Introduction

In most refineries, FCC gasoline is one of the largest, if not the largest contributor of sulfur to the overall gasoline pool. Regulations limiting the amount of sulfur in gasoline have highlighted the importance of reducing sulfur in the FCC gasoline stream. Grace Davison has been providing catalysts and additives to the industry that reduce FCC gasoline sulfur by 35% or more for over ten years. These technologies have been proven in 80 units worldwide. Another popular alternative to reduce gasoline sulfur is the installation of hardware. Increasingly stringent regulations have forced 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 refineries 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.

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.

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

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

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

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

Pre Turnaround Preparation

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

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

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

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

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

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

Another potential reason for differences between the pilot plant generated gasoline sulfur and that produced commercially is the method used to measure the sulfur concentration. Refiners typically measure gasoline sulfur by the bulk x-ray gasoline sulfur method. The measurement of gasoline sulfur pro-

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**Figure 5**
Feed Properties

**Table 1**
Interpolation at Constant Coke (3 wt.%)

<table>
<thead>
<tr>
<th></th>
<th>Routine Feed</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
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<td>81.8</td>
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</table>

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**Figure 6**
Feed Study Conversion vs. Coke
duced in the pilot plant utilizes a gas chromatograph to identify the individual sulfur species and total sulfur concentration.

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

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

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

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

**GSR-5 Additive Application**

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

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

**Economics**

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

After the pretreater was back 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 C3’s and C4’s before sending gasoline material directly to blending. The operation of the FCC unit is expected to shift in favor of more light olefins with the new equipment in service. The impact of the change in FCC operation on FCC gasoline sulfur and olefins will be evaluated to determine if GSR-5 economics remain favorable with the new process configuration.

**Conclusion**

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

The Valero, Wilmington case study presented here was made possible by incorporating discussions between Valero and Grace Davison into the planning stages of the FCC feed hydrotreater outage. Based on those discussions, pilot plant testing was completed which assisted Valero in selecting the purchased feeds they would run during the outage. Estimates provided by Grace Davison showed that the GSR-5 additive would allow Valero to achieve their shutdown objective of keeping their gasoline sulfur in compliance while running the higher sulfur purchased feeds. The use of GSR-5 additive during the outage resulted in $1.7 million in savings. With the proven product performance of the GSR-5 additive, Valero was then able to optimize their operation once the FCC feed hydrotreater was put back in service. The FCC feed hydrotreater unit severity was reduced, allowing for higher throughput, and the incremental hydrotreated gasoil was sold at a premium over regular gasoil. Additionally, Valero was also able to feed high sulfur VGO in place of medium sulfur VGO to the FCC feed hydrotreater without exceeding the FCC gasoline sulfur limits. Both operating changes resulted in a combined profit of over $8 million per year for the refinery.

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

Acknowledgements: The authors wish to thank Valero Energy and Grace Davison for permission to release this information. Natalie Petti (consultant), is gratefully acknowledged for her contribution of data evaluation and critique.