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Addressing Tier 3 Specifications in a Declining Gasoline Market: Options for the Future

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Addressing Tier 3 Regulations in a Declining Gasoline Market

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Introduction

Tier 3 gasoline regulations are expected to arrive in a market where the gasoline demand in the United States is forecasted to be stagnant or declining. Several factors contribute to the reduced demand including ethanol blending, market conditions, CAFE standards, and the increasing sales of hybrid cars along with import of surplus gasoline from Europe. At the same time, the market for middle distillates is expected to expand in the coming years. In many U.S. regions, the margins for middle distillate products are already significantly more profitable than for gasoline. As refineries reduce capacity or shut down to address the gasoline surplus, the diesel imbalance is not addressed and middle distillate supply suffers.

Staged implementation of Tier 2 gasoline regulations occurred in the early to mid 2000's when gasoline demand was strong and octane barrels were highly valued thereby making the investments more palatable. The current situation is different as many refineries have become octane long due to ethanol blending. The Tier 3 regulations are set to arrive in a market where gasoline is a lower margin product and octane loss is less of a concern. A minimum investment approach is typical for regulatory projects, but opportunities exist to increase profitability if gasoline can be shifted to distillate.

The Tier 3 regulation is expected to limit corporate average pool sulfur to 10 wppm which follows the worldwide trend. It is unclear whether the per gallon cap will be reduced from the current limit of 80 wppm. Implementation of the new regulations is expected between 2015 and 2018, and it is likely that incentives will be offered to reward early compliance. Additional restrictions on RVP and an increase in the minimum octane number are also possible and will affect the approach.

Addressing these complex issues and uncertainties will require innovative approaches and may offer opportunities to respond not just to Tier 3 but also the larger economic challenge of motor fuels imbalances.

Tier 2 Regulations

The current Tier 2 regulations require 30 wppm sulfur in the corporate gasoline pool. As the predominant source of sulfur in the gasoline pool, the FCC naphtha is the focus of Tier 2 efforts with 50 to 100 wppm sulfur typically required. The options for sulfur reduction in the FCC gasoline include pretreatment of the feed to the FCC and post-treatment of the FCC gasoline product. About 80% of refineries in the United States addressed the current regulations with post-treatment of the FCC gasoline alone or a combination of pretreatment and post-treatment.

Tier 3 Overview

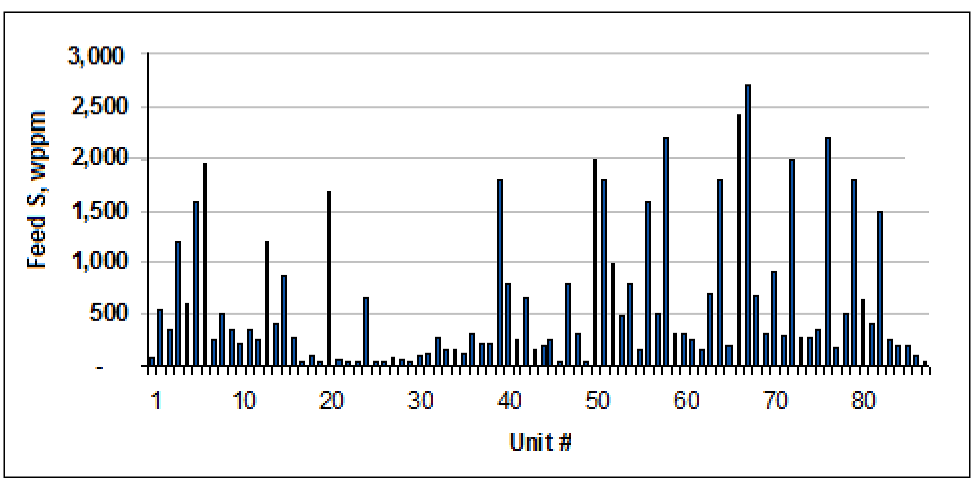
With the implementation of Tier 3 regulations, the requirement for the FCC naphtha will typically be 10-25 wppm sulfur with additional processing of orphan streams blended to the gasoline pool so that an overall pool sulfur limit of 10 wppm S is met. Many factors affect the optimum solution for Tier 3 in a particular refinery. In some cases, the existing Cat Feed Hydrotreater (CFHT) or FCC gasoline post-treater is capable of meeting the sulfur target for the FCC gasoline. However, the adequacy of existing facilities requires analysis beyond the ability of the unit to meet the sulfur target. The impact on product octane, hydrogen consumption, and cycle length are important for identification of a viable solution. The ability to synchronize with the FCC turnaround schedule is critical. The possibility of a future shift to a more sour crude slate should also be taken into account during Tier 3 planning.

The more stringent regulations will also limit the ability to blend low to moderate sulfur orphan streams directly to the pool. Raw Light Straight Run Naphtha (LSR), condensate gasoline (NGL), and pyrolysis gasoline will require hydrotreatment in most cases. The ability to handle Coker Naphtha at all times will also need to be addressed.

Worldwide Trend Towards 10 wppm Gasoline

The trend for lower sulfur fuels continues worldwide with Ultra Low Sulfur Gasoline (ULSG) already produced in California and other parts of the world. As noted previously, most refiners have chosen to meet Tier 2 regulations by installing FCC gasoline post-treatment units. About 90 of the 200 Axens licensed Prime-G+™ FCC gasoline selective hydrotreatment units were designed for 10 wppm sulfur in the gasoline pool. Prime-G+ units have been designed with feed sulfur as low as 30 wppm coming from high severity CFHT (Japan) and in refineries without pre-treatment processing a sour crude slate resulting in over 2,000 wppm feed sulfur to the Prime-G+ unit.

Figure 1: Prime-G+ Units Designed for 10 wppm Sulfur - Feed Sulfur Distribution



With many units in operation in Western Europe, Asia and California the performance at 10 wppm has been extensively proven. Several examples (USA and Europe) depict the ability of the Prime-G+ to produce ULS Light Cat Naphtha (LCN) and ULS Heavy Catalytic Naphtha (HCN). The Selective Hydrogenation reactor (SHU) offers extremely high conversion of light mercaptans and sulfides to heavier sulfur species, resulting in a light sweet ULS LCN cut to the gasoline pool. Production of ULS LCN is extremely important to achieve 10 wppm in the gasoline. High sulfur in the LCN would require overtreatment of the HCN and the resulting octane loss, hydrogen consumption and reduced cycle length.

Figure 2: Flow Scheme: Units A,B,C

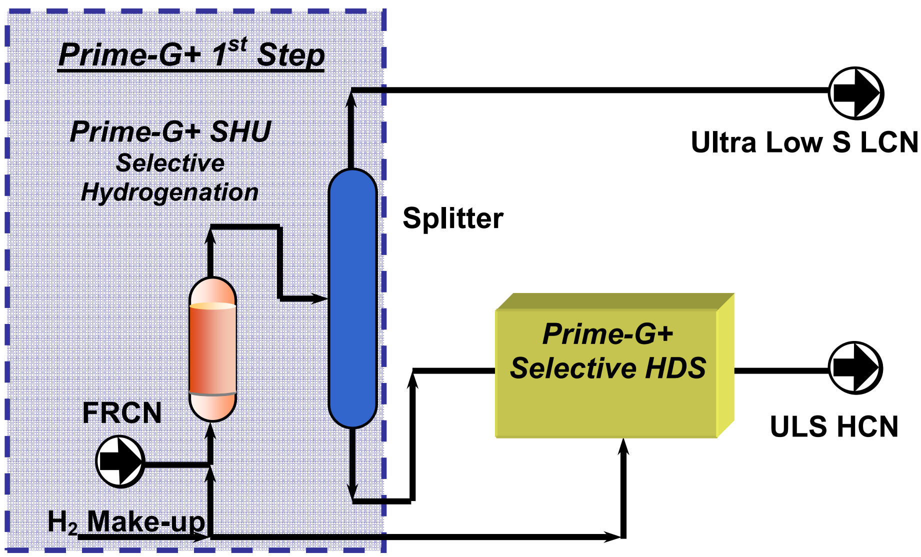


Figure 3: Unit A: ULS LCN

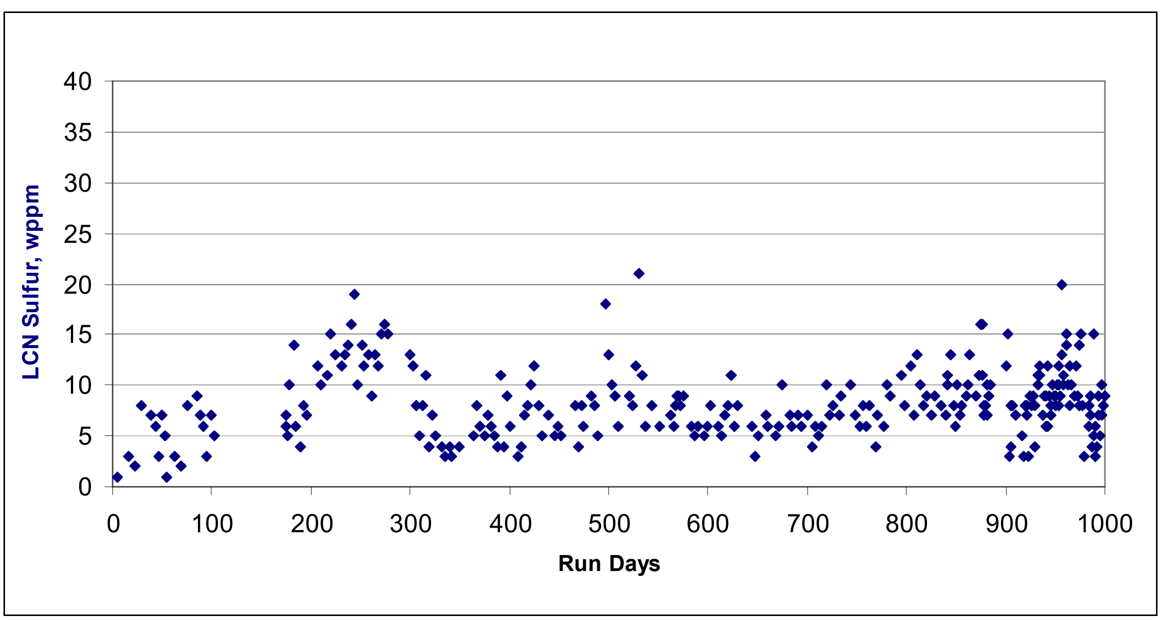
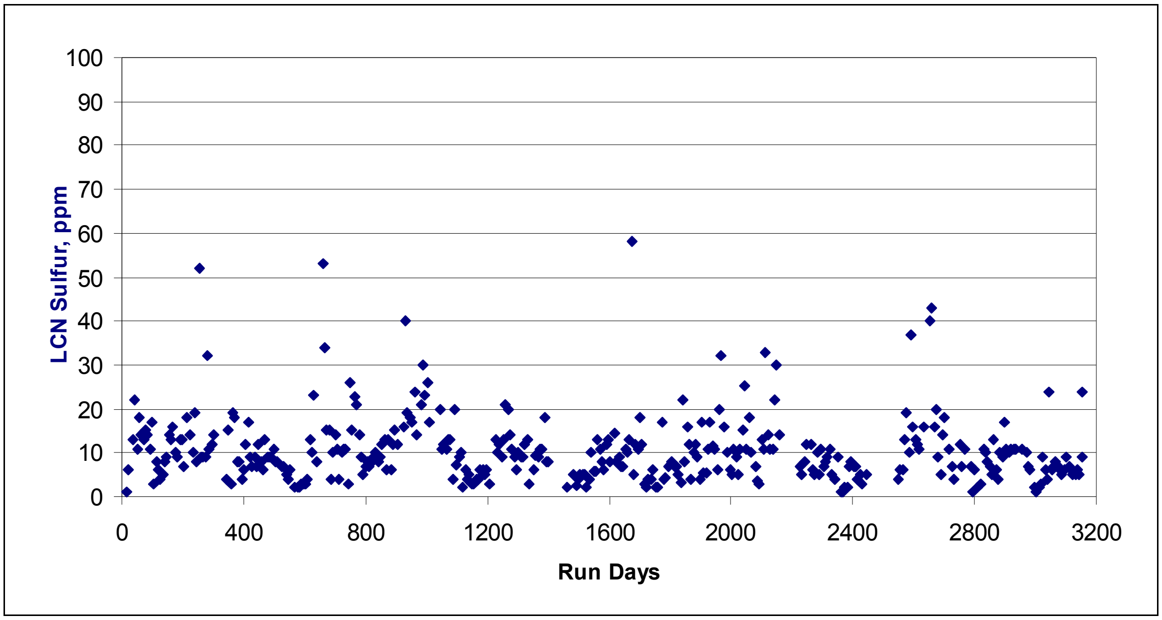


Figure 4: Unit B Cycle: ULS LCN



FCC gasoline post-treatment has proven effective for ULS FCC Gasoline production despite swings in the FCC gasoline feed quality. The example Unit A has consistently produced ULSG with great variation in the feed sulfur offering crude flexibility and protection from operational difficulty in the FCC. The operating data indicated are for the current cycle, which is on track to meet the FCC turnaround schedule. The Unit C also shows excellent product sulfur control at 20 wppm and below despite a wide variation in feed sulfur content.

Figure 5: Unit A ULS FCC Gasoline

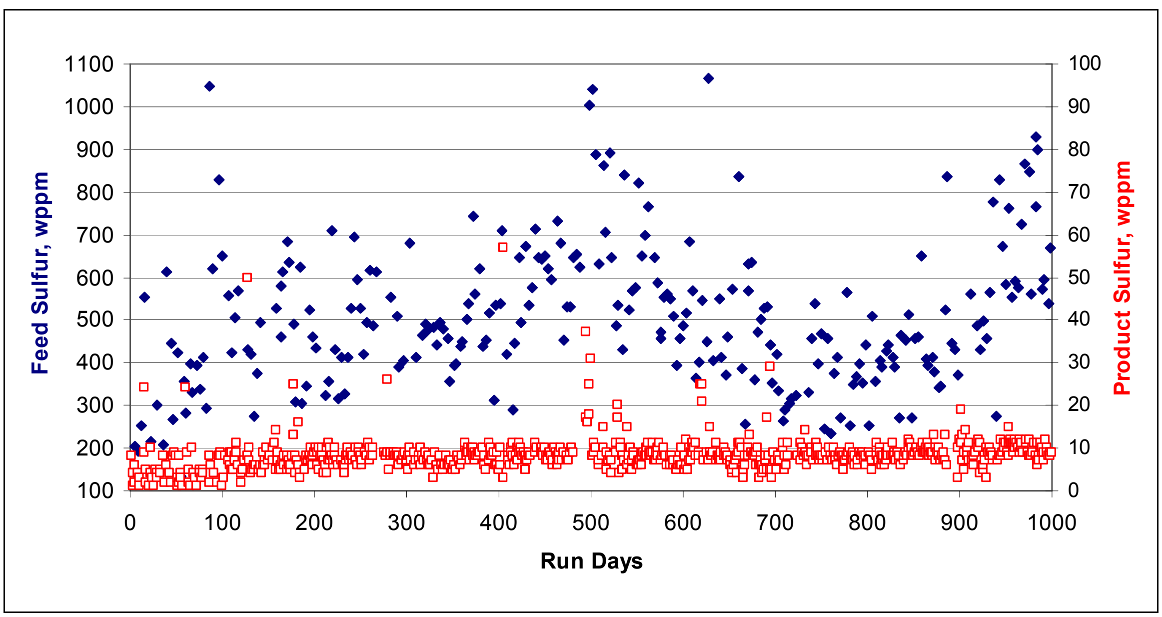
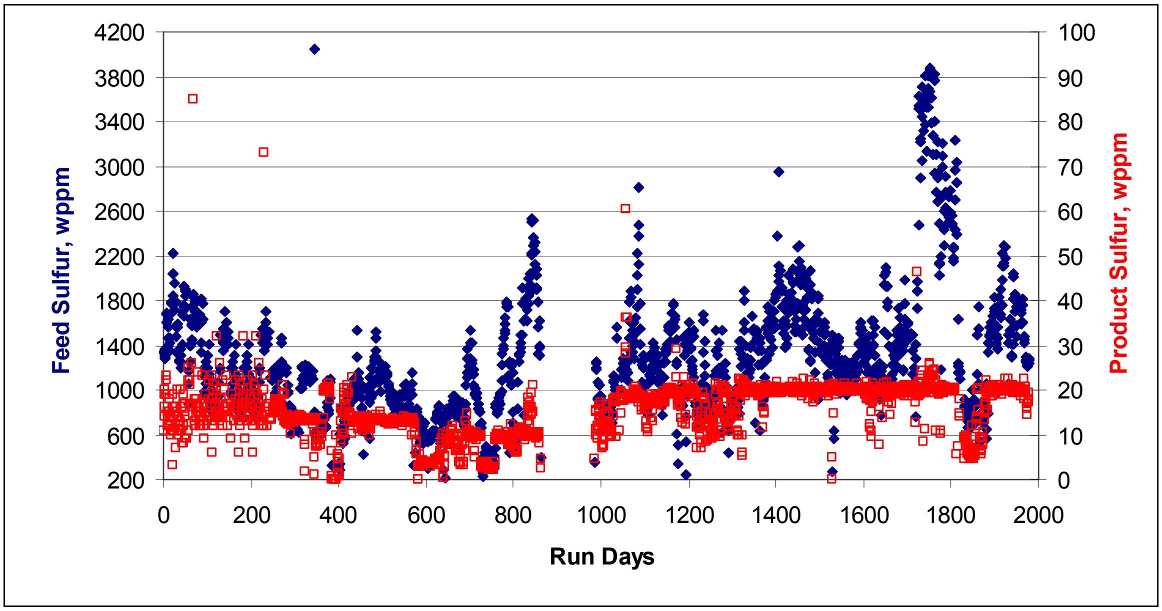


Figure 6: Unit C ULS HCN Production



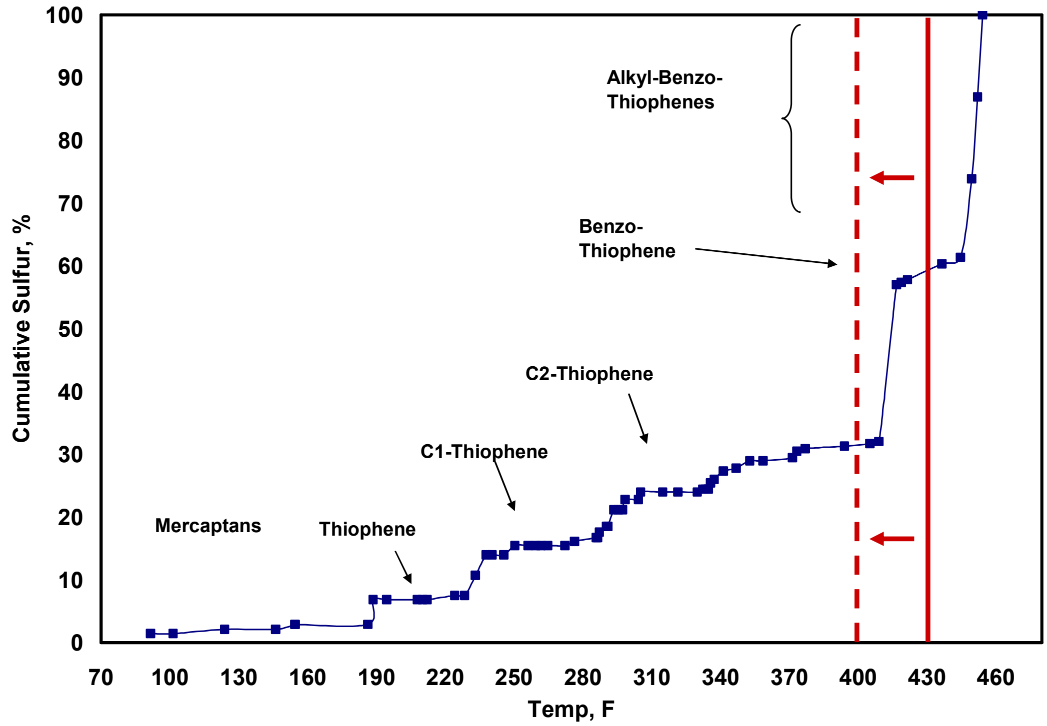
Post-treatment: Minimum Investment Options

In refineries with FCC gasoline post-treatment, the most basic strategy for Tier 3 is to increase the severity of the existing unit. If the unit is equipped with a splitter, the LCN cutpoint is modified to reduce the LCN sulfur. The result is increased feed rate and olefins content to the HDS section. The severity in the HDS section is increased to meet the product sulfur target. The impact of the higher load on the HDS section is an increase in octane loss and hydrogen consumption as well as reduced cycle length. If the refinery is octane long with sufficient hydrogen available, investment for Tier 3 may not be necessary if the unit is capable of achieving a cycle in sync with the FCC turnaround.

New catalysts have been developed to improve the capability of existing units for ULSG production. Higher selectivity catalysts reduce olefin saturation and the resulting octane loss and hydrogen consumption. Higher activity catalysts reduce the temperature requirement to meet the product spec, increasing the cycle length. The latest generation of Prime-G+ HDS catalyst HR846 offers both improved selectivity and activity. Control of recombinant mercaptans without any olefin saturation, a key part of ULSG production, is achieved by integrating polishing catalyst.

If the post-treater is not capable of meeting ULSG requirements without modification, reduction of the post-treater feed sulfur is an option. Operating with a low sulfur crude diet or using FCC catalyst additives are options, but the cost may not justify these methods as long term solutions. Another option is to modify the FCC Naphtha – Light Cycle Oil (LCO) cutpoint. Undercutting the FCC gasoline can significantly reduce the post-treater feed sulfur, and debottlenecks the unit. The increased LCO requires available distillate hydrotreating capacity, increases H_2 consumption and reduces the diesel pool cetane. The increased LCO production addresses the declining gasoline to distillate ratio; however, the heavy end of the FCC gasoline is valuable for gasoline RVP blending.

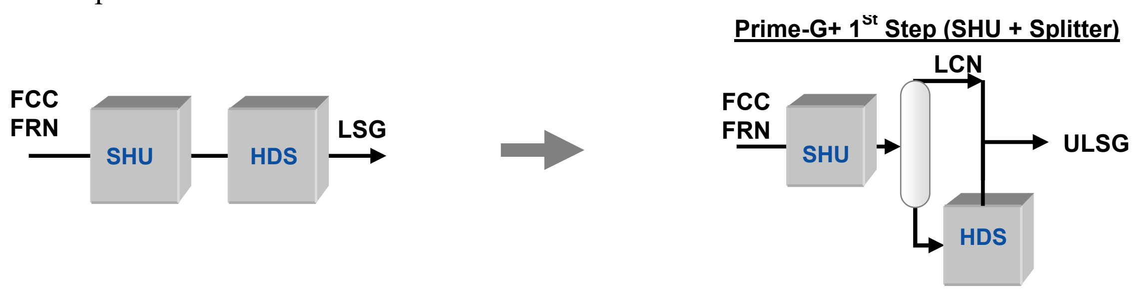
Figure 7: Impact of Reducing the FCC Gasoline Endpoint



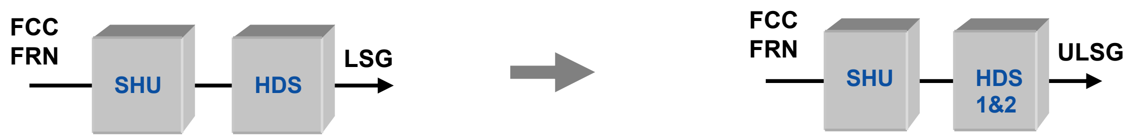
Post-treatment: Revamp Options

The primary drivers for revamp of the post-treater aim at addressing the following: cycle length, hydraulic bottlenecks, product octane, hydrogen consumption or increase blending flexibility. The three main options for post-treater revamp are to add a splitter, to add HDS catalyst volume, to add polishing catalyst volume, and to add an independent second HDS reaction section[1].

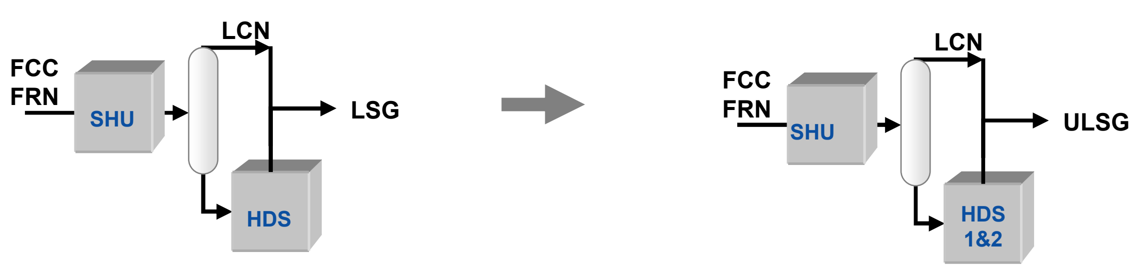
The simplest scheme for post-treatment is a Selective Hydrogenation Unit (SHU) followed by an HDS reaction section, with the SHU section protecting the HDS catalyst from gums formation from polymerization of diolefins. This scheme could be revamped to include a splitter in between the SHU and HDS sections. The Splitter debottlenecks the HDS section and removes olefins from the HDS section improving octane retention and cycle length as compared to the original scheme while minimizing hydrogen consumption.



Another route for revamp of the basic post-treater is to add a second HDS reaction section. Treating the FCC naphtha in two stages reduces octane loss and hydrogen consumption while increasing the cycle length.



The most common post-treatment scheme is the Prime-G+ 1st Step followed by a single HDS section. Revamping this scheme to include a second HDS reaction section offers the maximum octane retention, minimum hydrogen consumption and increased cycle.

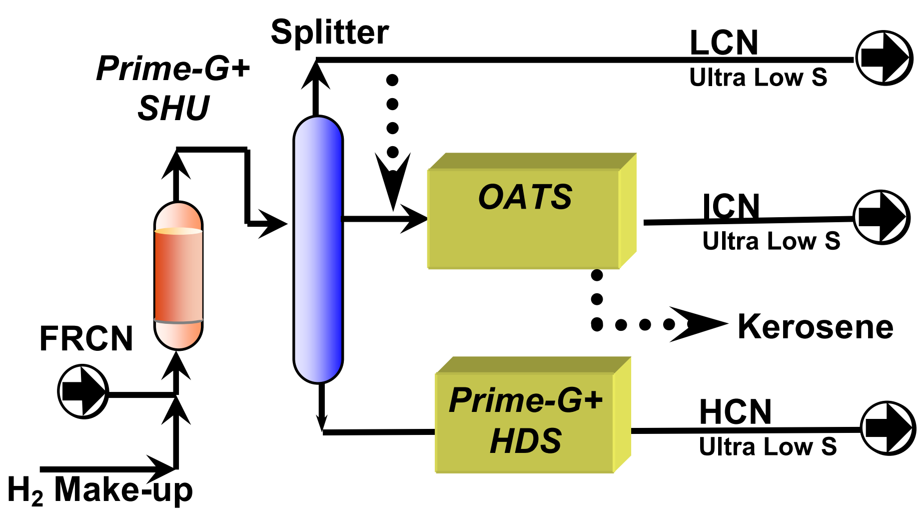


Post-treatment: Innovative Option - OATS

Another option for Tier 3 investment is application of the OATS (Olefins Alkylation of Thiophenic Sulfur) technology. The most common post-treatment scheme utilizes the Prime-G+ 1st Step, which couples a SHU reactor with a splitter to produce a light sweet LCN stream that can blend directly to the pool. In current Tier 2 operation, the LCN cutpoint is limited by the presence of Thiophene in the FCC naphtha. The OATS technology offers alkylation of the Thiophene with olefins creating heavier alkylated thiophenes.

The OATS technology can be integrated with the Prime-G+ 1st step to increase the LCN cutpoint to 190-230°F. Instead of reducing the LCN cutpoint and increasing the load on the HDS section, applying the OATS allows expansion of the Ultra-Low Sulfur LCN cut which reduces the load on the HDS section while minimizing the octane loss and the hydrogen consumption.

Figure 8: Integration of OATS with Prime-G+



An additional benefit of the OATS technology is an olefin shift. Light olefins dimerize to form a C_{10}-C_{12} product which shifts light gasoline to the distillate pool. The reduction of C_5 and C_6 olefins in the FCC gasoline also improves the RVP. Isomerization of olefins that do not dimerize makes the process octane neutral.

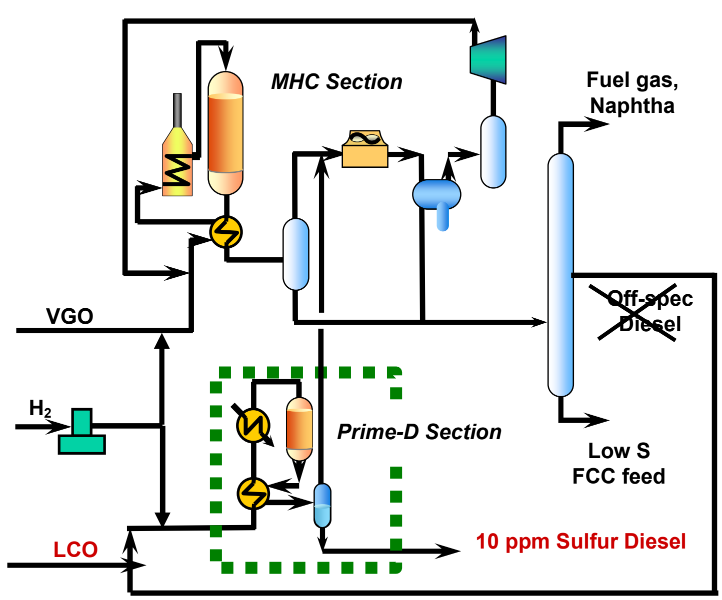
This is a commercially proven solution (3 units) offering low CAPEX and OPEX. The process uses a fixed bed solid acid catalyst operating with mild operating conditions and does not require any hydrogen.

Pretreatment: Refineries with CFHT

Refineries with FCC feed pre-treatment have the option to revamp the existing CFHT or to install or revamp a post-treater. One option for these refineries is to address Tier 3 with pre-treatment alone typically requiring reduction of the FCC feed sulfur to 200 – 300 wppm S. While possible, this is a difficult proposition for several reasons. Meeting a 4 to 5 year cycle is challenging with such high severity operation. Revamp of pre-treaters is usually not possible due to too low design pressure to meet sulfur and cycle length targets for Tier-3. Grassroots units will require very high investment and can only be justified by a complete shift towards a heavy crude diet. With pre-treat alone there is little margin for error in cycle length, unit operation or product fractionation when making ULSG. A grassroots or revamped post-treater is very likely the lower cost solution, adds flexibility, and greater compliance certainty. The post-treater can operate at higher severity during a CFHT catalyst change-out maintaining the target sulfur. Additionally, the post-treater can compensate for fluctuation in CFHT product quality.

Another option for refineries with high pressure CFHT is to revamp the unit into Mild Hydrocracking service (MHC). This is an attractive option as MHC increases middle distillate production. The revamp strategy is to avoid major changes to the reaction section, focusing on catalyst selection, managing increased hydrogen consumption and quench. Amorphous catalyst is often preferred over zeolite in this service due to the improved selectivity towards middle distillates. By limiting the revamp to the fractionation section, the investment is paid off by high middle distillate margins. Co-current production of ULSD along the whole cycle length may or may not be achieved depending on the unit design characteristics. Process arrangement such as that of Axens HyC-10™ allows decoupling MHC from ULSD production and greatly improves the unit operating window.

Figure 10: HyC-10 Scheme for Improved ULSD Production with MHC



Other Options in the FCC Complex

Traditionally, the FCC has been the refinery workhorse in the United States and its operation dictates the distribution of many refinery products. In the past, gasoline was the highest value product and was maximized. In the current market, middle distillates are generally more valuable. Fortunately options exist at various capital costs that increase the conversion of Vacuum Gas Oil to distillates.

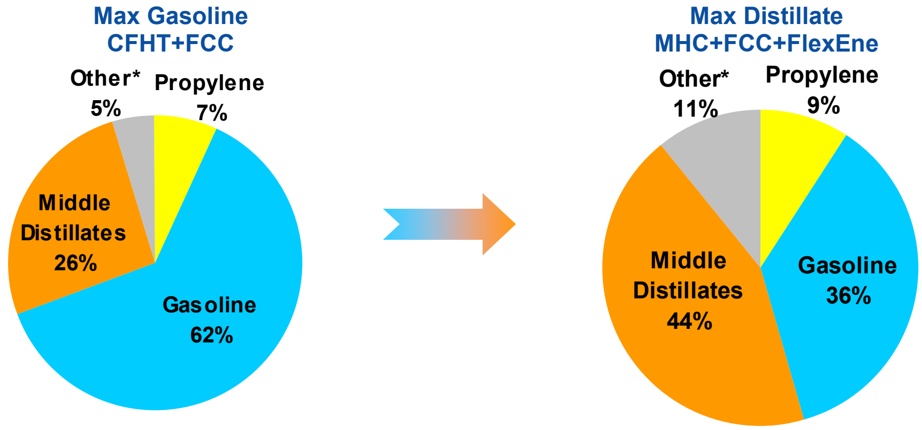
The operation of the FCC unit can be adjusted in several ways for optimizing the production of distillates[3]. Undercutting the FCC gasoline is the first step and represents the lowest cost option. Already discussed for its value in reducing the sulfur to the FCC gasoline post-treater, this option requires distillate hydrotreating capability for reduction of sulfur and olefins. The next step is to select an FCC catalyst that is the most compatible with operation of the FCC in a low-severity distillate or LCO mode. Management of the unconverted Heavy Cycle Oil is critical to effective distillate operation. The LCO – HCO cutpoint can be increased and the HCO recycled to the FCC reaction section to increase distillate production.

To further increase distillates production, Axens has developed a breakthrough technology offering oligomerization of the C_5 and C_6 olefins in the FCC naphtha to shift gasoline into a high quality kero/jet product. Oligomerization of the FCC LPG light olefins for fuels production is well known, however, the target has previously primarily been gasoline. In the past, the most commonly used technology used a Solid Phosphoric Acid (SPA) catalyst system which is difficult to handle and manage, suffering from low crush strength frequently leading to pressure drop problems and short cycle length. The new Axens technology, PolyFuel™, was born from the extensive industrial experience of Axens in LPG oligomerization through Polynaphtha™ and offers the ability to adjust the gasoline to distillate ratio and to reduce the gasoline RVP while maintaining a long cycle length to be in sync with the FCC turnaround. Typically 10% of the Full Range FCC gasoline can be converted to kero/jet.

Operation of the FCC in LCO mode will reduce the production of Propylene which may also be a refinery objective. This can be offset by the appropriate combination of the PolyFuel and recycle of the kero/jet oligomers to the FCC for selective conversion to propylene. The PolyFuel - FCC configuration is called FlexEne™. FlexEne is also effective when maximum propylene is the refinery objective.

The table below summarizes the potential overall shift in products with the combination of FCC in LCO mode, ZSM5 additives in the FCC catalyst, implementation of PolyFuel and FlexEne, and revamp of the CFHT into Mild Hydrocracking service.

Figure 11: Liquid Yields from VGO (vol%)



* LPG, naphtha, slurry

Conclusion

The preferred investment for meeting the expected 10 wppm gasoline pool S Tier 3 specification will once again be in post-treatment of the FCC gasoline. Maximization of existing assets reuse will be of paramount importance to minimize the investment. Proven new catalyst systems and revamp options for existing FCC gasoline post-treatment units offer refiners minimum cost solutions to meet anticipated new regulations. Further investment in new technology developments offers more comprehensive solutions to gasoline sulfur and RVP, shifting crude quality, declining gasoline demand versus diesel, and presents an opportunity to maximize profitability.

References

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2. Benazzi, E., "Gasoline and Diesel Imbalances in the Atlantic Basin – Part 1: Market Outlook", Petroleum Technology Quarterly, PTQ Q2 2011.
3. Fraysse, S. and Huchette, S., "Gasoline and Diesel Imbalances in the Atlantic Basin – Part 2: Options to Re-orient a Refinery's Production Towards Middle Distillates", Petroleum Technology Quarterly, PTQ Q4 2011.