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Turning a Tier 3 Profit

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Turning a Tier 3 Profit

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Introduction

In the highly competitive refining market, profitability is not a benefit of successful business, but rather a necessity to sustainable business. As such, profitable solutions and technologies are inherently key to a refiner's success, providing the driving force to transition from survival in tough markets to thriving sustainable development. The industry faces threats on many fronts which challenge profit margins and business development. Growth in challenging crude and product markets requires the careful application of best practices for asset utilization and strong technical solutions to adapt to changing constraints.

Environmental regulations have become increasingly challenging for refiners to adapt profitable solutions while maintaining feedstock and product flexibility. Notably, the continued reduction in refined product sulfur specifications has revolutionized the landscape of the industry over the last decade with the continued rise of importance for hydrotreating solutions within refinery complexes. This saga will continue as the industry moves toward the future Tier 3 regulations where the production of less than 10 ppm ultra-low sulfur gasoline (ULSG) will be required in 2017. However, technology has answered the call and responded with resounding success. Several refiners have already implemented strategies to meet Tier 3 blend stock requirements providing profitable, flexible solutions. This is a testament to the industry's commitment to enriching the environment and communities in which we provide energy solutions.

Tier 3 Strategies

Many of the blend components of typical gasoline product streams are very low in sulfur and thus achieving Tier 3 specifications for most refiners requires focus on a limited number of blend components in the gasoline pool. Generally these blend components being: untreated light straight run gasoline; straight run naphtha; natural gasoline; purchased blend stocks; and FCC (fluid catalytic cracking unit) gasoline. Most of these components are small portions of the overall pool and often fit into a simple model for sulfur reduction consisting of: inclusion in existing treating facilities; additional conventional treating; or exclusion from the blend pool. The primary target stream for reduction in sulfur is FCC gasoline, since in most refineries it is the largest blend component as well as the highest sulfur contributor to the blend. In most applications a target of 20-30 ppm sulfur in FCC gasoline is required to meet the less than 10 ppm specification in the blended gasoline product streams set by Tier 3 regulations. FCC gasoline is also a large contributor of octane barrels to the gasoline pool and retention of superior blend properties is highly important when considering options for stream sulfur reduction. This is where the challenge presents itself in providing profitable solutions for a superior blend component low in sulfur that does not result in the hydrogenation of valuable olefins found in FCC gasoline.

Reduction of FCC gasoline sulfur is achieved today in industry by way of multiple approaches; the pretreatment of FCC feed streams, the post treatment of FCC gasoline, or a combination of the two. The post treatment of FCC gasoline, unlike conventional hydrotreating, targets the selective removal of sulfur from the feed stream while limiting hydrogenation of the feed to minimize the reduction of valuable olefins in the stream. These olefins contribute to the higher octane of FCC gasoline and are inherently essential to the overall value of the stream as a blend component.

Established processes for post treatment have demonstrated successful production of Tier 2 blend components without significant losses of octane. However, there remains some degradation in product value for this method of sulfur reduction. Further reductions in sulfur using typical post treatment methods to achieve Tier 3 levels require increases in operating severity which can result in additional octane loss creating a significant economic penalty.

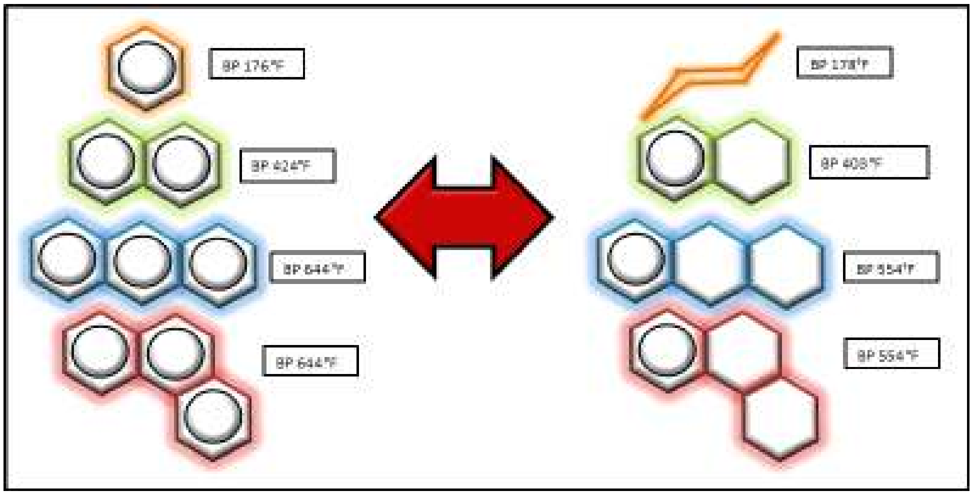
Alternatively, the pre-treatment of FCC feed streams removes heteroatoms including sulfur and nitrogen resulting in favorable reductions in product sulfur contents for all FCC products. In addition, pretreatment also removes metals and aromatics from the feed streams reducing FCC catalyst poison effects and improving feed crackability respectively. To achieve additional reductions from existing pre-treatment facilities requires higher severity operation which can result in reduced catalyst life cycles. Recent developments from Criterion for both processes have provided favorable results for the application of potential drop-in solutions in existing facilities.

Benefits of FCC Pretreat Strategy

Synergies between an FCC pretreat unit and an FCC may start with, but are not limited to, reduced sulfur in products. Pre-treatment of FCC feed provides significant upgrades in feed quality for an FCC resulting in improved yields and beneficial distribution of heteroatoms in the product streams. The hydrogenation of FCC feed streams is necessary for deep desulfurization especially when operating at higher sulfur conversion targets for Tier 3 FCC gasoline production. This hydrogenation of feed results in the removal of metals and nitrogen which are poisons to FCC catalysts as well as the saturation of aromatics, improving the conversion potential of feed streams. More highly hydrogenated feed streams achieve higher conversion in an FCC given constant operating conditions.

It is important to note also that conversion in any FCC is a choice, meaning that the desired product slate is flexible within heat balance constraints with the adjustment of operating parameters. Since an FCC must remain in heat balance, the introduction of upgraded feed streams results in lower coke production and thus higher catalyst to oil ratios. The unit responds by increasing the circulation of catalyst from the regenerator to the riser to generate similar coke make and remain in heat balance. The increased catalyst to oil ratio provides a boost in conversion of feed to saleable liquid products. Typically, day to day changes in FCC conversion are made by controlled adjustments in the riser top or reactor temperature. These changes influence the operation of the regenerator slide valve controlling the contact of hot catalyst with feed injected at the bottom of the riser. However, feed preheating is also used to influence conversion by pre-atomization of feed prior to entering the mixing zone of the riser. Feed preheat also impacts catalyst to oil ratio by playing a role in the amount of hot catalyst required to achieve the target riser top temperature. A higher degree of feed preheat results in a reduced need for hot catalyst from the regenerator and thusly a reduction in conversion by indirect effect on catalyst to oil ratio. Additionally, the recycling of products such as heavy cycle oil and slurry oil increases coke deposition on catalyst resulting in conversion control, regenerator heat balancing, and black oil minimization. Beyond day to day operating parameter control, the very nature of a circulating fluidized bed allows for the adjustment of catalyst formulations and custom control on catalytic activity throughout the operating cycle. It is this dynamic nature which plays well into the synergies of FCC pretreat and FCC operation yielding market trending control for profit maximization.

The addition of hydrogen to FCC feed results in an increase in feed API gravity due to aromatic saturation and removal of heteroatoms, which results in an increase in total liquid volume yield. This increase in feed gravity is associated with a shift in feed boiling range since the boiling point of the saturated aromatic structures is lower. The following graphic displays this effect:



Aromatic rings do not crack in the FCC, however saturated molecules do creating improved feed crackability. The saturation of rings in polynuclear aromatics increases the available molecules for conversion in the FCC. Additionally, the removal of nitrogen from FCC feed streams reduces the inhibition of cracking mechanisms critical to both FCC performance, as well as distribution of the remaining heteroatoms in FCC product streams. Targeting low FCC feed nitrogen levels results in more favorable distribution of sulfur in FCC product streams with lower FCC gasoline sulfur levels. This indicates that FCC pretreat hydrodenitrification (HDN) and hydrodearomatization (HDA) performance, not solely hydrodesulfurization (HDS), are critical influencing factors in the production of Tier 3 quality FCC gasoline.

When treating FCC feed streams the saturation of polynuclear aromatic species can be used to influence the distribution of aromatics in FCC product streams. The FCC will remove functional groups from aromatic rings, while leaving the rings intact. Since the boiling range of single-ring aromatics falls in the same range as gasoline, reducing polynuclear aromatics to single unsaturated aromatic species increases the production of FCC gasoline given the same operating conditions. Di and tri aromatic species have boiling points that fall in the typical LCO range resulting in conversion to LCO after functional groups and saturated species are removed. Thus the saturation of heavy polynuclear aromatic species provides an increase in conversion of feed to products in the FCC including gasoline and LCO. Inherently, this relates to the profitability achieved from feed treating, but the removal of aromatics is also essential in deep desulfurization and denitrification of feed streams. As higher conversion levels of sulfur and nitrogen are required in hydrotreating, the remaining molecules containing sulfur and nitrogen become increasingly more difficult to treat due to the molecular structure associated with aromatic species. In order to remove these heteroatoms, hydrogenation of the molecular structure is required to expose the occluded heteroatoms.

The influence of feed nitrogen in the FCC is key in understanding the synergy between FCC pretreat operation and FCC response. Nitrogen inhibits the catalytic function in an FCC and reduces catalytic cracking reactions, including secondary cracking mechanisms. This reduces the conversion of feed to products in the FCC, as well as the distribution of heteroatoms in FCC product streams. Since Tier 3 regulations are very stringent with respect to gasoline sulfur, the focus of heteroatom distribution is heavily weighted toward sulfur in FCC gasoline. When secondary cracking mechanisms are inhibited by higher feed nitrogen values there is an increase in sulfur found in the gasoline fraction. However, reducing feed nitrogen increases the conversion of organic sulfur molecules to H2S and liquid products. This relationship between feed sulfur and nitrogen implies that when feed streams are treated to reduce nitrogen, the feed sulfur can be increased while sustaining Tier 3 quality FCC gasoline production.

Case Studies

The following case studies explore the strategies of two separate refiners employing latest generation FCC pretreat catalyst technology to maximize profitability. The three main areas of profit generation when considering high severity FCC feed pre-treatment are: hydrotreater volume gain; FCC conversion enhancement; and, relevant to current trending markets, ultra-low sulfur diesel (ULSD) maximization.

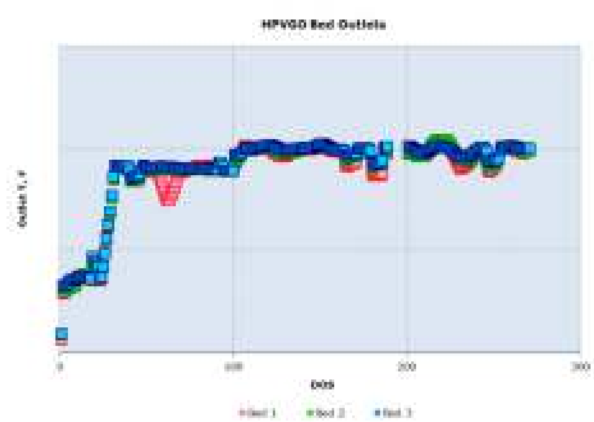
Marathon Petroleum Company (MPC) Catlettsburg

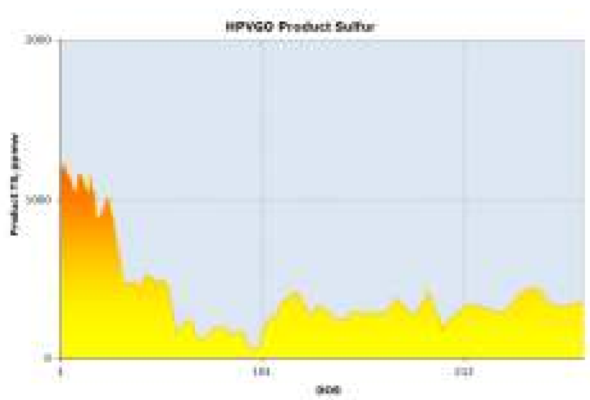
MPC operates the Catlettsburg refinery in Catlettsburg, Kentucky. The strategy for Tier 3 fuels production at the Catlettsburg refinery is higher severity FCC feed pre-treatment to reduce FCC gasoline sulfur for a combined gasoline pool blend below the required 10 ppm. The refinery recently replaced the catalyst in one of its two FCC pretreat units, upgrading to Criterion's latest generation CENTERA™ catalysts. The refinery operates two FCC pretreat units, the LPVGO and HPVGO, to hydrotreat 100% of the feed streams for the very large 100,000+ BPD FCC.

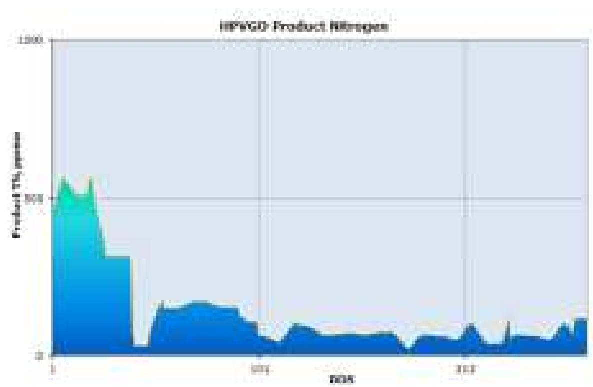
The two FCC pretreat units are operated in concert to reduce feed sulfur levels. The LPVGO operates at low pressure and is used to treat the "easy" feed streams sourced from the crude units including atmospheric gas oils and light vacuum gas oils. Processing roughly 40% of the FCC feed, this unit operates at lower conversion targets with a regenerated catalyst system. The HPVGO operates at higher pressure and severity to treat the more difficult feed streams including heavy vacuum gas oils and deasphalted oils. This unit processes roughly 60% of the FCC feed and is loaded with Criterion's latest generation CENTERA™ catalysts. With nearly a year of the anticipated four year cycle complete, the unit has provided stellar performance both with respect to hydrotreater operation as well as positive benefits for the FCC.

While MPC is not required to produce ULSG today, the team at Catlettsburg has been operating the HPVGO at higher temperatures and sulfur conversion to maximize unit profitability. The team is keen to recognize the value inherent to aromatics saturation of FCC feed streams and the conversion of excess hydrogen available to saleable liquid products.

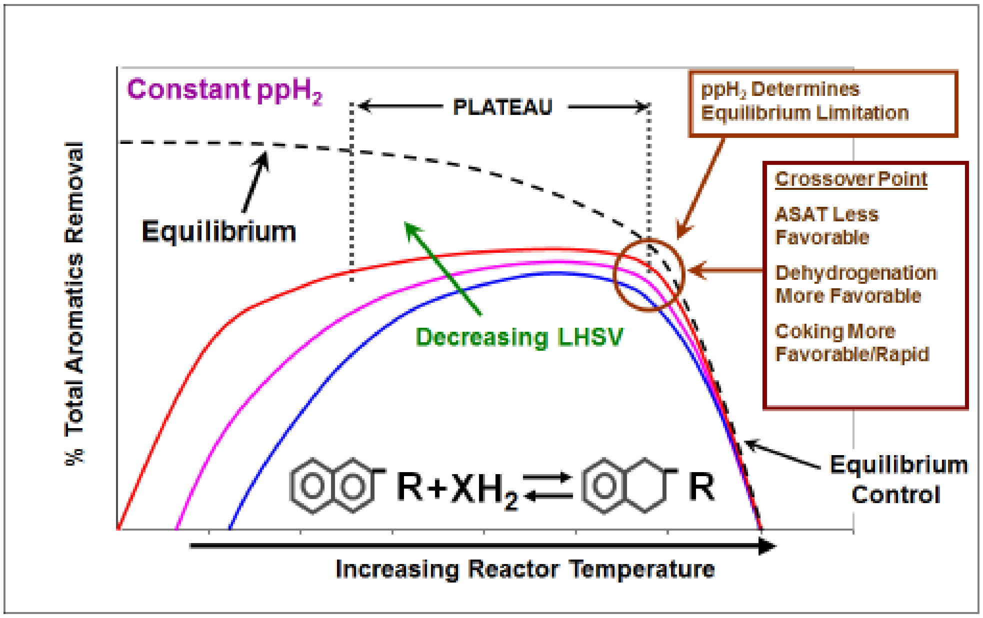
The refinery has a large volume of hydrogen generated from the production of reformate gasoline and a dedicated hydrogen plant. As such, this hydrogen is used by the various hydrotreaters in the refinery and is subsequently converted back into liquid products by the hydrogenation of hydrotreater feed streams. The HPVGO feed stream has excellent potential for upgrade by hydrogenation. The operation at elevated temperatures increases the saturation of aromatics due to the fact that the HDA reaction is kinetically driven up to an equilibrium constraint. Operation at elevated temperatures also further reduces FCC feed sulfur and nitrogen. Operating in this manner requires the careful attention of refinery engineering as well as operations staff, working in conjunction with Criterion to evaluate and maximize unit performance. These efforts are well rewarded with economic advantages for MPC.



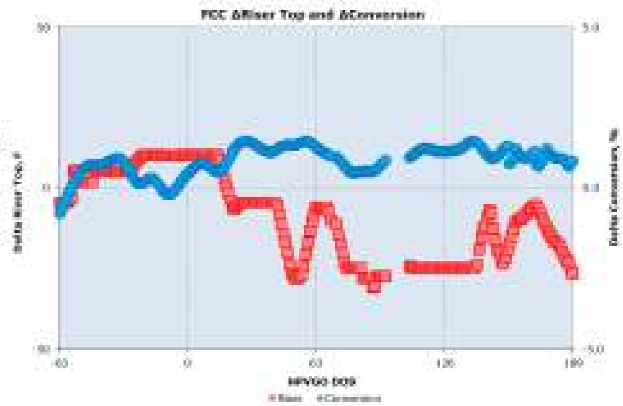


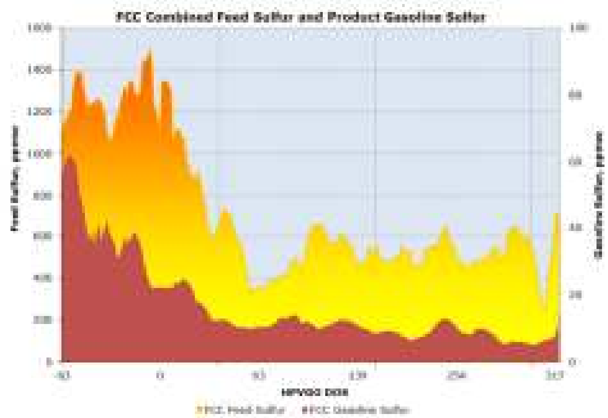


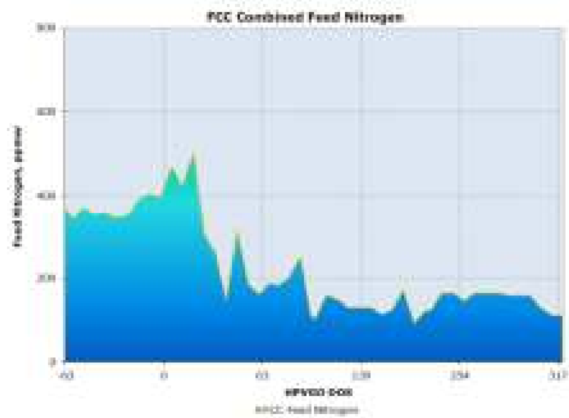
The previous charts depict the constant WABT of the HPVGO and associated product sulfur and nitrogen levels. The unit is expertly operated in such a manner to target equal bed outlet temperatures at the lowest point required to achieve the peak aromatic saturation. Peak aromatic saturation is a function of temperature and hydrogen partial pressure. This being the case, MPC strives to maintain the highest hydrogen partial pressure as operationally feasible, given a multitude of constraints. This is done while also minimizing reactor bed outlet temperatures within the peak window of aromatic saturation to minimize deactivation of the catalyst system. This rigorous attention to detail in operation results in excellent performance of the asset and long term stability of the catalyst system. The following chart displays aromatic saturation as a function of temperature and the influence of hydrogen partial pressure.

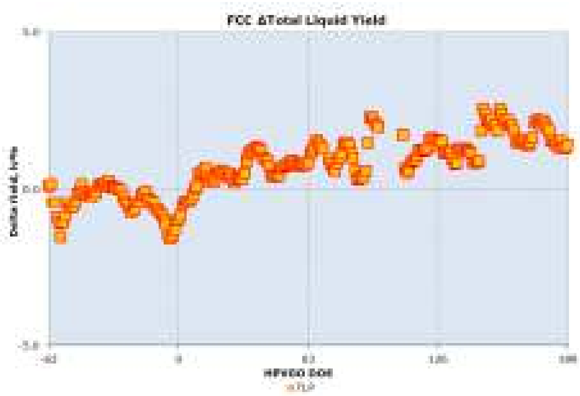


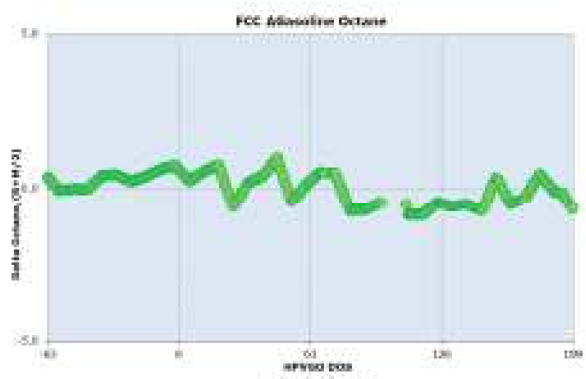
The subsequent value provided the FCC by operation of the HPVGO in aromatics saturation mode is shown in the following performance plots. The FCC feed rate has been increased significantly following the change in catalyst system in the HPVGO. Given constant feed properties and operating conditions, increasing feed rate in an FCC would typically result in reduced light olefin selectivity and gasoline olefinicity which relates directly to product octane due to a shift in riser hydrocarbon partial pressure. Increasing feed also can result in lower conversion due to residence time effects. However, the upgraded feed quality from feed pre-treatment has allowed the increase in feed rate, along with a reduction in riser top temperature with slightly elevated conversion and steady light olefins yield. Additionally, the FCC gasoline sulfur is extremely low, highlighting the benefits of exceptional HDN and HDA. The following plots depict changes from previous typical values for key performance indicators from the FCC as a function of time in relation to days on stream (DOS) for the HPVGO.



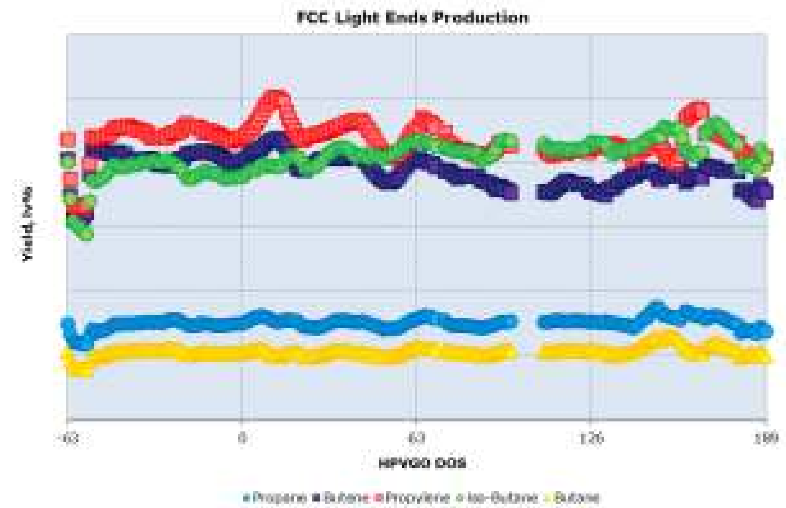




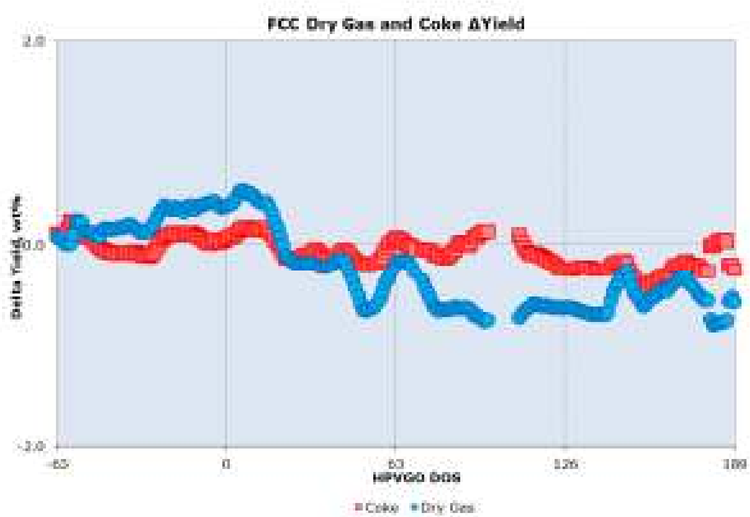




The FCC gasoline stream is not only very low in sulfur, but also retains superior blending qualities including high octane even at lower riser top temperatures. Reducing riser top temperature in the FCC reduces conversion of feed to gasoline and lighter products, but can also reduce the quality of the FCC gasoline. The retention of gasoline octane at lower riser top temperatures is a function of the increased feed crackability. Further, the retention of overall olefin selectivity illustrates the high potential value from feed pre-treatment associated with premium products such as alkylate and propylene.



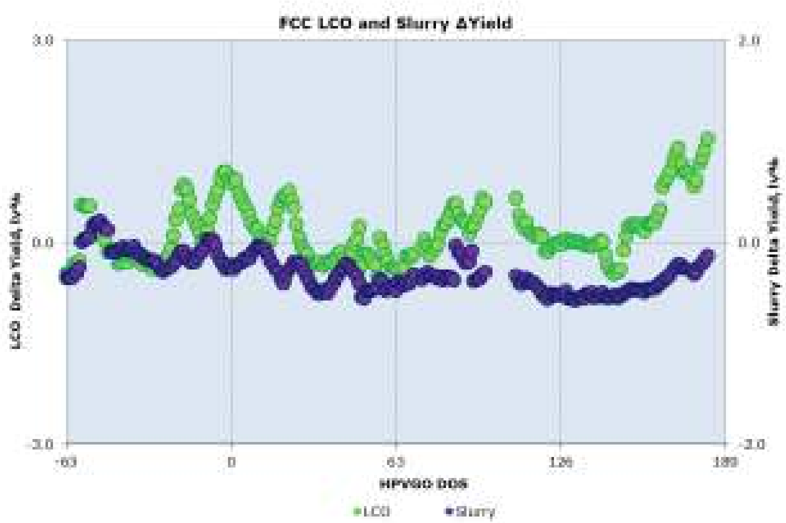
FCC units produce a large amount of low value light gases which typically are directed to fuel gas. These light gases (referred to as dry gas) are produced from over-cracking reactions which are enhanced by thermal cracking mechanisms. As regenerator temperatures increase, there is a higher ratio of thermal to catalytic cracking at the base of the riser. The increased feed hydrogen to hydrocarbon ratio for heavily hydrotreated feeds influences the coke deposition rate on catalyst, resulting in lower regenerator operating temperatures at a given conversion target. This in turn reduces the production of dry gases. This is illustrated by the significant reduction in dry gas yield following the upgrade in catalyst system and move to operation of the HPVGO in aromatics saturation mode. While the overall coke make remains similar to retain heat balance in the FCC and maintain similar conversion, the rate of coke deposited per pound of circulating catalyst is reduced, which leads to an increase in catalyst circulation rate and a reduction in regenerator temperatures.



Despite the potential advantages in gasoline production from increased severity hydrotreating in the HPVGO, MPC continues to operate the FCC at similar conversion targets primarily to capture margins in the distillate market. This flexibility allows MPC to capture margins in an either gasoline or diesel economy while continuing to make high quality gasoline streams. The maximization of distillate from an FCC can be accomplished via several routes:

- Fractionation adjustments to reduce gasoline end point and maximize LCO end point.
- Lowering Conversion By:
  - Decreasing reactor temperature
  - Decreasing catalyst activity
  - Higher feed preheat temperature
- Catalyst Optimization with respect to zeolite to matrix ratios
- Feedstock optimization:
  - Removal of diesel range material from feedstocks (general refinery distillate maximization)
  - Optimization of feed pre-treatment assets
  - Optimization of recycle streams

For MPC's Catlettsburg refinery, distillate maximization begins with optimization of crude fractions and is further extended to bottoms conversion. The conversion of FCC feed is adjusted to target balanced yields of both gasoline and LCO. LCO produced from an FCC must be further processed to meet ULSD specifications, but remains an incredibly valuable product from the FCC. Extending this flexibility further, accomplishing equal conversion at lower riser temperatures can allow for increased product recycle capability. The recycling of products, especially heavy cycle oil, can be employed to increase LCO production in an FCC and bottoms conversion resulting in black oil minimization. Note the observed slight reduction in Slurry and retention of LCO yields following the change out in catalyst system on the HPVGO.



The following tables offer a summary of the average benefits observed from operation of the HPVGO at higher severity for maximum aromatics saturation as well as the production of Tier 3 quality FCC gasoline:

FCCPT, HPVGO	Typical	Tier 3 Mode
Operating Mode	HDS	Arosat
TLP Volume Gain, lv% of Feed	Base	+1.25
Product Sulfur, ppmw	1000	300
Product Nitrogen, ppmw	500	100
API Gain, °	Base	+1.2
Diesel Make, lv% of Feed	Base	+2.1

FCC	Typical	Tier 3 Mode
Combined Feed Sulfur, ppmw	1200	570
Combined Feed Nitrogen, ppmw	360	160
Combined Feed API, °	Base	+0.7
Riser Top, °F	Base	-20
Conversion, %	Base	+0.5
Gasoline Sulfur, ppmw	46	10
Gasoline Octane, (R+M/2)	Base	Base
Dry Gas, wt% of Feed	Base	-0.51
TLP Volume Gain, lv% of Feed	Base	+1.75
Gasoline, lv% of Feed	Base	+2.34
LCO, lv% of Feed	Base	+0.18
Slurry Make, lv% of Feed	Base	-0.35

US Refiner

Another refiner operating a medium-high pressure FCC pretreat unit has employed an alternative strategy to capitalize on the value of high severity feed pre-treatment. The unit has been operating at high severity for quite some time with an alternative objective to the production of Tier 3 quality FCC gasoline. While the FCC downstream produces very low sulfur gasoline, the unit is primarily operated at high severity to produce a ULSD stream from the fractionation column work up section.

The unit was originally envisioned to solely treat gasoil streams for processing in the downstream FCC. However, the refinery has leveraged the unit's excess capacity and performance capability to increase overall distillate production refinery wide. This has enabled a significant increase in overall ULSD production from the refinery and has enabled increases in crude capacity, as well as flexibility.

The unit has been operating at higher severity with latest generation CENTERA™ catalysts to maximize overall refining yields. Not only does the unit produce a large volume of ULSD, but the unit also provides severely hydrotreated feed for the FCC. This FCC feed is significantly upgraded with very low nitrogen and sulfur as well as a significant degree of aromatic saturation. As such, the gasoline produced from the unit is very low in sulfur and suitable in blends to meet Tier 3 specifications.

Similar to MPC, this refiner capitalizes on the advantages afforded from the significant feed upgrade for the FCC unit. The unit is operated at very low riser top temperatures in the 930-945°F range achieving high levels of conversion. Additionally, this refiner employs the recycle of heavy cycle oil to maximize desired product yields from the FCC and minimize the production of slurry oil. In some cases the recycle of bottoms to extinction is accomplished with complete conversion of black oil to other saleable products.

Conclusions

The refining industry is rich with a tradition of technical solutions to strengthen our business when faced with challenging constraints and markets. In order to weather the cyclic nature of the business we must employ robust flexible solutions to meet future environmental regulations. Our market has become increasingly volatile, driving the need for flexible operating solutions which enable us to capture limited margins at the lowest possible capital investment. In many instances the application of latest generation catalytic advancements can provide both flexibility and low capital solutions for the production of Tier 3 fuels. Further, these catalyst systems can be used to provide flexibility and increase performance for existing assets. Many refiners have already transitioned to advanced catalytic solutions in the FCC pretreat arena. These can be used as a Tier 3 fuels strategy for the advantages afforded in FCC operation and yield selectivity, capitalizing on both clean fuels and profitability.

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