Catalytic strategies to meet gasoline sulphur limits

Stricter regulations reducing average gasoline sulphur content will require further reduction of FCC gasoline sulphur

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The US Environmental Protection Agency (EPA) has finalised new regulations designed to reduce air pollution from passenger cars and trucks. The regulations (commonly referred to as Tier 3) set new vehicle emission standards and lower the annual average sulphur content of gasoline from 30 ppm to 10 ppm (see Figure 1). Additionally, the regulations maintain the current 80 ppm refinery gate and 95 ppm downstream caps. The implementation date is 1 January 2017. These Tier 3 gasoline sulphur specifications are similar to levels already being achieved in California, Europe, Japan, South Korea and several other countries.

Implications for refinery processing

The gasoline pool is composed of gasoline boiling range hydrocarbons from several sources in the refinery. Typical gasoline pool blending components include butanes, ethanol, light straight run naphtha, isomerate, reformate, alkylate, FCC gasoline and hydrocracker gasoline. In addition, purchased blending components may also be present. Most of these components are very low in sulphur (typically <1 ppm) except for the FCC gasoline. Not only does the FCC gasoline have the highest sulphur content, but it is typically also the largest volume component of the gasoline pool. As a result, FCC gasoline sulphur will have to be reduced to 20-30 ppm in order for a typical refinery to meet the proposed Tier 3 regulations.

At present few, if any, refineries are able to blend significant amounts of FCC gasoline into the gasoline pool without employing hydrotreating to reduce sulphur. Options refiners are currently utilising to meet current Tier 2 regulations include:

- Pretreatment of FCC feed: pretreatment reduces the sulphur of the FCC feed, which in turn lowers the sulphur of the FCC products including FCC gasoline
- Post-treat FCC gasoline: post-treatment directly reduces FCC gasoline sulphur
- Combination of FCC feed

Figure 1 US gasoline sulphur requirements
pretreatment and FCC gasoline post-treatment.

Current unit constraints and relative economics of the available options will determine the technology selection for meeting Tier 3 regulations.

**Catalyst developments in FCC pretreatment**

To meet the demand for improved catalysts in FCC pretreatment service to meet Tier 2 regulations, Criterion Catalysts & Technologies L.P. (Criterion) developed and commercialised the Ascent family of catalysts with DN-3551 NiMo and DC-2551 CoMo. Criterion has also developed and commercialised the Centera family of catalysts for FCC pretreatment: DN-3651 NiMo and DC-2650 CoMo.

**Figure 2** highlights the continuing evolution of FCC pretreatment NiMo catalyst development by Criterion. Refiners were able to take advantage of the increased activity of DN-3551 to meet Tier 2 regulations and still achieve long catalyst life; similarly, the increased activity of the recently commercialised Centera DN-3651 will assist refiners in meeting the proposed Tier 3 regulations.

Criterion’s newest CoMo FCC pretreatment catalyst, Centera DC-2650, is often used in conjunction with Centera DN-3651, especially in lower pressure units to optimise hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN) performance.

These new catalytic developments allow current FCC pretreatment units to produce lower product sulphur at the same operating conditions and minimise the investments required to meet Tier 3 requirements.

**Capital avoidance from developments in FCC pretreatment**

Many refiners have invested heavily in robust FCC pretreatment units to meet Tier 2 regulations as well as MACT standards for FCC emissions. Leveraging advanced catalyst technologies with existing assets can, in many cases, provide attractive solutions to both minimise capital investment as well as improve refinery profitability. The FCC pretreatment unit plays a critical role in optimising FCC performance. Removal of sulphur from FCC feed improves FCC product quality while the removal of nitrogen and contaminant metals improves FCC catalyst performance and reduces catalyst usage. Additionally, hydrogenation of the FCC feed improves conversion by reducing the concentration of polynuclear aromatic species. In many applications, drop-in catalytic solutions for FCC pretreatment units can achieve higher severity with little to no capital investment and minimal change in cycle life.

There are several key factors to consider when evaluating FCC pretreatment units for higher severity operations:

- Hydrogen availability including recycle gas capacity to account for additional consumption
- Heat balance for operation at higher reactor temperatures
- Cycle life targets
- Current and future capacity targets as it relates to reactor space velocity
- Operating constraints such as fractionation limitations.

**Table 1** is derived from Criterion’s industry-wide database to illustrate a comparative analysis of the performance improvements expected for FCC pretreatment units using drop-in catalytic solutions with Centera products. In addition to product quality improvements, estimated improvements for FCC conversion are provided.

For a medium pressure unit with average feed properties and a typical 36-month cycle life currently producing 1000...
ppm product sulphur, the more severe FCC pretreatment operation to produce FCC gasoline sulphur in the 20-30 ppm range requires FCC pretreatment product sulphur to be in the 300 ppm range and when using Centera catalyst, a cycle life of 24 months or more can be achieved. In addition, the product nitrogen is reduced significantly and hydrogen consumption, FCC pretreatment volume gain and FCC conversion are increased.

The improvements in FCC performance and yields from higher severity operation of the FCC pretreatment unit are linked to the increased saturation of polynuclear aromatics. The saturation of aromatic rings in these complex molecules determines both the product distribution and the relative sulphur distribution in the FCC products. In the FCC, aromatic rings do not crack while functional groups attached to the aromatic rings can be removed. The number of unsaturated rings adjacent to each other is critical in determining the boiling range of the final FCC product. Molecules with one ring end up in the FCC naphtha cut, two- and some three-ring molecules go to the LCO cut while most three-ring and greater molecules are either found in the HCO and clarified oil streams or deposit as coke. Saturation of aromatics results in higher value products and greater conversion in the FCC. Saturation of aromatic rings starts from the centre of the molecule with a decrease in relative reaction rate as polynuclear aromatics are hydrogenated.

The critical operating parameters that influence these reaction rates are hydrogen partial pressure and operating temperature. In order to maximise aromatics saturation for a given unit, it is important to maximise hydrogen purity and hydrogen availability to optimise hydrogen partial pressure, particularly at the reactor outlet. In addition to maximising hydrogen partial pressure, operating temperatures must be increased to maximise saturation. However, saturation of aromatics is equilibrium limited at constant hydrogen partial pressure so there is an optimum temperature range for maximum saturation. This optimum temperature range is often referred to as the kinetic region or the aromatics saturation plateau. Operating in the kinetic region provides the best quality feed for the FCC.

When evaluating an increase in severity of a FCC pretreatment unit, there is typically a synergy between the additional temperature required and maximum aromatics saturation operating mode. The elevated desulphurisation severity drives the unit closer to maximum aromatics saturation mode, which results in improved yields in the FCC product slate. Additionally, the elevated desulphurisation severity early in the cycle capitalises on the maximum aromatic saturation activity of the catalyst system throughout the cycle which maximises overall yields.

Increased aromatic saturation has an impact on the distribution of the sulphur containing aromatic molecules in FCC products. The following discussion illustrates the impact of FCC pretreatment severity on a typical polynuclear aromatic species and the impacts on product sulphur distribution.

### Untreated feed (no FCC pretreatment)

For an untreated aromatic molecule, the FCC simply removes the functional group chains attached to the compound and leaves most of the molecule unconverted, resulting in higher coke and or cycle oil yield. This results in higher sulphur in the unconverted cycle oils or higher SOx in the flue gas after coke is
burned off the catalyst. There is a low probability of secondary thiophene cracking in the FCC, thus the sulphur in this molecule ends up in the cycle oil or coke. This is illustrated in Figure 3.

**Low severity FCC pretreatment**
When the same molecule is treated, but in a low severity operation, the resulting aromatic saturation result is an increase in gasoline yield. But because the sulphur atom remains integrated with the aromatic benzo thiophene, the probability of secondary cracking is low and it remains in the gasoline boiling range. This is illustrated in Figure 4.

**Higher severity FCC pretreatment**
Increased aromatic saturation by increasing severity in the FCC pretreatment unit converts the polynuclear aromatic (PNA) to a single ring compound. Secondary cracking of the thiophene yields H₂S, which removes the sulphur from the gasoline boiling range. This is illustrated in Figure 5.

This secondary thiophene cracking in the FCC is inhibited by the basic nitrogen in the FCC feed and, in the presence of basic nitrogen, the inhibition decreases the amount of sulphur removed from the gasoline fraction. This is illustrated in Figure 6.

The higher severity FCC pretreatment operation thus provides additional advantages by increasing the nitrogen and basic nitrogen removal from FCC feed. This impacts FCC cracking reactions and influences the distribution of sulphur in the FCC products. Thus, improved nitrogen removal also leads to a reduction in gasoline sulphur.
In conclusion, the increased HDS achieved by increased FCC pretreatment severity along with the higher saturation and denitrification are critical in reducing FCC gasoline sulphur while still achieving reasonable cycle life. Applying best available catalyst technologies opens the door to improved product quality and maximum profitability.

Several US refiners are already using Criterion’s industry leading catalysts to increase severity and are capturing the yield improvements while also producing low sulphur FCC gasoline streams that are suitable for blending to Tier 3 specifications. With the increased severity, the diesel side-stream off the FCC pretreatment unit has, in several cases, been of ULSD quality, thereby further improving the economics.

**Catalyst developments in FCC post-treatment**

Likewise Criterion has continued the development of FCC gasoline post-treatment catalysts with focus on maximising desulphurisation activity and selectivity with minimal olefin saturation. The company currently produces a Generation 1 FCC post-treatment catalyst that is employed in FCC gasoline post-treatment with a new catalyst in the development stage. The new catalyst is designed for maximum sulphur reduction while minimising octane loss.

The key challenge has been to develop catalyst nanostructures that selectively maximise desulphurisation sites, while minimising active sites associated with hydrogenation of olefins.

Generally, conventional metal sites (Co-Mo-S) on alumina favour both thiophenic compound desulphurisation and saturation of the olefinic species present. This type of processing results in high octane loss and hydrogen consumption. Increasing selectivity for desulphurisation, while suppressing olefin saturation, is key to increasing process efficiency, thus reducing costs and making post-treatment processing economically effective under the more stringent sulphur reduction specifications.

Selective post-treatment HDS is generally conducted in multiple stage reactors: in the first stage, some diolefins are removed and high mercaptan and high sulphur compounds are converted to heavier sulphur compounds. The effluent is fractionated to produce an olefin-rich light naphtha stream and a sulphur-rich heavy naphtha stream. In the second stage, the heavy naphtha fraction is desulphurised using selective catalysts. Depending on the process employed, effluent sulphur from this section can vary from tens to hundreds of ppm. Post-treatment processing in fixed bed units is employed in some processes to further reduce sulphur content of this effluent.

Catalyst development for the
finishing catalyst was conducted at Criterion’s R&D centres, where enhanced experimentation equipment was employed. This experimentation technique allows multiple experiments to be conducted simultaneously, while analysing and statistically organising data, thus enhancing the chances of a significant catalyst development breakthrough. Our focus in the development of this catalyst was to reduce the sites involved in hydrogenation and enhance the sites involved in the direct desulphurisation route. This involved both the development of new support material and enhanced surface metal chemistry to maximise selective desulphurisation, while minimising undesirable reactions.

Table 2 shows the properties of the feed used for post-treatment catalyst testing. This feed was collected from a Gulf Coast refiner and represented feed to a polishing reactor to reduce sulphur content.

Table 3 shows the product properties for two catalyst generations collected at various process operating conditions. Various studies were conducted where process parameters such as catalyst temperature, hydrogen partial pressure, gas circulation rate and system pressure were varied over an applicable range. Under all process conditions, the new generation catalyst showed superior activity for sulphur removal and olefin retention compared to the previous catalyst generation.

Conclusion
Proposed Tier 3 regulations reducing average gasoline sulphur content to 10 ppm will require further reduction of the FCC gasoline sulphur. Refiners are currently evaluating their options which include: increasing FCC pretreatment severity or expanding FCC pretreatment assets; increasing FCC gasoline post-treatment severity or expanding FCC post-treatment assets or a combination of the two.

Opportunities exist to minimise or eliminate these investments by use of advanced catalyst technologies to attain the longest possible cycle life at the increased desulphurisation requirements in the FCC pretreatment unit or to reduce the FCC gasoline sulphur in the FCC gasoline post-treatment unit while minimising octane loss.

Several US refiners are already using Criterion’s catalysts to increase severity and are capturing yield improvements while also producing low sulphur FCC gasoline streams that are suitable for blending to Tier 3 specifications.

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Further reading

### Table 2

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### Simulated distillation D-3710C-7890

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Table 3
Patrick Gripka is Regional Technical Services Manager for the Americas with Criterion Catalysts & Technologies. With over 25 years of experience, he provides technical support for Criterion’s customers via estimates, design bases, start-ups, unit monitoring, troubleshooting and value creation opportunities, primarily in the NHT, DHT and CFH technology areas. He holds BS and MS degrees in chemical engineering from the University of Missouri – Rolla. Opinder Bhan is a Senior Principal Advisor in the Catalysis Group at Shell. With over 27 years of experience with Shell, he has spent most of his career in catalyst research and development and is currently working on processes for more efficient removal of sulphur from petroleum feedstocks. He has received over 50 US patents, has commercialised over 20 catalysts, and holds a doctoral degree in chemical engineering. Wes Whitecotton is Criterion Catalysts & Technologies’ Regional Marketing & Business Development Manager for the Americas. He started his career with Criterion over 22 years ago and focuses on providing business support within Criterion and sales account management to customers via estimates, unit monitoring, troubleshooting and value creation opportunities primarily in refining technology. He holds a BS degree in business. James Esteban is a Senior Technical Service Engineer with Criterion Catalysts and Technologies, specialising in technical service and solutions for hydroprocessing applications, and is the global Subject Matter Expert for naphtha hydroprocessing with extensive experience in hydroprocessing applications for FCCPT, ULSD, ULSK and naphtha. He holds a BS degree in chemical and petroleum refining engineering from the Colorado School of Mines.