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

95% Confidence Intervals
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\textsuperscript{®} catalyst system. GENESIS\textsuperscript{®} catalysts provide a means to maximize yield potential through the optimization of discrete cracking catalyst functionality\textsuperscript{2}.

GENESIS\textsuperscript{®} catalyst systems offer refiners formulation flexibility and the ability to realize the desired yield shifts quickly in order to capture dynamic economic opportunities. GENESIS\textsuperscript{®} 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\textsuperscript{®} 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\textsuperscript{®} catalyst to change product slate. As product supply/demand balance shifts, GENESIS\textsuperscript{®} catalyst in the unit can be reformulated to maximize profitability and capture short term
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 can not 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 contaminate 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?
David Hunt
Grace Davison, Houston, TX

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.

absolute PM emission will depend, of course, on unit conditions such as the design characteristics, cyclone velocity, unit pressure and particulate loading of the third stage separator.

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