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Tier 3 Capital Avoidance with Catalytic Solutions

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Tier 3 Proposed Regulations

The U.S. Environmental Protection Agency (EPA) has proposed new regulations designed to reduce air pollution from passenger cars and trucks. The regulations (commonly referred to as Tier 3) would set new vehicle emission standards and lower the annual average sulfur content of gasoline from 30 to 10 ppm. Additionally, the EPA is proposing to either maintain the current 80 ppm refinery gate and 95 ppm downstream caps or lower them to 50 and 65 ppm, respectively. The current implementation date is January 1, 2017. These Tier 3 gasoline sulfur specifications are similar to levels already being achieved in California, Europe, Japan, South Korea and several other countries. Furthermore, the EPA also has proposed a three-year delay for small refiners and small-volume refineries processing 75,000 barrels of crude oil per day or less.

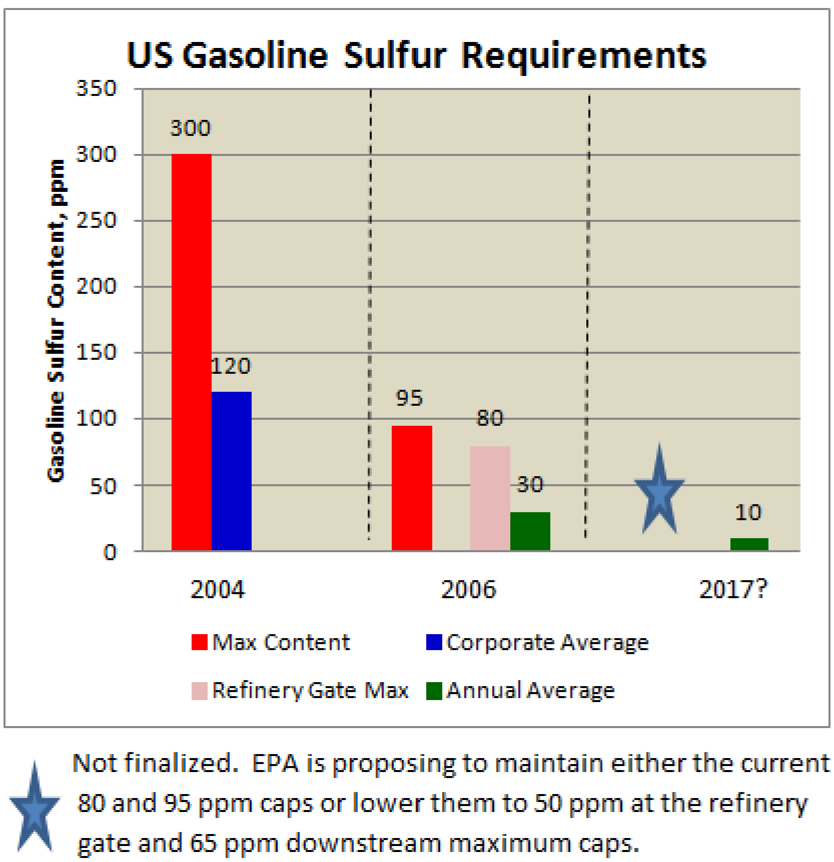

Figure 1 – US Gasoline Sulfur Requirements

Implications of Tier 3 on Refinery Processing

The gasoline pool is composed of gasoline boiling range hydrocarbons from several sources in the refinery. A simplified refinery configuration is shown in Figure 2 with typical gasoline pool blending components such as 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 sulfur (typically <1 ppm) except for the FCC gasoline. Not only does the FCC gasoline have the highest sulfur content, but it is typically also the largest volume component of the gasoline pool. As a result, FCC gasoline sulfur will have to be reduced to 20-30 ppm in order for a typical refinery to meet the proposed Tier 3 regulations.

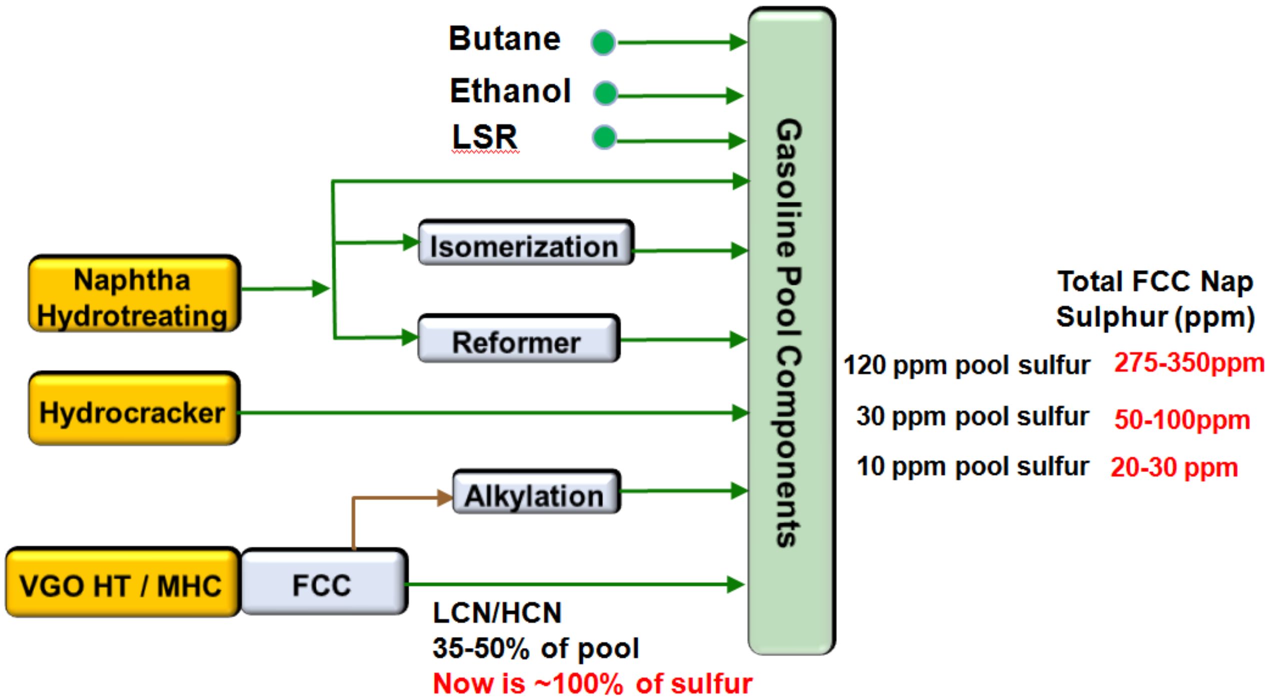

Figure 2 - Typical Gasoline Blending Pool Components

Current Industry Practices for Meeting Tier 2 Specifications

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

- ***Pretreatment of FCC feed***: Pretreatment reduces the sulfur of the FCC feed, which in turn lowers the sulfur of the FCC products including FCC gasoline.
- ***Post treat FCC gasoline:*** Post-treatment directly reduces FCC gasoline sulfur.
- ***Combination of FCC feed 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.

Comparison of the FCC Gasoline Sulfur Reduction Options

Most US refiners have FCC pretreat units which hydrotreat at least a portion of the FCC feed; however, very few U.S. refiners (less than 15%) are able to achieve Tier 2 specifications with just FCC pretreat. Approximately 70% of U.S. refiners utilize a combination of FCC pretreat and post-treatment to achieve the required sulfur level.

It is possible to produce Tier 3 quality FCC gasoline blend components by adding feed pretreatment or increasing the severity of an existing FCC pretreat unit. In addition to sulfur reductions of all the FCC products, adding or improving FCC pretreat saturates more aromatics, reduces nitrogen and removes metals, which improves crackability for increased FCC conversion and volume gain.

It is also possible to produce Tier 3 quality FCC gasoline blend components by adding FCC gasoline post-treatment or increasing the severity of the current post-treat unit. FCC gasoline contains a large amount of olefins, which are concentrated in the light fraction while the sulfur is concentrated in the heavy fraction. One of the unique features of the current post-treat technologies, as compared to conventional naphtha hydrotreating, is that they preferentially remove the sulfur in the heavy fraction while minimizing the olefin loss in the light fraction. Post-treatment does invariably result in octane loss due to saturation of some of the olefins, and increasing the severity to meet Tier 3 regulations can lead to increased octane loss.

The primary considerations when evaluating different options are capital investment, margin improvement, feedstock flexibility and cycle life duration and economics. Capital investment and operating costs are higher for a grassroots FCC pretreat unit versus post-treatment options. Increasing severity of a currently operating FCC pretreat unit may require capital investment to overcome unit limitations such as additional reactor volume to provide an acceptable cycle life at the more severe processing conditions, increased recycle or make-up gas compressor capacity, or heat train and furnace modifications. Likewise, increasing severity of a FCC post-treat unit may require capital investment to add additional hydrofinishing polishing capability to reduce the product sulfur to meet the proposed Tier 3 regulations.

Once the desired level of additional desulfurization required to meet Tier 3 gasoline specifications either by pretreatment or post-treatment is understood, the capital investment requirements for new construction or revamp of existing units can be evaluated versus economic return of each potential option. Figure 3 compares and summarizes the key characteristics of FCC feed pretreat versus FCC gasoline post-treat.

FCC Feed Pre Treatment

30 ppm FCC Gasoline Sulfur Achievable
10 ppm FCC Gasoline Sulfur Challenging
Reduced Sulfur in LCO
Reduced Sox Emissions
Increased FCC Conversion
Increased FCC Pre-Treat Volume Gain
Increased Feed Flexibility
Reduced FCC OPEX
Higher CAPEX
Higher FCC Pre-Treat OPEX

Post Treat FCC Naphtha

<10 ppm Sulfur Achievable
Lower CAPEX & OPEX than FCC Pre-Treat
Octane Impact on Pool

Figure 3 - Summary of FCC Pretreatment and Post-Treatment Key Characteristics

Today, all three options – FCC pretreatment, FCC post-treatment and a combination of the two processes – are currently employed in various refineries since similar economic evaluations were conducted when the industry invested a little more than a decade ago to meet Tier 2 regulations.

In parallel, catalyst technology providers have been focused on specific catalyst developments to improve the catalysts currently used in FCC pretreat and post-treat units in order to minimize and in some cases avoid capital investments to meet Tier 3 objectives.

Catalyst Developments in FCC PreTreat

To meet the demand for improved catalysts in FCC pretreat service to meet Tier 2 regulations, Criterion Catalysts & Technologies L.P. (Criterion) developed and commercialized the ASCENT™ family of catalysts with DN-3551 NiMo and DC-2551 CoMo. Criterion has continued to invest heavily in R&D and has developed and commercialized the CENTERA™ family of catalysts for FCC pretreatment: DN-3651 NiMo and DC-2650 CoMo.

Figure 4 below highlights the continuing evolution of FCC pretreat 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 commercialized CENTERA™ DN-3651 will assist refiners in meeting the proposed Tier 3 regulations.

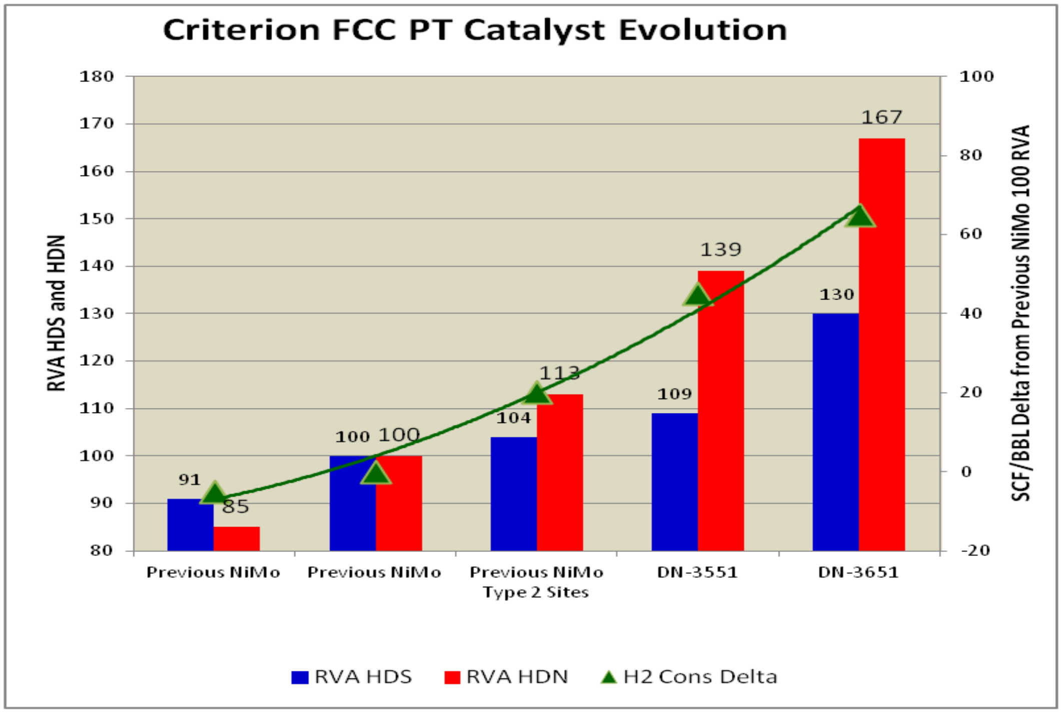

Figure 4 - Criterion FCC PT Continued Catalyst Evolution

Criterion's newest CoMo FCC pretreat catalyst, CENTERA™ DC-2650, is often used in conjunction with CENTERA™ DN-3651, especially in lower pressure units to optimize HDS and HDN performance.

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

Capital Avoidance from New Catalyst Developments in FCC Pretreat

Many refiners have invested heavily in robust FCC pretreat 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 minimize capital investment as well as improve refinery profitability. The FCC pretreat unit plays a critical role in optimizing FCC performance. Removal of sulfur 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 pretreat 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 pretreat 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

The following examples are derived from Criterion's industry-wide database to illustrate a comparative analysis of the performance improvements expected for FCC Pretreat units using drop in catalytic solutions with Criterion's CENTERA products. In addition to product quality improvements, estimated improvements for FCC conversion are also provided.

For a medium pressure unit with average feed properties and a typical 36 months cycle life currently producing 1000 ppm product sulfur, the more severe FCC pretreatment operation to produce FCC gasoline sulfur in the 20-30 ppm range requires FCC product sulfur to be in the 300 ppm range and cycle life is still more than 24 months. In addition, the product nitrogen is reduced significantly and both hydrogen consumption and FCC conversion are increased.

Feed Gravity, API	Feed Sulfur, wt%	Feed Nitrogen, ppm
20	2.0	2000

Operating Mode	Pressure, psig	LHSV, hr^{-1}	Cycle Life, mon	Product Sulfur, ppm	Product Nitrogen, ppm	H2 Consumption, SCFB	FCC Conversion, vol%	FCC Gasoline Sulfur, ppm
Current Typical	1000	1	36	1000	1000	500	Base	100
Tier 3	1000	1	26	300	500	600	+2.3	25

For a higher pressure unit with average feed properties and a typical 36 months cycle life currently producing ~600 ppm product sulfur, the more severe FCC pretreatment operation to produce FCC gasoline sulfur in the 20-30 ppm range requires FCC product sulfur to be in the 300 ppm range and cycle life is ~30 months. In addition the product nitrogen is reduced significantly and both hydrogen consumption and FCC conversion are increased.

Feed Gravity, API	Feed Sulfur, wt%	Feed Nitrogen, ppm
18	2.5	2500

Operating Mode	Pressure, psig	LHSV, hr^{-1}	Cycle Life, mon	Product Sulfur, ppm	Product Nitrogen, ppm	H2 Consumption, SCFB	FCC Conversion, vol%	FCC Gasoline Sulfur, ppm
Current Typical	1500	0.7	36	600	750	700	Base	60
Tier 3	1500	0.7	31	300	450	800	+1.9	20

The improvements in FCC performance and yields from higher severity operation of the FCC pretreat unit is 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 sulfur 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, 2 and some 3-ring molecules go to the LCO cut while most 3-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 center of the molecule with the relative reaction rates for saturation of a simple polynuclear aromatic compound depicted in Figure 5 below.

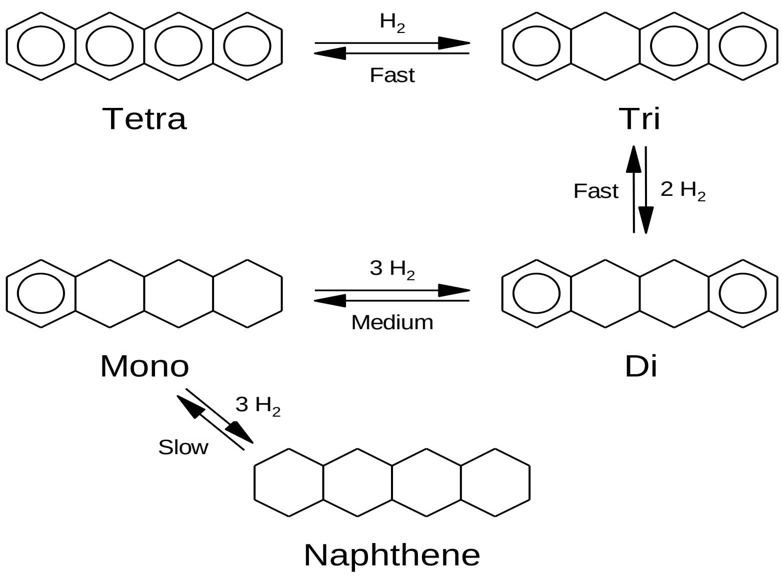

Figure 5 - Relative Aromatic Ring Saturation Rates

The critical operating parameters that influence these reaction rates are hydrogen partial pressure and operating temperature. In order to maximize aromatics saturation for a given unit, it is important to maximize hydrogen purity and hydrogen availability to optimize hydrogen partial pressure, particularly at the reactor outlet. In addition to maximizing hydrogen partial pressure, operating temperatures must be increased to maximize 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. Figure 6 depicts the relationship between aromatics saturation and operating temperature at a fixed hydrogen partial pressure.

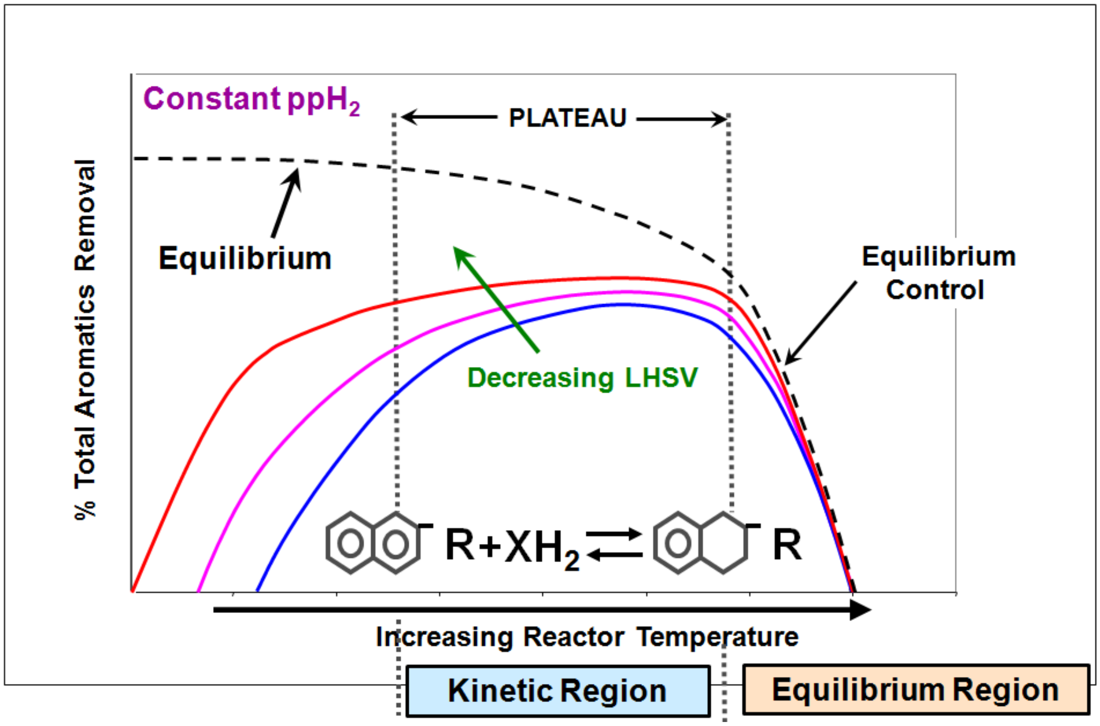

Figure 6 - Relationship Between Reactor Temperature and Aromatics Removal

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

Increased aromatic saturation has an impact on the distribution of the sulfur containing aromatic molecules in FCC products. The following discussion illustrates the impact of FCC pretreat severity on a typical polynuclear aromatic species and the impacts on product sulfur 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 the majority of the molecule unconverted, resulting in higher coke and or cycle oil yield. This results in higher sulfur in the unconverted cycle oils or higher SO_x 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 sulfur in this molecule ends up in the cycle oil or coke. This is illustrated in Figure 7.

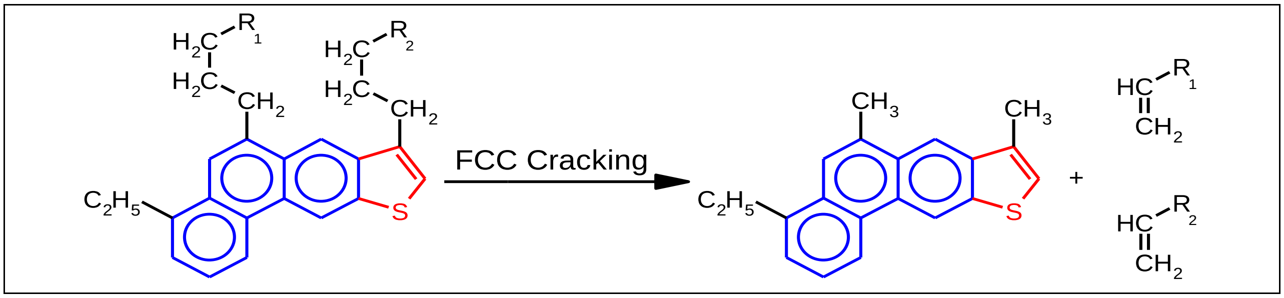

Figure 7 - Impact of Untreated Aromatic Molecule on FCC Products

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 sulfur atom remains integrated with the aromatic benzothiophene, the probability of secondary cracking is low and it remains in the gasoline boiling range. This is illustrated in Figure 8.

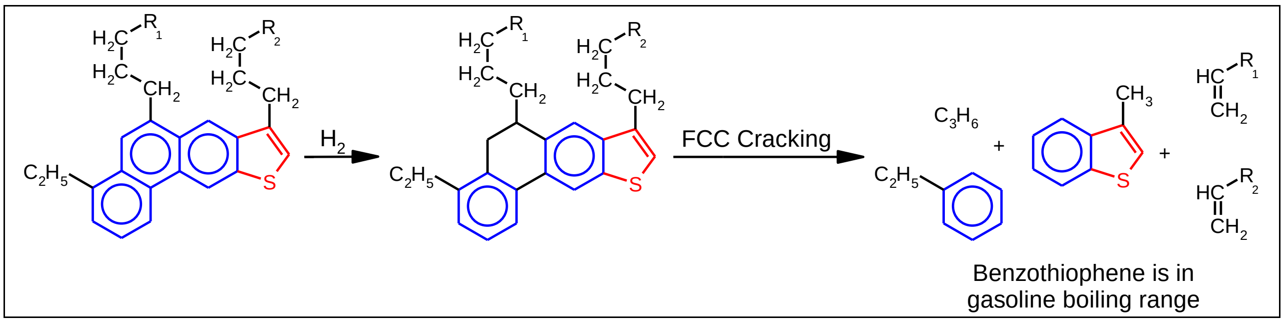

Figure 8 - Impact of Low Severity Aromatic Treatment on FCC Products

Higher Severity FCC Pretreatment

Increased aromatic saturation by increasing severity in the FCC pretreat unit converts the polynuclear aromatic (PNA) to a single ring compound. Secondary cracking of the thiophene yields H_2S, which removes the sulfur from the gasoline boiling range. This is illustrated in Figure 9.

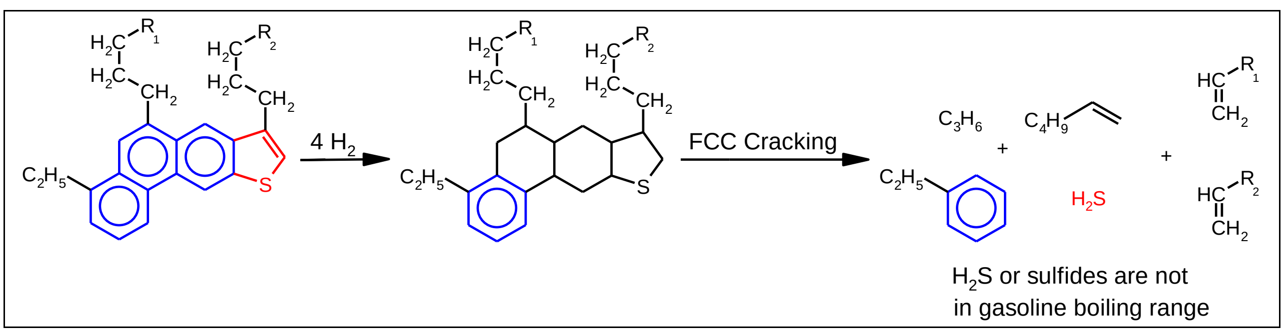

Figure 9 - Impact of Higher Severity Aromatic Treatment on FCC Products

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 sulfur removed from the gasoline fraction. This is illustrated in Figure 10.

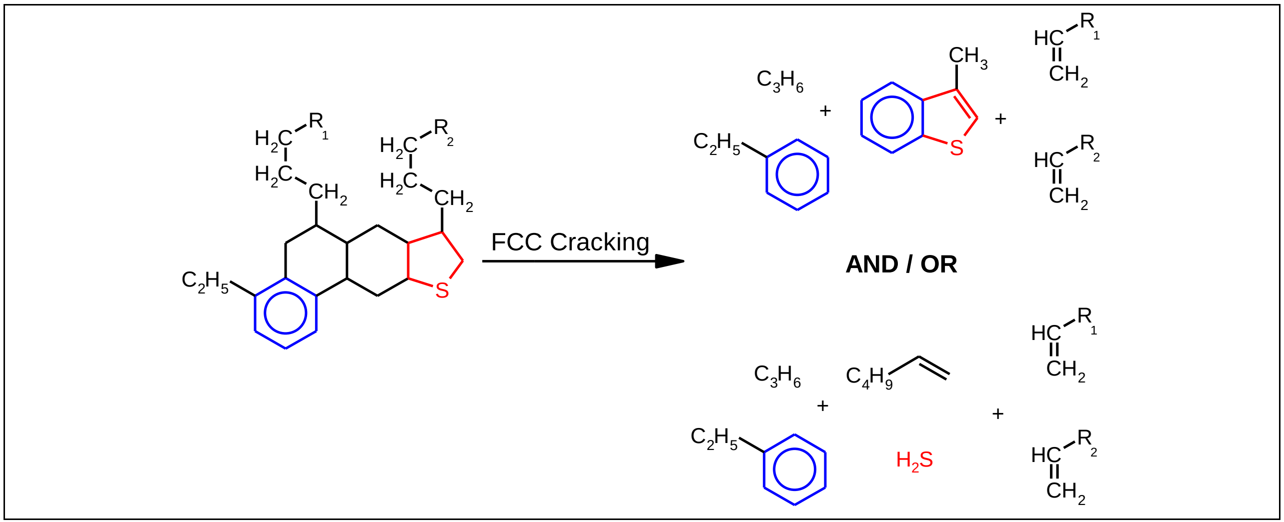

Figure 10 - Impact of Basic Nitrogen Inhibition on FCC Products

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 sulfur in the FCC products. Thus, improved nitrogen removal also leads to a reduction in gasoline sulfur.

In conclusion, the increased HDS achieved by increased FCC pretreat severity along with the higher saturation and denitrification are critical in reducing FCC gasoline sulfur while still achieving reasonable cycle life. Applying best available catalyst technologies opens the door to improved product quality and maximum profitability.

Another recent development that will impact options for meeting Tier 3 regulations is the increased use of light tight oil. The lower sulfur, lower aromatic vacuum gas oils from these crudes require less severe processing to meet the desired targets. However, it is important to note that pretreating FCC feed allows a greater degree of feed flexibility in terms of crude sources and quality. Adjustments in FCC pretreat operation can account for feed changes without impacting the FCC performance or product quality. This flexibility provides the refiner an opportunity to process a wide range of crudes to take advantage of market trends and maximize profitability of every asset.

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

Since each individual feed and set of operating conditions presents specific challenges, Criterion employs the use of detailed, customer-specific pilot testing in our extensive research and development facilities to ensure the reliability of estimates for the stable production of FCC feed streams that will meet the refiner's requirements for Tier 3 fuels. Some of the future challenges to this approach surround the complexity of blending and scheduling as it relates to catalyst changes for pretreat units, which may increase in frequency due to the changes in severity of operation. There are many creative solutions our customers employ to manage products during change out periods including management with storage facilities, changes in refinery crude slate as well as adjustments to cut points to reduce FCC naphtha sulfur. With the proper application of high-performance FCC pretreat catalysts and innovative solutions, Criterion catalysts offers an attractive option to meet future Tier 3 regulations.

Catalyst Developments in FCC Post-Treatment

Likewise Criterion has continued R&D development of FCC gasoline post-treat catalysts with focus on maximizing desulfurization activity and selectivity with minimal olefin saturation. Criterion currently produces a Generation 1 FCC post-treat catalyst that is employed in FCC gasoline post-treat with a new catalyst in the development stage. The new catalyst is designed for maximum sulfur reduction while minimizing octane loss.

The key challenge has been to develop catalyst nanostructures that selectively maximize desulfurization sites, while minimizing active sites associated with hydrogenation of molecules.

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

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

Catalyst development for the finishing catalyst was conducted at Criterion's R&D centers, where enhanced experimentation equipment were employed. This experimentation technique allows multiple experiments to be conducted simultaneously, while analyzing and statistically organizing data, thus enhancing the chances of a significant catalyst development break-through. Our focus in the development of this catalyst was to reduce the sites involved in hydrogenation and enhance the sites involved in the direct desulfurization route. This involved both the development of new support material and enhanced surface metal chemistry to maximize selective desulfurization, while minimizing undesirable reactions.

Table 1 shows the properties of the feed used for post-treat catalyst testing. This feed was collected from a Gulf Coast refiner and represented feed used for feed polishing to reduce sulfur content.

Table 2 shows the product properties for two catalyst generations collected at various process operating conditions Various studies were conducted where various 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 sulfur removal and olefin retention than the previous catalyst generation.

Total Sulfur, ppmw Mercaptan Sulfur, ppmw	159 52
Bromine Number	24
API	47.0
PIONA Analysis, wt.% Napthenes Iso-Paraffins n-Paraffins Cyclic Olefins iso-Olefins n-Olefins Aromatics	 14.55 21.32 8.47 4.62 4.37 2.86 44.12
Simulated Distillation D-3710C-7890	
IBP,F	140
5, wt.%	164
10	183
30	230
50	287
70	340
90	395
99	438
FBP	446

Table 1 – Polishing Reactor Feed Properties

Temp, F	Pressure, psig	LHSV , 1/hr	Gas Rate, SCF/Bbl	Gen 1 Catalyst		Gen 2 Catalyst	
				S ppm	Br. No	S ppm	Br. No
Base	Base	Base	Base	Base	Base	-	+
Base+	Base	Base -	Base	Base	Base	-	+
Base+	Base	Base +	Base	Base	Base	-	+
Base+	Base +	Base	Base	Base	Base	-	+
Base+	Base +	Base	Base +	Base	Base	-	+

Table 2 – Product Properties

Summary

Proposed Tier 3 regulations reducing average gasoline sulfur content to 10 ppm will require further reduction of the FCC gasoline sulfur. Refiners are currently evaluating their options which include (1) increasing FCC PT severity or expanding FCC pretreatment assets, (2) increasing FCC gasoline post-treatment severity or expanding FCC post-treat assets or a combination of the two.

Opportunities exist to minimize or eliminate these investments by use of advanced catalyst technologies to attain the longest possible cycle life at the reduced sulfur requirements in the FCC pretreatment products or to reduce the FCC gasoline sulfur in the FCC gasoline post-treatment unit while minimizing octane loss.

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[i] EPA, "EPA Proposes Tier 3 Tailpipe and Evaporative Emission and Vehicle Fuel Standards", May 2013

[ii] Vito Bavaro, Patrick Gripka, Dr. Alexei Gabrielov and Dr. Changan Zhang, "Value Driven Catalyst Developments in FCC Pretreatment Service", AIChE Sping Annual Meeting, April 2006

[iii] Carlson, Kevin D., De Haan, Desiree J., Jongkind, Herman H., Shivaram, Andy, "Continued Gains in FCC Pretreat Performance – Gains in Process Capability Used Effectively in Clean Fuels Production", ERTC, November 2008.

[iv] Gillespie, Bill, Gabrielov, Alexei, Weber, Thomas, Kraus, Larry, " Advances in FCC pretreatment catalysis", PTQ Catalysis, 2013, vol 18 No. 2.