A message from the editor...

Dear Refiners:

“We need to communicate more often and to communicate more information...Our small publication...will have material about what Davison is doing. But we hope to incorporate other values...a forum for discussion of matters of mutual interest to refiners and chemical suppliers.”

So said Grace Davison Vice President Robert Goodall in the editorial of the first issue of the Catalagram® in 1959. In the half-century since then, we’ve worked diligently to meet these goals through this publication.

Reviewing all the back issues, it’s interesting to note some major trends in FCC history:

• When the first Catalagram® was issued, it featured equilibrium catalyst analysis results. In 1959, our Ecat Testing Program was already over 10 years old (introduced in 1947). See page 30 for an update on how we keep this industry-standard testing program current for today’s refiner.

• The Catalagram’s® first guest editor was our Director of Research, Dr. Frank Ciapetta, in Issue #6, 1960. Dr. Ciapetta was only the first to highlight the commitment we have to design and commercialization of state-of-the-art FCC catalysts.

• In Issue #13, we introduced our first Glass Model Cat Cracker. The current iteration of this working model was just demonstrated at a Family Day at a major U.S. refiner and continues to educate everyone from young children to new FCC process engineers.

• Jim Blazek’s seminal article “Catalytic Cracking-Part One, History and Fundamentals” debuted in Issue #36, 1971. This and the two following parts, became the foundation of our famous “Silver Bullet” in the 1970’s and later, the “Grace Davison Guide to Fluid Catalytic Cracking, Parts I, II, and III,” which has become an industry-recognized training guide for FCC engineers in its ten-year history

To celebrate the 50th Anniversary Issue, we have pulled together several classic articles from past Catalagrams® that have stood the test of time. The introduction to each article highlights why that particular subject has remained relevant through the years.

Finally, our deepest thanks to you, our readers, for continuing to read, comment, and contribute to the Catalagram®. With your help, it will continue to be a valuable resource for another fifty years.

Joanne Deady
Vice President, Global Marketing
Grace Davison Refining Technologies
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Coke Selectivity Fundamentals
By Charles C. Wear
The 1980's saw the advent of more coke selective zeolites for increased resid processing and octane.
Reprinted from Catalagram #75, 1987

Trouble-Shooting FCC Standpipe Flow Problems
by Raymond W. Mott
A timeless classic on a critical FCC hardware issue from the early 90's.
Reprinted from Catalagram #83, 1992

IMPACT®: A Breakthrough Technology for Resid Processing
by Scott K. Purnell, Ph.D.
Coke selectivity is the hallmark of all Grace Davison FCC catalysts. Six years later and going strong, Impact is still the catalyst to beat for coke selectivity.
Reprinted from Catalagram #93, 2003

Use Hydrogen in Coke Number to Determine Coke Make Accuracy
by David Hunt
We saw a return to tech service/troubleshooting articles in the 2000's. This article also complements the coke selectivity article.
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Clean Fuels: An Opportunity for Profitability Using Gasoline Sulfur Reduction Technology
by Lauren Blanchard, Craig Borchert (Valero Energy) and Min Pu (Valero Energy)
A commercial example of the use of Grace Davison Clean Fuels Technologies to deal with hydrotreater outages.
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Grace Davison Refining Technologies
7500 Grace Drive • Columbia, MD 21044 • 410.531.4000
www.e-catalysts.com

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Editor’s Note:

The FCC cracking reaction is endothermic by nature. It is the unique trait of the FCC unit that the heat required for cracking is supplied primarily by the combustion of one of its products, coke. The challenge for catalyst suppliers is to provide FCC catalysts that will manage the delicate balance between heat required and heat supplied. Central for understanding the unit heat balance is a concept termed “delta coke”.

In this article, we discuss the relevance of coke selectivity and “delta coke” to overall unit performance and the eventual product slate. The article highlights the impact of FCC catalyst selection, feed quality, and operating conditions on delta coke and the overall coke selectivity.

Over the years Davison R&D has made significant improvements in catalytic technology to optimize coke selectivity. Coke selectivity is the most important consideration during the development of new FCC catalysts. Later in this issue, we will discuss the success of IMPACT® catalyst, which remains a breakthrough technology; delivering superior coke selectivity in many FCC’s worldwide.

Charles Wear, principle author of this article, is currently working in our hydroprocessing joint venture, Advanced Refining Technologies. This article first appeared in Issue #75, 1985
Coke selectivity is a term that often means different things to different people. So to lead off our discussion, let’s focus on a definition: Coke selectivity is the relative coke-making tendency of any given cracking catalyst. In the vernacular, a catalyst that has “good coke selectivity” means it produces lower coke compared to some reference catalyst. This is usually considered a favorable characteristic, since liquid yields are preferred.

That seems fairly straightforward, but the often misunderstood part is just what the phrase “coke-making tendency” really means. Many times it is confused with coke yield as expressed in say, weight percent of fresh feed. However, the coking tendency of a catalyst in the context of “coke selectivity” is actually its tendency to produce delta coke.

The Concept of Delta Coke

The concept of delta coke is neither novel nor complicated. It is simply the difference between coke on spent catalyst (at stripper outlet) and coke on regenerated catalyst, expressed as a weight percent of catalyst.

More correctly, delta coke can be thought of as the amount of coke formed on the catalyst for a single pass of the catalyst through the reactor which, in the continuous steady-state operation of a commercial FCCU, is also equal to the amount of coke burned off the catalyst in the regenerator.

Delta coke also has kinetic significance, especially on the reactor-side of the process where it formed. The coke on catalyst per pass is a
function of many variables, including but not limited to: feed quality and dispersion at the nozzle, reactor temperature and pressure, catalyst activity and contact time, and last but not least, catalyst coke selectivity.

Therefore, when all other variables affecting delta coke are more or less constant, a catalyst that possesses “coke selectivity” will exhibit lower delta coke at any given activity.

A “coke balance” around the regenerator results in a useful expression for delta coke. The coke yield must equal the difference in coke entering and leaving the regenerator. Therefore,

\[
\text{Coke Yield} = \frac{\text{C/O}}{(\text{CSC-CRC})} \quad \text{or} \quad \text{CSC-CRC} = \frac{\text{C/O}}{\text{Coke Yield}} - \Delta \text{Coke}
\]

where:
- Coke Yield is wt.% Feed
- C/O is Cat Circulation, lb Cat/lb. Feed
- CSC is Coke on Spent Catalyst, wt.% Catalyst
- CRC is Coke on Regenerated Catalyst, wt.% Catalyst

Note that coke yield and cat/oil must be expressed on the same feed basis, fresh or fresh plus recycle, to yield a meaningful number.

Since coke yield and cat/oil are related to delta coke in the abovementioned manner, it follows that a coke “selective” catalyst can decrease coke “yield”, but not necessarily. For instance, in many cases, coke selective catalysts will operate with higher cat/oil ratios with little or no change in coke yield. An understanding of this requires examination of the FCCU heat balance and the interaction of process operating variables.

**Heat Balance Effects**

A commercial unit, like all steady-state processes, must be in energy balance. This means that the total energy coming into the process must equal the energy leaving the process, as shown in Figure 1. The energy to heat the fresh feed, recycle feed and stripping steam to reactor outlet temperature, to heat the air to flue gas temperature, to supply the endothermic heat of reaction and any losses to the atmosphere—all of this must come from the coke’s heat of combustion. A portion of the feedstock is therefore “consumed” to supply the energy requirements of the process.

One consequence is that the coke yield as weight percent feed is determined by the sum of these energy requirements, not by the catalyst coke selectivity (or feed coking tendency for that matter). This is the key concept that distinguishes delta coke, which is catalyst and feed related, to coke yield, which is not. We will return to this concept in a moment.

The principle of energy balance holds for the individual reactor and regenerator as well as the overall process, as shown in Figure 2. Table I lists the simplified components to balance each vessel. By equating the regenerator heat production to the heat transferred by catalyst, a useful relationship can be derived:

\[
\text{Heat of Coke Combustion} + \text{Other Terms} = \text{Heat Transferred by Catalyst}
\]

\[
\text{Coke Yield (}\Delta \text{Hc}) = \frac{\text{C/O}}{\text{Cp}_{\text{Cat}} (T_{\text{Regen}} - T_{\text{Rs}})}
\]

\[
\Delta \text{Coke} = \frac{\text{Coke Yield}}{\text{C/O}} = \frac{\text{Cp}_{\text{Cat}}}{\Delta \text{Hc}} (T_{\text{Regen}} - T_{\text{Rs}})
\]

Noting that the catalyst heat capacity (\(\text{Cp}_{\text{Cat}}\)) is constant for any particular case, along with the coke’s specific heat of combus-
tion (Hc) when hydrogen in coke and degree of CO combustion are constant, the following proportionality holds:

\[ \text{Delta Coke} \propto (T_{\text{Regen}} - T_{\text{Rx}}) \]

This implies that a coke selective catalyst will, for a constant reactor temperature, reduce regenerator temperature. This is exactly what is observed commercially. Consider the unit in full combustion that has changed to a catalyst with different coke selectivity. Depending on the shift in delta coke, the changes shown in Figure 3 occur.

Of course, unit response to coke selective catalysts is not limited to regenerator temperature reductions. Consider the unit in partial CO combustion, where a drop in regenerator temperature could possibly result in an undesirable increase in regenerated catalyst carbon level. For this case, it would be wise for the operator to intervene--via increased promoter additions and/or air rate--to burn more CO to

---

**Figure 2**

Energy Balance of Reactor and Regenerator Involves Catalyst Circulation Rate

**Figure 3**

Typical Effect of Delta Coke on FCC Operation
CO₂ and thus return the dense bed to original temperature.

In this example, these “external stimuli” from the operator directly affect the overall heat balance by increasing the heat release per pound of coke burned (higher CO₂/CO). It therefore takes the combustion of less coke to satisfy the energy demand of the process. So, for this partial combustion case, coke yield will drop at the same or nearly the same reactor/regenerator temperatures (and therefore cat/oil). It has to, because the catalyst caused a reduction in the delta coke, and by definition coke yield must be lower if delta coke drops at constant cat/oil!

Remember earlier in this discussion it was stated that catalyst (and feed quality) have a direct effect on delta coke, but that the unit heat balance determines coke yield. As the preceding example showed, sometimes it’s difficult to separate what changes were caused directly by catalyst (or feed) as opposed to heat balance changes made by the operator.

In reality, the difference is not very important in many cases. The important point is that coke selective catalysts will, in more cases than not, allow an operator to have more flexibility in running his plant. Below are some of the ways we have seen operators use Davison coke selective catalysts to their fullest extent, and thus alleviate operating constraints and improve refinery profitability:

- Increase reactor temperature to produce maximum gasoline octane.
- Increase cat circulation for increased conversion.
- Increase resid content for additional bottoms destruction.
- Increase feed rate to satisfy increased product demand.
- Increase CO₂/CO for lower coke yield.

As with many things in life, “more” catalyst coke selectivity in all cases does not necessarily mean “better”. A thorough review of the base operation, including goals and constraints, should be performed before any catalyst change is considered. For example, some operations are precluded from the use of incremental catalyst coke selectivity. Consider the unit in full combustion, at maximum catalyst circulation and feed temperature, that cannot “heavy-up” the feed nor accept a lower reactor temperature. This obviously is not a unit that would profit from catalyst coke selectivity, it is a unit, however, which could greatly benefit by removing these limitations, and many have done exactly that via revamps.

### A Check on Data Consistency

The fact that delta coke can be measured directly by comparing the difference in coke levels between spent and regenerated catalyst samples was discussed earlier. Delta coke determined in this manner, versus the calculations of delta coke from the unit heat balance, can be a useful tool to check data consistency.

Most process engineers will calculate coke yield using air rate and flue gas composition, and then calculate catalyst circulation rate by heat balance. These coke yield and cat/oil results can then be used to calculate a delta coke. If this “heat balance method” to obtain delta coke differs substantially from the direct sampling method, it could mean one or more of the following:

- Incorrect flue gas analysis or air rate (the most common problem).
- Nonrepresentative catalyst samples (also a common problem).
- Error in heat balance method, data or assumptions.
- Excessive entrainment of interstitial hydrocarbons through the stripper.

### Types of Delta Coke

It is convenient to define components of delta coke as to source, and several proposed breakdowns have been published. A sampling is listed in Table II. The three components of delta coke defined below can be influenced by proper catalyst design:

1. Catalytic-the coke deposit formed when hydrocarbon is cracked via acid site catalysis.
2. Cat/Oil-adsorbed/unstripped hydrocarbons entrained by catalyst flowing through the stripper.
3. Contaminant-coke produced as byproduct of contaminant metal (V, Ni, Cu, Fe) dehydrogenation activity.

**Catalytic Delta Coke**

Most cracking catalysts have two sources of acid sites, and therefore two types of activity—zeolite and matrix. Zeolite is crystalline silica/alumina with a specific structure. In the usual case it is where most of the overall catalyst activity resides.

The balance of the catalyst particle is defined as the matrix. It may be similar to the zeolite in composition (silica/alumina), but does not have the particular crystalline structure unique to zeolites. Many of today’s matrices resemble the amorphous catalysts of the 1950’s and 60’s.†

The activity associated with the zeolite and the matrix have very different selectivity patterns, especially in regard to coke. This is illustrated in Figure 4. As matrix activity relative to zeolite is minimized, delta coke at constant activity decreases—the catalyst becomes more “coke selective”.

Differences in zeolite type also affect coke selectivity. The key issue is the chemical composition (Si/Al ratio) of the *equilibrated* zeolite, which is measured by X-ray as the unit cell size. Zeolites that equilibrate with high Si/Al ratios (low cell sizes) exhibit retarded hydrogen transfer rates which, among other things (such as increasing gasoline octane), reduce catalytic coke make. Davison’s experience with these zeolites, generically referred to as “ultrastable” or USY types, is unmatched in the industry. The premium form of USY, patented by Davison as “Z-14US”, is the core technology behind Davison’s current octane catalyst product line. The coke selective properties of these octane catalysts have been thoroughly treated in earlier *Catalagrams* (Numbers 73 and 74).

**Table II**

**Typical Delta Coke Breakdowns** *(1, 2)*

<table>
<thead>
<tr>
<th>UNIT</th>
<th>CATALYST FEED TYPE</th>
<th>DELTA COKE TYPES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zeolite-Low Metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zeolite-High Metals</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Wt.% Cat</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic</td>
<td>0.52</td>
<td>65</td>
</tr>
<tr>
<td>Cat/Oil</td>
<td>0.12</td>
<td>15</td>
</tr>
<tr>
<td>Contaminant</td>
<td>0.12</td>
<td>5</td>
</tr>
<tr>
<td>Feed/Nondistillable</td>
<td>0.04</td>
<td>15</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.80</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1.40</td>
<td>100</td>
</tr>
</tbody>
</table>

**Cat/Oil Coke**

Cat/oil coke is perhaps the most insidious component of delta coke because† it is totally independent of any beneficial chemical reaction taking place, such as making gasoline, and² it has the highest heat of combustion (highest hydrogen content) which leads to high intraparticle temperatures during regeneration.

A properly designed and operated catalyst stripper will minimize the amount of hydrocarbons that flow into the regenerator along with the circulating spent catalyst. Stripping steam rates of at least two lb. per 1000 lb. of catalyst circulated are typically recommended. Increasing catalyst level (residence time) in the stripper can also be effective in minimizing carry-over. The common commercial practice is to increase steam rate and/or stripper level until no further reduction in regenerator temperature is observed, providing, of course, reactor-side catalyst losses do not increase.

†In the 1980’s most high matrix catalysts were neither selective nor metals tolerant. Today’s high MSA MIDAS® catalysts have been shown to improve coke selectivity by eliminating and cracking coke precursors.
Steam injection displaces hydrocarbon vapor between catalyst particles—it is not very effective in reversing surface adsorption or pore condensation. In some cases, higher reactor (stripper) temperatures have been found to reduce cat/oil coke. The mechanism may involve volatilizing and/or further cracking of desorbed material.\(^3\)

Cat/oil coke is also influenced by catalyst matrix pore size and surface area. Catalyst “strippability” can be measured in the lab by subjecting an inert porous material to heavy oil, followed by nitrogen stripping at typical reactor operating conditions. The results is shown in Table III as a function of stripping time and temperature.

High intraparticle temperatures associated with adsorbed hydrocarbon have been the subject of several studies,\(^4,5\) which showed that high surface area (hence, more adsorptive) catalyst particles are prone to deactivate rapidly when regenerated. Particle temperatures several hundred degrees higher than average regenerator bed temperatures were calculated.

To summarize, catalysts designed to minimize the cat/oil component of delta coke should have low surface area, large average pore diameter matrices to discourage hydrocarbon adsorption and enhance “strippability”.

### Table III

**Effect of Surface Area on Hydrocarbon Stripping**

<table>
<thead>
<tr>
<th>Surface Area, M(^2)/g</th>
<th>439</th>
<th>389</th>
<th>105</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Volume, cc/g</td>
<td>0.89</td>
<td>1.8</td>
<td>1.14</td>
</tr>
<tr>
<td>Volume Avg. Pore Diameter, A</td>
<td>72</td>
<td>184</td>
<td>436</td>
</tr>
<tr>
<td>Stripping Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900°F</td>
<td>17.3</td>
<td>17.7</td>
<td>6.4</td>
</tr>
<tr>
<td>990°F</td>
<td>2.0</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Unstripped Coke (Wt.% FF) After 1 Minute</td>
<td>1.5</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Unstripped Coke (Wt.% FF) After 15 Minutes</td>
<td>1.7</td>
<td>0.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Conditions: MAT REACTOR: 5 gm. Charge, 16 WHSV, 3 C/O, WEST COAST FEED, N\(_2\) STRIPPING AT 30 SCCM,

Volume Avg. Pore Diameter: 40,000 (pore Volume)

To summarize, catalysts designed to minimize the cat/oil component of delta coke should have low surface area, large average pore diameter matrices to discourage hydrocarbon adsorption and enhance “strippability”.

**Contaminant Delta Coke**

The hydrogen-producing effect of feed metals-particularly that of nickel, copper, and vanadium-deposited on the cracking catalyst is well known. Coke is a companion product of dehydrogenation, and from Table II it is clear that contaminant coke can be a substantial percentage of the overall delta coke for metals-laden catalysts.

The passivation of nickel by antimony (licensed by Phillips Petroleum Co.) and of vanadium by tin additives is being practiced commercially.\(^6\) Claims of a 50% reduction in hydrogen and coke produced by contaminant metals have been published.\(^6,7,8,9\)

We have found that the level of hydrogen and coke production due to contaminant metals is also a function of catalyst matrix composition. Matrices with low alumina content and low surface areas are more effective in minimizing contaminant metal dispersion and dehydrogenation activity\(^i\) (Table IV).

### Table IV

**Metal Aging Study Results\(^{10}\)**

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>500 ppm Ni (Impregnated After Steam Deactivation(^1))</th>
<th>500 ppm Ni + Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Aged(^2)</td>
</tr>
<tr>
<td>Super-D (50 m(^2)/gm)(^3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA, V%</td>
<td>68.5</td>
<td>69.5</td>
</tr>
<tr>
<td>H(_2), Wt.%</td>
<td>0.21</td>
<td>0.08</td>
</tr>
<tr>
<td>Coke, Wt.%</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Competitor B (115 m(^2)/gm)(^3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA, V%</td>
<td>70.0</td>
<td>68.0</td>
</tr>
<tr>
<td>H(_2), Wt.%</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>Coke, Wt.%</td>
<td>4.15</td>
<td>4.2</td>
</tr>
<tr>
<td>Competitor A (220 m(^2)/gm)(^3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA, V%</td>
<td>79.0</td>
<td>78.0</td>
</tr>
<tr>
<td>H(_2), Wt.%</td>
<td>0.45</td>
<td>0.35</td>
</tr>
<tr>
<td>Coke, Wt.%</td>
<td>4.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

\(^1\)Deactivation Conditions: 1350˚F, 100% Steam, 15 psig, 8 Hrs.

\(^2\)Aged 13 Cycles in Cyclic Fixed-Fluid Bed Pilot Units; 40 WHSV, 3 c/o, 1000˚F Reaction/1100˚F Regeneration

\(^3\)Typical Matrix Surface Area

\(^{10}\)See note on page 7.
Coke Selective Catalyst Properties

As can be seen from the preceding discussion, catalyst design has a direct bearing on the formation of various components of the overall “delta coke”. Certain catalyst properties, associated with the true “coke selective” catalyst system, act to minimize delta coke for any given activity level. The essential ingredients are¹ a zeolite that will equilibrate at low unit cell size, while retaining the appropriate activity level to dominate that of the matrix and² a matrix of controlled surface area with large pores to maximize strippability and control dispersion and dehydrogenation activity of contaminant metals.

Davison has used these principles for years to design a wide range of catalysts. Current examples are members of the Octacat, GXO, and Nova families that have led the industry in coke selectivity, as well as octane enhancement. Davison R&D is focused on a continuous program of improving these products, as well as on the design of new coke selective grades such as the DXB family.

References

Gatte Named North American General Manager

Bob Gatte has been appointed General Manager - North America, Refining Technologies. In his new role, Bob will have overall responsibility for the North American business activities in support of the global Refining Technologies strategy. Bob will also be a member of the Refining Technologies global management team.

Bob has worked in key roles at Grace for the last 21 years. He has previously held positions as the Vice President Sustainability and New Ventures; Vice President and General Manager of the Discovery Sciences business, General Manager Grace Catalyst AB in Stenungsund, Sweden, and Vice President and COO of e-Catalysts, Inc. In the earlier part of his career, Bob held positions as Technical Sales Manager for FCC, and a Manager of Business Development for Davison Catalysts.

Bob has a Ph.D in Chemical Engineering from the Pennsylvania State University and a Bachelor of Science in Chemical Engineering from Rensselaer Polytechnic Institute.
Editor’s Note:

The most profitable operation of an FCCU requires the integration of a superior FCC catalyst as well as optimized operating conditions for a given feed stream. However, the physical characteristics of the unit also play an important role in achieving optimal unit product yields and profitability.

It is necessary to operate the FCCU at steady conditions to ensure the heat balance required to achieve these goals. This means that, along with other operating parameters, steady catalyst circulation is necessary to guarantee a smooth operation that will produce a product slate of maximum earnings for the refiner.

Occasionally, problems with catalyst flow in the standpipes can hinder continuous catalyst circulation from the regenerator to the riser, causing major problems in the unit and in extreme cases, a unit shutdown.

In this article we discuss how to diagnose and solve flow problems in the FCC standpipes. We will look at the importance of pressure profiles in the standpipes, catalyst compression mechanisms, and show an example of the calculation of standpipe tap aeration requirements.

This article, originally published over 15 years ago is still a trusted reference for the industry when evaluating and solving catalyst fluidization problems in the FCCU.

Principal author Ray Mott is a recognized FCC expert who consults for Grace Davison. This article was first published in 1992, issue #83.
Troubleshooting FCC Standpipe Flow Problems

Introduction

Troubleshooting the performance of an ill-behaved FCC standpipe can present one of the most difficult challenges that the FCC process engineer faces. Not only is the nature of the catalyst circulation problem very nebulous, but the existence of a catalyst circulation problem places a great deal of technical and economic pressure on the process engineer’s shoulders.

This paper will discuss how to systematically diagnose the operation of an FCC standpipe with chronic problems. In the process, some of the causes for the behaviors observed in standpipe operation will be investigated, and some engineering benchmarks against which the operation of the FCC standpipe can be compared will be presented.

Symptoms of Standpipe Flow Problems

There are a whole range of catalyst circulation symptoms that show up in FCC standpipes. Many of these symptoms are interrelated, and there are several distinctly different problems that exhibit the same symptoms. All of this makes troubleshooting standpipe flow problems extremely challenging.

Some of the symptoms of catalyst circulation problems that commonly occur in standpipes include:

- Low slide valve (or plug valve) differential pressure.
- An inability to circulate additional catalyst despite changes in slide valve position. Often this is accompanied by an inability to control reactor temperature.
- Erratic slide valve differential pressure that threatens the loss of catalyst circulation.
- Physical bouncing or hopping of catalyst standpipes.

Any of these symptoms can make smooth FCC operations impossible. However, before we dive into troubleshooting, it is worth looking into the detailed mechanics of catalyst flow in standpipes to establish a framework for investigation.
Pressure Profiles in the FCC Standpipe

One way to glimpse into the workings of the FCC standpipe is to conduct a pressure survey along its length. Usually, the most readily available way to do this is to conduct a single gauge survey. In this type of survey, a single calibrated pressure gauge is carried up and down the FCC structure to measure the pressure at various locations along the length of the vessels and standpipes. This helps reduce the errors that reading many separate gauges would introduce.

In principle, the FCC standpipe is expected to behave analogously to a pipe full of water. The pressure measured at any depth in the standpipe should be roughly proportional to the density of the fluidized catalyst and the height of the catalyst above the point where the pressure is being measured. Figure 1 shows the “idealized” pressure profile that would be observed in a perfectly behaved FCC standpipe. The pressure is linearly increasing with respect to depth in the standpipe.

In practice, when a standpipe is experiencing operating difficulty, the pressures observed at any point along the length of the standpipe may be going through wild gyrations. So, taking a meaningful single gauge pressure survey will require patience.

Obviously, FCC catalyst differs from water in the important sense that it is actually a fluidized solid. Less obvious is the fact that non-fluidized powders can support their own weight against the walls of their container. For example, as an empty storage silo is filled with corn or wheat, the pressure on the floor of the silo initially increases as the height of grain in the silo increases. However, when the grain reaches a depth of approximately three times the diameter of the silo, the pressure on the floor of the silo stops increasing. The grain in the upper levels of the silo supports most of its own weight against the silo walls instead of the floor!

The implications for FCC catalyst flow in a standpipe are dramatic. If the catalyst loses its fluidization, it, too can start supporting a portion of its weight against the standpipe walls, and the slide valve at the bottom of the standpipe will see a reduced pressure buildup. A pressure survey will provide a better idea of what is going on inside the standpipe, and may help isolate where such local problems as defluidization are occurring.

Figure 2 shows the pressure profile for a standpipe that is experiencing moderate circulation difficulties. At first, the pressure is increasing normally as you descend the standpipe; however, this standpipe has trouble building additional pressure below the second aeration tap (counting from the top down).

A more extreme problem is shown in Figure 3. In this standpipe, the pressure profile actually shows a loss of pressure below the second aeration tap, and an inability to build up much pressure below this point.

The single gauge pressure surveys shown in Figures 2 and 3 suggest that the catalyst flow may be obstructed by a foreign object or by bubbles. Another possibility is that the catalyst may be losing its fluidization in some sections of the standpipe so that a portion of the catalyst weight is supported against the walls.
The Narrow Operating Window of the FCC Catalyst

FCC catalyst only has a narrow range of conditions under which it will flow well in standpipes. At one end of this operating range, the catalyst is at the point of incipient bubbling. If any more gas were present in the fluidized catalyst emulsion, then there would be a tendency for the system to generate bubbles. In standpipes, bubble formation tends to impede catalyst flow because the bubbles act as obstacles that the catalyst must flow around.

Incipient fluidization represents the other end of the well-behaved operating spectrum. If there were any less gas present in the catalyst emulsion at this point, the fluidized catalyst would then revert back to a packed bed.

These two extremes of fluidization are often measured in terms of velocity, and many articles have been written on measuring the superficial gas velocity at incipient bubbling \( U_{ib} \) and the superficial gas velocity at incipient fluidization \( U_{if} \) in beds of FCC catalyst. In an operating FCC standpipe, however, gas velocity has only a very nebulous meaning because it is difficult to determine what the relevant gas velocity is.

Fortunately, the well-behaved operating range can also be defined in terms of the density of the fluidized emulsion. Thus, the range of densities between the density of the emulsion at its point of incipient fluidization \( \rho_{if} \), and its point of incipient bubbling \( \rho_{ib} \) can be considered the range of densities over which a fluidized FCC catalyst will be well-behaved in a standpipe.

The catalyst beds encountered in commercial FCC units do not generally operate as quiescent fluidized beds that are confined to operate within the range of densities mentioned above. The typical catalyst bed found in the average FCC regenerator, for example, is usually operating as a very active bubbling bed. In open fluidized beds, bubbles do not present a fluidization problem. However, in a standpipe, bubbles need to be avoided. Thus, as the bubbling bed of catalyst begins to enter an FCC standpipe, it needs to shed itself of the excess gas bubbles to avoid dragging them down into the standpipe. The standpipe inlet geometry and location of the standpipe inlets should be carefully designed to allow this initial shedding of excess gas to take place in an orderly fashion.

It is beyond the scope of this paper to go into how the specific inlet geometry should be arranged; however, from the troubleshooting point of view, the process engineer needs to be aware that this process of shedding excess gas is taking place at the inlet to the standpipe. Thus, introducing aeration right at the standpipe inlet often causes more problems than it solves.

The Compression of Catalyst in a Standpipe

After the fluidized FCC catalyst emulsion enters the top of the standpipe and begins its descent, it starts to undergo a form of compression. As the catalyst descends the standpipe, the pressure head that is seen at any given depth in the standpipe increases. This increasing pressure compresses the interstitial gas that is surrounding the catalyst particles, as well as the gas that is in the pores of the catalyst particles. The net result of all this gas compression, is that the volume of the fluidizing gas surrounding the catalyst particles is reduced. So the catalyst particles move closer together, and the density of the emulsion increases.

If the standpipe is long enough, and if no aeration is introduced along the length of the standpipe, then this process of compression will continue as the catalyst travels deeper and deeper into the standpipe. This will cause the density of the catalyst emulsion to continue to increase until the catalyst emulsion reaches its incipient fluidization.
density. If the catalyst emulsion is compressed past this point, the emulsion will change phase from a fluidized bed to a packed bed, and the catalyst will have trouble circulating.

On FCC units that use standpipe aeration, the purpose of the standpipe aeration is to supply just enough additional gas to the catalyst as it passes each aeration tap to restore the catalyst emulsion to its original volume, as in Figure 4.

The ratio of $\rho_{if}/\rho_{ib}$ is known as the “Stable Expansion Ratio” for a fluidized catalyst. The higher this ratio, the more forgiving the fluidized catalyst is to changes in density, and the more easily it will tend to circulate in an FCC unit.

Another way of interpreting this ratio is to realize that it represents the maximum compression factor that the catalyst emulsion can be expected to tolerate as it descends the standpipe before losing its fluidization.

Abrahamsen and Geldart\(^1\) have shown that the ratio of the superficial gas velocity at incipient bubbling to the superficial gas velocity at incipient fluidization is a function of the physical properties of the catalyst as shown below.

$$\frac{U_{ib}}{U_{if}} = \frac{2300 \rho_g^{0.126} \mu^{0.833} e^{0.716 F}}{\rho_p \rho_g^{0.8}}$$  \hspace{1cm} (1)

Where:

- $U_{if}$ = Superficial Gas Velocity at Incipient Fluidization, m/sec.
- $U_{ib}$ = Superficial Gas Velocity at Incipient Bubbling, m/sec.
- $\rho_g$ = Gas Density, kg/m\(^3\).
- $\rho_p$ = Particle Density, kg/m\(^3\).
- $\mu$ = Gas Viscosity, kg/m sec.
- $F$ = 0-45 micron Fines Fraction in Catalyst.

$dp$ = Mean Particle Diameter, meters.
$g$ = Gravitational Constant, 9.81 m/sec\(^2\).

They also show that the Maximum Stable Expansion Ratio (MSER) can be estimated from the equation below:

$$\text{MSER} = \frac{\rho_{if}}{\rho_{ib}} = \left( \frac{U_{ib}}{U_{if}} \right)$$  \hspace{1cm} (2)

The measured Maximum Stable Expansion Ratio for a series of equilibrium FCC catalysts at room temperature and pressure. The sensitivity of the measured MSER in Figure 5 to changes in ABD and the 0-40 micron fines fraction appears to be significantly greater than what Equation 2 would predict. This lack of precise agreement is common in the field of fluidization. It is mentioned here to illustrate that published correlations and measurements need to be applied cautiously.

Both of these effects are clearly illustrated in Figure 5 which is taken from work published by Magnusson\(^2\). Figure 5 shows the measured Maximum Stable Expansion Ratios for a series of equilibrium FCC catalysts under “ideal” conditions. In actual practice, the effective MSER aggravate standpipe circulation problems because the maximum stable expansion ratio decreases with increasing catalyst particle density\(^1\).

Equation 2 and Figure 5 both provide estimates of the MSER for FCC catalysts under “ideal” conditions. In actual practice, the effective MSER

\(^1\)High apparent bulk density (ABD), typically correlates with high particle density in equilibrium FCC catalyst.
of the catalyst in the FCC standpipe appears to be only a fraction of this estimated number, so the MSER should not be taken at full face value when looking at standpipe compression. However, the relative changes predicted in MSER by Equation 2 and Figure 5 due to particle size, ABD, viscosity, and gas density are very real effects. It is these relative movements in MSER that are very useful for troubleshooting.

In an operating FCC unit, one of the ramifications of Equations 2 and Figure 5 is that the ability of the equilibrium catalyst to tolerate compression can change dramatically due to subtle effects like a loss of fines, or an increase in ABD that might accompany a catalyst change out.

The limited ability of equilibrium FCC catalyst to tolerate compression places a great deal of importance on proper standpipe design and aeration practices.

With these ideas in mind, let’s move on to troubleshooting standpipe circulation problems.

Assess the Situation; Gather Facts and Figures

When troubleshooting, a good way to get started is to gather some facts about the status of the standpipe’s operation for comparison against useful benchmarks. In the process, ask as many questions as possible about the history, and recent operation of the troubled standpipe. Some of the typical avenues of investigation are outlined below.

Catalyst Flux

A quick calculation of the catalyst flux passing through the standpipe will help indicate how high the duty of the standpipe is. Calculate the catalyst flux rate (kg/m² second) at which the standpipe is operating. How does this compare with past operating experience for the unit in question? Many FCC standpipes will operate with a flux as high as 980-1220 kg/m² second (200-250 lbs/ft² sec). Some standpipes have been observed operating as high as 1465 kg/m² second (300 lbs/ft² sec). If your catalyst flux is up at these levels you may be operating near the practical capacity of your FCC standpipe. If, on the other hand, the catalyst flux is significantly lower than this, then it is likely that something other than a sheer capacity limitation is causing the catalyst circulation problem.

Look at the Standpipe Pressure Profile

Conduct a single gauge pressure survey along the length of the standpipe and the vessel from which it is coming. What type of pressure profile is the standpipe generating? How does this compare with the idealized profiles discussed earlier? Usually, you are looking for a section of standpipe that is not generating the expected pressure head as a clue to where the problem is located.

Sometimes it is difficult to visualize what is going on inside those sections of the standpipe that are not building pressure. There are really several different phenomena that can create this type of pressure profile.

- The catalyst might be defluidized so that it is supporting its weight against the walls.
- There may be stationary bubbles in the standpipe that are acting as obstructions.
- There may be a real obstruction like a piece of dropped refractory or a workman’s shovel.

In any case, the section of the standpipe immediately below an obstruction will have a tendency to operate with a dilute rain of catalyst falling through an essentially empty standpipe. This type of flow does not generate the pressure buildup that the standpipe needs to produce.

Check the Standpipe Aeration Practices

The aeration rates being used on the standpipes should be checked against the theoretical aeration rates calculated in the next section. Defluidization of the catalyst from under-aeration, or obstructions in the form of bubbles from over-aeration, can both be caused by errors in the standpipe aeration. Unfortunately the symptoms for

---

Figure 5

Maximum Stable Expansion Ratio Versus Fines Content of Equilibrium Catalyst

---

2Unlike the gas contained in the continuous emulsion phase, bubbles can arise at velocities that are competitive with the velocity of the descending catalyst emulsion in the standpipe. Thus, if bubbles form in the FCC standpipe, they can rise against the flowing catalyst, be pulled down by the flowing catalyst, or remain stationary in the standpipe, depending on the relative bubble and catalyst emulsion velocities involved.
both these problems are very similar, so it is necessary to use a theoretical aeration rate as a point of reference.

It is very important to calculate the aeration required by each individual aeration tap location along the length of the standpipe. This information provides a great deal of insight into how the standpipe wants to operate, and provides a basis for comparing the actual aeration rates. Not calculating the individual aeration tap requirements is a serious mistake because the opportunity to look at the operating requirements for each section of the standpipe may be missed.

Also, ask as many questions as possible about the standpipe aeration. Some questions that come to mind are:

- How much aeration is being used in the standpipe?
- Is steam, air, or some other gas being used for aeration? Why is this particular media being used?
- If the standpipe is being aerated with steam, is it absolutely dry steam, or could there be condensate slugging into the standpipe?
- How much aeration is being supplied to each individual tap?
- How does the aeration rate compare with the theoretical aeration rate calculated for each individual tap?
- Could some of the aeration taps be plugged?
- How is the aeration being distributed to the taps?
- Does the aeration system use rotometers for each tap, or are orifices being used to obtain distribution?
- How confident are you that the aeration is going where you think it is going?

Figure 6
Calculation of Aeration Requirements

![Diagram showing the calculation of aeration requirements]

Operating Conditions of Regenerator:
- Catalyst Circulation, Metric Tons/Min.: 12.0
- Regenerator Pressure, kPa gauge: 87.2
- Regenerated Catalyst Temperature, °C: 682
- Molecular Wt. of Aeration Medium: 18.0 (Steam)

Standpipe Inlet
Distance from Top of Bed to Inlet is 1.83 m

Assume that the Standpipe Density will be 560.65 kg/m³

You need to know the skeletal density of the catalyst. This can either be measured or estimated from composition. For this example use 2549.9 kg/m³

If the standpipe does not have aeration, read on, since this is where the plot thickens.

Calculation of Standpipe Aeration Requirements

The calculation of the aeration, needed at any one of the pressure taps, is relatively straightforward. The steps required are outlined below, followed by a worked example.

1) Calculate the volume of catalyst that is descending the standpipe.
2) Calculate the volume of voids that are circulated with the catalyst.
3) Calculate the absolute pressure that should be observed at the standpipe inlet and at the various aeration taps along the standpipe length using an assumed emulsion density.
4) Calculate the change in gas volume due to the pressure increase between adjacent aeration taps.

This is the theoretical volume of gas that should be introduced into the tap under investigation. However, in practice only about 60-70% of this quantity of aeration is usually needed.

The example discussed below is illustrated in Figure 6.

Example 1

Calculate the steam required to aerate the first aeration tap in a regen-

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Footnote:
3 The circulation of the catalyst in the standpipe actually pumps the gas that occupies the spaces between (and inside) the particles down the standpipe with the catalyst. The minimum fluidization velocity of FCC catalyst is on the order of 0.003 m/second, while the velocity of the catalyst descending the standpipe is several orders of magnitude higher than this. So the gas that is in the continuous emulsion phase between and inside the catalyst particles is, in effect, dragged down the standpipe with the catalyst.
The distance from the surface of the catalyst bed in the regenerator vessel to the inlet of the standpipe is 1.83 meters (6 ft).

The distance from the inlet of the standpipe to the first aeration tap below the inlet is 2.85 meters (9.35 ft).

You will need to assume a density for the fluidized catalyst inside the standpipe, for the sake of these calculations, it is customary to assume a density of 560.65 kg/m$^3$ (35 lbs/ft$^3$).

You will also need to know the skeletal density of the equilibrium (not fresh) FCC catalyst being used. This can either be measured using helium pycnometry, or the skeletal density can be approximated from the calculation below:

$$\rho_{\text{skeletal}} = \frac{1000}{\frac{\text{Al}_2\text{O}_3}{3.4} + \frac{\text{SiO}_2}{2.1}}$$

Where:

- $\rho_{\text{skeletal}}$ = Skeletal density of catalyst, kg/m$^3$.
- $\text{Al}_2\text{O}_3$ = Weight fraction Alumina in catalyst.
- $\text{SiO}_2$ = Weight fraction silica in catalyst.

For this example, a skeletal density of 2549.9 kg/m$^3$ was measured using the equilibrium catalyst.

1) Calculate the volume of the catalyst emulsion that is traveling down the standpipe per minute:

$$1000 \frac{Q_{\text{Catalyst}}}{\rho_{\text{emulsion}}} = V_{\text{emulsion}}$$

Or

$$V_{\text{emulsion}} = 1000 \left(\frac{12.0}{560.65}\right) = 21.40 \text{ m}^3/\text{min}$$

Where:

- $Q_{\text{Catalyst}}$ = Catalyst circulation, metric tons per minute.
- $V_{\text{emulsion}}$ = Volume of fluidized catalyst emulsion m$^3$/min.
- $\rho_{\text{emulsion}}$ = The assumed standpipe fluidized density of 560.65 kg/m$^3$.

2) Calculate the total volume of interstitial and intraparticle gas that is circulated with the catalyst:

$$V_{\text{gas}} = V_{\text{emulsion}} \left(1 - \frac{\rho_{\text{emulsion}}}{\rho_{\text{skeletal}}}\right)$$

Or

$$V_{\text{gas}} = 21.40 \left(1 - \frac{560.65}{2549.9}\right)$$

Where:

- $V_{\text{gas}}$ = Volume of gas circulated down the standpipe with the catalyst, m$^3$/min.

3) Calculate the absolute pressure at the standpipe inlet, and the first aeration tap:

The Pressure At The Inlet Is:

$$P_{\text{Inlet}} = P_{\text{Dilute}} - \frac{\rho_{\text{emulsion}} (g) (\Delta H_{\text{Inlet-Surface}})}{1000}$$

Or

$$P_{\text{Inlet}} = (82.74 + 101.32) + \frac{(560.65)(9.81)(1.83)}{1000} = 194.12 \text{ kPa Absolute}$$

The Pressure At Tap 1 Is:

$$P_{\text{Tap 1}} = P_{\text{Inlet}} - \frac{\rho_{\text{emulsion}} (g) (\Delta H_{\text{Tap 1-Inlet}})}{1000}$$

Or

$$P_{\text{Tap 1}} = 194.12 + \frac{(560.65)(9.81)(2.85)}{1000} = 209.80 \text{ kPa}$$

4) The change in gas volume due the pressure increase can then be calculated:

$$\Delta V_{\text{gas}} = V_{\text{gas}} \frac{P_{\text{Tap 1}}}{P_{\text{Inlet}}}$$

Or

$$\Delta V_{\text{gas}} = 16.70 \left(\frac{209.80}{82.74}\right) = 1.25 \text{ m}^3/\text{min}$$

Where:

- $\Delta V_{\text{gas}}$ = The change in gas volume at the temperature and pressure of the standpipe due to compression.

In order to counteract the compression effect and restore the needed volume to the catalyst emulsion, an incremental 1.25 m$^3$ of gas per minute (at 682.2°C., 209.80 kPa absolute) must be injected into the standpipe at Tap 1. Using a molecular weight of 18.0 and PV=nRT this works out to 0.59 kg/min of steam at this tap location.

The theoretical aeration requirement serves as a useful bench mark to judge aeration rates when first examining the operation of the standpipe. However, few FCC units actually operate with exactly this...
quantity of aeration. In the real world, the actual aeration rate should initially be set to approximately 60-70% of this theoretical aeration requirement. Subsequent adjustment of the aeration rates from this initial point can then be used to seek out additional improvements. Some FCC units will end up operating somewhat above the theoretical aeration requirement, while others will operate below this theoretical aeration rate. In any case the best place to start is with an aeration rate that is 60-70% of theoretical.

Figure 7 which is taken from a paper by R.E. Wrench, J.W. Wilson, and G. Guglietta\(^3\) shows how the pressure generated in a standpipe responds to variations in aeration rates. Note that over-aeration produces a dramatic loss of standpipe pressure. This behavior provides another good reason to use less than the full theoretical aeration rate when first setting up standpipe aeration.

It should be expected that as the physical properties of the equilibrium catalyst change, the shape of the aeration response curve shown in Figure 7 will also change. As the MSER of the equilibrium catalyst increases, the more tolerant it becomes to improper aeration.

Note that the aeration requirements of a standpipe is dependent on the catalyst circulation rate. So it is convenient to calculate the aeration requirement in terms of kg aeration per metric ton of catalyst circulated. In this example, the theoretical aeration at the first tap is 0.049 kg steam/metric ton of catalyst circulation.

The aeration calculation should be repeated incrementally from tap to tap down the length of the entire FCC standpipe. All of the actual aeration rates can then be compared to the theoretical bench marks provided by the calculation. Often this exercise will reveal that some portion of the standpipe is being improperly aerated.

When doing these aeration calculations along the length of the standpipe, it is handy to know that if the distances between the taps are equal, then the theoretical aeration required by the equally spaced taps will all be the same. Table I illustrates this for the regenerator used in the example above. Aeration taps 2 through 10 are all equally spaced at a distance of 3.5 meters from each other.

### Table I

<table>
<thead>
<tr>
<th>Tap #</th>
<th>Tap Location, Meters Below Bed Surface</th>
<th>∆H, Meters</th>
<th>Aeration Required, kg/min of Steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>1.83</td>
<td>1.83</td>
<td>None</td>
</tr>
<tr>
<td>1</td>
<td>4.68</td>
<td>2.85</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>8.18</td>
<td>3.50</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>11.68</td>
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<td>0.73</td>
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<td>15.18</td>
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<td>3.50</td>
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<td>0.73</td>
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<td>3.50</td>
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</tr>
<tr>
<td>10</td>
<td>36.18</td>
<td>3.50</td>
<td>0.73</td>
</tr>
</tbody>
</table>

### Standpipe Compression Requirements

Calculating the change in catalyst emulsion density that is taking place in the standpipe from tap to tap is also very revealing. As was mentioned earlier, there is only a very limited range of densities over which FCC catalyst will remain fluid. If the increase in pressure from tap to tap is too large, the catalyst will be compressed past its point of incipient fluidization.

Using data from the previous example, the percent change in catalyst density required from tap to tap can be calculated from:

\[
\Delta \rho_{\text{Emulsion}}\% = 100 \times \frac{\Delta V_{\text{Gas}}}{V_{\text{Emulsion}}}
\]

Or using the numbers from Example 1:

\[
\Delta \rho_{\text{Emulsion}} = 100 \times \frac{1.25}{21.40} = 5.84\%
\]

Where:

\[\Delta \rho_{\text{Emulsion}} = \text{The percent change in emulsion density that is taking place from tap to tap.}\]
What we are really doing here is calculating the amount of compression that the standpipe is requiring the catalyst to undergo. The greater the required percentage increase in density from tap to tap, the more prone the standpipe is to circulation difficulties. Calculating the percentage compression from tap to tap, often pinpoints where the FCC standpipe will be most likely to experience compression problems. FCC units that are suffering from catalyst over-compression, and the subsequent loss of fluidization that it brings on, will often find that these problems are occurring in the upper half of the standpipe because this is where the greatest amount of compression per meter of descent takes place in the standpipe.

This standpipe compression requirement is a function of the FCC design pressure, and the spacing between the taps on the FCC standpipes. For example, it is commonly observed that lower pressure FCC units, where the regenerator may be designed to operate at 82 kPa gauge (12 psig), generally have much more difficulty circulating catalyst in standpipes than do higher pressure designs where the regenerator may be operating at 207 kPa gauge (30 psig). A quick calculation of standpipe compression requirements reveals that the low pressure designs inherently have much higher standpipe compression requirement, per meter of standpipe descent, than do the higher pressure designs.

Table II shows how the compression requirements for a standpipe change dramatically with respect to the dilute phase pressure of the vessel from which they are drawing catalyst.

The standpipe that is operating at the lower design pressure requires the catalyst to undergo significantly more compression between the aeration taps. In fact, at the top of the standpipe where the compression requirements are greatest, the low pressure design shown here requires 58% more catalyst compression per meter of standpipe descent.

One way to mitigate this compression requirement when the unit is designed for lower pressure, is to place the aeration taps closer together along the length of the standpipe.

As a rule, the aeration taps for low pressure standpipes should normally be spaced so that less than 4.5-5.0 percent compression is required between the taps. By keeping the compression requirement low, the standpipe circulation will be more tolerant of the changes in catalyst particle size distribution that accompany cyclone deterioration at the end of a run.

In terms of absolute numbers, 4.5 or 5.0 percent compression does not seem very high. However, if the unit is circulating a catalyst with a low stable expansion ratio (Low 0-40 fines content and high ABD), then a 5.0 percent compression requirement in the standpipe can create catalyst circulation problems very quickly.

### Choice of Aeration Media

Inspection of Equations 1 and 2 suggests that if the aeration media has a higher density and a higher viscosity, then the MSER for the system will be higher. Air is significantly higher than steam in both viscosity and density.

Thus, changing the aeration media from steam to air in regenerator standpipes that are suffering from compression problems has sometimes produced a dramatic improvement in catalyst circulation. If, due to poor cyclone performance, the particle size distribution and density of the catalyst have moved into a region where the catalyst has trouble circulating in a standpipe with a 5.0 percent compression requirement, then changing the aeration media from steam to air can increase the compression tolerance (Effective MSER) to almost 1.08. This type of change in compression tolerance from 1.05 to 1.08 represents almost 60 percent improvement.

The possibility of condensate slugging into the standpipe is also greatly reduced by using air instead of steam.

The refiner should be aware that there are occasional gasoline gum or stability problems that can arise from the additional oxygen that is
carried into the reactor by air in the regenerator standpipe. But these problems are relatively infrequent, and if they do occur, then the standpipe can be switched back to steam.

Note that this change in aeration medium is only appropriate in units that are operating with complete combustion in the regenerator.

**Catalyst Design**

In order to help mitigate a refiners’ catalyst circulation problems, there are a number of things that the catalyst manufacturer can do to the catalyst.

First of all, if the FCC unit is limited in the amount of catalyst that it can circulate, then an increase in equilibrium catalyst activity should be considered. This will allow the refiner to achieve his best possible conversion with the limited catalyst circulation that is available. Increasing the activity of the equilibrium catalyst will also raise the regenerator temperature, which in turn will reduce the amount of catalyst that must be circulated at a given set of operating conditions. These two effects complement each other nicely.

Equations 1 and 2 along with Figure 5 clearly show that the Maximum Stable Expansion Ratio of the equilibrium FCC catalyst is a function of catalyst ABD and the 0-40 micron fines content of the inventory. Manufacturers of FCC catalyst have a great deal of flexibility in their manufacturing process which allows them to modify the ABD of the equilibrium catalyst without changing the chemical composition, or the catalytic selectivity patterns of the catalyst. Thus, a reduction of the equilibrium ABD can be designed into the fresh catalyst so that the MSER of the equilibrium catalyst can be enhanced.

In addition, the particle size distribution of the fresh catalyst can be modified in favor of a smaller average particle size with a higher 0-40 micron fines content which also tends to aid circulation.

Attrition resistance of the catalyst is another feature that can be modified so that the tendency to generate 0-40 micron fines can be enhanced. This is sometimes helpful when the cyclones have deteriorated and the ability of the FCC unit to hold the necessary 0-40 micron fines in its inventory is diminished.

By judicious application of these principles, the catalyst manufacturer can provide the refiner with a great deal of relief from standpipe circulation problems.

**Pulling it All Together**

From the foregoing discussion it should be clear that there are really four disciplines that need to be examined when trouble-shooting catalyst circulation problems in standpipes:

1. The Design of the FCC Unit Itself.
2. The FCC Unit Operations.
3. The Fluidization properties of the Equilibrium FCC Catalyst.
4. The Design of the Fresh Catalyst.

The FCC standpipe design needs to be looked at to confirm that its compression requirements are reasonable, to determine where the standpipe is making the most demands on the circulating catalyst, and to determine what the theoretical aeration bench marks are.

FCC operations need to be looked at to insure that the standpipe is being operated properly, and to insure that the rest of the FCC hardware is really doing what it is suppose to be doing. For example, a false level reading can trigger circulation difficulty by upsetting the bed levels which may uncover the cyclone diplegs, etc. One thing leads to another, and soon the fines have been lost from the inventory, and the standpipe circulation is in jeopardy.

Since the cyclone operation determines the particle size distribution of the equilibrium catalyst, an examination of cyclone performance should be considered an integral part of trouble-shooting standpipe circulation problems.

As shown above, the equilibrium catalyst properties provide much indirect information about how compression tolerant the catalyst will be in the standpipe. Thus, the equilibrium catalyst properties should be closely scrutinized for any subtle changes that may have triggered the standpipe upset.

Since a great deal of relief can often be obtained by modifying the fresh catalyst design, the catalyst manufacturer should be consulted to determine how much latitude is available for changing physical properties or activity. Modification of the fresh catalyst design to mitigate circulation difficulties is just another example of the benefits that accrue from close cooperation between the refiner and the FCC catalyst manufacturer.

**References**

Have you ever wished it were this easy to remove sulfur?

With the products and expertise available through Grace Davison and Advanced Refining Technologies, our team now offers a one-stop shop for clean fuels solutions.

Grace Davison GSR® technologies continue to provide 30%-45% gasoline sulfur reduction in the FCC. This success has been proven in over 85 commercial units worldwide and is the result of over 15 years of continuous R&D efforts. Our clean fuels product portfolio currently includes D-PriSM® and GSR-5 additives, as well as SuRCA® and Neptune™ catalysts.

Our GSR technologies are used around the world in a variety of FCC operations, with and without hydrotreating hardware, to provide feedstock flexibility, operating flexibility during hydrotreater outages, gasoline stream blending options, and gasoline octane preservation. In-unit reduction of FCC gasoline sulfur continues to create a variety of opportunities and options for refiners to drive profitability.

For refiners with FCC pretreaters, the ApART™ Catalyst System utilizing combinations of AT575, AT775 and AT792 offers the opportunity to significantly increase sulfur removal in the hydrotreater while at the same time maximizing FCC feed quality. The improved performance of the pretreater results in higher gasoline potential in addition to decreasing FCC gasoline sulfur.

For ULSD processing, the SmART Catalyst System® utilizes state-of-the-art catalyst technology which is staged in the proper proportions to provide the best performance, while at the same time meeting individual refiner requirements. The catalyst staging is designed to selectively take advantage of the different reaction mechanisms for sulfur removal with efficient hydrogen usage. CDXi and 420DX, our newest generation of high activity CoMo catalysts, efficiently removes the unhindered, easy sulfur via the direct abstraction route, while NDXi, our high activity NiMo catalyst, then attacks the remaining sterically hindered, hard sulfur. The SmART system provides higher activity than either the traditional CoMo or NiMo catalyst alone while effectively helping the refiner manage hydrogen utilization.
Editor’s Note:

FCC catalyst optimization has taken different directions over the years but a recurring goal has been improving coke selectivity. Ultimately, this would allow the refiner to process heavier feedstocks, increase unit throughput, and operate within hardware limitations exacerbated by the deleterious effects of contaminants such as nickel and vanadium. Over half of refiners blend some resid into their feed.

Intense R&D efforts have resulted in multiple generations of successful catalyst families with improved coke selectivity. One such success story is the IMPACT® series of catalysts. In this article, we discuss the application of IMPACT catalyst in its early phase of commercialization. It is clear that expectations of enhanced coke-to-bottoms based on pilot plant studies were exceeded in the first commercial application some six years ago. IMPACT contains the only integral vanadium trap in the industry. In the years since, IMPACT has delivered enhanced coke and gas selectivity in a broad range of applications, from severely hydrotreated gasoils to heavy resid feeds.

Since its initial commercial launch, we have sold over 200,000 tons of IMPACT catalyst and have employed the technology successfully in over 70 units worldwide.

Scott Purnell, principal author, serves as General Manager and Managing Director of Advanced Refining Technologies. This article first appeared in Issue #93, 2003.
As the availability of light, sweet crudes has declined and prices have increased, refiners have reconfigured their operations in order to be able to upgrade heavier, less desirable feedstocks into lighter, more valuable products. Declining fuel oil demand has only added to the urgency for effective upgrading of heavy resid. Fluid catalytic cracking is one of the most efficient and economic ways of achieving this upgrading, and it is estimated that about half of the refiners blend some amount of resid into their FCC feeds.

For resid operations, optimal design of the FCC catalyst is critical. Obviously, minimizing diffusional limitations for the large molecules found in vacuum residue is an important consideration in the design of resid catalysts, but coke selectivity remains paramount. These units processing resid are impacted by high levels of contaminant metals and Conradson carbon, and are often limited by air blower capacity and/or regenerator temperatures, making coke selectivity the most important catalyst performance characteristic. Coke selectivity determines the FCC unit conversion level at a given set of conditions, and improvements in coke selectivity have the greatest value to the refiner. Improvements in coke selectivity can allow the refiner to increase feed rate, increase conversion, or process heavier, less expensive feedstocks, all of which lead to increased profit margins.
In this article we will describe a breakthrough new resid catalyst technology with unsurpassed coke selectivity, known as IMPACT®, and share data from the first commercial applications of this promising new technology.

Breakthrough New Resid Catalyst: IMPACT

Technology Description

Grace Davison is highly committed to its FCC catalyst business and has an active R&D program to develop and commercialize higher performing products. Through our stage-gate new product development process, we have successfully commercialized the AURORA, ATLAS, ADVANTA, and VANGUARD catalyst families within the last two to three years. Recent efforts have focused on further raising the performance bar for resid catalysts. Our scientists have strived to combine all the important catalyst functionalities for resid cracking into one superior catalyst. The goal was to invent a catalyst with step-out improvements in coke selectivity and stability over current industry benchmarks, VANGUARD and AURORA-LC, while optimizing the matrix design for additional bottoms cracking. Industry leading unit retention characteristics and resistance to iron poisoning were also desired.

These efforts have led to the development of a breakthrough new resid catalyst family, known as IMPACT. IMPACT combines next-generation integral vanadium trapping, advanced zeolite stabilization, and superior matrix metals passivation to achieve the ultimate in coke selectivity, and has demonstrated truly remarkable performance in laboratory testing. Figure 1 illustrates one comparison between state-of-the-art technology and IMPACT. These data were generated in the Davison Circulating Riser (DCR) pilot plant with a heavy resid feedstock. The catalysts were deactivated with 2,500 ppm nickel and 5,000 ppm vanadium using our CPS cyclic deactivation protocol. This figure indicates that the IMPACT technology offers nearly 30% improvement in coke selectivity. Improvements of this magnitude over industry-leading technology are extraordinary.

In addition to coke selectivity, we have also compared the stability of IMPACT to industry benchmarks. Figure 2 summarizes a metals deactivation study that compares IMPACT to a state-of-the-art coke selective resid catalyst and a conventional FCC catalyst at increasing levels of vanadium. This figure shows that both the resid benchmark and IMPACT technologies offer a much higher tolerance to vanadium than conventional catalysts (the curves are much flatter). Note however, that the activity curve of IMPACT is slightly flatter than the industry standard, and the base activity achieved at 9,000 ppm total metals (Ni + V) is also higher. Comparing the zero metals case to 9,000 ppm total metals, the microactivity of IMPACT declined only about 2 numbers, while a
decline of 25-30 numbers was observed for the conventional catalyst. This phenomenal stability will give IMPACT even better commercial coke selectivity as it resists the zeolite deactivation and metals poisoning found in resid operations.

Furthermore, IMPACT is based on the Grace Davison proprietary aluminia sol catalyst platform. Thus, in addition to the truly step-out coke selectivity and stability performance, users of IMPACT will enjoy the additional benefits characteristic of Davison alumina sol catalysts, namely industry-leading unit retention, maximum resistance to iron poisoning, and enhanced bottoms cracking.

In fact, IMPACT further distinguishes its performance through step-out improvements in coke-to-bottoms selectivity. When formulating resid catalysts, coke-to-bottoms performance often tends to fall on a single line with some catalysts demonstrating outstanding coke selectivity, but with poor bottoms cracking, and yet other catalysts showing excellent bottoms upgrading, but with high coke yields. This phenomenon is illustrated in Figure 3 where the coke-to-bottoms performance of IMPACT is gauged against other industry benchmarks.

This chart shows the bottoms yields measured vs. coke in a riser pilot plant study where the catalysts were deactivated via cyclic propylene steaming (CPS) at 1450°F with 4,000 ppm vanadium and 4,000 ppm nickel and run with a resid feedstock. In this study, the two industry benchmark catalysts can be seen to fall on essentially the same line, one with better coke selectivity and the other with better bottoms cracking. However, IMPACT showed a dramatic improvement over these technologies, demonstrating a step-change in both bottoms cracking and coke selectivity. At a constant coke yield of 4 wt.%, IMPACT showed a 2.0 wt.% reduction in bottoms (25% relative) over the coke selective resid catalyst benchmark, while at a constant bottoms yield of 6 wt.%, IMPACT showed a 2.3 wt.% reduction in coke (37% relative) over the bottoms cracking resid catalyst benchmark. When this bottoms cracking capability is combined with its phenomenal coke selectivity, the coke-to-bottoms performance of IMPACT is nothing short of extraordinary.

The superior performance characteristics of IMPACT, as described above, will lead to enhanced operating flexibility and increased profitability for the refiner. The coke selectivity improvement alone would allow many refiners to increase throughput, increase conversion, or process heavier, less expensive feedstocks. Table I shows the estimated yield shifts for a refiner contemplating a switch from a very successful operation with an industry-leading resid catalyst technology to IMPACT. In this

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<th>Estimated Economic Benefit from IMPACT (based on a 50,000 bpd RFCCU)</th>
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<td><strong>Base Case</strong></td>
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<td>Total C3’s, wt.%</td>
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particular case, the premium coke selectivity of IMPACT is projected to give an astonishing conversion increase of 4.0 wt.%. Using typical product values, this conversion increase would translate into a $0.45/bbl advantage for IMPACT, or $22,500/day (greater than $8 million annually) for a 50,000 bpd resid FCCU.

Commercial Experience

IMPACT is in the "Commercial Testing" stage of our new product development process and is currently being evaluated in four commercial FCCU’s. Data are still preliminary, but initial results are very promising, meeting our high expectations for this exciting new technology. We will share some of the highlights here.

In the first application, IMPACT was added to a UOP High Efficiency unit in the US Gulf Coast. The unit runs more than 60,000 bpd of feed and operates in full combustion. At only 30% turnover to IMPACT, a reduction in regenerator temperature and an increase in catalyst circulation rate were observed (Table II). These observations are clearly consistent with the superior coke selectivity of IMPACT.

The reduction in fresh catalyst additions combined with increased contaminants in the feed led to an increase in equilibrium catalyst Ni + V levels of 30%. However, at only 30% turnover and at the higher metals level, IMPACT maintained ecat microactivity and increased conversion by 1.3 vol.% while reducing dry gas. IMPACT also dramatically reduced slurry. Yield shifts are summarized in Table III.
additions and the other at 20% turnover to IMPACT. The yield shifts observed in this study are summarized in Table IV. In this ACE study, the IMPACT-containing equilibrium catalyst showed a 2.0 wt.% increase in conversion at constant coke. Again, the conversion increase came mainly through upgrading of slurry, while hydrogen and dry gas were also reduced.

It may seem remarkable that these large yield shifts were observed at relatively low levels of IMPACT in circulating inventory. However, the performance benefits of IMPACT have been shown to track turnover and are apparent almost from the first additions. Figures 4-6 show improvements in equilibrium catalyst performance observed for Ecats taken from a third IMPACT application and tested in Grace Davison’s standard equilibrium catalyst monitoring program. This third IMPACT application is in yet another UOP High Efficiency FCCU operating at a rate of more than 70,000 bpd.

Status

Although early in the commercialization process, IMPACT is now readily available in commercial quantities. The completion of a multi-million dollar expansion to the fluid cracking catalyst (FCC) facility at the flagship Lake Charles, Louisiana manufacturing complex will allow Davison to meet anticipated future demand for IMPACT. The expanded facility (Figure 7), which went on-stream in May, 2003, will also allow Davison to produce other premium cracking catalysts characterized by superior coke selectivity, including AURORA™-XLC, a further enhancement of the very successful AURORA catalyst family.

Summary

In the optimal design of resid cracking catalysts, coke selectivity remains paramount. Recent R&D efforts focusing on coke selectivity in resid applications have led to the development of a truly break-
through new resid catalyst known as IMPACT. IMPACT has shown extraordinary enhancements in both coke selectivity and stability over current industry benchmarks in pilot plant testing, while also providing step-out improvements in coke-to-bottoms selectivity. Since IMPACT is based on Davison’s proprietary alumina sol technology, industry-leading unit retention and resistance to iron poisoning are additional benefits. IMPACT is now available in commercial quantities and is currently being evaluated in four FCCU’s. Data are still preliminary, but initial results are very promising. Dramatic improvements in coke and gas selectivities have been observed in the Ecat data from the start of IMPACT additions and track with turnover. In two of the applications, increases in conversion of 1-2 vol.% (mainly gasoline at the expense of slurry) have been observed with only 20-30% IMPACT in inventory.

Figure 7
Expansion at Davison’s Lake Charles Plant to Produce IMPACT
Maximize yield with Grace Davison’s GENESIS™ FCC catalyst.

Most refiners need flexible catalyst systems that allow them to take advantage of changing economic scenarios. Grace Davison delivers this flexibility with the GENESIS™ catalyst system. GENESIS™ catalysts provide a means to maximize yield potential through optimization of discrete cracking catalyst functionality. GENESIS™ catalysts are a blend of two catalyst types. The key component is MIDAS®, which maximizes conversion of bottoms and improves coke selectivity by eliminating coke precursors. The other GENESIS™ component is most often an IMPACT® catalyst. The inclusion of IMPACT® provides critical zeolite surface area and activity as well as superior coke and gas selectivity in a broad range of applications, from severely hydrotreated gosols to heavy resid feeds.

GENESIS™ catalysts demonstrate a true yield synergy with a superior coke to bottoms relationship than either component alone. The synergy exists because each component cracks specific feed species.

GENESIS™ catalyst provides the ultimate in formulation and FCC operational flexibility.

For more information, contact your Grace Davison Technical Sales Manager

www.grace.com  7500 Grace Drive • Columbia, MD 21044 USA
Grace Davison’s Equilibrium Catalyst Analysis Program

Grace Davison recognized the importance of equilibrium catalysts analyses early in the history of cat cracking. That’s why we instituted the industry’s first Equilibrium Catalyst Analysis (Ecatal) program in 1947, only five years after the startup of the first FCCU.

As analytical technology has advanced, we’ve installed sophisticated equipment and included many more critical tests for the program. Through the years, we developed and reported many analysis of Ecatal chemical and physical properties that have helped FCC operators understand their circulating catalyst health and use this information to optimize their operations.
Continuous improvements to our system have evolved into recent developments including online access to immediate test results through www.e-Catalysts.com. Currently, we analyze for the following properties:

- Microactivity
- Surface Area
- Elemental Analysis
- Pore Volume
- Carbon
- Apparent Bulk Density
- Particle Size Distribution
- Unit Cell Size

For more information on Grace Davison’s industry-leading Equilibrium Catalyst Analysis program, contact your technical sales rep or log on to www.e-Catalysts.com.
Editor’s Note:

Over the years we have focused on the refiners’ needs to optimize FCC performance as it impacts product slate and product quality. We have also supplied valuable information on the interaction of unit operating parameters and catalyst technology.

The basic concept of fluid catalytic cracking is the cracking of hydrocarbon molecules, followed by the eventual transfer of hydrogen to produce products that are lighter and more valuable than the feed. Simultaneously, heavier products, such as coke, are generated.

Hydrogen in coke is a necessary parameter for the calculations of the unit coke yield. It can also be an indicator of inefficient stripping that can cause fluctuations in regenerator temperature. Accurate flue gas analysis is also important for many emissions regulations, such as MACT II, which are based on coke yield.

In this article, we discuss that hydrogen in coke is more than a measure of stripper efficiency; it is a reflection of other key unit operating parameters and controls.

Our Technical Service Manager, David Hunt, is the principal author of this article, which originally appeared in issue #100, 2006.
Refiners often use hydrogen in coke as a parameter to judge the performance of their FCC catalyst stripper. However, the use of this parameter for process monitoring is often the subject of significant debate. The main questions are what hydrogen in coke number truly indicates good catalyst stripping and how valid is the number itself.

I propose refiners use the hydrogen in coke number to help confirm the accuracy of their coke make, other heat balance parameters and flue gas analysis. Any hydrogen in coke value less than 5 wt.% or greater than 9 wt.% is likely due to poor flue gas analysis.

Since the flue gas analysis is the basis for the heat balance calculations, it influences many of the calculated operating parameters such as the unit coke production, heat of reaction, catalyst circulation rate, and most dramatically, the hydrogen in coke. An artificially low hydrogen in coke number resulting from an incorrect flue gas analysis will result in a calculated coke production from the unit that is higher than actual.

An accurate flue gas analysis and hydrogen in coke number is especially important when you consider that many throughput limitations are set by emission regulations based on coke production. When considering this, the use of the hydrogen in coke number to judge stripping efficiency should be a secondary concern.

Calculating Hydrogen in Coke Practical Limits

If your heat balance calculations yield a hydrogen in coke result of 4 wt.% does this mean you have a world-class stripper? Or if your hydrogen in coke is 12 wt.% should you plan on a stripper revamp during the next turnaround? The answer to both questions is likely "no".
Generally the industry accepts 5 to 6 wt.% hydrogen in coke as the lowest attainable from ideal stripping. This is based on the assumption that if the FCC stripper performed perfectly it would only allow coke consisting of highly unsaturated hydrocarbons to pass through to the regenerator.

In order to define the upper reasonable limit for hydrogen in coke, you might consider a case where a substantial amount of product is burned in the regenerator. Burning the equivalent of slurry oil (main fractionator bottoms) in the regenerator as coke could be considered an extreme case. In this circumstance, the hydrogen in coke would be \( \sim 9.0 \) wt.%, which is the nominal hydrogen content of a slurry oil with an API of \( \sim 0^1 \).

So, at best you may argue that the stripper produces coke with a hydrogen content of 5 wt.% and at an extreme case it might produce up to 9 wt.%. Data outside this range is likely explained by bad flue gas data. An inaccurate value of CO\(_2\) is often the culprit; however, poor O\(_2\) results will cause errors in the calculations as well.

### The Influence of CO\(_2\) on Hydrogen in Coke

Figure 10 shows the calculated hydrogen in coke and coke yield as a function of the measured flue gas CO\(_2\) content for a FCC operating in full combustion with constant excess O\(_2\). Questionable data is indicated by the dashed lines for hydrogen in coke data outside of the 5 to 9 wt.% range.

The impact of CO\(_2\) is significant and can affect not only the hydrogen in coke value but perhaps more importantly the calculated coke yield. Figure 10 suggests that coke yield could be off more than 10% due to bad flue gas data. Many FCC emission regulations, like MACT II, are based on coke production so accurate coke measurement is critical.

The coke yield was calculated using the method described in the Grace Davison Guide to Fluid Catalytic Cracking, Part One.

Next time you see a high or low hydrogen in coke number in your operating data, instead of immediately thinking about your stripper performance, you may want to check the validity of your flue gas analyses and realize that the reported coke yield (as well as other heat balance parameters) may be in error.

### References


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**Figure 10**

Influence of Flue Gas CO\(_2\) Value on Hydrogen in Coke and Coke Yield
The recognized industry source for fundamental FCC process, hardware and catalyst knowledge.

Grace Davison’s commitment to the refining industry extends beyond that of a traditional catalyst supplier. It has always been our philosophy to complement the use of our premium, value-added FCC catalysts with the industry’s finest technical support.

The Guide features the following articles:

**Part One**
1. History of Cracking
2. Cracking Reaction Mechanism
3. The Fluid Catalytic Cracking Process
4. Vessel and Mechanical Equipment
5. Feedstock
6. FCC Operation

**Part Two**
7. Fluid Cracking Catalysts
8. Equilibrium Catalyst Analysis
9. Fluid Cracking Catalyst Additives
10. Reformulated Gasoline and the FCC Unit

**Part Three**
11. Laboratory Evaluations of Fluid Catalytic Cracking
12. Yield Estimates
13. Cat Cracker Problems and Solutions

All three parts of the Guide are now available on CD as searchable PDF documents. To order a copy of the Guide on CD, contact your Grace Davison sales representative or betsy.mettee@grace.com.
Editor’s Note:

The use of Grace Davison FCC catalysts and additives has provided improved operating flexibility to refiners for decades. Fluctuating product values, some seasonal, others triggered by evolving economic parameters, have created a dynamic market for products that can address short term and long term operating objectives. With the application of new strict environmental regulations on a global level, and the ever changing feed slate, the refiner must adapt quickly in order to maintain a profitable and acceptable operation.

One such challenge is meeting regulations with respect to sulfur levels in products like gasoline and cycle oils. There are obvious hardware options such as hydrotreating and hydroprocessing units but there are also catalytic options that a refiner can implement to complement the refinery configurations. Grace Davison innovation resulted in our patented gasoline sulfur reduction or GSR® family of products designed specifically to achieve compliance with new fuels regulations.

In this article we will discuss a scenario where a FCC feed hydrotreater planned shutdown caused a burden on the refiner to meet gasoline sulfur specifications during the unit outage. We will present the step-by-step approach that was implemented by Grace Davison and the refiner in providing the refiner an action plan including the use of GSR to allow them to continue meeting the product sulfur specification while processing a poorer quality feed during the outage.

The short-term application was such a success that the refiner decided to continue GSR usage even after starting up the FCC feed hydrotreater.

Principal author Lauren Blanchard is currently Strategic Global Marketing Manager for Advanced Refining Technologies. This article first appeared in Issue #101, 2007.
Introduction

In most refineries, FCC gasoline is one of the largest, if not the largest contributor of sulfur to the overall gasoline pool. Regulations limiting the amount of sulfur in gasoline have highlighted the importance of reducing sulfur in the FCC gasoline stream. Grace Davison has been providing catalysts and additives to the industry that reduce FCC gasoline sulfur by 35% or more for over ten years. These technologies have been proven in 80 units worldwide. Another popular alternative to reduce gasoline sulfur is the installation of hardware. Increasingly stringent regulations have forced refiners to install FCC feed hydrotreaters and gasoline post-treaters to meet ultra-low sulfur gasoline regulations. Interestingly, the phase-in of hardware has not eliminated the benefit of sulfur reducing catalysts and additives. Grace Davison’s gasoline sulfur reduction technologies are complementary to hardware solutions. They are being used at numerous refineries around the world in conjunction with hardware to drive refinery profitability by providing feedstock flexibility, minimizing octane loss and providing operational flexibility during hydrotreater outages.

Proper management of FCC feed hydrotreater outages is becoming increasingly important as more and more refiners rely on hydrotreating to meet their per-gallon gasoline sulfur limits. About half of all FCC units now have feed hydrotreaters. Some are run at higher severity than in the past to achieve these new ultra-low gasoline sulfur targets. Running at higher severity increases the frequency of turnarounds. Conventional methods of ensuring that the gasoline pool stays below the sulfur limit during the
Hydrotreater turnaround are purchasing low sulfur feed or reducing FCC throughput. Either approach can significantly reduce refinery profitability. Another option is to use one of Grace Davison’s sulfur reducing technologies during the outage to provide feedstock flexibility while maintaining sulfur compliance.

This paper presents a case study in which Grace Davison and Valero Energy’s, Wilmington, California, USA refinery worked closely together to minimize the impact of a FCC feed hydrotreater outage. Significant planning and preparation took place, including selecting the best purchased feeds to run during the outage as well as the best sulfur reduction technology to use to meet their objectives given the sulfur species in the FCC gasoline. The use of Grace Davison’s GSR-5 sulfur reduction additive allowed Valero to process feed that was higher in sulfur than their routine feed yet remain in gasoline pool sulfur compliance. Valero estimates that the use of GSR-5 additive saved them $1.7 million during the hydrotreater outage. The results were so encouraging that Valero has elected to use GSR-5 additive on an on-going basis and estimates increased profits of over $8 million annually.

Evolution of Sulfur Reduction Technologies

In 1992, well before the industry realized the need to reduce FCC gasoline sulfur, Grace Davison anticipated this requirement and began a research and development effort for catalytic reduction of FCC gasoline sulfur. The objective was to develop a family of FCC catalysts and additives to help refiners meet clean fuels specifications. Established technologies that evolved from over 14 years of continuous R&D include D-PriSM additive, SuRCA catalyst, GSR-5 additive, and Neptune catalyst.

A road map for product selection is shown in Figure 1. When formulating a solution for a customer, Grace Davison experts consider the FCC gasoline stream targeted for sulfur reduction, the desired level of gasoline sulfur reduction, and whether a catalyst or an additive is preferred. Careful selection of the appropriately engineered solution for each application has resulted in consistent product performance and meeting or exceeding customer expectations. Twenty-three refiners are currently using Grace Davison gasoline sulfur reduction products worldwide, making Grace Davison the leading supplier of gasoline sulfur reduction catalysts and additives. Many of these refiners have been using these products on a continuous basis as part of their overall sulfur reduction strategy. (Figure 2).

For refiners who desire FCC additives for maximum operating flexibility, Grace Davison’s D-PriSM additive is effective at reducing sulfur species in light and intermediate FCC gasoline. It has been used in more than 25 refineries worldwide. D-PriSM additive has provided up to 35% sulfur reduction on light FCC gasoline with no FCC yield deterioration.

Figure 1
Grace Davison’s Portfolio of Gasoline Sulfur Reduction Products

Figure 2
Grace Davison Experience in Sulfur Reduction Applications
Grace Davison’s SuRCA catalyst family is designed to completely replace the conventional FCC catalyst in the circulating inventory. This product provides gasoline sulfur reduction of up to 35% on full range gasoline while maintaining or even enhancing existing yields and selectivities. Additionally, reductions of 10-15% in LCO sulfur have been observed in some applications. Over 45 SuRCA catalyst applications have occurred worldwide, with 10 current users having employed the technology for an average of more than three years. These refiners have incorporated SuRCA catalyst into their operating strategies for long-term profitability and operating flexibility.

Appreciating refiners’ desire for a product that provides the performance of SuRCA catalyst but can be used as an additive for maximum operating flexibility, Grace Davison commercialized the GSR-5 additive in 2004. It is based on the SuRCA catalyst chemistry and provides similar gasoline sulfur reduction with base cracking catalyst functionality. There are currently five refiners benefiting from the use of GSR-5 additive.

To further expand the sulfur reduction portfolio for continuous improvements in both performance and cost effectiveness, Grace Davison has recently commercialized a new gasoline sulfur reduction catalyst family. This next generation technology, Neptune, is a step out improvement, providing 35-50% full range gasoline sulfur reduction commercially with full catalyst formulation flexibility.

Pre Turnaround Preparation

The Valero, Wilmington refinery approached Grace Davison four months prior to their scheduled FCC feed hydrotreater shutdown to help them get a better understanding of their options during the outage. Valero and Grace Davison worked together to determine if the use of a gasoline sulfur reducing technology would enable Valero to improve their economics and remain within their FCC gasoline sulfur limit during the shutdown.

During the outage, the refinery planned to purchase several hydrotreated feeds. These would be different than the pretreated feed normally charged to the FCC unit. The refinery planned to blend purchased feeds with their routine feed. The candidate feeds were sent to Grace Davison for testing to compare the potential effects of the feeds on the refinery’s FCC yields and gasoline sulfur.

Analysis of the candidate feeds and Valero, Wilmington’s pretreated Routine Feed is shown in Figures 3-5. Candidate feeds (Samples A, B, and C) were heavier and more aromatic than the Valero, Wilmington Routine Feed (Figure 4) making them more difficult to crack (Figure 3). Additionally, the three sample feeds contained significantly more sulfur and nitrogen species, while concarbon levels were similar to the Routine Feed (Figure 5).

The four feeds were tested using a representative Valero, Wilmington equilibrium catalyst (Ecat) sample in the pilot plant. The results suggested that all of the candidate feeds would suppress conversion by at least 4 wt.% (Figure 6). Yields interpolated at constant coke are shown in Table I. All feeds showed the potential for increased LCO and bottoms. These feeds also yielded significantly less gasoline with slightly lower octane.
In addition to shifting yields toward less favorable products, the feeds also increased gasoline sulfur. Samples B and C increased sulfur by 200%, while Sample A more than tripled FCC gasoline sulfur relative to the Routine Feed (Figure 7).

The gasoline sulfur concentration for the Routine Feed produced in the pilot plant is significantly lower than what is sent to blending from the Wilmington FCC unit. A number of “tramp” gasoline streams generated at other process units are currently processed in the FCC gas plant. These streams elevate the apparent “FCC gasoline sulfur” as it is received in blending.

To help align the estimated FCC gasoline sulfur that would result from processing the candidate feeds with predicted commercial performance, the gasoline sulfur species produced in the pilot plant using the Routine Feed were compared to the commercially produced gasoline samples. The commercial gasoline samples were produced in the Valero, Wilmington FCC unit while processing two different feeds (Figure 8). There is good agreement for both individual sulfur species, and the relative amount of each species present when comparing the two sets of samples. Therefore, we can reasonably replicate the sulfur distribution of the commercially produced gasolines in the pilot plant. Cut gasoline sulfur is the sum of the species (mercaptans through C₄ thiophenes) and is higher for the commercially produced gasoline, suggesting the presence of additional sulfur from the “tramp” streams.

Another potential reason for differences between the pilot plant generated gasoline sulfur and that produced commercially is the method used to measure the sulfur concentration. Refiners typically measure gasoline sulfur by the bulk x-ray gasoline sulfur method. The measurement of gasoline sulfur pro-
duced in the pilot plant utilizes a gas chromatograph to identify the individual sulfur species and total sulfur concentration.

Sulfur species in the gasolines produced by the candidate feeds were compared to species present in gasoline generated by the Routine Feed. The candidate feeds all produced the same gasoline species as the gasoline generated from the Routine Feed except in higher concentrations (Figure 9).

Gasoline samples for each candidate feed in Figure 9 were normalized to account for the delta between FCC-produced and pilot plant-produced methods (from Figure 8). Additionally, data was normalized to an x-ray basis to reflect the levels of sulfur that would be observed on the FCC unit. Finally, gasoline sulfur for each candidate feed was adjusted to maintain the same gasoline sulfur to feed sulfur ratio observed on the Wilmington FCC unit resulting in the data in Figure 10.

The results from the pilot plant study, along with information on the Valero, Wilmington FCC unit operation (both routine and during a previous pretreater outage) were then used by Grace Davison to evaluate the performance of various gasoline sulfur reduction technology options. The GSR-5 additive, which contains base cracking functionality, was determined to be the best solution. Based on the normalized species in the gasoline produced by Samples A through C, Grace Davison estimated that the GSR-5 additive would reduce gasoline sulfur by 19-23%. This narrow range reflects extensive understanding of the customer’s operation and the up-front pilot plant work.

The Valero, Wilmington refinery pool gasoline sulfur limit is 30 ppm. The refinery also must produce gasoline below California NOx emissions limits, which are influenced heavily by the sulfur and olefins content of the
gasoline streams blended into the pool. The results of the pilot plant testing confirmed that the refinery would need to store Routine Feed to blend with candidate feeds during the pretreater outage to keep FCC feed sulfur levels low enough to remain below their limits. Based on the pilot plant results, Valero concluded that Feed A was too risky in both gasoline sulfur and FCC yields/selectivities. The decision was made to purchase the other feeds and blend them at various ratios with available Routine Feed during the outage.

**GSR-5 Additive Application**

As is common in many refineries, the FCC gas plant at Valero’s Wilmington facility processes streams from outside the FCC unit. These streams contain sulfur that is not affected by the GSR-5 additive since the additive works by participating in the cracking reactions that take place in the FCC unit. Unfortunately, the Wilmington refinery sampling configuration does not allow for direct sampling of the FCC gasoline prior to the inclusion of the “tramp” streams. The presence of these streams in the gasoline samples used to evaluate GSR-5 additive performance reduces the apparent performance by reducing the calculated percentage sulfur reduction.

Valero began use of GSR-5 additive two months prior to the 45-day feed hydrotreater outage. Coordinated efforts with Grace Davison allowed Valero to receive material and base-load their inventory in 14 days. A blend of the candidate feeds along with the Routine Feed was fed to the FCC prior to the outage, which increased feed sulfur by 20-35%. Additive additions proceeded smoothly and the projected performance was exceeded in less than 30 days with gasoline sulfur reduction of 20-25%. Figure 11 depicts a year’s worth of normalized gasoline data vs endpoint. The three periods represented are typical operation (Base Period), GSR-5 additive before and during the outage, and finally GSR-5 additive following the outage. Throughout the outage, Valero remained within their FCC gasoline sulfur limits while processing all candidate feeds. After the outage, continued addition of GSR-5 additive allowed them to run 10-15% higher feed sulfur.

**Economics**

The candidate feeds also increased the FCC gasoline olefins content, which combined with the increase in the projected gasoline sulfur would have forced Valero to hydrotreat approximately five MBPD of FCC gasoline to comply with California NOx emission specifications. The loss of octane from hydrotreating the FCC gasoline would have reduced the amount of low octane streams, such as Light Straight Run (LSR) and Heavy Cat Naphtha (HCN), that could be blended into the pool. The sulfur reduction provided by the GSR-5 additive allowed Valero to avoid hydrotreating the five MBPD FCC gasoline stream, the value of which was calculated to be $0.25/BBL or $1.7 million over the three month period surrounding the outage.

After the pretreater was back on-line, Valero evaluated the economics of continued GSR-5 additive usage. They determined that by continuing to use it, they could consistently feed high sulfur VGO to their FCC feed hydrotreater instead of medium sulfur VGO and remain...
under the refinery pool gasoline sulfur limit of 30 ppm. Valero estimates the incremental profit for processing high sulfur VGO is $4.4 million per year (using a conservative 3 cents per gallon differential between high and medium sulfur VGO). Accounting for the cost of the GSR-5 additive and incremental SOx additive required to remain in SOx emission compliance (higher FCC feed sulfur yields higher SOx emissions) the net profit is $3.8 million.

The Wilmington refinery targets a two-year cycle on the FCC feed hydrotreater. The cycle length is determined by the catalyst activity, which is influenced by operating severity and throughput. Valero determined that by using the GSR-5 additive to control FCC gasoline sulfur, they could reduce hydrotreater severity (even with higher sulfur VGO feed to the hydrotreater), which allowed them to process more VGO through the unit. Valero was able to increase hydrotreater throughput by 4%. The excess hydrotreated FCC feed is periodically sold at a premium over regular gasoil (using a seven cents per gallon differential between hydrotreated and regular gasoil) for an estimated annual profit of $4.5 million.

The total benefit from the GSR-5 additive for the Wilmington refinery is calculated to be $8.3 million per year - a return of over 18 times the incremental cost of the GSR additive technology.

The refinery has also determined that managing the tramp gasoline streams using a different process, rather than processing them in the FCC gas plant, will allow them to achieve significant flexibility in their gasoline pool blending operation. They plan to revamp an existing tower into an LSR splitter, which will remove C3’s and C4’s before sending gasoline material directly to blending. The operation of the FCC unit is expected to shift in favor of more light olefins with the new equipment in service. The impact of the change in FCC operation on FCC gasoline sulfur and olefins will be evaluated to determine if GSR-5 economics remain favorable with the new process configuration.

Conclusion

Proper management of hydrotreater outages is becoming increasingly important as more and more refiners rely on hydrotreating to meet gasoline sulfur limits. Outages of either FCC feed hydrotreaters or gasoline post-hydrotreaters create opportunities for refiners to incorporate Grace Davison’s sulfur reduction catalysts and additives into their planning. This would allow for significant savings in purchased feeds or mitigation of the cost of constraints caused by non-routine operation leading up to and during the outage. With hydrotreating equipment in service, these technologies can generate significant revenue for refineries who want to optimize operations to drive profitability. Reduction of FCC gasoline sulfur allows for higher feed sulfur to the FCC unit or to an upstream FCC feed hydrotreating unit without risking gasoline sulfur non-compliance. Lower FCC gasoline sulfur can also allow for reduced severity operation on either the FCC feed hydrotreater or the gasoline treating units, creating revenue in the form of octane recovery, higher throughput, or extended cycle life.

The Valero, Wilmington case study presented here was made possible by incorporating discussions between Valero and Grace Davison into the planning stages of the FCC feed hydrotreater outage. Based on those discussions, pilot plant testing was completed which assisted Valero in selecting the purchased feeds they would run during the outage. Estimates provided by Grace Davison showed that the GSR-5 additive would allow Valero to achieve their shutdown objective of keeping their gasoline sulfur in compliance while running the higher sulfur purchased feeds. The use of GSR-5 additive during the outage resulted in $1.7 million in savings.

With the proven product performance of the GSR-5 additive, Valero was then able to optimize their operation once the FCC feed hydrotreater was put back in service. The FCC feed hydrotreater unit severity was reduced, allowing for higher throughput, and the incremental hydrotreated gasoil was sold at a premium over regular gasoil. Additionally, Valero was also able to feed high sulfur VGO in place of medium sulfur VGO to the FCC feed hydrotreater without exceeding the FCC gasoline sulfur limits. Both operating changes resulted in a combined profit of over $8 million per year for the refinery.

While each refinery configuration is unique, and the economics presented here are specific to the Valero Wilmington refinery, this example demonstrates that Grace Davison’s gasoline sulfur reduction products can provide enhanced operating flexibility in any operation and significantly improve refinery profitability.

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Grace Davison Refining Technologies
7500 Grace Drive
Columbia, Maryland 21044 USA
+1.410.531.4000 • +1.410.531.8245 (fax)
www.e-catalysts.com