Cracking the Bottom of the Barrel with MIDAS® Technology
Break the bottom of your barrel with Grace Davison's MIDAS® FCC catalyst.

Grace Davison's revolutionary MIDAS®-300 catalyst is commercially proven to upgrade the bottom of your FCC barrel. Designed by Grace Davison specifically for today's diesel-driven market, MIDAS®-300 offers high activity matrix surface area, balanced with an optimized zeolite level.

MIDAS®-300 FCC catalyst is just the latest result of our 60+ year commitment to understanding bottoms cracking mechanisms and catalysts. Contact us for information on how Grace Davison can provide catalytic solutions to your bottoms cracking needs.
A message from the editor...

Dear Refiners:

As the demand for diesel fuel grows, many of you are faced with the challenge of re-optimizing your operations to maximize light cycle oil (LCO) yield. This issue of the Catalagram® is devoted to strategies for our customers to tap the bottom of the barrel and expand their LCO output and then process this feed for maximum ultra low sulfur diesel (ULSD) yield.

Grace Davison has recently commercialized a max LCO version of our industry-leading MIDAS® FCC catalyst technology. MIDAS®-300, together with the operating strategies presented here, will allow any refiner to ensure profitable maximum LCO operations while maintaining high C₃+ liquid yield and gasoline octane. For an additive approach, BX™-450 can help maximize distillate yield.

Hydroprocessing LCO from the FCCU, as well as synthetic crudes and other pre-processed streams, can present problems that impact unit performance. As discussed in the article “Maximizing ULSD Unit Performance when Processing LCO and other Previously Processed Feeds”, ADVANCED REFINING TECHNOLOGIES can work closely with refining technical staff to help plan for processing these opportunity feeds.

If you want more information on the best catalysts and strategies for bottom-of-the-barrel upgrading, contact your Grace Davison technical sales representative or me at joanne.deady@grace.com.

Joanne Deady
Vice President
Marketing/R&D
Grace Davison Refining Technologies


Anyone who works in the FCC business has been touched by Jim’s work at some point. Shortly after joining Grace Davison, he formed the first Technical Service Team in the industry. A half-century later, refiners worldwide rely on Grace Davison’s Technical Service to optimize their operations. Jim was also instrumental in starting the Catalogram in 1959, as well as the Equilibrium Catalyst Analysis Program in the late 1950’s at Grace Davison. In the early 1970’s, Jim also co-wrote and edited the first “Grace Davison Guide to Fluid Catalytic Cracking” (known as the “Silver Bullet”) that served as the basis for our widely-used, three-part Guide of the same name.

He received his B.S.Ch.E. from Purdue University and worked for Atlantic Refining in Philadelphia, PA. He served in the U.S. Army during the Korean War. Following his military service, Jim worked for Standard Oil of New Jersey’s Esso Refinery in Baltimore, MD until he joined Grace Davison. Jim co-authored numerous technical articles and papers during his years here.

His wife, Terry, passed away in 1999. Jim and Terry are survived by their son, Matt, who works at Grace Davison’s Columbia, MD headquarters in FCC R&D; daughter, Barbara Regan, and sons, Jim and Paul.

Jim hired and mentored some of the best talent in the FCC business during his time here. He continued to encourage and inspire us until his passing. He and his wife, Terry, were well-loved and well-respected members of our Grace Davison FCC "Family."
Maximizing FCC Light Cycle Oil Operating Strategies: Introducing MIDA$^{\text{®}}$-300 Catalyst for Increased LCO Selectivity
By David Hunt, Rosann Schiller, and Matthew Chang, Grace Davison Refining Technologies
Maximizing LCO yield is largely a slurry management process. Refiners can reduce FCC operating severity, optimize fractionator conditions, and/or change feedstocks in an effort to increase LCO yields. Grace Davison’s experienced technical service engineers can assist with these unit-specific optimizations. LCO volume yield could be further increased with Grace Davison’s new MIDA$^{\text{®}}$-300 catalysts. Our new technology is also available in a specially formulated additive. BX$^{\text{TM}}$-450, the industry’s first LCO maximization additive.

Maximizing ULSD Unit Performance when Processing LCO and other Previously Processed Feeds
By Brian Watkins, Advanced Refining Technologies
ULSD has evolved from simply meeting the diesel sulfur specification to a constant awareness of unit performance in order to process difficult streams such as FCC light cycle oil (LCO) and other thermally cracked stocks; synthetic crudes; and various other pre-processed feed sources. It is important to understand the impacts of processing new feed streams, and this paper highlights a few examples demonstrating significant differences in feed reactivity, which are not necessarily anticipated from the usual bulk feed analyses.

Grace Davison Issues New Shipping Guidelines for Hydrocarbon Samples
By Larry Langan, Grace Davison Refining Technologies
This article provides an overview of the shipping guidelines recommended by Grace Davison for materials being sent to U.S. locations for analysis and testing from customers and potential customers.

Answers to Questions from the 2008 NPRA Q&A Session-FCC Section
By Kristen Wagner, Grace Davison Refining Technologies

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rev.1/09
Grace Davison Refining Technologies announces new MIDAS® catalyst technology designed to tap the value at the bottom of the barrel and maximize unit profitability with higher LCO yield. MIDAS®-300 FCC catalyst is the latest result of Grace Davison’s 60+ year commitment to defining bottoms cracking mechanisms and catalysis. MIDAS®-300, together with the operating strategies presented here, will allow any refiner to ensure profitable maximum LCO operations while maintaining high C₃+ liquid yield and gasoline octane.

Adoption of clean fuel standards in the United States shifted economic conditions such that the value of ultra low sulfur diesel (ULSD) is equivalent to or exceeds the value of gasoline. Demand shifts have meant new objectives for FCC units, shifting production away from gasoline and towards LCO (light cycle oil). Designed to produce high volumes of gasoline, many FCC units are now being re-optimized to boost yields of LCO to meet the increased distillate demand.

Since 2002, the growth in distillate demand has been more than double that of gasoline (Figure 1). This trend is not occurring only in the United States and developed regions, but also in developing regions such as South America, the former Soviet Union, Middle East...
and Asia Pacific (Figure 2). Future demand of distillate relative to gasoline in North America is expected to increase, as shown in Figure 3, largely due to the Energy Independence and Security Act of 2007. New Corporate Average Fuel Economy (CAFE) standards require auto manufacturers to boost fuel mileage to 35 mpg by 2020. This applies to all passenger automobiles, including light trucks. To meet this challenging fuel mileage standard, more efficient vehicles powered by hybrid and diesel engines are expected. The Energy Independence and Security Act also requires the total amount of biofuels added to gasoline to increase to 36 billion gallons by 2022, up from 4.7 billion gallons in 2007.

**Technical Challenges**

The primary challenge in the FCC unit is increasing LCO, yet minimizing any incremental slurry yield. Figure 4 shows how LCO and slurry yield change with conversion. LCO, like gasoline, is an intermediate product increasing with conversion at very low conversion levels, eventually reaching an over-cracking point. Past the over-cracking point, LCO yield declines with increasing conversion. This high conversion regime represents the traditional FCC unit-operating window.

The optimal LCO yield may not be at the maximum LCO point due to increased amounts of slurry at lower conversion. As a result, maximizing LCO yield is largely a slurry management process.

Refiners tend to focus on the following strategies to maximize LCO production:

1. **Operating Conditions**
   - LCO and gasoline cut point shifts
   - Reactor and feedstock temperatures and equilibrium activity optimization

2. **Recycle Streams**
   - Heavy Cycle Oil (HCO) or slurry
3. Feedstock
   - Removal of diesel range material from the FCC feedstock
   - Feed hydrotreater severity optimization
   - Residual feedstock optimization

4. Catalyst Optimization
   - Increasing bottoms conversion
   - Maintaining C\textsubscript{3+} liquid yield and gasoline octane

In the following sections we discuss these commonly employed operating strategies to increase FCC LCO yield and unit profitability.

**Operating Conditions**

Gasoline end point reduction is the most common operating strategy for increased LCO production. Approximately 10% of the gasoline can be moved to LCO by reducing the gasoline cut point from 430°F to 350°F TBP, limited often by a minimum main fractionator top temperature and maximum LCO flash point. The LCO cut point should be increased within the maximum main fractionator bottoms temperature and diesel hydrotreater constraints. Many refiners operate with LCO endpoints near 700°F.

Figures 5, 6 and 7 shows the effect of reactor temperature, feedstock temperature and equilibrium catalyst (Ecat) activity on the yield of LCO and slurry yield. (These data were generated using a commercial FCC model). Operating at lower conversion (by re-optimizing these operating conditions) can increase LCO. Figures 5-7, like Figure 4, confirm that the true challenge of maximum LCO operations is minimizing incremental slurry yield.

Air blower and wet gas compressor demand is reduced at lower reactor temperature or higher feed temperatures. As a result, the refinery may choose to increase feed rate or introduce a recycle stream to push the unit back to an operating constraint during maximum LCO operations.
Recycle

Operating with a recycle stream of 700+ °F material can increase LCO yield without producing incremental slurry yield during lower conversion operations. HCO in the 700-850°F range is preferred over slurry (700°F+) due to its lower Conradson carbon and higher saturate content. Table I shows pilot plant data where HCO was cracked neat over Ecat. The HCO feed had an API gravity of 10°, carbon level of 0.1 wt.%, and an endpoint of 790°F. At a reactor temperature of 970°F and an Ecat microactivity (MAT) of 72%, conversion was only 37 wt.%, yet resulted in 33 wt.% LCO and 19 wt.% gasoline. The coke yield is quite high for such a low conversion.

Table II shows commercial data for one cat cracker that operated in both gasoline and LCO maximization modes. With recycle and lower Ecat activity, LCO increased ~14 vol%. Note that dry gas and coke yields also rose with increased recycle. Lower air blower and wet gas compressor demand by operating at lower reactor temperature and higher feedstock temperature, however, may allow the refinery to operate with a recycle stream.

Ideally, recycle should be introduced to the riser in dedicated injectors above the fresh feed injectors. This practice increases the riser mix zone temperature for a given riser outlet temperature. Higher mixed temperature of the feedstock and catalyst at the base of riser in order to ensure good feedstock vaporization at low riser temperatures in order to minimize slurry yield. Using dedicated injectors for recycle, instead of processing the recycle through the primary fresh feed injectors, also eliminates any damage of the fresh feed injectors due to catalyst particles present in slurry recycle.

Table I
HCO Cracking Riser Pilot Plant Data

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>Dry gas</td>
<td>3.0</td>
</tr>
<tr>
<td>LPG</td>
<td>8.0</td>
</tr>
<tr>
<td>Gasoline</td>
<td>19.0</td>
</tr>
<tr>
<td>LCO (430-660°F)</td>
<td>33.0</td>
</tr>
<tr>
<td>Slurry</td>
<td>30.0</td>
</tr>
<tr>
<td>Coke</td>
<td>7.0</td>
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Table II
Effect of Recycle and Lower Ecat Activity on LCO Production

<table>
<thead>
<tr>
<th></th>
<th>Gasoline Mode</th>
<th>Diesel Mode</th>
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</thead>
<tbody>
<tr>
<td>Combined Feed Ratio</td>
<td>1.07</td>
<td>1.25</td>
</tr>
<tr>
<td>Yields, wt.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Gas</td>
<td>3.4</td>
<td>4.0</td>
</tr>
<tr>
<td>LPG</td>
<td>15.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Gasoline (C_{5}-420°F)</td>
<td>43.7</td>
<td>32.1</td>
</tr>
<tr>
<td>LCO (420 to 700°F)</td>
<td>22.9 (≈21.3 vol.%)</td>
<td>36.8 (≈35.6 vol.%)</td>
</tr>
<tr>
<td>Slurry (700°F+)</td>
<td>8.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Coke</td>
<td>6.1</td>
<td>6.7</td>
</tr>
<tr>
<td>Conversion (420°F)</td>
<td>69.8</td>
<td>55.9</td>
</tr>
<tr>
<td>Riser Temperature, °F</td>
<td>950</td>
<td>950</td>
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<tr>
<td>Feed Concarbon, wt.%</td>
<td>3.75</td>
<td>3.75</td>
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<tr>
<td>ECAT Activity</td>
<td>Base</td>
<td>Base-4</td>
</tr>
</tbody>
</table>
Feedstock composition has a very significant effect on LCO yield and quality. In general, the LCO yield and quality decline with improved feedstock quality.

Feedstock with increased amounts of di- and tri-aromatic cores will increase the yield of LCO. Aromatic cores are inert to catalytic cracking and once the alky groups and naphthenic rings are cracked from the cores, the di- and tri-aromatic cores will remain in heavy cat naphtha and LCO boiling ranges (total cycle oil).

Table III shows two FCC feedstocks (A and B) with similar API gravity and hydrogen content. Feedstock B, however, has higher content of di- and tri-aromatic cores but similar levels of tetra+-aromatics.

Table IV shows the product yields when feedstocks A and B were cracked over a standard Ecat in a bench scale MAT reactor. Both catalysts produced similar coke and slurry. However, LCO yield was higher for feedstock B. The increase in LCO was nearly proportional to the higher amount di- and tri-aromatic cores in feedstock B.

Refiners who hydrotreat FCC feedstock may consider re-optimizing polynuclear aromatic (PNA) saturation levels to increase LCO yield. Figure 8 shows the effect of feedstock PNA saturation on LCO and slurry yields at constant coke yield. An ACE unit was used to generate this data by cracking three FCC feedstocks produced over a range of hydrotreating severities. Lower hydrotreating severity will increase the amount of di- and tri-aromatics in the FCC feedstock and consequently raise the LCO yield. Tetra+-aromatics also increase at lower severity, which can lead to additional slurry yield.

Figure 8 also illustrates how an optimized catalyst system can be used.
to crack incremental slurry to LCO. Hydrotreated feeds contain higher levels of naphthenoaromatics than typical gasolines. The proper design of matrix activity is a crucial factor in optimizing the catalyst feed interaction. In this example LCO is increased by ~4 wt.% through a combination of lower VGO hydrotreating severity and an FCC catalyst reformulation.

**C₃+ Liquid Yield and Gasoline Octane**

We have focused primarily on the means to increase LCO yield while mitigating the incremental slurry yield that is associated with severity changes. Maintaining liquid yield and gasoline octane during maximum LCO operation is equally critical to ensure overall profitability. Grace Davison’s OlefinsMax® additive can be used to achieve the desired octane levels at lower reactor temperature. OlefinsMax® additive is currently the most widely used ZSM-5 additive technology in the refining industry, enabling refiners to substantially increase yields of valuable light olefins, as well as the octane value of the FCC naphtha.

Operating at reduced conversion to maximum LCO will reduce the volume expansion of the FCC due to the higher density of LCO relative to gasoline and LPG. Table V shows three yield cases. Case 1 represents a traditional catalyst reformulation for reduced activity that increases LCO yield at the base reactor temperature. Case 2 is an operation with Grace Davison’s MIDAS®-300, our maximum LCO catalyst and OlefinsMax® additive.

Despite a two volume percent increase of LCO in Case 1 and less slurry, the product value is neutral compared to the base operation due to lower C₃+ total liquid yield. The MIDAS®-300 operation in Case 2 shows an increase product value of $1.50/bbl over the base due to enhanced bottoms cracking, higher LCO yield, similar C₃+ liquid yield, and higher gasoline octane. In this case, OlefinsMax® additive was added until a wet gas compressor constraint was reached, increasing C₃+ liquid yield over the Case 1 operation. Recent 2008 Gulf Coast economics, with a 40¢/gallon incremental value of LCO over gasoline, were used.

**Table V**

Maximize Product Value with MIDAS®-300

<table>
<thead>
<tr>
<th>Case</th>
<th>Base</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Base</td>
<td>Traditional LCO Catalyst</td>
<td>MIDAS®-300 with OlefinsMax®</td>
</tr>
<tr>
<td>Reactor Temperature, °F</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Yield, vol.% FF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>74.6</td>
<td>72.8</td>
<td>72.8</td>
</tr>
<tr>
<td>LPG</td>
<td>33.4</td>
<td>31.9</td>
<td>34.4</td>
</tr>
<tr>
<td>Gasoline</td>
<td>51.5</td>
<td>50.7</td>
<td>48.8</td>
</tr>
<tr>
<td>LCO</td>
<td>20.1</td>
<td>22.0</td>
<td>22.9</td>
</tr>
<tr>
<td>Slurry</td>
<td>5.3</td>
<td>5.2</td>
<td>4.3</td>
</tr>
<tr>
<td>C₃+</td>
<td>110.3</td>
<td>109.8</td>
<td>110.4</td>
</tr>
<tr>
<td>RON</td>
<td>91.0</td>
<td>91.2</td>
<td>93.2</td>
</tr>
<tr>
<td>MON</td>
<td>80.0</td>
<td>80.1</td>
<td>81.1</td>
</tr>
<tr>
<td>Incremental $/bbl</td>
<td>Base</td>
<td>$0.00</td>
<td>$1.50</td>
</tr>
</tbody>
</table>

The different types of reactions involved in cracking the bottom of the barrel require different catalyst functionalities. Overall, a balanced approach is required to achieve maximum bottoms upgrading. The goal is to convert the bottoms to higher value products and not coke. Premium Grace Davison MIDAS® catalysts have been proven to reduce slurry yield without a coke or gas penalty and we have recently commercialized MIDAS®-300 catalyst specifically designed for today’s distillate driven market.

MIDAS®-300 catalyst is the result of Grace’s long commitment to defining bottoms cracking mechanisms and catalysis. This research project produced the MIDAS®-100 series of catalysts in 2005. In 2007, Grace Davison introduced the MIDAS®-200 series for increased activity. Today, we are pleased to announce the development of MIDAS®-300 series, designed to maximize LCO selectivity and bottoms cracking.

MIDAS®-300 catalysts offer high activity matrix surface area, balanced with an optimized zeolite level. This new formulation maximizes LCO selectivity via the three-step bottoms cracking mechanism (Figure 9). The majority of matrix porosity in MIDAS®-300 catalysts is found in the crucial 100-600 Å pore diameter range, ensuring selective cracking of heavy ends.

As previously discussed, a common means to shift selectivity to gasoline+distillate rather than gasoline+LPG is to lower operating severity. Reduced reactor temperature achieves the desired increase in LCO by reducing conversion, but it comes with a price – reduced cracking temperature also reduces feed vaporization, allowing unvaporized liquid hydrocarbons to bypass the riser and condense as coke in the reactor vessel.
Feed vaporization must be maintained when operating at reduced cracking severity. At low operating severity, optimization of Type I cracking becomes more critical due to the reduction in mix zone temperature. Catalyst design plays an important role in maintaining the right conditions. Since resid feeds contain a high percentage of molecules boiling above mix zone temperature, pre-cracking is necessary to achieve complete vaporization. Porosity in the 100-600Å range is essential for the pre-cracking reactions that facilitate vaporization. MIDAS®-300 catalysts have the highest porosity in this critical range of any cracking catalyst, ensuring that feed is properly vaporized even at low severity.

Most of the LPG and gasoline produced in an FCC comes from dealkylation of aromatics or Type II cracking. Zeolite is much more effective than matrix in cracking long chain alkyl aromatics. Type II cracking is important to reduce the molecular size and promote eventual conversion of bottoms; however, we must prevent any LCO that is produced from being over-converted to lighter components. The zeolite level in MIDAS®-300 has been optimized to provide sufficient dealkylation activity yet maintain the product yield as distillate rather than LPG and gasoline.

Finally, Type III cracking destroys naphthene rings in naphthenoaromatic compounds. The size of typical naphthenoaromatic molecules is too large to easily fit into the zeolite. The cracking of these molecules will occur on the matrix sites or on the external surface of the zeolite. The selective cracking of this type of molecule requires the proper design of matrix activity and the interaction of matrix and zeolite. The high mesoporosity of MIDAS®-300 catalysts improves LCO selectivity by converting coke precursors into valuable liquid product.

The increased matrix activity and porosity of MIDAS®-300 catalysts enhances LCO selectivity and bottoms cracking relative to MIDAS®-100 (Table VI) while maintaining equivalent activity, light ends, gasoline and coke, increasing unit profitability by $0.31/bbl.

**Flexibility**

Grace Davison can also deliver enhanced LCO selectivity in an additive form. BX™-450 additive is Grace's newest catalytic additive offering and is the first of its kind designed specifically for maximum distillate yield. BX™-450 additive is based on MIDAS®-300 catalyst technology and offers high activity matrix surface area balanced with an optimized zeolite level to quickly maximize LCO selectivity as refining economics swing between distillate and gasoline. As described earlier, proper zeolite to matrix ratio is critical to selectively destroy bottoms and minimize coke precursors. However, to maximize LCO with an additive, the amount and type of zeolite is critical; too much zeolite and any LCO that is produced can be over-converted to lower value products. The optimized zeolite level in BX™-450 additive provides sufficient catalytic activity, enabling 1:1 replacement of fresh catalyst.

**Commercial Performance**

Typically we recommend addition rates of BX™-450 additive up to 20% of overall fresh catalyst usage. However, improved selectivity has been reported with as little as 10% in inventory.

Selective conversion of bottoms to LCO at constant gasoline, LPG, and coke has been demonstrated with BX™-450 additive [Figure 10]. At constant conditions, 1.5 lv.% of slurry was shifted to LCO. BX™-450 additive, by converting coke precursors into liquid product, actually decreased regenerator temperature and Ecat coke factor. Using recent spot economics, the addition of 10% BX™-450 additive improves profitability by $1.14/bbl. Further increases in yield can be attained through a detailed unit severity optimization.

**Conclusions**

Maximizing LCO yield is largely a slurry management process. Refiners can reduce FCC operating severity, optimize fractionator conditions, and/or change feedstocks in a effort to increase LCO yields. Grace Davison's experienced technical service engineers can assist with these unit-specific optimizations.

LCO volume yield could be further increased with Grace Davison's new MIDAS®-300 catalysts. MIDAS®-300
Catalysts allow refiners to maximize LCO production via enhanced matrix activity and porosity that optimize the three-step bottoms cracking mechanism. MIDAS®-300 catalyst technology selectively shifts slurry into LCO without a coke or gas penalty. Our new technology is also available in a specially formulated additive. BX™-450, the industry’s first LCO maximization additive, delivers flexibility as refining economics swing between gasoline and distillate. Contact your Grace Davison sales representative today to learn how MIDAS®-300 can enhance your refinery’s profitability.

References

1. D. Bhattacharyya et al., Indian Oil Corporation LTD, Middle Distillate Maximization in FCC Unit – 6º Encuentro Sudamericano de Craqueo Catalítico

Table VI
Maximum LCO Product Value

<table>
<thead>
<tr>
<th></th>
<th>MIDAS®-100</th>
<th>MIDAS®-300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat/Oil</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>C₄’s &amp; lighter</td>
<td>18.1</td>
<td>18.1</td>
</tr>
<tr>
<td>Gasoline</td>
<td>53.6</td>
<td>53.6</td>
</tr>
<tr>
<td>LCO</td>
<td>20.5</td>
<td>21.0</td>
</tr>
<tr>
<td>Bottoms</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Coke</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Incremental Profit</td>
<td>----</td>
<td>$0.31/bbl</td>
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Figure 10
BX™-450 Selectivity Shifts Slurry into LCO
Maximizing ULSD Unit Performance when Processing LCO and Other Previously Processed Feeds

With demands for increased production of ultra-low sulfur diesel (ULSD) and the rise in crude prices, unit operation and performance have become significantly more challenging. This has prompted refiners to look for ways to maximize their diesel pool by using opportunity feedstocks. However, use of these feedstocks may lead to other problems which impact unit performance. ULSD has evolved from simply meeting the diesel sulfur specification to a constant awareness of unit performance in order to process difficult streams such as FCC light cycle oil (LCO) and other cracked stocks; synthetic crudes; and various other pre-processed feed sources. It is important to understand the impact of processing new feed streams, and this paper highlights a few examples demonstrating significant differences in feed reactivity, which are not necessarily anticipated from the usual bulk feed analyses.

Background

It has been documented for some time that desulfurization of dibenzothiophene and substituted dibenzothiophenes occurs through two reaction pathways: the direct sulfur abstraction route and the hydrogenation abstraction route. The former involves adsorption of the molecule on the catalyst surface via the sulfur atom followed by C-S bond scission. This path is favored when using cobalt-molybdenum (CoMo) based hydrotreating catalysts. The second pathway involves saturation of one aromatic ring of the diben-
zothiophene species followed by the extraction of the sulfur atom. Nickel-molybdenum (NiMo) catalysts have a higher selectivity for desulfurization via this route.

It is both expedient and efficient to model ULSD kinetic schemes by grouping the various sulfur species into “easy sulfur” and “hard sulfur” categories. The so-called easy sulfur is made up of compounds which are readily desulfurized via direct abstraction and boil below about 680°F, while hard sulfur is made up of compounds which are more readily removed via hydrogenation followed by abstraction. These compounds include 4,6 dimethyl-dibenzothiophene and other di- and tri-substituted dibenzothiophenes. The relative amounts of easy and hard sulfur in a feed are critical properties to consider since the concentration of each can vary significantly from feed to feed depending on crude source, boiling range and the prior thermal or catalytic treatment of the feedstock. Further details can be found in the 2007 ERTC paper by ART entitled “SmART Strategies for Maximizing ULSD Unit Performance: Tuning Hydrogen Utilization for Flexibility with Cracked Stocks.”

The use of thermal or catalytic treatment of feedstocks that will be sent to a ULSD unit can have varying effects depending on the severity of the pre-treatment. LCO and coker diesels have long been common elements combined with a straight run (SR) feed source to produce ULSD products. LCO generated from an FCC can vary depending on the severity of the pre-treatment of the FCC feed. However, the common element is the increase in polynuclear aromatic compounds relative to other feeds. The amount of LCO blended into the diesel hydrotreater has a much greater effect on catalyst performance when producing ULSD than when operating under prior, less restrictive, low-sulfur regulations. Use of diesel range products from ebulliating bed resid or fixed bed resid desulfurizers can also have a significant impact on catalyst activity if not clearly identified as to their origin. The general properties of diesel streams from these units often indicate that they may be fairly easy to hydrotreat due to their unusually low sulfur content. Table I lists the general properties for examples of each of the base feeds used in pilot testing at ART.

Note that Ebulliating Bed Diesel represents a diesel fraction from the product of an LC-FINER or H-Oil Unit, and Fixed Bed Diesel is the diesel fraction coming from a Fixed Bed Resid Unit.

The diesel product from an Ebullating Bed Resid (EB) Unit and the Fixed Bed Resid (FB) Unit provide very different sulfur distribution patterns compared to the other feeds in Figure 1. It is clear that

<table>
<thead>
<tr>
<th>Type</th>
<th>SR</th>
<th>LCO</th>
<th>Ebullating Diesel</th>
<th>Fixed Bed Diesel</th>
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</thead>
<tbody>
<tr>
<td>°API</td>
<td>37.72</td>
<td>15.31</td>
<td>32.24</td>
<td>30.9</td>
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<td>Sulfur, wt.%</td>
<td>1.096</td>
<td>1.041</td>
<td>0.143</td>
<td>0.344</td>
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<tr>
<td>Nitrogen, ppm</td>
<td>46</td>
<td>837</td>
<td>940</td>
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<td>Aromatics, lv.%</td>
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<td>68.81</td>
<td>40.38</td>
<td>38.54</td>
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<tr>
<td>Mono-, lv.%</td>
<td>14.43</td>
<td>18.44</td>
<td>32.05</td>
<td>27.28</td>
</tr>
<tr>
<td>Poly-, lv.%</td>
<td>7.88</td>
<td>50.37</td>
<td>8.34</td>
<td>11.26</td>
</tr>
</tbody>
</table>

**Table I**

Base Feed Properties

<table>
<thead>
<tr>
<th>Dist., D86, °F</th>
<th>IBP</th>
<th>10%</th>
<th>50%</th>
<th>70%</th>
<th>90%</th>
<th>FBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO</td>
<td>404</td>
<td>470</td>
<td>532</td>
<td>558</td>
<td>612</td>
<td>678</td>
</tr>
<tr>
<td>Fixed Bed Resid</td>
<td>387</td>
<td>462</td>
<td>542</td>
<td>598</td>
<td>660</td>
<td>712</td>
</tr>
<tr>
<td>SR</td>
<td>366</td>
<td>440</td>
<td>524</td>
<td>552</td>
<td>591</td>
<td>637</td>
</tr>
<tr>
<td>489</td>
<td>538</td>
<td>589</td>
<td>614</td>
<td>649</td>
<td>704</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1

Sulfur Distribution in the Four Distillate Feedstocks

![Sulfur Distribution in the Four Distillate Feedstocks](image-url)
although the total sulfur is much lower for the two resid diesel materials, a majority of the sulfur species that are present are all the so-called hard sulfur species.

To help explain how the HDS activity changes with product sulfur for these feeds, pilot work was completed using 100% SR diesel as the base feed. The individual components were blended into the base feed to show the individual, as well as some cumulative effects on catalyst performance. Two different concentrations (15% and 30% by volume) of LCO were used. The blends containing LCO produced a five to seven number decrease in API, as well as decreases in total sulfur of 2500 to 2700 ppm, respectively. Feed nitrogen content, however, increases by 150 to 250 ppm, and the total aromatic content in each of the blends increases 10 to 18 volume percent. The resid diesel streams were blended into the SR at a 25% by volume concentration. This gave a similar 1.5 to 2 number decrease in API for each of the FB and EB diesel streams, with a significant increase in total nitrogen of 120 to 220 ppm, respectively. Feed aromatic content showed a three to four number increase in mono-aromatics.

At low severity hydrotreating (higher product sulfur), there is little difference between the straight run and the blended resid diesel streams. Figure 2 is a plot of the EB and FB diesel blends at different levels of sulfur removal. The impact of adding EB diesel is little more than 4°F higher temperature relative to the SR, while the FB diesel required just over 10°F for low sulfur products. As the product sulfur is decreased the required temperatures start to diverge: 17°F higher temperature is required for the EB diesel blend feed at 200 ppm sulfur and 22°F for the FB diesel. Clearly, there is a different temperature response for each feed which is most likely an indication that although the total sulfur is lower, the additional nitrogen from the EB unit is hindering the catalytic ability to saturate the more difficult sulfur compounds required to produce ULSD. The FB diesel feed also has an impact, due to the fact that it contains additional refractory sulfur which is harder to remove.

As product sulfur continues to trend toward ULSD, the difference increases to over 35°F. A comparison of the feedstock inspections shown in Table I shows that the two feeds are quite similar with no obvious explanation for a 30°F increase in required temperature relative to the base feed to achieve ULSD sulfur levels. This underscores the importance of the source (or history) of a feedstock, and how significant this can be on unit performance.

Figure 3 summarizes data using the 15% and 30% LCO feeds. The impact of even a small amount of LCO is again readily apparent.
Initially about 20°F higher temperature is required compared to the SR feed for 15% LCO, and 40°F higher temperature is required at the 30% LCO level as compared to the base feed at 500 ppm product sulfur. Although not obvious from the chart, there are also small differences in the temperature response between the SR and LCO containing feeds. Using 15% LCO there is a 20°F loss in HDS activity at 500 ppm sulfur which increases to 50°F at 200 ppm sulfur and to over 90°F for ULSD. With a 30% LCO blend, the activity differences are much greater: 37 °F at 500 ppm sulfur increasing to 70°F at 200 ppm sulfur and over 115°F for ULSD. As mentioned above, this is an indication that as LCO is added to the feed, the concentration of refractory, sterically hindered sulfur compounds increases making it more difficult to desulfurize. The presence of more refractory compounds decreases the temperature response relative to the base SR feed. That means that a much larger temperature increase is required for the LCO feed to achieve the same sulfur removal as the base feed.

The effects of combining the various diesel sources are not necessarily a cumulative effect on catalyst performance. The effect of adding 15% LCO into a feedstock that already contains 25% FB diesel has only an additional 10°F impact compared to the 20°F increase in required temperature discussed above. The use of 30% LCO blended into the 25% FB feed has an impact of 28°F increase in required temperature which is almost 10°F lower than 30% LCO by itself. This impact can be seen through the entire range of operation as shown in Figure 4.

One possible option to gain back some of the lost activity is to change the end point of the feed to be used. ART was able to conduct duplicate pilot plant testing on this same LCO, but with a 30°F end point reduction to simulate how this can affect catalyst performance. Table II lists the major component analysis between the two LCO feed sources. The decrease in endpoint lowers the total sulfur by almost 1000 ppm, where total nitrogen decreases by 129 ppm.

The impact this reduction has on ULSD performance is over 30°F in restored catalyst activity which corresponds to additional life in the hydrotreater. A comparison of the two LCO feeds blended at 30% into the SR base feed is shown in Figure 5.

<table>
<thead>
<tr>
<th>Type</th>
<th>LCO (Low FBP)</th>
<th>LCO (High FBP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>°API</td>
<td>18.31</td>
<td>15.31</td>
</tr>
<tr>
<td>Sulfur, wt.%</td>
<td>0.948</td>
<td>1.041</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>708</td>
<td>837</td>
</tr>
<tr>
<td>Aromatics, lv.%</td>
<td>66.86</td>
<td>68.81</td>
</tr>
<tr>
<td>Mono-, lv.%</td>
<td>22.65</td>
<td>18.44</td>
</tr>
<tr>
<td>Poly-, lv.%</td>
<td>44.21</td>
<td>50.37</td>
</tr>
<tr>
<td>Dist., D86, °F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>380</td>
<td>387</td>
</tr>
<tr>
<td>10%</td>
<td>450</td>
<td>462</td>
</tr>
<tr>
<td>50%</td>
<td>522</td>
<td>542</td>
</tr>
<tr>
<td>70%</td>
<td>579</td>
<td>598</td>
</tr>
<tr>
<td>90%</td>
<td>638</td>
<td>660</td>
</tr>
<tr>
<td>FBP</td>
<td>682</td>
<td>712</td>
</tr>
</tbody>
</table>
The addition of LCO has a major impact on activity for both the low and high endpoint materials. The required temperature increase for ULSD in going from 0 to 30% LCO for the lower endpoint material is about 1.2°F per percent LCO. Processing the higher endpoint LCO increases the required temperature to about 1.4°F per percent LCO. Notice from the chart that the activity effects are not exactly linear with increasing LCO content. The first 15% LCO has a larger impact on activity than the next 15%. Figure 6 demonstrates this more clearly in the form of a plot of activity lost as a function of LCO content. It clearly shows much higher activity losses for the first few percent LCO as compared to the last few percent added to the feed.

ADVANCED REFINING TECHNOLOGIES can work closely with refining technical staff to help plan for processing opportunity feeds such as those discussed above. One of the keys is being aware of the potential impact processing certain feeds will have on unit performance. Feeds which have been previously processed present unique challenges and ART is well positioned to provide assistance on how best to maximize unit performance and take advantage of these oppor-
Grace Davison Issues New Shipping Guidelines for Hydrocarbon Samples

Introduction

Grace Davison’s Columbia, MD, USA facility handles about 4000 oil samples per year from customers. Many of them arrive without incident; however, we are seeing an increase in the number of samples that are packaged improperly. The photographs accompanying this article give some examples of improperly packaged samples.

Acceptable Sample Sizes

Grace Davison’s Columbia, MD facility will accept for testing flammable and other liquids such as gas oil, feed, petroleum distillates, LCO, diesel fuel, naphtha, gasoline, motor spirits, petrol, slurry oil, scrubber water etc. with proper labels, documentation and in suitable shipping containers consistent with the IATA manual and CFR49 DOT regulations.

For these type of materials Grace Davison prefers 4 oz. packages for evaluation in our Oils Lab and for microactivity testing. If more extensive testing is requested, then an 8 oz. package will be acceptable. These quantities are more than adequate to perform any necessary
testing to be performed, while also eliminating the need to dispose of large quantities of unused sample. Use of smaller samples should also decrease shipment costs for our customers.

The customer must use packaging that meets CFR49 DOT regulations and include a leak containment barrier. Loose sample container lids, paint cans sent improperly without lid locks, glass bottles of scrubbing water of scrubber water that freeze in the winter and boxes dripping with oil in the delivery truck are examples of why leak containment is required.

For other testing and use, the sample size required may be larger or smaller. The amount to be sent to Grace Davison should be discussed in advance with the Grace Davison personnel who will receive the material. Samples larger than needed increase costs to both Grace Davison, who must dispose of the material, and to the shipper, who must pay for shipment costs. Grace Davison personnel can also be contacted to provide assistance in determining the appropriate type of container or package to maintain sample quality; however, the shipper must be aware that compliance with all applicable shipping regulations is the responsibility of the shipper.

Packaging, Paperwork and Labeling

All samples shipped to Columbia, MD must include on the shipping papers the correct chemical identification information. This permits Grace Davison personnel to properly follow any applicable chemical handling requirements.

All samples must be appropriately labeled with hazard, composition and other identification information. A relevant MSDS shipped with the samples or reference to an MSDS already on file, is also required.
It is critical that samples are shipped with proper packaging and protection as the Columbia site shipping and receiving department may reject samples that leak during transport and have them returned to the shipper. Samples that leak are also often comprised and therefore cannot be analyzed and will be immediately disposed of.

**Shipments from Overseas**

Grace Davison personnel should be informed in advance of any shipments of materials coming to Columbia, MD from overseas so that proper TSCA import certification documentation can be prepared. Failure to provide such information will slow the passage of the material through customs and can often result in the sample being refused entry into the U.S. A TSCA certification is required for import of any chemical into the U.S. It is also important to note that only U.S. citizens can authorize TSCA certifications. Most problems occur when the customer does not specify the shipping sample name with an accepted shipping regulation name. They may use something such as “Unit 5 feed” instead of a regulation name such as “Gas Oil”.

**Summary**

Compliance with all applicable shipping regulations is the responsibility of the shipper. Adoption of these shipping guidelines will ensure sample integrity and result in accurate analyses. Most important, proper packaging guarantees the safety of everyone who touches the sample.
Introducing PINNACLE®-XLC: An FCC Catalyst for Even Lower Delta Coke

Grace Davison has introduced PINNACLE®-XLC to the Asia Pacific Market. PINNACLE®-XLC is an alumina-sol catalyst formulated with a novel zeolite technology, Grace Davison’s nickel resistant matrix, TRM-400, and the commercially-proven integral vanadium trap, IVT-4, that is utilized in the IMPACT® catalyst series.

The alumina-sol technology platform provides excellent physical properties and catalyst retention. The proprietary zeolite modifications utilized in PINNACLE®-XLC deliver enhanced stability and activity compared to previous resid processing benchmarks and shifts light ends into gasoline. Incorporation of Grace Davison’s integral vanadium trap further enhances stability and activity retention, while Grace Davison’s nickel resistant matrix, TRM-400, provides superior coke and gas selectivity in the presence of high levels of contaminant nickel.

The overall result is an extremely stable, coke-selective catalyst offering maximum gasoline selectivity at constant coke yield in high contaminant metals operations.

Based on our lab testing and commercial experience, we have found that the use of PINNACLE®-XLC shows, even at high metals level, excellent activity retention (Figure 1) and better coke selectivity (Figure 2) compared to resid benchmark catalysts.
CATALYST

33. How much gasoline sulfur reduction can be achieved with the use of additives? Have you seen sulfur reduction in the LCO fraction? How well do these additives perform? Where does the sulfur end up?

a. Grace Davison gasoline sulfur reduction applications provide 20%-35% gasoline sulfur reduction commercially. Current customers have been applying this technology for an average of 2.5 years, including one refiner who has been benefiting from Davison gasoline sulfur reduction for over seven years now. Neptune™ catalyst, our most recent step-out GSR® technology, has commercially lowered gasoline sulfur by 45%.

b. In some applications, sulfur reduction has been seen in the LCO cut, but only for lower boiling point LCO fractions. Grace Davison GSR® products are designed to reduce sulfur species from the gasoline boiling range. If the IBP of the LCO is low, there may be gasoline sulfur species in the LCO stream, and therefore sulfur reduction will occur.

c. The sulfur that is removed from the FCC gasoline boiling range is converted to H₂S in the reactor. This equates to an increase of approximately 1%-2% overall H₂S generation from the FCCU.

PROCESS TECHNOLOGY

37. What are the typical sulfur contents of FCC products for various FCC feed types and sulfur levels?

Sulfur content of FCC products is derived from the sulfur present in the FCC feed. Gasoline sulfur typically contains 2%-10% of the FCC feed sulfur, but there are additional variables that can affect the level of sulfur in the gasoline. Those variables include the selectivity of the feed to crack into gasoline range sulfur species, the FCCU operating conditions, FCC catalyst properties, and the gasoline cut point in the main fractionator. One FCC feed type can result in different gasoline sulfur levels in different FCC operations.

Additionally, two different feeds with the same sulfur content can yield different gasoline sulfur levels in the same FCC unit, due to differences in the sulfur selectivities of the feeds.

In Grace Davison GSR® product applications, FCC feed sulfur levels have varied from 0.15% to 2.40% feed sulfur, while gasoline sulfur reduction levels remain consistent at 20%-35% sulfur reduction. Based on a range of data and experience, Grace Davison has not found a direct correlation between FCC feed sulfur content and gasoline sulfur content or gasoline sulfur reduction levels.

Grace Davison GSR® catalysts and additives are successfully used in several different FCC unit operations, in conjunction with a variety of FCC catalyst types and FCC feed types, to provide 20%-45% gasoline sulfur reduction.

GSR®-5 Reduces Gasoline Sulfur by More Than 40% in India

In two recent applications of Grace Davison’s gasoline sulfur reduction additive, GSR®-5, in India, gasoline sulfur was reduced by more than 40% without affecting activity and conversion.

GSR®-5 additive can be used with any base FCC catalyst. Typically, GSR®-5 additive is used in place of 25% of catalyst additions. There have been more than 85 worldwide applications of Grace Davison’s gasoline sulfur reduction catalysts and additives since the technology was first introduced to the market in 1996.
Grace Davison Refining Technologies is pleased to welcome Ann Benoit, Matt Chang, and Mike Federspiel to our Technical Sales and Marketing Team.

**Ann Benoit**, Technical Service Representative headquartered out of our Houston office. A B.S.Ch.E. graduate of Tennessee Technological University, Ann joins us from Citgo’s Lake Charles, LA refinery, where she served as a process engineer, economic analyst, and logistic manager.

**Matt Chang**, who recently completed the Grace Marketing Leadership Program, is Marketing Manager, Light Olefins. He received his B.S. in Chemical Engineering and a B.A. in Economics from Rutgers University, as well as an MBA in Marketing and Finance from Georgetown University. Previously, Matt held production, quality and R&D engineering positions at JM Manufacturing and PlastPro.

**Mike Federspiel**, Technical Sales Manager, joins us from Hovensa, where he was Assistant Area Manager, FCC Engineer. Prior to that, he was Chief Technical Advisor, Development Engineer at UOP. Mike holds a B.S.Ch.E. from the University of Wisconsin and is based in the Chicago area.

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**Olsen to Serve on Q&A Panel**

Advanced Refining Technologies (ART) is pleased to announce that Dr. Charles W. Olsen, Worldwide Technical Services Manager, has been selected to 2008 National Petrochemical and Refiners’ Association Question and Answer panel. Chuck, who has over 15 years of experience in hydroprocessing, has held a variety of technical service, research and technical management positions in Chevron and Grace Davison before joining ART. Olsen holds a B.S.Ch.E degree from the University of Minnesota, and M.S. and Ph.D. degrees in chemical engineering from the University of Illinois in Champaign-Urbana.

The 2008 NPRA Q&A session will be held October 5-8 at the Omni Champions Gate Resort in Orlando, Florida. For more information, go to www.npra.org/meetings.
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