Almost one year after first proposing the stricter vehicle emissions standards known as Tier 3, the US Environmental Protection Agency (EPA) finalized the new regulations on March 3, 2014¹. Tier 3 requires the U.S. oil industry to reduce the average sulfur level in gasoline by more than 60 percent, to just 10 parts per million (ppm) in 2017, from the current 30 ppm. Unlike regulations in parts of Europe and Japan, the U.S. regulations allow for refinery gate sulfur levels as high as 80 ppm so long as the volume weighted average is maintained at or below 10 ppm.

Based on Tier 2 compliance experience, the EPA projects that an average standard gasoline target, combined with a higher cap will allow refiners batch-to-batch flexibility while reducing the overall sulfur level. The EPA also believes that this system will allow refiners to minimize operating costs. Tier 2 experience supports these assumptions. In 2012, under Tier 2, the national gasoline average pool sulfur was 26.7 ppm, 3.3 ppm below the target of 30 ppm.

Tier 3 continues the Tier 2 credit trading plan, where credits are generated for gasoline produced below the average target gasoline sulfur. Also, credits accumulated under Tier 2, which have a five year life, can be carried over for Tier 3 compliance.

At current gasoline sulfur levels, if refiners continue to accrue credits at the current rate until 2017, Tier 3 implementation could potentially be delayed 1 year. By averaging 20 ppm for 2.5 years leading up to 2017, refiners could delay implementation of Tier 3 standards until mid 2019. Adding the 3.3 ppm of credits accumulated in 2012, 2013, and the first quarter of 2014, refineries could possibly delay investments in capital to meet Tier 3 compliance until 2020. Also, small volume refineries, representing approximately 1/3 of U.S. refineries, are exempted from compliance until 2020.

Credit trading is described by the EPA as “robust and fluid”. According to EPA data, 56% of 2012 credits were transferred intercompany and 44% of 2012 credits were traded intracompany, that is, traded outside the company where they were generated. Credits allow refiners to delay capital spending, and in some cases may allow refiners to minimize capital spending.

To meet Tier 3 targets, the EPA predicts that average FCC gasoline sulfur will have to be equal to or lower than 25 ppm, compared to the current average FCC gasoline sulfur of 80 ppm, assuming that FCC gasoline represents 36% of the total gasoline pool.

Much of the Tier 3 gasoline sulfur compliance focus is on FCC gasoline. With the exception of the combined Light Straight Run (LSR) and Natural Gas Liquids (NGL) stream, which currently represents 5.2% of the gasoline pool with a current average sulfur level of 15 ppm, the FCC stream is the only stream that does not meet the new Tier 3, 30 ppm average sulfur target.

Compliance with Tier 3 regulations will require adjustments to operating strategies and, most likely, capital investment for new or upgraded equipment. Hardware options available to reduce FCC gasoline sulfur include FCC feed pre-treatment or gasoline post-treatment.
FCC Feed Pre-Treatment

FCC feed hydrotreating typically lowers FCC feed sulfur by 70-90%. FCC units running hydrotreated feedstocks produce gasoline in the range of 200 to 500 ppm. If the hydrotreater is operated at high severity – high temperature and pressure – the resulting FCC gasoline sulfur level would typically be in the range of 75 to 100 ppm. Operating at higher severity requires more frequent catalyst change outs, increased hydrogen, and increased maintenance, and, therefore, increased operating cost. And to meet Tier 3 levels, other changes in the pre-treater operation might need to be considered.

To address these needs, Advanced Refining Technologies LLC (ART) utilizes the ApART™ catalyst system for FCC pre-treatment. This technology is designed to provide significant increased HDS conversion while at the same time providing significant upgrading of FCC feedstock quality and yields. In essence, an ApART™ catalyst system is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each catalyst are optimized to meet individual refiner’s goals and constraints. ART continues to develop a better understanding of the reactions and kinetics involved in FCC pre-treating, and through its relationship with Grace, a detailed understanding of the effects of hydrotreating on downstream FCC performance.

The hydrotreating catalyst system and the operating strategy for the pre-treater are critical to providing the highest quality feed for the FCC.

FCC pre-treating plays an important part in reducing the sulfur content of FCC products. ART has completed many studies looking into the effects of hydrotreating on FCC performance and the quality of the FCC products. This work confirms that increased severity of the pre-treater operation results in a reduction in FCC gasoline sulfur.

Figure 1 shows the relationship between FCC feed sulfur and the resulting sulfur of the FCC gasoline. This presented in Figure 1 was generated using a variety of FCC feeds that had been hydrotreated over several types of catalysts and catalyst systems. The results demonstrate good correlation between FCC feed sulfur and the corresponding FCC gasoline sulfur.

However, increasing the severity of the pre-treater operation to reduce product sulfur will tend to move the catalyst towards more of a poly nuclear aromatic (PNA) mode of operation. The PNA mode of operation, while beneficial to the FCC in many ways, can shorten the cycle length of the pre-treater catalyst due to the increased temperatures.

Operating the hydrotreater to remove nitrogen and PNA’s improves FCC product value when targeting gasoline production, but this needs to be balanced against the increased costs of higher hydrogen consumption and shorter cycle. Tailored ApART™ catalyst systems with 586DX and AT795 optimizes the production of high quality feeds to the FCC and production of lower sulfur FCC gasoline, providing additional benefit if the FCC gasoline sulfur is low enough to be blended directly into the gasoline pool without additional post treating, or requires less severe post treating.

Post-Treating FCC Gasoline

Hydrotreating FCC gasoline can have a dramatic, negative effect on the gasoline octane due to the additional olefin saturation that occurs when removing the last amount of sulfur. The impact of gasoline post treatment on gasoline octane is related to the severity of the post treater operation. In the range of 96-99% sulfur removal, the impact on octane and hydrogen use is exponential. The impact on gasoline octane across all technologies, operated at moderate severity, is approximately 0.8 R+M/2.

Undercutting Gasoline

The EPA estimates that 22% of FCC gasoline was undercut to distillate in 2009 and expects that to increase to 68% by 2018. With much of the FCC gasoline sulfur concentrated in the high boiling point tail, undercutting can significantly lower gasoline sulfur. The EPA predicts that if the naphtha swing cut is fully cut into the distillate pool, that FCC gasoline volume could be reduced by 16%, and that FCC gasoline sulfur could be reduced by 50%. However, the EPA believes that market forces will drive undercutting gasoline to diesel, as diesel demand increases amid decreasing gasoline demand.
Refiners around the world have demonstrated that use of gasoline sulfur reduction catalysts and additives is a cost-effective component of their clean fuels strategy.

Grace GSR® technologies: D-PrISM®, SuRCA®, and GSR® 5, are the result of almost two decades of innovation. Grace’s gasoline sulfur reduction products have been used in over 100 FCC applications worldwide to provide 20%-40% sulfur reduction in FCC naphtha, including applications in Japan and Europe, where gasoline sulfur is already regulated to a 10 ppm cap.

With much of Tier 3 compliance focused on the high sulfur FCC gasoline stream, in-unit reduction of FCC gasoline sulfur with Grace’s patented gasoline sulfur reduction technologies creates a variety of opportunities and options for refiners to drive profitability while meeting Tier 3 gasoline requirements.

Grace’s clean fuels solutions create economic advantages around feedstock blending and asset optimization to:

- Preserve octane
- Maximize throughput
- Extend pre-treatment and/or post-treatment hydrotreater life
- Provide more flexible gasoline stream blending options
- Provide operating flexibility during hydrotreater outages
- Generate gasoline sulfur ABT credits to defer capital investment

The benefits of in-unit catalytic FCC gasoline sulfur reduction are specific to the refinery’s configuration, yield targets, and financial goals. However, some examples can be drawn from current applications.

**Commercial Application of Grace FCC Gasoline Sulfur Reduction Technologies**

In the mid 2000’s, Japan committed to lower gasoline sulfur. As early adopters of more stringent gasoline quality regulations, Japanese refiners faced similar challenges that US refiners face today in meeting Tier 3. Since 2005, Japanese refiners have successfully utilized Grace’s gasoline sulfur reduction products to maintain compliance and meet the 10 ppmw gasoline specifications².

Most refiners in Japan have elected to heavily hydrotreat FCC feedstocks and therefore base gasoline sulfur levels are extremely low by worldwide standards. The sulfur content of FCC gasoline blended into the gasoline pool typically must be 15 ppm or less, but varies with each refinery.

Most refiners in Japan have also elected to install FCC gasoline hydrotreaters and have taken steps to modify FCC feed properties to meet the stricter gasoline sulfur limits.

The sulfur content of hydrotreated FCC feed is typically in the range of 700 ppm to 3000 ppm. The severity of the hydrotreating operation needed to achieve these levels limits the life of the hydrotreating catalyst to 1-2 years.
The use of SuRCA® in the FCC unit reduces gasoline sulfur levels by 20-40 percent. By using SuRCA®, FCC feed sulfur could be increased and the refiner would achieve the same FCC gasoline product sulfur as was produced on the lower sulfur feed.

Increasing FCC feed sulfur accomplished by reducing the severity of the upstream FCC feed hydrotreater will extend the life of the FCC feed hydrotreater catalyst.

SuRCA® catalyst technology can also be used to reduce the severity of FCC gasoline hydrotreaters. Lower sulfur in the feed to the gasoline hydrotreater allows lower severity operation to achieve a given product sulfur level. Lower severity has the benefit of reducing octane loss across the gasoline hydrotreater.

Other benefits of FCC gasoline sulfur reduction technology include the potential to increase cut point (T90) of the FCC gasoline, which increases gasoline yield. Some refiners in Japan are also hydrotreating only a portion of the FCC gasoline stream and using SuRCA® catalyst to optimize overall refinery production of low sulfur gasoline.

**Case Study: Japanese Refiner (Ongoing User)**

This FCC unit processes 100% hydrotreated VGO feed. The unit charge rate is 40,000 barrels per day and it is operated in full burn.

Using SuRCA, the refinery realized a 40% reduction of HCG (gasoline) sulfur at constant feed sulfur. The ratio of gasoline sulfur to feed sulfur at constant gasolineT99 is shown in Figure 2.

SuRCA was applied over a base Grace catalyst. No shifts in product selectivities or gasoline octane were observed. Yields and selectivities of any SuRCA catalyst can be adjusted through reformulation of the catalyst.

This refiner continues to use SuRCA today to allow them to either blend high sulfur coker gasoline into their gasoline pool or extend the catalyst life of their FCC feed VGO hydrotreater.

**Conclusions**

Grace’s multiple product offerings allow for a truly custom clean fuels solution for your refinery’s Tier 3 compliance plan. Grace’s current range of FCC gasoline sulfur reduction products is shown in Table I.

In challenging environments like Japan, where gasoline sulfur specifications are more severe than the new U.S. Tier 3 regulations, refiners use Grace products to realize 20-40% reductions in gasoline sulfur, and provide feedstock and operating flexibility. With the new Tier 3 regulations in the U.S., Grace’s gasoline sulfur reduction products can also be used to generate credits to optimize investment options. Additionally, ART, Grace’s JV with Chevron, provides a full slate of FCC feed pretreatment products to optimize product sulfur levels and yields.

Ask your Grace representative which solution is best for your operation.

**References**
