Hydroprocessing/FCC Synergy
Dear Refiner:

Recently, you have been demanding to know more about the synergy between the fluid catalytic cracking process and hydroprocessing. With the formation of ART in 2001 and our long-standing premier position in the FCC business, Grace Davison and ART have lead the industry in these critical areas.

In light of clean fuels and ultra low sulfur diesel requirements, you have expressed particular interest in the dynamics between cat feed hydrotreating and fluid catalytic cracking. Chuck Olsen, ART's Worldwide Manager of Technical Service, has co-authored our lead article titled, "Balancing the Need for FCC Product HDS and Opportunities for Improving FCC Performance," which highlights the RT/ART efforts. Chuck was joined by Joanne Deady, George Yaluris and Natalie Petti in preparing the paper, which will be presented at the NPRA Annual Meeting in San Antonio in March 2007.

With our extensive experience in refining, Grace Davison and ART's Technical Team are ready to assist you with optimizing your hydroprocessing and FCC units to get the best yields possible. Please contact your technical team or go to our website www.e-catalysts.com for more information. We are dedicated to meeting your challenges.

Regards,

Robert H. Bullard
Vice-President and General Manager, Grace Davison
Managing Director, Advanced Refining Technologies
IN THIS ISSUE

Balancing the Need for FCC Product HDS and Opportunities for Improving FCC Performance
Chuck Olsen, Worldwide Technical Services Manager, Advanced Refining Technologies
Joanne Deady, Vice President Marketing and R&D, Grace Davison, Columbia, MD
George Yaluris, Marketing Manager, Grace Davison, Columbia, MD
Natalie Petti, Consultant
Clean fuels regulatory demands have brought a focus on the importance of optimized FCC feed pretreating in efforts to facilitate compliance. The proper selection of FCC Pretreater catalyst and severity integrated with the selection of the appropriate FCC catalyst design and operating conditions offer a refiner the opportunity for an optimized refining operation.

Catalytic FCC Gasoline Sulfur Reduction
Citgo’s Corpus Christi refinery reduces FCC gasoline sulfur by up to 31% using Grace Davison’s GSR®-5 additive
Lauren Blanchard, Strategic Business Marketing Manager, Advanced Refining Technologies, Columbia, MD
Michael Ziebarth, Research Manager, Grace Davison, Columbia, MD
Timothy Dougan, Marketing Manager, Grace Davison, Columbia, MD
Low gasoline sulfur is key to operating successfully in today’s environment. In order to define an effective sulfur reduction strategy a good understanding of the sulfur species present in the gasoline streams is essential. Grace Davison Catalysts and Additives are designed to remove specific compounds present at different boiling ranges in the gasoline. A Citgo Refinery successfully used an additive and reached gasoline sulfur reduction of 44% with undercutting (31% without undercutting).

Clean Fuels: An Opportunity for Profitability Using Gasoline Sulfur Reduction Technology
Lauren Blanchard, Strategic Business Marketing Manager, Advanced Refining Technologies, Columbia, MD
Craig Borchert, Valero Energy, Wilmington, CA
Min Pu, Valero Energy, Wilmington, CA
FCC Gasoline Sulfur is an important operating parameter for a refinery operation in efforts to meet strict regulations. Outages of processes upstream and downstream of the FCC can impact continued compliance with these regulations. Grace Davison and Valero Wilmington worked closely together to develop a successful strategy involving feed and catalyst selection to stay within gasoline sulfur compliance during an FCC Feed Pretreater Outage.

Understanding and Minimizing FCC Slurry Exchanger Fouling
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Bill Minyard, National Technical Sales Manager, Grace Davison, Houston, TX
Jeff Koebel, Technical Service Manager, Grace Davison, Chicago, IL
Slurry Exchanger fouling can impact FCC operation by causing reduced feedrate, loss conversion and increased maintenance costs. A good understanding of the fouling mechanisms involved is important. The selection of appropriate operating conditions and FCC catalyst selection can reduce the incidents of exchanger fouling and improve unit profitability.

The information presented herein is derived from our testing and experience. It is offered, free of charge, for your consideration, investigation and verification. Since operating conditions vary significantly, and since they are not under our control, we disclaim any and all warranties on the results which might be obtained from the use of our products. You should make no assumption that all safety or environmental protection measures are indicated or that other measures may not be required.
Introduction

The benefits of hydrotreating FCC feed on product yields and sulfur content were recognized some time ago and described in earlier publications. Recently, regulatory demands and the drive towards clean fuels have renewed interest in FCC feed hydrotreating to facilitate compliance and satisfy the need for improved yields. To address these needs, Advanced Refining Technologies (ART) introduced the ApART Catalyst System™ for FCC pretreatment in 2001. This technology was developed to provide increases in HDS conversion while at the same time providing significant upgrading of FCC feeds. In essence, an ApART Catalyst System is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each are optimized to meet individual refiner goals and constraints. The ApART technology has been described in detail previously. ART has continued to
develop a better understanding of the reactions and kinetics involved in FCC pretreating, and, through our partnering with Grace Davison Refining Technologies, a detailed understanding of the effects of hydrotreating on FCC unit performance. The complexity of combinations of catalyst design and operating conditions for both the FCC feed hydrotreater and the FCC unit presents a significant optimization opportunity for refiners to drive the combined operation to maximum product value.

FCC Pretreating

There are numerous reactions that occur during hydrotreating of heavy gas oils making it a challenging process to model. A partial list of reactions includes sulfur and nitrogen removal, aromatics saturation, carbon (MCR) removal, and contaminant metals removal. The progression of several of these reactions as a function of the hydrotreater temperature is shown in Figure 1. Each reactant in the figure shows a unique response to temperature which indicates that different reaction kinetics are involved for each species. A wide range of conversion levels is achieved, with some reactants at 50% conversion and others at 90%+ conversion. As shown in Figure 1, the conversion of polynuclear aromatics (PNA’s) passes through a maximum as temperature increases, and begins to decrease as temperature increases beyond that point. The conversion of total aromatics follows a similar profile with increasing temperature.

The data in Figure 2 examines the conversion of aromatics in more detail. This figure shows how the aromatics’ conversion varies with temperature and LHSV when hydrotreating a coker gas oil feed blend. The existence of a maximum in conversion is readily apparent. At higher temperatures the conversion begins to decrease, and this is due to thermodynamic equilibrium constraints. The temperature where the conversion becomes thermodynamically limited is a strong function of feedstock, hydrogen partial pressure and LHSV. As indicated in Figure 2, the temperature of maximum conversion increases as LHSV increases and, not surprisingly, the overall conversion level decreases. A similar trend is observed for the PNA conversion although in that case the conversion levels are higher compared to total aromatics conversion. It is important to note that the aromatics conversion trends observed with increasing LHSV are similar to what is observed as the hydrotreating catalyst ages. The temperature for the maximum in PNA conversion (and aromatics) gradually increases as the catalyst ages from start of run (SOR) to end of run (EOR).

It is generally accepted that removing PNA’s and nitrogen from the FCC feed will improve FCC performance. As an example, Figure 3 summarizes FCC pilot plant data for several hydrotreated FCC feeds. The left y-axis represents the FCC conversion and the right axis represents the FCC feed quality, shown as a ratio of either product nitrogen content to feed nitrogen content or product PNA content to feed PNA content. Clearly, the PNA and nitrogen content of the FCC feed have a strong effect on FCC performance. At the highest pretreater severity the FCC conversion actually decreases
by about 1 wt.% relative to the previous severity in the chart. The decrease in FCC conversion coincides with an increase in PNA content from 0.48 to 0.55. Notice also that the conversion decreases despite the fact that the FCC feed nitrogen content is at the lowest level suggesting the PNA feed content has the larger impact on FCC conversion.

It has been previously shown\(^6\) that the type of hydrotreating catalyst or catalyst system used in the pretreater is critical for FCC unit performance. However, it is not enough to simply have the right FCC pretreat catalyst as there is also an operating window for the pretreater which maximizes the performance of the FCC. ART and Grace Davison Refining Technologies have recently collaborated on a study examining the synergy between the FCC pretreater and the FCC unit. The scope of the study covered the effects of catalyst type (both pretreater and FCC catalysts) as well as pretreater operating severity. A typical FCC feed sample was hydrotreated in the pilot plant with both NiMo and CoMo hydrotreating catalysts across a range of operating severity levels, and the hydrotreated product samples were then catalytically cracked in the FCC pilot plant. A variety of FCC catalyst types were tested to evaluate the combined effects of hydrotreating catalyst type, pretreater operating severity, and FCC catalyst design on FCC yields.

I. FCC Pretreating Pilot Plant Results

A VGO/coker gas oil blend was used as the feedstock for the FCC pretreater in this case study. The properties for the feedstock, along with the pilot plant test conditions are summarized in Table I. The hydrotreating catalyst systems included a NiMo catalyst (ART AT575) and a CoMo catalyst (ART AT775). Both catalysts have had extensive use in FCC feed pretreat applications around the world. Several hydrotreating severities were investigated that cover the typical range encountered in FCC pretreating, and both catalysts were tested across the same range of severities. The resulting hydrotreated products were then used as FCC feed in subsequent FCC pilot plant testing.

Figure 4 shows how the product sulfur from the pretreater changes with temperature for both catalysts. At the lowest severity, the CoMo catalyst removes more sulfur than the NiMo catalyst, as expected. At the higher severities the NiMo catalyst slightly outperforms the CoMo catalyst with this feed and these operating conditions. The product sulfur content spans the range from 1000 ppm down to around 50 ppm.

<table>
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<tr>
<th>Operating Conditions</th>
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<tr>
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<td>H(_2) Pressure, Psi</td>
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<td>Feedstock</td>
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<td>Total Aromatics, wt.%</td>
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<td>PNA, wt.%</td>
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<tr>
<td>Distillation, °F (ASTM D-1160)</td>
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<td>95</td>
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Figure 5 shows how the product nitrogen varies with temperature for both catalysts and, as expected, the NiMo catalyst significantly outperforms the CoMo catalyst throughout the temperature range investigated. The product nitrogen covers the range from about 600 ppm down to <100 ppm. The wide range in nitrogen content suggests that clear differences might be expected in the subsequent FCC pilot plant testing.

Figure 6 shows how the PNA conversion varies for both catalysts. Again the NiMo catalyst significantly outperforms the CoMo catalyst for saturation of PNA's. The range of hydrotreater severity was chosen to cover the range where PNA conversion is thermodynamically limited, and thus, PNA conversion for both catalysts is seen to decrease at the higher temperatures in the study. The PNA conversion for the NiMo catalyst varied from around 77% to 86% compared to the CoMo catalyst range of only 70% to 78%. Again, these ranges suggest substantial differences in FCC feed quality which should result in differences in FCC performance.

Figure 7 shows the HDS and PNA data for the NiMo catalyst on one chart. It is useful to view the data in this way when discussing FCC pretreater operating modes. The maximum PNA conversion is about 86%, and at that temperature the product sulfur (i.e. FCC feed sulfur) is about 200 ppm. This represents the FCC feed quality for a pretreater running in maximum PNA saturation mode. Another common way to operate the FCC pretreater is constant HDS mode. Assuming the target sulfur is 0.1 wt.%, the sulfur target is met at significantly lower temperature than required for the maximum PNA saturation mode. At that temperature the corresponding PNA conversion is nearly 10 wt.% lower than that obtained in PNA saturation mode.
Given the lower nitrogen and PNA contents achieved from operating in PNA mode it is expected that the FCC feed will result in significantly higher FCC conversion and higher gasoline yield compared to running in HDS mode. This improvement, however, does come with some additional operating costs for the pretreater. The PNA mode of operation will result in higher hydrogen consumption and a shorter run length compared to the HDS mode of operation.

The pretreater pilot plant data was used to calibrate the ART FCC pretreatment model for the feed whose properties are summarized in Table I. The model was then used to predict the hydrogen consumption and FCC pretreater cycle length for both the HDS and PNA modes of operation shown in Figure 7. The results are listed in Table II.

Figure 8 shows the results of modeling the differences in FCC pretreater temperature profiles for the two operating strategies. In HDS mode, the reactor temperature is increased to maintain a constant product sulfur, 0.10 wt.% in this example. The end of run (EOR) is typically determined by a maximum outlet temperature, which is reached in about 36 months in this case. In PNA mode, the reactor temperature is ramped up to the conditions resulting in maximum PNA conversion. The temperature is then adjusted to maintain constant PNA conversion. PNA saturation activity deactivates at a slower rate relative to HDS activity, so the rate of temperature increase in PNA mode is much slower than for the HDS mode.

The EOR for the PNA mode of operation is determined by the required sulfur level in the FCC feed. Figure 9 shows how the sulfur conversion changes throughout the cycle for each mode of operation. In HDS mode the conversion remains constant throughout the
run. In PNA mode the sulfur conversion at SOR is much higher than required due to the higher SOR temperature, and because HDS activity deactivates at a higher rate than PNA saturation activity, the HDS conversion decreases as the cycle progresses. The EOR is reached when HDS conversion has decreased to the target sulfur level, 24 months in this case.

Figure 10 shows how the PNA conversion changes through the cycle for both modes of operation. In PNA mode the conversion stays nearly constant until close to EOR when equilibrium constraints start to limit conversion. In HDS mode, the PNA conversion starts out relatively low, and increases as the cycle progresses. The PNA conversion reaches a maximum and then begins to decrease through the last part of the cycle due to equilibrium limits. In this mode of operation the maximum PNA conversion (i.e. maximum FCC feed upgrade) is only achieved for a small fraction of the total cycle.

As Figure 11 shows, the nitrogen conversion decreases from SOR to EOR for either operating mode. Under these operating conditions HDN activity deactivates at a higher rate than HDS activity or PNA saturation activity, so HDN conversion is much lower at EOR compared to SOR. For the HDS operating mode HDN activity decreases from around 72% to 45% from SOR to EOR, while for the PNA mode the HDN conversion declines from 87% to about 57% from SOR to EOR.

These data clearly show that there are significant differences in FCC feed quality as the cycle moves from SOR to EOR in either mode of operation, and this indicates that FCC performance will change as the cycle progresses regardless of the operating strategy. To investigate this further, the ART model was used to simulate the FCC feed properties as the pretreater cycle progressed from
SOR to EOR for both modes of pretreater operation. The FCC feed properties were then used to estimate FCC conversion, the results of which are shown in Figure 12. Operating the pretreater in PNA mode provides significantly higher FCC conversion for most of the cycle, but again it comes at the cost of shorter pretreater run length and increased hydrogen consumption. These costs need to be weighed against the benefits in FCC performance to determine the best operating strategy.

There is the potential to extend the cycle length of the pretreater when operating in PNA mode through the use of sulfur reduction technologies in the FCC unit. FCC gasoline sulfur can be reduced by 20%-35% commercially\textsuperscript{7,8,9} which would enable the pretreater to run to a higher sulfur level. Figure 13 shows the impact of using a sulfur reduction product in the FCC unit that delivers 20% reduction in FCC gasoline sulfur (such as D-PriSM\textsuperscript{®} or GSR\textsuperscript{®}-5 additives, or SuRCA\textsuperscript{®} catalyst) while operating the pretreater in PNA mode. The pretreater product sulfur is allowed to increase in months 24 through 28 while the FCC gasoline sulfur remains constant because the sulfur reduction product is used to control FCC gasoline sulfur during those months.

The results of estimating the FCC conversion for the FCC sulfur reduction case are shown in Figure 14. This chart demonstrates that the use of a sulfur reduction product in the FCC can extend the pretreater cycle length in PNA mode while at the same time maintain the benefits of increased FCC conversion.

Figures 9 through 14 show how changes in pretreater operating mode can influence FCC feed sulfur, nitrogen and PNA content which directly effects FCC unit conversion. As the pretreater progresses from SOR to EOR in either mode of operation, the FCC feed properties
change, again directly influencing FCC unit conversion. The next section will show how the FCC catalyst formulation can potentially be used to offset pretreater product property shifts, as well as to optimize the joint operation of the pretreater and FCC units for maximum profitability.

II. FCC Unit Pilot Plant Results

The next phase of the study involved taking the hydrotreated products and using them as FCC feed in an FCC pilot plant. The FCC feeds were cracked over three different FCC equilibrium catalyst types. The pilot unit was run at a constant reactor temperature of 990 °F, and each of the FCC e-cat samples was tested at three catalyst-to-oil ratios (4, 6, and 8) in the pilot unit.

The yields resulting from FCC equilibrium catalyst Type 1 will be discussed first. The properties of the Type 1 Ecat are shown in Table III.

Type 1 catalyst is high rare earth, high zeolite to matrix (Z/M) ratio, and high equilibrium unit cell size (UCS) designed for maximum gasoline selectivity. Ecat metals levels are moderate, and the catalyst has a relatively high Ecat activity (MAT). The yields for the FCC feeds from the NiMo catalyst in HDS and PNA modes with Type 1 Ecat are shown in Figure 15, and are presented at constant coke yield (2.0 wt.%).

The trends indicate that the PNA mode of pretreater operation results in higher overall conversion (the maximum value on the y-axis). Selectivity of gasoline and LPG also increase, while dry gas yield is essentially unchanged. The lower PNA and nitrogen contents of the FCC feed generated by the PNA mode of operation result in higher FCC conversion, and production of more valuable products.

### Table III

<table>
<thead>
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<th>Property</th>
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<tbody>
<tr>
<td>MAT (wt.%)</td>
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<tr>
<td>Total Surface Area (m2/g)</td>
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<td>Zeolite Surface Area (m2/g)</td>
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<td>Matrix Surface Area (m2/g)</td>
<td>32</td>
</tr>
<tr>
<td>Nickel (ppm)</td>
<td>183</td>
</tr>
<tr>
<td>Vanadium (ppm)</td>
<td>1527</td>
</tr>
<tr>
<td>Unit Cell Size (Å)</td>
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<tr>
<td>Rare Earth (wt.%)</td>
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<tr>
<td>Alumina (wt.%)</td>
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</table>

### Figure 15

FCC Yields for NiMo Treated Feed Reacted over Type 1 Ecat

### Figure 16

C₃ & C₄ Olefinicity of FCC Products from NiMo Treated Feed Reacted over Type 1 Ecat
Figure 16 shows that olefinicity of both C3’s and C4’s is lower in PNA mode than HDS mode, which supports previously observed trends for hydrotreated feeds. Hydrotreated FCC feeds are more hydrogen rich, and the resulting products are therefore more hydrogen rich.

Comparing the performance of the FCC feed produced by the CoMo catalyst, shown in Figure 17, shows lower overall conversion and lower selectivities for gasoline, C3’s and C4’s than the NiMo produced feed. Again, operating the hydrotreater in PNA mode (i.e. higher severity) instead of HDS mode results in higher conversion and selectivities for gasoline and LPG. This is due to the increased HDN and PNA removal at higher temperature. Both NiMo and CoMo will remove more nitrogen and PNA’s from the FCC feed at the elevated temperatures of the PNA mode, although the NiMo catalyst removes significantly more compared to the CoMo catalyst. This results in significantly higher FCC conversion (1.4 wt.% in either mode) for the NiMo than the CoMo catalyst.

Similar trends showing reduced C3 and C4 olefinicity for the hydrotreater in PNA operating mode are observed for CoMo produced FCC feed (Figure 18). Overall the C3 and C4 olefins produced by FCC feed from the two hydrotreating catalyst types are essentially equal.

Applying typical Gulf Coast economics to the FCC yields allows a comparison of the value associated with each pretreater catalyst type and each operating mode. In the following figures, the NiMo produced FCC feed in HDS mode is used as the base case assuming a 50,000 BPD FCC unit. Figure 19 shows the observed trends in FCC product value for Type 1 Ecat.

The NiMo catalyst produces FCC feed that results in $0.19 to $0.23/BBL higher total product...
value than the CoMo catalyst. In addition, the PNA operating mode yields $0.37 to $0.41/BBL higher product value than HDS mode. Note that this excludes any value associated with lower sulfur FCC products which result from the lower sulfur content of feeds treated in PNA operation. However, these product value benefits of operating in PNA mode must be considered against the higher hydrogen consumption cost and the associated costs of the reduction in the hydrotreater run length resulting from higher severity operation, as discussed previously.

Even after adjusting these product values to account for increased hydrogen consumption, the NiMo produced FCC feed in PNA mode still yields higher product values. Accounting for the higher hydrogen consumption cost for NiMo relative to CoMo, the delta FCC product value for NiMo catalyst is $0.14/BBL higher than the CoMo product value in PNA mode (Figure 20), and $0.16 to $0.39/BBL higher than either catalyst in HDS mode.

To determine the point at which the incremental conversion from increasing pretreater severity diminishes from reduced PNA conversion and/or unfavorable hydrotreater operating costs for the feed in Table I, additional modeling was conducted using the pilot plant results. Starting with an FCC feed produced by a pretreater with NiMo catalyst, assuming a 50,000 BPD pretreater with a catalyst change out cost of $7 MM and a four-year FCC unit shutdown cycle, running in higher severity mode would cause additional pretreater outage and hydrogen consumption costs. As shown in Figure 21, higher FCC product value can be obtained by running the hydrotreater at higher severity. The HDS operating mode and Type 1 Ecat represents the base operation. Increasing the severity of the hydrotreater operation toward optimum PNA mode results in higher operating costs for the hydrotreater, which are more than justified by the

<table>
<thead>
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<th>Table IV</th>
<th>Equilibrium Catalyst Properties - Type 2</th>
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<tbody>
<tr>
<td>MAT (wt.%)</td>
<td>73</td>
</tr>
<tr>
<td>Total Surface Area (m²/g)</td>
<td>175</td>
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<td>Zeolite Surface Area (m²/g)</td>
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<td>Rare Earth (wt.%)</td>
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<td>Alumina (wt.%)</td>
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</table>
higher FCC product value. At the optimum PNA point, $0.10/BBL higher profit would be realized after accounting for the higher cost of running the hydrotreater in that mode. Beyond the optimum PNA point, however, the incremental FCC product value begins to level off, and eventually begins to decline due to the higher PNA levels in the feed (as was observed in Figure 3). The increasing cost of higher severity operation of the hydrotreater is not justified as it more than offsets the FCC product value realized.

FCC catalyst can also be designed to further enhance yield advantages of hydrotreating catalyst type or hydrotreater mode/severity of operation. As an example, the resulting yields for FCC feed produced by NiMo catalyst in HDS and PNA operating modes over FCC equilibrium catalyst Type 2 were investigated. The properties of the Type 2 Ecata are shown in Table IV.

Type 2 catalyst has moderate rare earth, with a lower zeolite to matrix (Z/M) ratio and lower unit cell size than Type 1 catalyst. Shifts in Z/M and UCS will result in a yield slate with more olefins and octane than Type 1. For some hydrotreated feeds, Type 2 catalyst will yield higher overall conversion (see Figure 22), as the matrix contribution from the catalyst will crack more of the heavier feed molecules.

Comparing Figure 22 to Figure 15, switching to Type 2 FCC catalyst boosts conversion by 1.9 wt.% in HDS mode and 2.7 wt.% in PNA mode. Compared to Type 1 catalyst in HDS mode, the higher conversion for Type 2 results in $0.66/BBL higher product value, and that increases to $0.89/BBL higher product value in PNA mode (Figure 23).

Figure 24 shows the product value increase along with the costs associated with the higher severity pretreater operation with Type 2 catalyst. In this case, there
appears to be a smaller window of pretreater operation where the gain in product value exceeds the increasing operating costs. The point at which the cost of higher severity operation for the pretreater overwhelms the incremental FCC product value is closer to the base HDS operating mode, so the refiner running Type 2 FCC catalyst could make up to $0.12/BBL more profit at the optimum PNA point, but the operating window is much narrower than it was for Type 1 catalyst. Obviously the economics of each combination of FCC catalyst, pretreater catalyst, and hydrotreater severity are unique to each refinery.

For the last comparison case, the resulting yields for an FCC feed produced by NiMo hydrotreating catalyst in HDS and PNA operating modes over FCC equilibrium catalyst Type 3 are presented. The properties of the Type 3 Ecat are shown in Table V.

Type 3 catalyst properties look similar to Type 1, but Type 3 has a higher Z/M ratio. Type 3 also has slightly higher rare earth levels and a UCS that favor gasoline selectivity. The metals levels are appreciably lower than Type 1 and the MAT activity is higher. For the feed produced by the NiMo catalyst in PNA or HDS mode, Type 3 catalyst yields significantly higher conversion than Type 1 (2.7 wt.% on average over yields presented in Figure 18), and slightly higher conversion than Type 2 (0.4 wt.% on average over yields presented in Figure 22). However, as Figure 26 shows, the delta product values for Type 2 catalyst are higher due to the higher olefins yield for this type of catalyst.

Modeling Type 3 catalyst yields and selectivities for increasing severity of pretreater operation shows that Type 3 will increase in delta product value and then level off across the range of severity analyzed (Figure 26). The benefits of increased severity level off sooner for Type 2 than Type 3 catalyst, and then Type

| MAT (wt.%) | 78 |
| Total Surface Area (m2/g) | 164 |
| Zeolite Surface Area (m2/g) | 134 |
| Matrix Surface Area (m2/g) | 30 |
| Nickel (ppm) | 110 |
| Vanadium (ppm) | 235 |
| Unit Cell Size (Å) | 24.32 |
| Rare Earth (wt.%) | 3.88 |
| Alumina (wt.%) | 43.2 |

Table V
Equilibrium Catalyst Properties - Type 3

Figure 25
FCC Yields for NiMo Pretreater Feed Reacted over Type 3 Ecat

Figure 26
Delta Economics for FCC Products from NiMo Pretreater Feed Reacted over Type 1, Type 2 and Type 3 Ecat
2 catalyst product value actually declines with the further increase in severity while Type 3 catalyst product value levels off. The higher matrix surface area of Type 2 catalyst creates diminishing returns on FCC conversion as the pretreater severity increases (simulating the pretreating catalyst progressing toward EOR). This is because the declining pretreater product quality at end of run causes higher FCC coke yield and Type 3 catalyst designed with the higher Z/M ratio will be more coke selective with this feed trend.

Figure 26 indicates that there are significant opportunities to adjust FCC catalyst formulations as pretreater cycles move from start of run to end of run, however, the data presented are specific to the feed in Table I, the FCC catalyst types tested, and the range of severities tested. Each refinery operation requires individual analysis of candidate catalysts and operating conditions of both FCC feed pretreater and FCC units to determine the optimum combination which maximizes profitability.

Conclusion

FCC feed pretreating offers the potential to significantly improve refinery economics. Both the hydrotreating catalyst system and the operating strategy for the pretreater are critical to providing the highest quality feed for the FCC. In general, NiMo based catalysts produce better FCC feed, with both lower nitrogen and PNA content. The operating mode of the hydrotreater can be used to further improve the FCC feed. Driving the hydrotreater to remove nitrogen and PNA’s improves FCC product value, but this needs to be balanced against the increased costs of higher hydrogen consumption and shorter cycle length that result from this mode of operation.

The shorter run lengths from operating in PNA mode can be extended with the use of a sulfur reduction catalyst or additive in the downstream FCC unit. FCC gasoline sulfur reduction of 20% or higher from a product such as D-PriSM® or GSR®-5 additives, or SuRCA® catalyst would enable the pretreater to run beyond the point when product sulfur levels exceed target levels, while FCC gasoline product sulfur remains within the limits needed for gasoline pool sulfur compliance. Extending operation in PNA mode closes the gap in run length versus a hydrotreater in the HDS mode of operation, while continuing to provide FCC feed of higher quality than HDS mode.

FCC catalyst formulation can also be included as one of the variables that can be adjusted to maximize profitability. With constant hydrotreater product properties, FCC catalyst formulation can provide up to $0.90/BBL higher product value. Pushing hydrotreater severity to an optimum with constant FCC catalyst can yield in excess of $0.10/BBL net product value, which includes the cost of higher severity operation of the hydrotreater. Finally, adjusting FCC catalyst formulation as the hydrotreater moves from start of run to end of run can significantly offset decline in product quality, and preserve product value.

All of the combinations presented show the need for refiners to follow an integrated approach to managing the catalysts and operation of the FCC pretreater and FCC units. FCC and hydroprocessing operation can be continuously optimized throughout the course of the hydrotreater run, to significantly increase refiner revenue.

References

Increasingly stringent gasoline sulfur regulations such as the 30 ppm sulfur limit imposed on most U.S. refiners in 2006 present yet another challenge to the refining industry. Refiners not only have to comply with the new specifications but they need to determine the most economical method to reduce gasoline sulfur while preserving as much operating flexibility as possible. The fluid catalytic cracking (FCC) unit is a significant contributor to the gasoline pool and one of largest sources of gasoline sulfur. Therefore, reducing FCC gasoline sulfur is a key component of a refiner’s overall compliance strategy. While pre-treating the feed or post-treating the FCC gasoline are popular approaches, the use of catalysts and additives for sulfur reduction can provide increased flexibility and improved profitability.

Grace Davison first commercialized gasoline sulfur reduction catalysts and additives in 1996 and has been successful in introducing new products to the market. These products have been used in 85 commercial applications and have demonstrated the ability to reduce FCC gasoline sulfur by up to 46%. When combined with under-cutting, gasoline sulfur reduction approaches 60%. Refiners have found numerous ways to incorporate these products into their short-term and long-term strategies to:

- Improve profitability
- Extend feed hydrotreater run-life
- Manage FCC feed hydrotreater outages
- Process higher sulfur opportunity feeds
- Increase FCC feed hydrotreater throughput
- Minimize under-cutting
- Comply with pipeline specifications
- Minimize octane loss from post treatment
- Reduce hydrotreater hydrogen consumption

Grace Davison’s, SuRCA® catalyst, which is designed to replace conventional FCC catalyst, has been Grace Davison’s most successful gasoline sulfur reduction product. SuRCA catalyst has been used in over 45 applications worldwide. In addition to reducing...
gasoline sulfur, it has, in some instances, reduced LCO sulfur by 10-15%. Grace Davison also offers GSR-5® gasoline sulfur reduction additive, which is based on similar technology embodied in SuRCA catalyst. This product provides comparable performance with the increased flexibility and the convenience of an additive. Typically, GSR-5 additive is used in place of 25% of catalyst additions. Grace Davison has had seven commercial applications of GSR-5. Citgo Petroleum Corporation’s Corpus Christi, TX refinery successfully used the additive for over a year and was able to reduce gasoline sulfur by up to 31%. Results from this application are summarized in this paper.

The Origin of FCC Gasoline Sulfur

The proper application of existing products, as well as the development of new technologies, requires an understanding of gasoline sulfur formation pathways, the species that are formed and the effect of FCC feed sulfur speciation on the resulting gasoline sulfur. Sulfur compounds in FCC feed include mercaptans, sulfides, alkyl substituted thiophenes, thiophenols, benzothiophenes and multi-ring aromatic thiophenes. The amount and relative quantity of each of these species is dependent on a wide range of factors. These factors include feed source, type of feed pretreatment (hydro-treating, etc.), and whether or not other refinery streams such as coker gas oil have been blended into the FCC feed.

In the FCC unit, typically 35-45% of the feed sulfur is converted into H₂S, 45-55% ends up in the light cycle oil (LCO) and bottoms and 5% in the coke. Only about 5% ends up in the gasoline. Gasoline sulfur species can be determined using a Gas Chromatograph (GC) equipped with an Atomic Emission Detector (AED). The typical sulfur compounds found in FCC gasoline are presented in Figure 27 as a function of their boiling point. The gasoline range sulfur species include mercaptans, sulfides, alkyl substituted thiophenes, thiophenols, and, depending on the gasoline cut point, benzothiophene and alkylbenzothiophenes.

The importance of the feed sulfur type on the amount of gasoline sulfur produced is shown in Figure 28. Two FCC gas oil feeds with similar sulfur levels were cracked in an FCC pilot plant and the resulting gasoline analyzed for sulfur. The gasoline produced from Gas Oil B has about 75% higher sulfur than the gasoline produced from Gas Oil A, despite the fact that both starting gas oils had similar sulfur levels.

The two gas oils were analyzed by High Resolution Mass Spectrometry (HRMS) and X-ray Photoelectron Spectroscopy (XPS) to determine the types of sulfur species present. The HRMS determines the type and amount of aromatic thiophenes present by measuring the quantity and mass of the molecular species. XPS measures the binding energy of the feed sulfur species and allows quantification of the amount of aromatic and aliphatic sulfur species. An analysis of the two feeds by these methods shows the differences in the types of sulfur species present in each feed (Table VI). Gas Oil B has about twice the level of alkylthiophenes, twice the level of aliphatic sulfur species and about 10% higher alkylbenzothiophenes, compared to Gas Oil A. Gas Oil A has more multi-ring benzothiophenes.
the biggest contributors to gasoline range alkylthiophenes, while the other feed sulfur molecules are more modest contributors. The alkylbenzothiophene and multi-ring thiophenes are the main source of benzothiophene which may not appear in the FCC gasoline, depending on the end-point.

Understanding the mechanisms by which gasoline sulfur is formed has allowed Grace Davison to develop a range of different products that target the different sulfur producing pathways.

Based on the feed sulfur analysis, experiments were designed to determine if feed alkylthiophenes, alkylbenzothiophenes and saturated sulfur compounds are more likely to end up in the gasoline as compared to multi-ring alkylbenzothiophenes. A hydrotreated, low sulfur gas oil was spiked with one of four model sulfur compounds; a mercaptan, an alkylthiophene, an alkylbenzothiophene and an alkyl dibenzothiophene. These feeds were cracked in an FCC pilot plant and the resulting gasoline was analyzed for sulfur. The results are shown in Figure 29. The data shows that the alkylthiophenes in the feed contribute significantly to gasoline range sulfur species. The alkyl chains on the thiophene are cracked and isomerized to produce a range of alkylated thiophene species. The alkyl group can also cyclize and dehydrogenate to form benzothiophene. The mercaptans are cracked mainly to H2S and only a small quantity ends up as gasoline range sulfur. The alkylbenzothiophene and alkyl dibenzothiophene produce some benzothiophene but essentially no gasoline range alkylthiophenes.

In summary, this data shows that (C₅+) alkylthiophenes in the feed are the biggest contributors to gasoline range alkylthiophenes, while the other feed sulfur molecules are more modest contributors. The alkylbenzothiophene and multi-ring thiophenes are the main source of benzothiophene which may not appear in the FCC gasoline, depending on the end-point.

Understanding the mechanisms by which gasoline sulfur is formed has allowed Grace Davison to develop a range of different products that target the different sulfur producing pathways.

When formulating a solution for a customer, we consider the FCC gasoline speciation, the desired level of gasoline sulfur reduction, and whether a catalyst or an additive is preferred. Careful selection of the appropriate technology for each application has resulted in consistent product performance that has met or exceeded customer expectations. As a result, these technologies tend to be used on a long-term, continuous basis. The average length for all 85 commercial applications is 388 days, with one user at 6 years. Over one-half of the applications have lasted 100

<table>
<thead>
<tr>
<th>Table VI</th>
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<tbody>
<tr>
<td>Sulfur Characteristics of Gas Oil A and B</td>
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</table>

<table>
<thead>
<tr>
<th>Sulfur Compounds by High Resolution Mass Spec (ppm)</th>
<th>Gas Oil A</th>
<th>Gas Oil B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(N)H(2N-4)S THIOPHENES</td>
<td>526</td>
<td>980</td>
</tr>
<tr>
<td>C(N)H(2N-10)S BENZOTHIOPHENES</td>
<td>13918</td>
<td>12702</td>
</tr>
<tr>
<td>C(N)H(2N-16)S DIBENZOTHIOPHENES</td>
<td>9439</td>
<td>7317</td>
</tr>
<tr>
<td>C(N)H(2N-22)S NAPHTHOBENZOTHIOPHENES</td>
<td>1517</td>
<td>0</td>
</tr>
</tbody>
</table>

| Total Sulfur XPS Analysis (wt.%)                     |           |           |
| ALIPHATIC SULFUR                                     | 0.23%     | 0.50%     |
| AROMATIC SULFUR                                      | 2.54%     | 2.09%     |

Catalytic Gasoline Sulfur Reduction Options

D-PriSM® sulfur reduction additive, another product from Grace Davison, is effective at removing an intermediate that converts to alkylthiophene and therefore is more effective at reducing light gasoline sulfur. This product has been used in more than 25 refineries worldwide. The SuRCA® catalyst family, GSR-5 additive and the recently commercialized NEPTUNE™ catalyst are designed to reduce a broader range of gasoline sulfur species (Figure 30).

When formulating a solution for a customer, we consider the FCC gasoline speciation, the desired level of gasoline sulfur reduction, and whether a catalyst or an additive is preferred. Careful selection of the appropriate technology for each application has resulted in consistent product performance that has met or exceeded customer expectations. As a result, these technologies tend to be used on a long-term, continuous basis. The average length for all 85 commercial applications is 388 days, with one user at 6 years. Over one-half of the applications have lasted 100
days and over one-quarter used the technologies for more than a year. Grace Davison currently has 25 gasoline sulfur reduction applications worldwide.

**Citgo Corpus Christi**

Citgo, Corpus Christi needed to reduce FCC gasoline sulfur to keep their overall refinery gasoline pool in compliance. Citgo and Grace Davison worked together to determine if catalytic sulfur reduction technologies could achieve the necessary reduction on their 67,000 barrel per day UOP High-Efficiency unit. The unit processes 100% hydrotreated vacuum gas oil and operates in full combustion. After careful evaluation of their unit operation and objectives, and Citgo’s preference for an additive approach, GSR-5 additive was recommended. Citgo began baseloading the product to achieve 25% in the circulating inventory. Maintenance dosage was also at the recommended level of 25% additions in place of normal catalyst additions.

Unit data, including feed quality, operating conditions, yields and yield quality was collected for eight months that encompassed both the base period, prior to additive additions and the GSR-5 additive period. Sulfur reduction on the heavy gasoline stream is shown in Figure 31. The data was normalized for changes in feed sulfur and endpoint. Sulfur reduction ranged from 21-31% depending on endpoint with an average reduction of 26%. Combining the effect of undercutting with the GSR-5 additive reduced gasoline sulfur by 44%.

To supplement the data generated by the refinery, FCC feed and heavy gasoline samples were collected by Citgo and sent to Grace Davison both before and during the trial. The samples were analyzed by Gas Chromatograph (GC) to determine the sulfur species present.
The performance of the GSR-5 additive on individual sulfur species is shown in Figure 32. Both sets of samples were normalized to account for variation in feed sulfur. The baseline is steeper at the points A through E than the GSR-5 additive line illustrating the performance across the entire range of sulfur species present in the heavy gasoline. Total gasoline sulfur reduction as measured by speciation is 30%. There were no adverse yield shifts with the GSR-5 additive when incorporated into Citgo’s operation at 25% of the unit inventory. The product was baseloaded into the unit allowing for quick results. This is achievable because the GSR-5 additive contains catalytic cracking functionality, which for Citgo resulted in a conversion increase of 0.7 Iv% and slurry decrease of 0.5 Iv%.

Citgo will use the GSR-5 additive for about a year to help cost effectively meet pool gasoline sulfur limits until alternative technologies can be commissioned. Then they will evaluate using GSR-5 on a long-term basis in conjunction with the hardware that is installed.

Citgo’s experience with GSR-5 additive technology is representative of other commercial applications. Table VII contains a list of refiners that have employed the product. With this additive, refiners can take advantage of FCC gasoline sulfur reduction on either a short or a long-term opportunity basis. Because the product is an additive, the application is independent of the base catalyst technology used by the refiner.

### Table VII

<table>
<thead>
<tr>
<th>Refiner</th>
<th>Region</th>
<th>Unit Type</th>
<th>% Sulfur Reduction</th>
<th>Days Used</th>
<th>Feed S, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A*</td>
<td>NA</td>
<td>UOP HIGH EFF</td>
<td>26</td>
<td>382</td>
<td>0.2 0.5 0.3</td>
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<tr>
<td>B*</td>
<td>NA</td>
<td>TEXACO DESIGN</td>
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<td>398</td>
<td>0.2 0.4 0.3</td>
</tr>
<tr>
<td>C*</td>
<td>NA</td>
<td>UOP HIGH EFF</td>
<td>23</td>
<td>368</td>
<td>0.3 0.5 0.3</td>
</tr>
<tr>
<td>D*</td>
<td>NA</td>
<td>UOP SBS</td>
<td>15</td>
<td>96</td>
<td>0.8 1.6 1.4</td>
</tr>
<tr>
<td>E*</td>
<td>NA</td>
<td>UOP MOD V</td>
<td>29</td>
<td>231</td>
<td>0.2 0.4 0.3</td>
</tr>
<tr>
<td>F*</td>
<td>NA</td>
<td>EXXON FLEXI</td>
<td>50</td>
<td>196</td>
<td>0.4 1.2 0.8</td>
</tr>
<tr>
<td>G*</td>
<td>NA</td>
<td>EXXON FLEXI</td>
<td>8</td>
<td>196</td>
<td>0.9 2.3 1.3</td>
</tr>
</tbody>
</table>

*Current Users*

### Summary

Gasoline sulfur regulations are becoming increasingly stringent worldwide. Since the FCC unit is such a large contributor of sulfur to the gasoline pool, effective means of reducing FCC gasoline sulfur can significantly improve refinery profitability and flexibility. Catalysts and additives for FCC gasoline sulfur reduction have been commercially proven in 85 units worldwide. Understanding the pathways of FCC gasoline sulfur formation as well as the species present is crucial in selecting the most appropriate technology. Proper application leads to successful results like those achieved at Citgo’s Corpus Christi refinery.
Grace Davison: Your proven FCCU emissions solution.

Grace Davison environmental technologies have helped refiners reduce FCCU emissions for over a quarter of a century.

The FCCU is often the largest point source within the refinery for SOx and NOx emissions. The use of innovative catalytic technologies reduces emissions from the FCCU regenerator, without the need for capital intensive “end-of-pipe” hardware solutions.

Super DESOX® provides industry leading SOx removal effectiveness. More and more refiners are finding that Super DESOX can cost effectively control SOx emissions below 25 vppm from a wide range of uncontrolled SOx baseline emissions.

Grace Davison researchers have studied the complex formation of NOx and developed two additives to reduce NOx. XNOx® is a low NOx combustion promoter designed to replace conventional promoters, which often cause increased NOx formation. For units not using a promoter, or requiring additional NOx reduction, DENOX® is the additive of choice. NOx reductions in excess of 50% have been observed commercially with both products. With more than 50 commercial applications of NOx additives, Davison has more experience than the rest of the industry combined and would be happy to assist you in reducing FCCU NOx emissions.

Extensive customer-driven research efforts at Grace are providing new insights into improving SOx and NOx removal. Want to find out more about our environmental technologies? Contact us at www.e-catalysts.com or call us at (410) 531-8226. Let Grace Davison help you meet your FCCU emission challenges.
Your **Clean Fuels** Solutions

When it comes to commercially proven technology to meet increasingly stringent Clean Fuels regulations, make Grace Davison and Advanced Refining Technologies your one-stop shop for FCC catalysts, additives and hydroprocessing catalysts.

For gasoline sulfur reduction, today’s refiners are challenged more than ever before to blend various refinery streams to meet stringent product specifications and government regulations for clean air. Proven in over 75 commercial units, Grace Davison’s portfolio of FCC gasoline sulfur reduction technologies includes the D-PriSM® and GSR®-5 additives and the SuRCA®, SATURN® and Neptune™ catalyst families.

> Recently commercialized, NEPTUNE catalyst further expands our sulfur reduction technologies to continuously improve both performance and cost effectiveness. This next generation technology is a step out improvement over earlier technologies, providing 35-50% full range gasoline sulfur reduction commercially with full catalyst formulation flexibility.

> For refiners with FCC pretreaters, the ApART Catalyst System™ utilizing combinations of ART 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. ART CDXi, our newest generation of high activity CoMo catalyst, efficiently removes the unhindered, easy sulfur via the direct abstraction route, while ART 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.

Have questions about our clean fuels technology? Contact us at [www.e-catalysts.com](http://www.e-catalysts.com) or call us at (410) 531-8226. Let Grace Davison and Advanced Refining Technologies give you the custom catalytic solution to your clean fuels challenges.
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 refineries 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 refineries 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.

Figure 33
Grace Davison’s Portfolio of Gasoline Sulfur Reduction Products

Figure 34
Grace Davison Experience in Sulfur Reduction Applications

A road map for product selection is shown in Figure 33. 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 34).

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.

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 35-37. Candidate feeds (Samples A, B, and C) were heavier and more aromatic than the Valero Wilmington Routine Feed (Figure 36) 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 37).

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 38). Yields interpolated at constant coke are shown in Table VIII. 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 39).

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 produced 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 41).

Gasoline samples for each candidate feed in Figure 41 were normalized to account for the delta between FCC-produced and pilot plant-produced methods (from Figure 40). 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 42.

The results from the pilot plant study, along with information on the Valero, Wilmington FCC unit operation (both routine and during a previous pretreater outag) 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. The decision was made to purchase the other feeds and blend them at various ratios with available Routine Feed during the outage. 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. 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.

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 baseload 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 43 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 online, 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 Cs's and Cs+ 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 refineries rely on hydrotreating to meet gasoline sulfur limits. Outages of either FCC feed hydrotreaters or gasoline post-hydrotreaters create opportunities for refineries 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 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 & 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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Understanding and Minimizing FCC Slurry Exchanger Fouling

Slurry exchanger fouling is often considered the worst fouling service in the FCC process. The primary problem that results from slurry exchanger fouling is reduced heat exchanger duty in the slurry/FCC feed preheat exchanger or the steam generators. The reduction in feed preheat temperature that can result from just mild fouling of the FCC slurry/feedstock exchangers can result in reduced unit feed rate or conversion.* Additionally, excessive pressure drop or inability to cool the slurry to the necessary rundown temperature can also require reducing the feed rate. Certainly excessive slurry exchanger fouling can be very costly to the refinery in terms of lost feed rate, lower conversion and higher maintenance expenses.

The purpose of this article is to present potential sources of slurry exchanger fouling and suggestions on how to prevent or minimize fouling. We will draw on industry experience from several sources to present a broad review of the subject. Our readers may consider this information and case study experience as they work to understand and minimize slurry exchanger fouling at their refinery.

Figure 44 illustrates a typical FCC Main Fractionator Slurry circuit. Superheated FCC product vapor is quenched as it enters the main fractionator using the reflux from the slurry pumparound circuit. Slurry exchangers, which recover this energy by heating the feedstock and generating steam, are often subject to fouling through a number of mechanisms. When slurry exchangers foul, feed rate or reactor temperature must often be reduced.

*For those FCC units that do not have a fired feed heater and are air blower limited.

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Figure 45 shows how quickly a slurry/feed exchanger heat transfer coefficient can deteriorate. Over a ten-week period, this refiner needed to clean their FCC slurry exchanger three times. During each cleaning cycle they were forced to significantly reduce feed rate.

Potential causes of FCC slurry exchanger fouling are shown in Figure 46. Fouling can be generally classified as either “organic” or “inorganic” based. Several organic or inorganic slurry fouling mechanisms are possible. Each of these possible fouling sources will be discussed and suggestions to prevent or reduce each type will be presented.

**ORGANIC BASED FOULING**

Organic based fouling is the most common fouling type. The potential causes of organic based fouling are very broad. It is helpful to classify organic fouling into two general sub-types: “hard” and “soft” coke fouling.

**Hard Coke Fouling**

Solid coke fragments circulating to the slurry exchanger tubes that restrict the flow through the exchanger is an example of hard coke fouling. This type of fouling results in excessive pressure drop and a loss of heat transfer duty. These shiny coke fragments generally accumulate on the exchanger tube sheets at the inlet to the tubes. Figure 47 shows how pieces of coke can block the exchanger tubes, increasing exchanger pressure drop.

These coke fragments can originate in the reactor overhead line or the main fractionator. The coke often becomes dislodged following an FCC shutdown because of the thermal cycling of the surface that the coke is adhered to. If the coke fragments are small enough to pass through the suction strainers on the slurry pumparound pumps, they...
can eventually foul the first slurry exchanger in the pumparound loop. Another scenario that can result is excessive hard coke accumulation in the bottom head of the main column that restricts the suction of the circulating slurry pumps.

Smaller coke fragments that pass through the exchanger tubes can still be problematic. These coke particles are either smaller coke particles from the main fractionator or are formed by polymerization reactions in the slurry pumparound circuit at high main fractionator bottoms temperatures. Small coke fragments can settle onto the tube surface and further polymerize, resulting in a barrier to heat transfer and slurry flow.

In some cases, formation of a very thin, hard layer of deposit has been observed on the tube walls. This type of deposit has a hard, shiny appearance similar to varnish. These deposits are formed by polymerization reactions on the tube surface. This type of fouling can reduce the heat transfer coefficient.

Preventing Hard Coke Fouling

Poor feed/catalyst contacting can be a significant source of hard coke formation in the vapor line. This is particularly true in units that process resid feeds. Feed/catalyst contacting can be improved in several ways:

- Improve feed atomization;
- Increase feed dispersion steam within the limits of the feed distributor design;
- Repair damaged feed distributors or replace with a more modern design;
- Increase the feed temperature to avoid high feed viscosity at the injection distributors. This is particularly applicable to resid operations.

A hot wall reactor vapor line must be properly insulated to reduce the likelihood of liquid condensation at cool spots. Insulation must be properly anchored and should be watertight. Once oil droplets form, they eventually dehydrogenate to form coke. The reactor vapor line blind flange and all the vapor line pipe supports should also be insulated if the designs allow, as coke can accumulate at these locations. Do not insulate the bolts of the blind flange, however, as this can result in the flange opening due to bolt creep.

Reactors vapor line vapor velocities less than 100 fps should be avoided to minimize coke formation. The exception to this is the velocity right at the inlet nozzle to the main column, where lower velocities are permitted. Higher velocities will reduce the likelihood of un-vaporized oil accumulating along the wall of the vapor line and eventually forming coke. Vapor line velocities between 100 to 120 fps are a good compromise to minimize both coke formation and pressure drop. (4)

Self-draining reactor overhead lines are a design feature often used to minimize coke formation and subsequent slurry exchanger fouling.

The maximum main fractionator bottoms temperature is typically between 680˚F and 700˚F to avoid coke formation and slurry exchanger fouling. The maximum safe bottoms temperature for any unit is unit and feedstock specific. It is also important to note that the bottoms temperature is often based on a single temperature indicator (TI) at the outlet line of the main fractionator. Poor pumparound distribution and liquid mixing may result in locally hotter temperatures than what is actually measured in the bottoms outlet line, increasing the likelihood of coking. This can be particularly true in operations where quench is used to cool the bottom of the main column.

Long liquid residence time in the slurry circuit will also influence coking. Reducing bottoms liquid level can minimize slurry residence time. Also note that increasing main fractionator bottoms temperature
and slurry pumparound rate both increase the liquid residence time.\(^{(5)}\)

FCC feedstock, particularly feed containing resid, can form coke at typical main fractionator bottom temperatures. As a result, refiners should ensure that no feedstock is leaking into the slurry pumparound circuit through an emergency feed by-pass valve or slurry/feed exchanger.\(^{(5)}\)

The slurry pumparound return should be properly distributed to minimize hot spots. The pumparound rate should be sufficient to ensure the grid zone is well wetted. Local areas devoid of liquid flow will allow hard coke to form. A minimum flux rate of 6 gpm/ft\(^2\) has been recommended.\(^{(6)}\)

A slurry pumparound rate of 1.2 to 1.5 times the feed rate is a rule of thumb that has also been suggested to ensure good liquid distribution in the bottom of the main fractionator.\(^{(5)}\)

Slurry quench, as shown in Figure 48, can be used to sub-cool the main fractionator bottoms temperature and reduce hard coke formation.\(^{(6)}\) A quench distributor should be used to minimize hot spots. Slurry quench, however, is commonly injected from a nozzle that terminates near the wall of the fractionator. As a result, the returning quench liquid is often not well distributed. Therefore, do not rely on perfect mixing of the slurry quench, as zones of high temperature could still be present. The refiner may consider monitoring bottoms temperature on a quench-free basis to account for potential high temperature zones.\(^{(6)}\)

Maintaining slurry exchanger tube velocities greater than 6 fps will help minimize any settling of small coke fragments or FCC catalyst onto the tube service.\(^{(8)}\) Units often have spillback valves on the slurry product exchangers to help maintain minimum slurry flows during times of turndown operation. Tube velocities should be less than 10 fps to avoid erosion.\(^{(8)}\)

Using an elevated slurry exit nozzle can reduce the likelihood of coke being entrained into the slurry pumparound loop.\(^{(8)}\) However, this results in the bottom head of the main column filling with accumulated coke and catalyst. On units where the liquid draw is on the bottom head, a coke trap should be employed in the bottoms suction nozzle on the column and/or upstream of the slurry exchanger as shown in Figure 48 to trap any entrained coke particles before they can foul the exchanger. G. Walker discussed application of a coke trap and resulting reduction in slurry exchanger fouling.\(^{(9)}\)

**Soft Coke Fouling**

Soft coke fouling is organically based where commonly an insulating barrier is deposited inside the exchanger tubes, reducing the exchanger heat transfer coefficient. The insulating barrier can be found throughout the tube service.\(^{(10)}\) Figures 49 and 50 show examples of soft coke fouling. Just a thin layer of material can result in a costly reduction of the exchanger heat transfer coefficient. In some cases, soft coke fouling can also result in increased exchanger pressure drop.\(^{(10)}\) Generally, however, reduced heat transfer is apparent before excessive pressure drop with this type of fouling.

Precipitated asphaltenes are a common source of soft coke fouling. Asphaltenes are highly condensed polyaromatics typically insoluble in a saturated hydrocarbon such as heptane.\(^{(11)}\) The concentration of these multi-ring aromatics in the slurry can be

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\(^{(6)}\) Ibid.

\(^{(8)}\) Ibid.

\(^{(9)}\) Ibid.

\(^{(10)}\) Ibid.

\(^{(11)}\) Ibid.
increased by thermal condensation reactions in the slurry circuit.

Asphaltenes can become insoluble in the slurry oil and begin to precipitate onto the tube surface. The tar-like layer on the tube surface can also trap coke and catalyst particles that are present in the slurry.\(^{(12)}\) Figure 51, an abbreviated version of Figure 46, illustrates the sequence. Analyzing such tube deposits and slurry for fused aromatics can be insightful. Higher amounts of fused aromatics in the deposit relative to the slurry can confirm asphaltene precipitation.\(^{(13)}\)

Slurry viscosities increase at the tube wall due to the locally cooler temperature. The higher viscosity can cause material to adhere to the tubes, resulting in exchanger fouling.\(^{(12)}\) Slurry with a higher paraffinic content may be more prone to fouling due to the inherently higher viscosity.

**Preventing Soft Coke Fouling**

Two sources suggest minimizing asphaltene content of the slurry in order to minimize fouling.\(^{(6,14)}\) ASTM D3279 can be used to determine asphaltene content. The asphaltene content is defined as those components in the sample that are not soluble in n-heptane. This procedure gives the combined amount of asphaltenes and particulate matter.

Maintaining asphaltenes in solution is key to preventing soft coke fouling. The composition of the slurry will affect the solubility of the asphaltenes. Generally higher aromatic content of the slurry tends to keep asphaltenes in solution. As such, changing the slurry composition by dropping some LCO down the tower can increase the solubility of asphaltenes in the bottoms material. This also has the benefit of reducing the temperature at the bottom of the main column.

It is often necessary to adjust the bottoms composition and temperature in this manner during changes in feed composition. For example, slurry produced from paraffinic feedstocks tends to be more prone to fouling and requires lower main fractionator bottoms temperature to minimize fouling.

Many refiners will also adjust bottoms temperature with conversion shifts to minimize fouling. A drop in conversion could result in higher slurry exchanger fouling. Slurry with higher API gravity, generally due to lower conversion, contains more saturated compounds, which can reduce asphaltene solubility and increase soft coke fouling. Slurry with a high API gravity is also more viscous and more prone to fouling.

Feedstock leaking into the slurry circuit can cause asphaltene precipitation. This occurs because the feedstock is more paraffinic than the slurry and reduces the solubility of the slurry asphaltenes. The refiner should take all precautions necessary to ensure that the feed emergency by-pass valve and the slurry/feed preheat exchangers do not leak feedstock into the slurry circuit.

The FCC catalyst can be formulated with features to minimize fouling. Catalyst matrix design can be optimized to improve slurry exchanger fouling by increasing Type III cracking as described by Zhao.\(^{(3)}\) Minimizing naphtheno-aromatics and paraffinic content of the slurry by increased Type III cracking may improve asphaltene solubility and reduce slurry exchanger fouling. Using a catalyst with proper tolerance to contaminant metals will help avoid fouling as well. Increased catalyst contaminants that result in a loss of FCC conversion can increase the likelihood of fouling as discussed above.

Hot Cycle Oil Flush at the inlet of the slurry exchangers can help keep asphaltenes in solution and increase tube velocity, both of which will help reduce slurry exchanger fouling.\(^{(5)}\)

**INORGANIC BASED FOULING**

Inorganic fouling can include fouling prompted from corrosion or iron scale, catalyst or precipitated metals. Catalyst is often found in tube deposits and can be identified by the presence of alumina, silica, and rare earth. Catalyst in the deposits is often a result of organic based fouling, since catalyst generally accumulates onto viscous precipitated asphaltenes or other hydrocarbons already present on the tubes.

Another inorganic foulant in FCC slurry service is antimony. Antimony present in the slurry has been found
on tube deposits. In one instance, 20 wt.% antimony was found in a deposit.\(^{(15)}\) The antimony source was from antimony injection into the FCC feedstock to passivate equilibrium catalyst nickel.

**Preventing Inorganic Based Fouling**

Catalyst losses to the main fractionator should be minimized by proper reactor cyclone operation and good reactor cyclone mechanical integrity. The catalyst itself can also be designed to minimize losses to the main fractionator. To maximize catalyst retention, the following catalyst design parameters should be considered:

- Low Attrition Index (Low DI);
- Low 0 to 40 micron content;
- High Particle Density.

Antimony levels in the slurry should be closely monitored to minimize the possibility of antimony depositing onto the tube service. FCC equilibrium catalyst antimony to nickel ratio is generally between 0.10 and 0.60 by weight. The antimony chemical should be injected to maintain the target level on the equilibrium catalyst without significant overfeed.

Proper metallurgy in the main fractionator, slurry piping and slurry exchanger should be used to minimize corrosion. Below is a summary of suggested materials:\(^{(6)}\)

- Main fractionator internals
  - TP 410 SS;
- Exchanger tubes
  - TP 405 or TP 410 SS;
- Slurry Lines 5 Cr - 1/2 Mo with 1/4" CA.

**Antifoulants**

Antifoulants have been successfully used to prevent FCC slurry exchanger fouling. Antifoulants can be generally classified as follows:

- Organic dispersants - prevent the agglomeration and deposition of asphaltenes;
- Inorganic dispersants - prevent the deposition of catalyst fines or other inorganic foulants such as Fe compounds;
- Coke suppressants - inhibit condensation reactions, which lead to hard coke-like deposits in exchangers.

A combination of antifoulants can be used. However, the likely source of the fouling should be identified before a specific antifoulant is applied.

Note that there can be some downstream effects when using an antifoulant. For example, in some cases catalyst fines settling in slurry tanks can be impacted if an inorganic dispersant is used.

**Additional Design and Operation Considerations**

There are many design considerations for exchanges in slurry service that can help to minimize the potential for exchanger fouling.

Slurry exchanger tube velocities should be 6 to 10 fps.\(^{(8)}\) Velocities below six fps can result in catalyst, coke or other particulates settling onto the tube surface, resulting in fouling. The minimum slurry exchanger tube diameter should be one inch.\(^{(5)}\) Smaller tubes can be subject to excessive fouling and are difficult to clean.

Spill back control can be used on net product exchangers in turndown conditions to keep tube velocities above minimum values.

Slurry should be present only on the exchanger tube side. With slurry on the shell side, it is impossible to prevent catalyst settling in the exchanger because of low local velocities.

Vertical and Spiral slurry pumparound exchanger designs tend to be less prone to slurry exchanger fouling.

Finally, having spare slurry exchangers should be considered to minimize turndown during exchanger cleaning.

**Case Study**

An FCC unit began observing severe fouling of their Slurry Steam Generator exchangers. The fouling began suddenly and continued for approximately two weeks and then stopped. During that time, it was necessary to clean the exchangers several times. The exchangers exhibited a reduction in heat transfer coefficient. Exchanger pressure drop was not affected.

The FCC was a modern design employing a modern riser termination device and state-of-the-art feed injection nozzles. The reactor temperature operated at 980˚F and main fractionator bottoms temperature was typically 690˚F. Conversion normally was ~78 vol.\% with a slurry API gravity of -2 API.

The feedstock was a vacuum gas oil and resid blend with the following nominal feedstock properties:

- API 22˚ to 24˚;
- K Factor 11.7 to 11.8;
- Conradson Carbon ~1.0 wt.%;
- 10% Greater than 1050˚F.

A deposit was taken from the fouled exchanger. Analysis of the deposit showed the following:

- 87% Carbon, 94% Organic Based (C, H, N);
- <1% Alumina;
- 1 wt.% Antimony;
- <1 wt.% Iron;
- 52% of the sample was Asphaltenes.
The refinery does use antimony to passivate nickel. However, antimony had been used for several years without any previous issues. No recent change in antimony injection was made and consequently antimony was likely not the cause of the fouling.

The deposit itself did not contain catalyst, as evident by the low amount of alumina.

The high amount of asphaltenes in the deposit confirmed asphaltene precipitation as the likely fouling mechanism.

A review of feedstock properties showed the feedstock had recently become more paraffinic, as evident by the higher API gravity and K Factor during the same time as the exchanger fouling. Figure 52 shows how feedstock API and K factor shifted. When the refinery changed the feed source the feedstock properties returned to typical values and the fouling stopped.

Many refineries recognize that some feed and crude sources can result in increased FCC slurry exchanger fouling. Those sources are either avoided, the main fractionator temperature is reduced, and/or antifoulants are used to minimize fouling while those feedstocks are processed.

**Final Remarks**

Continuous monitoring of the overall heat transfer coefficients is critical to catch a slurry exchanger fouling problem early. Monitoring slurry properties such as API gravity, ash content, asphaltene content, and viscosity can also alert the refiner when the FCC unit may be more susceptible to slurry exchanger fouling. A shift of feedstock properties or unit conversion may also increase slurry exchanger fouling.

Slurry exchanger fouling often occurs during start-up or at turnaround conditions when feedstock and operating conditions may be atypical. Special precautions may be considered during these unusual operations.

Reducing slurry exchanger fouling by lower main fractionator bottoms temperature and higher slurry product rate can be costly in terms of lower product value. Grace Davison can work with the refiner to adjust catalyst properties and operating strategy to minimize fouling and any subsequent yield loss.

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