Question 52: What strategies have you employed to profitably manage Tier III regulations (i.e. crude purchasing strategy, pre/post treating, FCC operational changes, sulfur reducing additives, etc.)?

TODD HOCHHEISER (Johnson Matthey)

Hydrotreating has been the major way that refineries have achieved Tier III sulfur compliance. Pretreating FCC feed improves yields and lowers sulfur in all products but has higher capital cost than post-treating. Post-treating is less capital intensive but reduces gasoline octane and also has no impact on FCC yields or the sulfur in other FCC products. Most new hydrotreating units for Tier III compliance were post-treating. If post-treating is used for sulfur reduction, it is beneficial to have multiple gasoline cuts. Excluding light FCC naphtha from hydrotreating will reduce overall octane loss as most olefins are found in the light FCC naphtha. For refineries with existing feed hydrotreaters, some have increased severity to comply with Tier III leading to a shorter catalyst cycle length.

The most significant FCC operational change to reduce gasoline sulfur has been to reduce the gasoline cutpoint. This removes the fraction of gasoline with the highest sulfur concentration. Additionally, some FCCs have been able to reduce gasoline sulfur by increasing conversion.

The quality of the gasoline / LCO fractionation can also have significant impact on gasoline sulfur. Benzothiophene boils at 430 degrees F. For units that are under-cutting gasoline, benzothiophene should be in the LCO stream. For one refinery, over 60% of the gasoline sulfur species were benzothiophene and alkyl-benzothiophenes. A fractionation improvement project would shift a significant amount of these sulfur molecules to LCO where they belong.

Sulfur reduction additives have been used to reduce FCC gasoline sulfur by 15-30%. Many gasoline sulfur reduction additives utilize technology that saturate thiophenes to tetrahydrothiophenes which are cracked to H2S and non-sulfur containing hydrocarbons. Gasoline sulfur reduction additives are usually less effective when the base catalyst contains high rare earth and high vanadium or when the feed contains previously cracked hydrocarbons. For most refineries, gasoline sulfur reduction additives are not the sole answer for Tier III compliance but rather are used in conjunction with other strategies.

Finally, sulfur credits have also been used to meet Tier III compliance. These credits can be from other refineries in the corporation or can be purchased in the open market.

COLIN BAILLIE (W. R. Grace & Co.)

Refiners have various options to comply with Tier 3 regulations for gasoline sulfur, though post treatment of FCC gasoline lies at the heart of many refiners' strategies. As there are limited capital projects for new installations relating to Tier 3 that have been announced, it would appear that many refiners have opted to revamp, expand capacity, or simply increase the severity of existing hydrotreaters. Post-

treatment of gasoline can involve various process configurations, including Selective Hydrogenation Units, Splitters, and Hydrodesulfurization units (HDS), to best fit the gasoline pool requirement and maximize refinery profitability. The downside of post-treating gasoline is the resulting loss of octane. This can be alleviated when pretreating feed upstream of the FCCU through FCC feed hydrotreaters and/or hydrocrackers, which allows the HDS unit to run at lower severity.

In terms of FCC operational changes, if the unit is equipped with a splitter the LCN cut point can be decreased to reduce the LCN sulfur, which is typically blended directly into the refinery gasoline pool. However, this results in a higher volume of HCN to the HDS section, which increases hydrogen consumption. Another option is to reduce the overall FCC gasoline cut point. This can significantly reduce the sulfur content of the FCC gasoline, and therefore allow a lower severity of post-treatment with benefits for octane preservation. However, gasoline yield is reduced, and the increased yield of LCO requires available distillate hydrotreating capacity and increases hydrogen consumption.

Switching to lower sulfur feeds can allow refiners to more easily achieve gasoline sulfur targets, though many refiners may not have the flexibility to do this. However, the ramping up of IMO 2020 legislation, combined with a lightening global crude slate, could be additional drivers for refiners to move to a lower sulfur crude diet, which would also have benefits for Tier 3 compliance.

Another way refiners in North America have approached Tier 3 is through the use of sulfur credits. EPA's sulfur credit program allows refiners to accumulate credits by achieving lower sulfur levels than required. The credits can then either be "cashed in" at a later date to offset higher sulfur levels or be sold to other refiners who are struggling to meet the 10-ppm sulfur target. For example, Tier 2 credits generated prior to 2017 (by achieving less than the required 50 ppm gasoline sulfur) are being used by some refiners to bring them within Tier 3 compliance, though these Tier 2 credits are only valid until the end of 2019. Refiners can continue to generate credits by achieving less than 10 ppm sulfur, which are valid beyond 2019. However, due to the difficulty of achieving <10 ppm sulfur, significantly less Tier 3 credits will be generated compared to Tier 2 credits. With a low supply of credits, and an expected high demand, this is likely to be a very costly strategy for refiners to rely on.

Finally, FCC gasoline sulfur reduction catalyst and additive technologies can be used by refiners to complement the strategies described above. Grace 's GSR® technologies include D-PriSM® and GSR® 5 additives, as well as SuRCA® catalysts, and have been used by more than 70 refineries worldwide to successfully reduce gasoline sulfur. Many of these applications have included heavily hydrotreated feedstocks where the FCC gasoline sulfur is already low reducing or eliminating the need for post treatment. The lower gasoline sulfur obtained with GSR® technologies can allow a reduction in FCC gasoline post-treatment severity, thus minimizing octane loss and reducing hydrogen consumption. They also allow a reduction in the undercutting of FCC gasoline, resulting in increased volume while maintaining overall sulfur level. They can also be used to help generate additional sulfur credits, for example by allowing the LCN cut point to be extended without increasing sulfur. Finally, GSR® technologies allow higher sulfur feeds to be processed, which improves feedstock flexibility.

GEORGE HOEKSTRA (Hoekstra Trading LLC)

Tier 3 puts high value on reducing octane loss in FCC gasoline desulfurizers. It is possible to reduce

octane loss by making unit changes that reduce olefin saturation at constant product sulfur. An effective way to do this is to add a feed splitter, which can be done with low capital investment. This also provides opportunity to adjust the light/heavy naphtha cut point to optimize desulfurization/saturation selectivity.

Our pilot plant, laboratory, and field testing has shown that adjusting the heavy naphtha end point can also improve selectivity by driving heavy sulfur and/or octane-enhancing aromatics into or out of the gasoline.

These cut point optimization steps are strongly dependent on feed composition and are facilitated by use of detailed hydrocarbon type analysis and sulfur speciation data.

Other operating variables also affect sulfur/octane selectivity in ways that can be measured with modern analytical methods and adjusted beneficially. We describe unit performance with a performance curve showing RON octane loss versus product sulfur. Here is the performance curve for one commercial unit that doesn't have a feed splitter:

This next chart shows our estimate of how this curve can be shifted up by the combined effects of

- 1. adding a feed splitter
- 2. optimizing feed end point
- 3. employing operating conditions that improve sulfur/octane selectivity.

In this case, the combined effect saves 4 RON octane at 10 ppm product sulfur, which is more than enough to pay for a feed splitter and LOTS of laboratory analyses.

These optimization tools, and the data on which they are based, are available to anyone at negligible cost through Hoekstra Trading.

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