.56
Another symptom of Fe contamination is lower Ecat apparent bulk density (ABD), as shown in the figure on page 28.

The shift in Ecat ABD is due to the presence of nodules on the catalyst particle at high iron levels. The SEM image on page 28 illustrates the FCC nodules.

The shift in ABD, possible sticking of catalyst particles and pore plugging due to iron contamination have caused catalyst circulation instability in some units.

Grace recommends MIDAS® catalyst for units that are subject to iron contamination. High surface Al₂O₃ levels present in Grace’s MIDAS® technology and Al-Sol catalysts do not form low melting temperature phases and, as a result, are less prone to iron contamination.

Finally, high SOx emissions have been linked to iron contamination in some units. Fe is believed to react with H₂S in the riser to form FeS, which in the regenerator is oxidized and is eventually released as SOx.
In your experience, what are the best catalyst practices to shift FCC yields rapidly between gasoline and diesel maximization and then back again? Many catalyst suppliers are recommending blended catalyst systems. Do you believe this catalyst/additive blending is the best approach?

Rosann Schiller  
Grace Davison, Columbia, MD

In these challenging times, refiners more than ever need flexibility. Grace Davison delivers the flexibility most refiners need with the GENESIS® catalyst system. GENESIS® catalysts provide a means to maximize yield potential through the optimization of discrete cracking catalyst functionality.

GENESIS® catalyst systems offer refiners formulation flexibility and the ability to realize the desired yield shifts quickly in order to capture dynamic economic opportunities. GENESIS® is one of Grace Davison’s most successful catalysts, with 20% of the world’s FCC capacity having utilized the technology.

For new applications, Grace’s experienced technical service carefully formulates the GENESIS® catalyst to achieve the stated goals of the refiner. Often, several scenarios (e.g., max gasoline or max LCO) are prepared and presented to illustrate the flexibility and the power of GENESIS® catalyst to change product slate. As product supply/demand balance shifts, GENESIS® catalyst in the unit can be reformulated to maximize profitability and capture short term opportunities.
economic opportunities. To speed implementation, formulation adjustment often takes place in the fresh hopper, minimizing the delay often associated with a catalyst change out.

GENESIS® catalyst has also provided the flexibility to maximize profitability based on current supply/demand economics. Since introduction to the unit, the refiner in the table above has reformulated GENESIS® catalyst twice; first to maximize LCO and again to return to a gasoline operation. In the max LCO operation, the percentage of MIDAS® catalyst was increased in the blend to maximize bottoms cracking and reduce Z/M. GENESIS® 2 catalyst, formulated for max LCO, delivered an additional 3.5 lv. % yield for a net increase of 5 lv.% LCO and 2.2 lv.% reduction in slurry relative to the competitive base catalyst (see table above). When economics became favorable for gasoline, the refiner returned to the original formulation. Overall, these yield shifts were worth between $0.45 and $1.00/bbl, depending on the operating mode and the refining margins at the time.

For both catalyst reformulations, the blend ratio of MIDAS® and IMPACT® catalysts was adjusted to achieve the desired yield shift. Grace was able to reduce turnover time by working with the refiner to readjust the formulation within the fresh catalyst hopper.

GENESIS® FCC catalyst offers customers the ultimate in formulation flexibility and the option to realize those changes quickly. A decision to reformulate within a GENESIS® catalyst system typically happens 80% quicker than with a traditional catalyst because simply changing the blend ratio presents a lower risk option than a new catalyst or even a new additive. Catalyst Z/M ratio can be optimized to match the specific unit feedstock and operating constraints. In addition to optimizing the blend ratio, the activity levels of the individual components are carefully selected to match the operating mode and feed types. This formulation flexibility can deliver a significant selectivity change, allowing a refiner to accommodate a seasonal operation, manage a swing feedstock or even a hydrotreater outage, and most importantly, GENESIS® catalyst systems allow refiners to capture short term economic opportunities.

87. In your experience, how does catalyst activity affect the catalyst’s coke selectivity and the FCCU’s delta coke? How are the coke selectivity and delta coke related? Lastly, discuss how to determine the proper activity to maximize conversion.

Rosann Schiller
Grace Davison, Columbia, MD

When designing an FCC catalyst, one must consider coke selectivity, delta coke and total coke yield. Coke selectivity is the relative coke-making tendency of the catalyst, or in other words, a catalyst with good coke selectivity produces higher conversion per unit of coke make than the reference catalyst. Delta coke is, simply put, the difference between carbon on spent catalyst after stripping and carbon on regenerated catalyst. Delta coke is expressed as a percentage of the catalyst. Generally, the delta coke is higher for catalysts with poor coke selectivity, but is also higher for more active catalysts and with heavier feeds. Higher delta coke translates to higher regenerator temperatures.

Total coke yield is the delta coke times the catalyst-to-oil ratio. In other words, total coke yield is the amount of coke burned in the regenerator, expressed as a percentage of the feed rate. Burning this coke, total coke, is responsible for fulfilling all the heat requirements, including the heat of reaction, in the
FCC process. Total coke cannot change unless there is a change in these heat requirements. Consequently, if these heat requirements are held constant, a change in delta coke will cause an opposing change in cat/oil ratio to maintain the total coke yield constant.

There are four contributions to total coke: feed carbon, contaminant, stripping and catalytic. The feed coke can be approximated by the Conradson Carbon level. Stripping or cat-to-oil coke results from the carry-over of occluded hydrocarbons after stripping. Stripping and feed coke are non-catalytic. Contaminant coke results from the metals in the feed, primarily nickel and vanadium. Lastly, catalytic coke is the intrinsic coke making tendency of the catalyst and feed. While both contaminant and catalytic coke appear to be controlled via catalyst, they are also dependent on the Cat/Oil ratio, which always adjusts to maintain the exact amount of total coke yield required for heat balance.

Catalyst design has a direct bearing on the formation of variable components of total coke. The needs for in-unit activity (catalytic coke) must be balanced against the contributions to coke from feed carbon and contaminant metals. For a resid application, a catalyst with "good coke selectivity" would typically have moderate activity and exhibit superior stability to metals deactivation as well as the ability to crack and convert coke precursors into liquid product. In this case, the effect of contaminant metals is minimized, and the catalytic activity is balanced against the contribution from feed carbon. A heavily hydrotreated feed application, where there is minimal contribution to total coke from feed or metals, requires a higher catalyst activity to satisfy a given heat balance. If the catalyst is not active enough, torch oil or recycle must be utilized to achieve the equivalent targeted coke yield per unit of feed, often to the detriment of the overall operation. For these hydrotreated feeds, the recommended catalyst still must possess excellent coke selectivity (that is achieve high conversion for a given coke yield) but have enough activity (delta coke) to deliver the prescribed total coke for the application. At Grace Davison, we strive to deliver the most coke selective catalyst for each application, in order to maximize liquid yield and profitability.

88. What options exist for the disposition of FCC equilibrium catalyst and fines? For refineries processing residual feedstocks, what are the limitations on the contaminant levels for the various disposal options?

Stuart Kipnis
Grace Davison, Columbia, MD

There are generally three disposition options for FCC equilibrium catalyst (Ecat) and fines.

1. Selling of Ecat is an option if the quality is deemed suitable for reuse. With Grace’s ENCORE™ catalyst program, the catalyst technology embodied in the Ecat is appropriately matched to another refinery’s needs. Resale of Ecat fines, normally limited to refineries in need of improved circulation is much less common.

2. Recycling of Ecat and fines through cement kilns is a common practice for material coming from residual feedstock operations where metals contamination is much higher. Claude Kennard from Metaloy states that in order to dispose of Ecat and fines at a cement kiln, the material must be non-pyrophoric. As such, most kilns will require a full TCLP analysis prior to accepting Ecat. In general, acceptable contaminant levels will vary with each cement kiln and will need to be investigated on a case-by-case basis.

3. The last option is to dispose of Ecat and fines at a landfill. This becomes a viable alternative when a local cement kiln is perhaps too small to accept the volume of Ecat or if there is no local kiln.

89. In shifting from partial burn to full burn in a side by side unit, what has been your observed impact on the NOx emissions? What is necessary to achieve 20 ppm NOx?
Several Grace customers successfully operate with NOx emissions less than 20 ppm in full combustion without the use of NOx removal hardware in the flue gas circuit.

These units have the following common theme:

- Regenerator flue gas excess O2 levels are less than 1.5 vol.%.
- If necessary, a non Pt combustion promoter like Grace’s CP® P promoter is used to control afterburn and/or CO emissions. Additions of promoter are minimized since excessive additions of any CO combustion promoter can increase NOx.
- Some of these units inject ammonia into the flue gas stream to meet NOx limits.
- Some of these units use a NOx reduction additive such as Grace’s DENOX® additive.
- The regenerator combustion air and spent catalyst are extremely well mixed.

To ensure low emissions from a third stage separator, an exhaustive review of the following FCC operations should be confirmed:

1. No excessive catalyst attrition sources are present:
   a. Vapor velocities should be less than 300 fps and preferably less than 100 fps
   b. Restriction orifices are present and the correct size
2. Regenerator cyclone velocities are within acceptable operating limits.
3. Regenerator bed level should provide the correct burial requirements for the cyclone dipleg valves and the transport disengaging zone should terminate below the cyclone inlet.
4. Secondary cyclone dipleg levels should terminate well below the top of the dipleg (3ft).
5. All steam sources are dry.
6. Regenerator superficial velocity is minimized.

91. Assuming the FCCU already has a third stage separator, what are the various options you consider for further reduction of particulate emissions (PM) and what is the expected level of PM to be achieved?

David Hunt
Grace Davison, Houston, TX

Many FCC units which use third stage separators operate with particulate limits <1 lb/1000 lb of coke burn. The
7. Regenerator air and spent catalyst distribution is adequate to ensure the diplegs terminate in well fluidized zones and each primary cyclone has similar catalyst entrainment.

The catalyst design can also be optimized to minimize particulate entrainment to the third stage separators to ensure maximum third stage separator efficiency.

Catalyst attrition is likely the most important catalyst property to consider; however, consideration of the amount of micron fines (<1 micron) generated during catalyst attrition is more important.

The figure at right confirms that the cyclone efficiency falls by almost a factor of 10 for a 20 micron particle versus a one micron particle. As a result, two catalysts which have the same attrition index can have much different particulate emissions, depending on whether micro fines are generated during attrition versus particles in the 5 to 20 micron range.

The 0 to 20 micron and 0 to 40 micron content of the fresh catalyst is also critical to ensure low particulate emissions from a third stage separator. These particulate fractions should be minimized within the constraints of the catalyst circulation system. (Many units need higher fresh fines content to ensure stable catalyst circulation.)

A catalyst with a higher particle density, not necessarily higher apparent bulk density, will increase TSS efficiency.

**Al₂O₃** content can be used to increase the particle density.

An article entitled “Optimizing your FCC Regenerator Operation and Catalyst Design Can Minimize Catalyst Losses” provides a detailed review of many of the issues discussed above.

Grace recommends our Al-Sol catalysts such as ALCYON®, IMPACT®, GENESIS®, AURO-RA®, and AdVANTA® catalysts for units which use third stage separators. Worldwide, Grace supplies more FCC units with third stage separators than any other catalyst supplier. While we are the world’s largest supplier of FCC catalyst, our market share of units using third stage separator devices is even larger. This market advantage is a testament to the fundamental advantage of Grace catalyst and our Al-Sol catalyst, in particular, for minimizing emissions from third stage separators.

**References**

Summary

CITGO has successfully applied CP® P, Grace Davison’s third generation Low NOx FCC combustion promoter, at their Lake Charles refinery. CP® P promoter replaced Grace Davison’s first generation low NOx promoter, XNOX®, and Grace’s second generation low NOx promoter XNOX® 2, and built on the successful application of these products.

CP® P promoter allowed CITGO to reduce regenerator excess O₂ levels by ~0.3% and improve CO emissions at similar NOx levels. Operating with lower excess O₂ provided additional operating flexibility in terms of feed rate and conversion. CP® P promoter steady state additions were 75% lower than the base XNOX® promoter, resulting in significant cost savings as well as improved product performance.

Table VI summarizes the results of the evaluation.
Table VI
Low NOx Promoter Evaluation Data Summary

<table>
<thead>
<tr>
<th>Low NOx Promoter</th>
<th>Additive Additions</th>
<th>NOx</th>
<th>CO (1)</th>
<th>O2</th>
<th>Afterburn</th>
</tr>
</thead>
<tbody>
<tr>
<td>XNOX® Base</td>
<td>Base</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XNOX® 2 50% Base</td>
<td>~ Lower</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP® P 25% Base</td>
<td>~ Lower</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

(1) CITGO could have elected to operate at similar CO levels and lower NOx levels by re-optimization of the promoter additions and excess O2 levels.

Grace Davison’s low NOx promoter, XNOX®, and NOx reduction additive, DENOX®, were identified as the best performing products during those short-term trials. CITGO then conducted an optimization evaluation with both products, followed by a demonstration period with the optimized addition rates.

During the demonstration period, it was evident that CITGO was successfully meeting EPA target NOx emission levels with the application of XNOX®, DENOX®, and tight control of flue gas excess O2. As a result, CITGO elected to stop the demonstration period and accept EPA standard NOx limits of 20 ppm/40 ppm.

Low NOx Promoter Optimization

The use of combustion promoter is critical to meet FCC emission limits at CITGO’s Lake Charles Refinery. With NOx limits established, Grace Davison recommended that CITGO evaluate new, more active, non-platinum promoter additives available from Grace Davison.

The FCCU’s at CITGO operate within a narrow range between its NOx and CO emissions limits. CITGO typically minimizes flue gas excess O2 to inhibit NOx formation. However, as O2 is reduced, CO eventually begins to increase. CITGO is careful to add just enough combustion promoter to meet CO limits, but not excessive amounts that would risk elevated NOx formation. CITGO
has found that twice daily additions of CO combustion promoter are optimal to meet CO, NOx, and regeneration afterburn objectives.

After the conclusion of the test period, CITGO elected to further optimize promoter additions by testing a second generation low NOx CO promoter from Grace Davison, XNOX\textsuperscript{®} 2, followed by Grace Davison’s newest low NOx CO promoter CP\textsuperscript{®} P. CITGO and Grace Davison established a test plan which included product addition rates, data monitoring, and milestones.

XNOX\textsuperscript{®} 2 Combustion Promoter

XNOX\textsuperscript{®} 2 promoter is more active than XNOX\textsuperscript{®} promoter and CITGO immediately reduced promoter additions by half, once they began using XNOX\textsuperscript{®} 2 promoter.

CITGO noted a fundamental shift in the relationship between CO and O\textsubscript{2} in the FCC flue gas with XNOX\textsuperscript{®} 2 promoter. Figure 22 shows that XNOX\textsuperscript{®} 2 promoter shifted the CO vs. O\textsubscript{2} curve to a more favorable position. With XNOX\textsuperscript{®} 2 promoter, CITGO was able to reduce excess O\textsubscript{2} for the same level of CO. By operating at lower excess O\textsubscript{2}, CITGO was afforded additional operating flexibility in terms of rate and conversion within NOx emission limits and air blower constraints.

Flue gas NOx levels and Afterburn were maintained with XNOX\textsuperscript{®} 2 promoter at half of the promoter additions as shown in Figures 23 and 24.
Data shown in Figures 22, 23 and 24 represents data from one of the three FCC units at the CITGO Lake Charles Facility. Similar conclusions were also made in CITGO’s other two FCCU’s.

**CP® P Combustion Promoter**

CITGO evaluated CP® P promoter after a successful application of XNOX® 2 promoter. CP® P promoter was more active than XNOX® 2 promoter and CITGO reduced additions of CP® P promoter by 75% relative to the base XNOX® promoter additions.

CP® P promoter was able to maintain the favorable relationship of CO versus O₂ that XNOX® 2 promoter provided as shown in Figure 25. As a result, CITGO continued to minimize excess O₂ without a CO penalty.

NOx production and afterburn continued to be controlled with CP® P promoter as shown in Figures 23 and 24.

**Acknowledgements**

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**References**

We don’t just make FCC catalysts, we make FCC catalysts for you.

Only Grace Davison offers refiners a full portfolio of high technology, state-of-the-art FCC catalysts and additives. Driven by our world-class research and development in the U.S. and Europe, only Grace Davison can customize products designed specifically to optimize your operation.

Our industry-leading technical service provides support including unit monitoring and troubleshooting, backed by our high level of analytical services including Ecat, spent catalyst and fines analysis.

We have been the leader in FCC catalysis since inventing the first FCC catalyst over 65 years ago and we are committed to the future of the refining industry.

Have Grace Davison design your optimal catalyst. Contact us.
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