Introduction

New U. S. regulations requiring 30 ppm sulfur gasoline phase in beginning in 2004. In 2006 regulations requiring 15 ppm sulfur diesel take effect. The technology to achieve the required sulfur levels has focused primarily on improved hydrotreating technology, with a few novel processes being introduced and even commercialized. A combination of these technologies will form the backbone for the industry's approach to meeting these requirements. Very little has been written regarding the potential clean fuels benefits of improved refinery fractionation. Much of the data available in the public domain suggest that improved fractionation could have tremendous benefits. However, most of what has been written focuses on either splitting Fluid Catalytic Cracking (FCC) Unit naphtha to minimize hydrotreating requirements and olefin saturation or on under-cutting the naphtha to reduce the amount of sulfur that makes it into the gasoline pool. Both of these approaches neglect the potential of simply improving the existing splits between the FCC products while maintaining constant yields. Although the potential to reduce sulfur concentration through improved fractionation has been suggested,[1] it has not been investigated in detail. Through laboratory analysis and simulation studies of a commercial FCC Main Fractionator this paper will attempt to highlight the potential value of improved product fractionation.

Background

Low sulfur gasoline and diesel have dominated industry discussion in the three years since the EPA began rolling out proposed new regulations for gasoline. Prior to that, California refineries have been meeting ultra low sulfur gasoline specifications since the mid 1990's. FCC naphtha, generally the largest source of sulfur in the gasoline pool, is the primary focus for most refiners. Refiners who already fully hydrotreat their FCC feed may be able to meet the new regulations through increased FCC feed hydrotreater severity. The capital required for a grassroots FCC feed hydrotreater will probably be prohibitive for most refiners who don't already have one. Many refiners will therefore probably employ some sort of post-treatment on their FCC gasoline. Conventional hydrotreating cannot be directly applied because of the octane downgrade that would occur due to olefin saturation. This leaves the refiner to select from selective hydrotreating/isomerization processes or newer technologies developed specifically for FCC naphtha desulfurization. All of these processes suffer some degree of octane or yield loss.

The typical role of distillation in any of these processes is to split the naphtha into fractions to either minimize the size of the naphtha treater, minimize the octane loss, or both. A popular way of accomplishing this is pulling a heavy naphtha side draw from the Main Fractionator[2]. This reduces the overhead temperature in the Main Fractionator which may result in ammonium chloride salt deposition and related corrosion. Alternatively the full range FCC naphtha can be fed to a downstream splitter. Naphtha can also be split using a two drum overhead system as is common in crude units.[3] In any case the naphtha streams are then fed to a sulfur removal unit tailored to the type of sulfur in the stream. This can minimize capital and operating cost for some refiners but still may carry an octane penalty. Other refiners are undercutting the FCC naphtha to control sulfur. This has the downside of reducing FCC naphtha yield, as well as potential fouling and corrosion problems in the main fractionator due to the lower overhead temperature. In addition, the heavy tail makes poor distillate due to the high aromatic content.[4]

Little work has been presented which considers reducing the sulfur content by improved fractionation in the Main Fractionator. However, much of the data presented suggest that FCC naphtha sulfur can be reduced with little or no yield or octane loss through improved fractionation. A typical FCC naphtha sulfur and olefin distribution is shown in Figure 1. The sulfur is concentrated in the heavy portion of the naphtha with the olefins more concentrated in the lighter portion. The data suggests undercutting the naphtha will reduce sulfur without significantly reducing the olefin concentration (and therefore the octane). What is not clear is the potential to reduce the sulfur by improved fractionation or what impact this might have on yield.

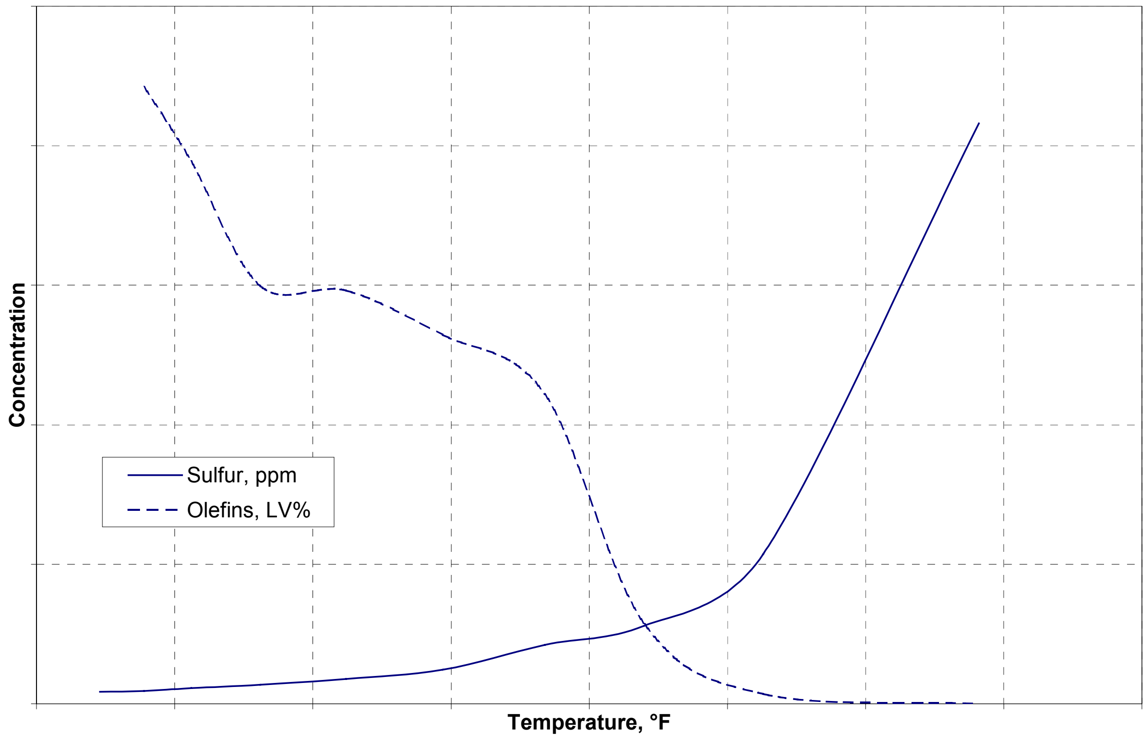

Figure 1: Typical FCC Naphtha Sulfur and Olefins Distribution

Closer inspection of the sulfur in FCC naphtha using mass spectrometry provides more insight into what benefits improved fractionation might provide. Figure 2 shows the cumulative FCC naphtha sulfur concentration versus the normal boiling point of the sulfur component for a typical FCC naphtha. Approximately 20% of the sulfur is contributed by benzothiophene (bp = 430 °F) alone. An additional 40% is from species - primarily alkyl benzothiophenes - with boiling points greater than 430 °F. These components are contained in the heavy "tail" on most full range FCC naphtha streams. Benzothiophenes are the most difficult components to hydrotreat in FCC naphtha[5]. Most FCC's have a significant overlap between the naphtha and LCO fractions as shown in Figure 3. Refiners have typically considered this poor separation to be acceptable. However, with the new regulations this may have to change.

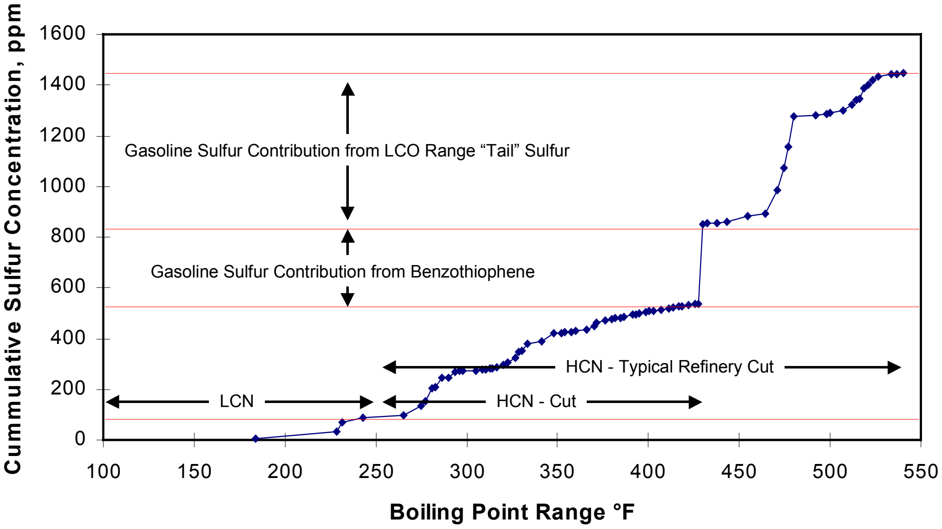

Figure 2: FCC Sulfur Distribution by Component Boiling Point
(Graph Courtesy of GRACE Davison)

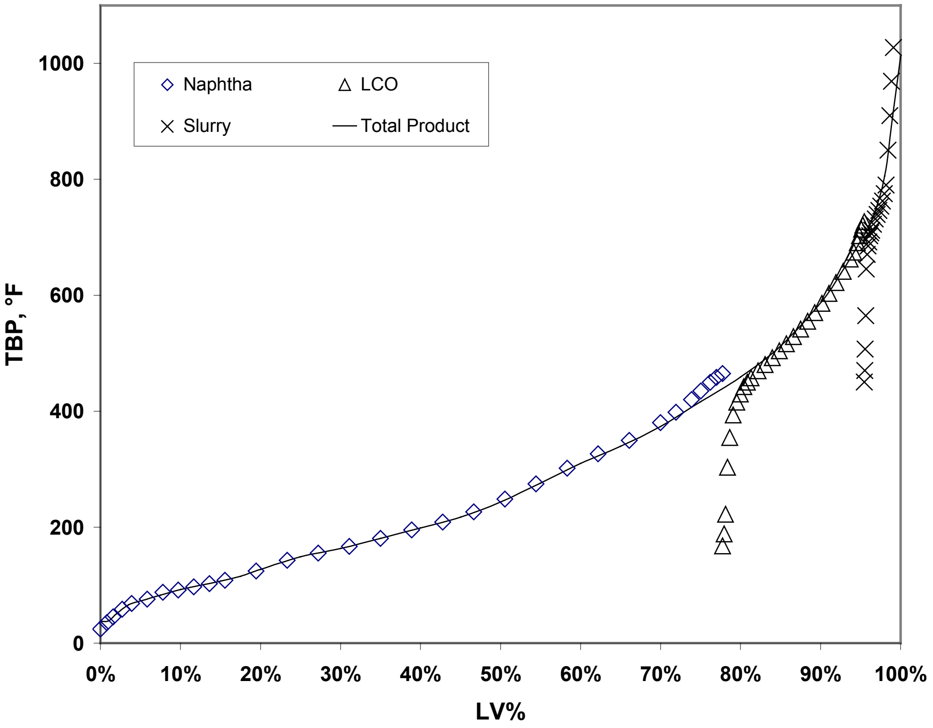

Figure 3: Typical FCC Product Distillations

FCC Light Cycle Oil (LCO) is not necessarily the largest contributor of sulfur to the overall diesel pool in a refinery. However, LCO does contain a large fraction of dibenzothiophenes, the most difficult molecule to desulfurize due to the sterically hindered sulfur - especially 4,6-dibenzothiophene.[1] Prior work has shown that in deep hydro-desulfurization of diesel fuels virtually all of the sulfur left is contained in dibenzothiophene with alkyl groups in the 4, 6, or both positions.[6] These species boil above 630 °F[7]. Again, the tail contains the most difficult sulfur species for conventional hydrotreating.[8]

Since the tail for both FCC naphtha and LCO present the biggest challenge for reducing the sulfur from these streams it was decided to further investigate the potential for reducing the sulfur content through improved fractionation.

Experimental Work

The experiment designed to further understand the potential benefits of improved fractionation for reducing the sulfur content of FCC naphtha and LCO consists of three parts:

1. Laboratory blending and re-distillation of the C_5^+ liquid products from a commercial FCC followed by analysis of the laboratory and commercial cuts for sulfur content and speciation.
2. Detailed simulation studies of the effect of theoretical stage count and reflux on the sulfur distribution in the products from a hypothetical FCC Main Fractionator.
3. Field test runs to determine the impact of increased reflux on the sulfur distribution in the products from an actual commercial FCC Main Fractionator with a fixed number of theoretical stages.

This paper presents the results of the first two parts. The third part could not be completed in time for this paper due to scheduling difficulties.

Part 1: Laboratory Distillation Studies

Samples of FCC Naphtha, LCO, and Slurry Oil were collected from a commercial FCC. This unit processes a blend of coker and virgin gas oil. The feed to this particular FCC is fully hydrotreated. However, since the sulfur distribution in FCC products is similar whether or not the feed is hydrotreated the results from the study should be generally applicable. The samples were blended in the laboratory to produce a C_5^+ stream with the same volumetric composition as the commercial unit. This stream was then distilled in a standard TBP distillation apparatus[9] to the same naphtha and LCO cutpoints as the commercial unit. Recovery from the laboratory distillation was 99.7%. Yield and cutpoint data are shown in Table 1. There is a slight discrepancy between the laboratory blend and the commercial compositions that is negligible for the purpose of this study. The laboratory distillation yields compare very closely to the commercial composition and the laboratory blend.

Table 1: Commercial C_5^+ Composition Compared to Laboratory Blend and Cuts

		Field	Blend	Lab Cut	Cutpoint
Naphtha	LV%	Base	-0.39%	-0.29%	415 °F
	Wt%	Base	-0.42%	-0.85%	
LCO	LV%	Base	0.50%	0.15%	675 °F
	Wt%	Base	0.57%	0.05%	
Slurry	LV%	Base	-0.11%	0.34%	
	Wt%	Base	-0.15%	0.50%	

The commercial and laboratory Naphtha, LCO, and Slurry distillations are shown in Figure 4 and Figure 5. As expected the commercial distillations have more overlap between the cuts. In the laboratory distillation this overlap is largely eliminated. Note that the fractionation is improved on both the front and back ends of the fraction, thus maintaining the yield of each cut while reducing the amount of heavy material in the lighter cuts. This is the exact opposite of undercutting, which sacrifices the heavy tail of the lighter cut to maintain a desired endpoint without improving recovery of light ends from the heavier cut.

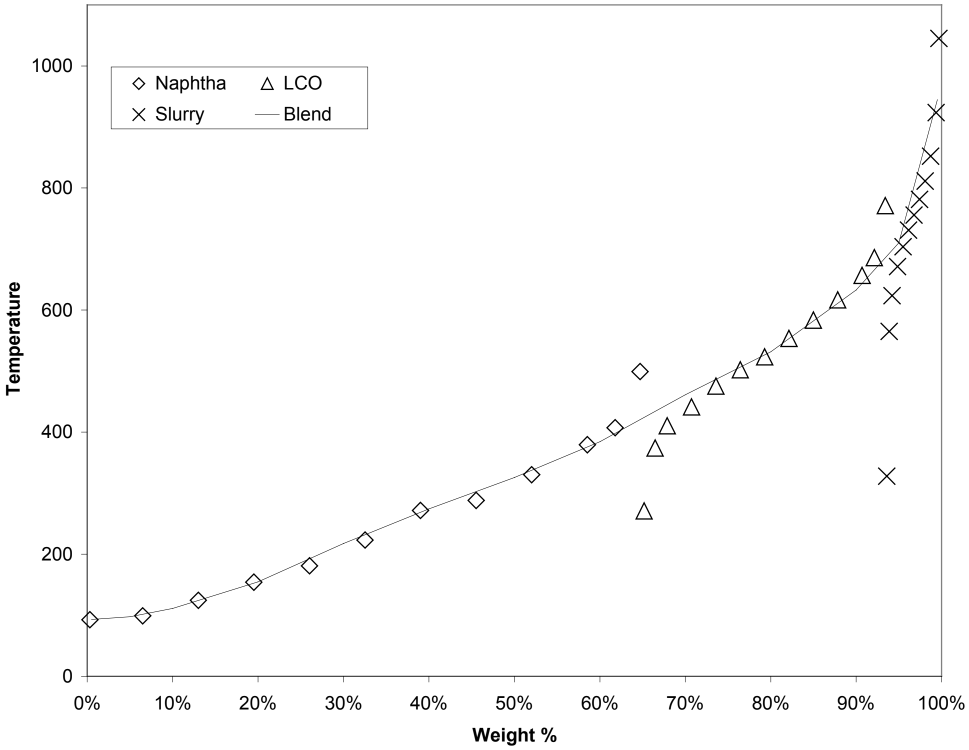

Figure 4: Commercial FCC Product Distillations

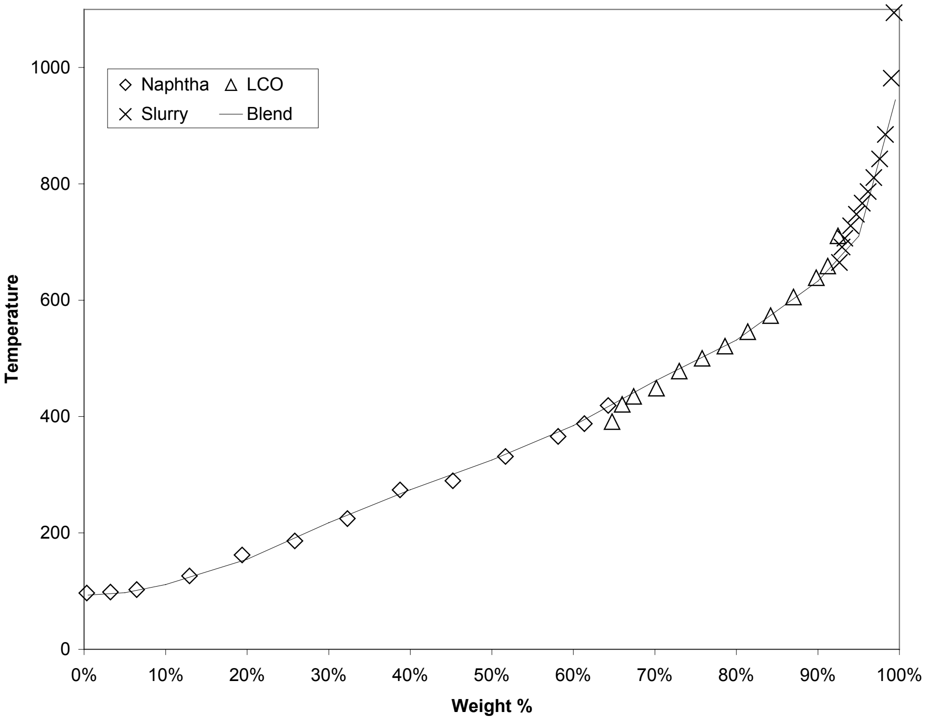

Figure 5: Laboratory FCC Product Distillations

Each cut was analyzed for total sulfur content. The sulfur content of the individual blend components and the laboratory cuts balanced to within four weight percent of the overall blend concentration. As shown in Table 2 the bulk sulfur concentration in the naphtha cut was reduced by over 40% with essentially no loss of octane. One study has shown a 15 LV% volume reduction required to obtain a similar decrease in sulfur by simply undercutting.[10]

Table 2: Commercial and Laboratory Cut Bulk Analysis

	Commercial			Laboratory		
	Sulfur, ppm	°API	RON	Sulfur, ppm	°API	RON
Naphtha	150	55.4	93.4	85	56.0	93.3
LCO	4450	12.7		4510	12.3	
Slurry	9160	-3.0		8150	-4.7	
Blend				1890	38.8	

The commercial and laboratory Naphtha samples were analyzed to determine the type of sulfur species present. Table 3 shows that virtually all of the reduction is in species heavier than benzothiophene. In fact, there is an increase in the concentration of species lighter than benzothiophene. This is primarily due to lighter naphtha range thiophenes that were present in the commercial LCO sample but were recovered in the laboratory Naphtha fraction due to the more efficient distillation. It is this aspect of improved fractionation (rather than simply undercutting) that maintains Naphtha yield and octane while rejecting undesirable components.

Table 3: Commercial and Laboratory Cut Sulfur Speciation

	Commercial ppm	Laboratory ppm	Δ ppm	%
Lighter than Benzothiophene	46.4	57.4	10.9	23.6%
Benzothiophene	13.3	11.2	-2.0	-15.2%
Alkyl Benzothiophenes	43.4	0.7	-42.7	-98.3%
Heavier than Alkyl Benzothiophene	17.1	11.6	-5.5	-32.3%
Total	120.2	80.9	-39.3	-32.7%

It is highly unlikely that fractionation alone will allow a refiner to meet new gasoline sulfur specifications even if a commercial unit is able to approach a laboratory quality split. However, these results indicate that fractionation improvements can significantly reduce the amount of sulfur present in the Naphtha fraction and therefore reduce the cost associated with compliance. In addition, fractionation improvements offer a potential low capital option for refiners who plan on undercutting FCC Naphtha all or part of the time as part of their compliance strategy to accomplish the same goal without sacrificing yield. Finally, the sulfur species removed by improved fractionation are the most difficult to hydrotreat. This reduces the operating expense and potentially the capital cost of any post-treatment for the Naphtha stream.

At first glance, better fractionation did not significantly influence LCO sulfur as shown in Table 2. The LCO bulk sulfur did not change significantly between the commercial and laboratory cuts. However, with LCO the type of sulfur present is as important as the quantity. LCO is rich in sterically hindered dibenzothiophenes which are especially difficult to hydrotreat. As discussed earlier, studies have shown that these compounds account for virtually all of the sulfur remaining in diesel that has been hydrotreated to 500 ppm sulfur. These compounds are especially concentrated in the heavy tail of the LCO. Undercutting diesel has proven to be an effective low capital approach to meeting low sulfur diesel requirements, even with low severity hydrotreating.[1] Undercutting LCO directly has the disadvantage of reducing diesel yield and increasing slurry oil yield, neither of which is desireable.

The commercial and laboratory samples were analyzed using sulfur simdist, which provides a sulfur versus boiling point distribution for the oil. As shown in Figure 6, the commercial LCO contains sulfur species with boiling points above 800 °F, while the laboratory cut species end below 750 °F. Nearly 50% of the sulfur species from diesel cuts above 670 °F are sterically hindered dibenzothiophenes.[11] However, the sulfur simdist does not provide a direct measure of the type of sulfur molecules present.

To better determine the impact of the improved distillation we analyzed the LCO samples to determine the exact sulfur species present. The results are presented in Table 4. The discrepancy between total sulfur reported from the sulfur speciation and the total sulfur analysis is due to differences in the analytical method. As expected, non-dibenzothiophene sulfur increases due to the sulfur species that were fractionated out of the naphtha. Also as expected dibenzothiophene and mono-substituted dibenzothiophene sulfur increased as these components were preferentially fractionated into the LCO from the slurry as well as from the naphtha. Because of the high cutpoint (700 °F) the improved distillation also resulted in an increase in di-substituted dibenzothiophenes (b.p. ~ 640 - 680 °F). Better fractionation did reduce the concentration of higher (C_3+) substituted dibenzothiophenes (b.p. > 680 °F).

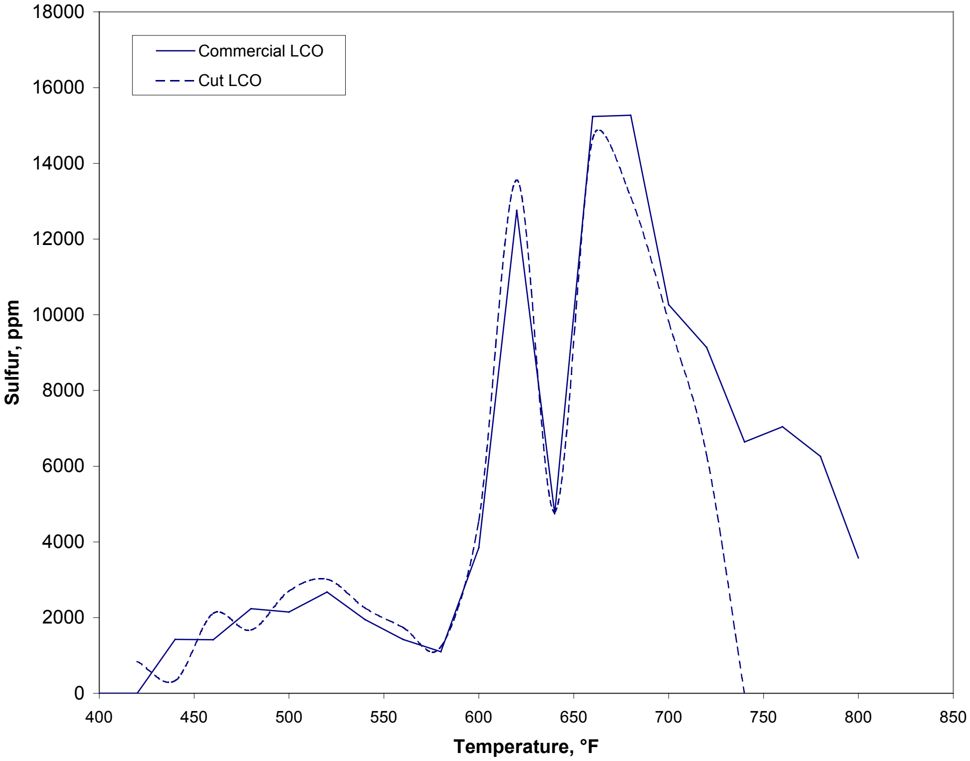

Figure 6: Sulfur Simdist for Commercial and Laboratory Cut LCO

Table 4: Sulfur Species in Commercial and Laboratory Cut LCO

	Commercial ppm	Laboratory ppm	Δ ppm	%
Non-Dibenzothiophene	1302	1682	380	29.2%
Dibenzothiophene	208	231	23	10.8%
C_1 Substituted Dibenzothiophenes	791	913	122	15.4%
C_2 Substituted Dibenzothiophene	1278	1533	255	20.0%
C_3+ Substituted Dibenzothiophene	2050	1716	-334	-16.3%
Total	5629	6075	446	7.9%

A reduction in C_3+ substituted dibenzothiophenes is desirable because of the difficulty in desulfurizing these molecules. However, it does not offset the increase in di-substituted dibenzothiophenes which almost certainly corresponds to an increase in 4,6-dibenzothiophene. To significantly reduce the concentration of this component some reduction in LCO cutpoint will probably be required to significantly reduce the difficulty of hydrotreating to meet new diesel sulfur requirements.

Part 2: Simulation Studies

The detailed sulfur distribution data obtained during Part 1 were used to construct a process simulation of the commercial main fractionator that matches the commercial heat and material balance and product sulfur distribution. This simulation was then used to study the effect of reflux and theoretical stage count on Naphtha and LCO sulfur concentration.

The sulfur species in the simulation were represented as a continuous boiling point distribution as part of the petroleum pseudocomponents rather than as discrete pure components. This has the advantage of requiring minimal input. However, it does not allow the examination of individual species in boiling point ranges where a complex mixture of species exists. This imposes limitations on the conclusions that can be drawn from the simulation results.

For the purpose of the study C_5^+ Naphtha and LCO product volumes were held constant. Internal reflux ratios were adjusted by reducing slurry pumparound duty and allowing the condenser duty and overhead reflux to increase to maintain the same product volumes and overhead accumulator temperature. The LCO side stripper in this unit is reboiled and the reboiler duty was held constant. The changes we evaluated were kept modest, especially compared to the 15 stage, 5 L/V of the TBP distillation. This is to ensure that our comparisons can potentially be applied to commercial units. Obviously, if sufficient incentive exists or if a refiner is purchasing a new fractionator for mechanical reasons or for increased throughput the conclusions can be extrapolated to evaluate the incentive for even further fractionation improvements.

Reflux ratio in the Naphtha/LCO section of the tower was varied from approximately 0.18 to 0.30 mol/mol averaged at the top and bottom theoretical stage of the section. Theoretical stages were increased up to five theoretical stages from the base. The impact of these changes on total Naphtha sulfur concentration is shown in Figure 7. Reflux has a much greater impact on Naphtha sulfur content than tray count. This is not surprising given the low reflux ratio in this section and is typical of refinery fractionators. A 60% increase in reflux ratio reduces the sulfur content by approximately 15%. The corresponding increase in condenser (or top pumparound duty) is about 30% with the increase in internal vapor traffic approximately 17%.

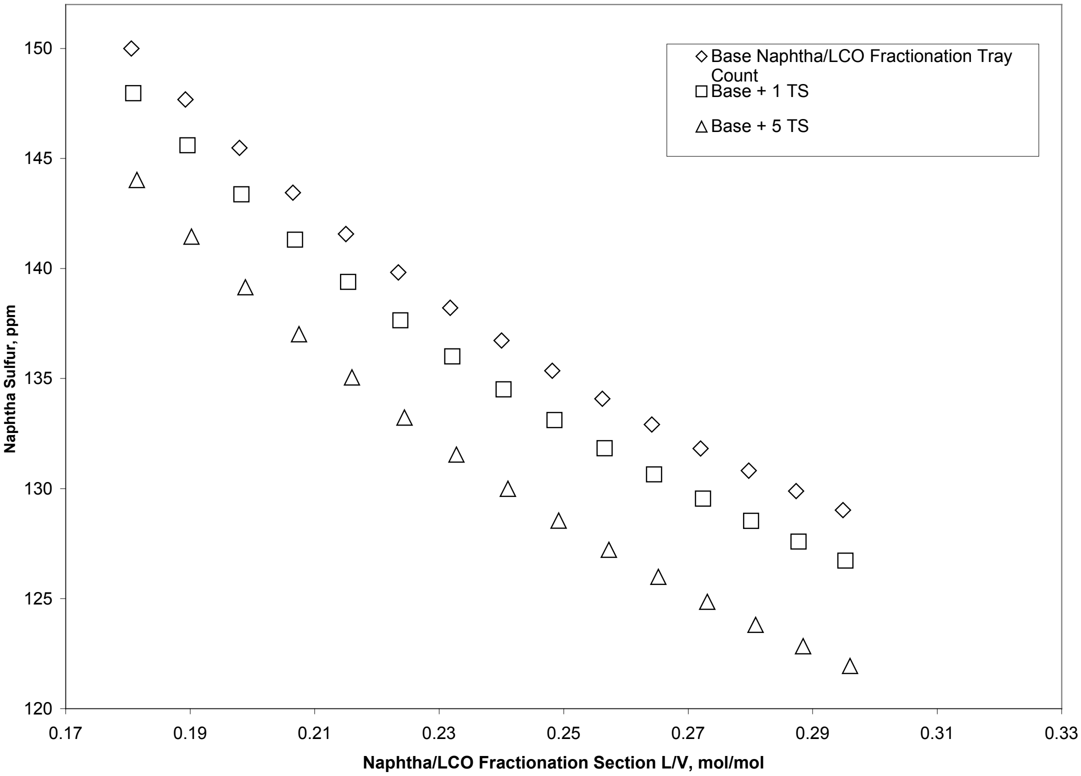

Figure 7: Impact of Tray Count and Reflux on FCC Naphtha Sulfur Content

The simulation also shows that species lighter than benzothiophene (b.p. 430 °F) tended to increase in concentration, while those heavier than benzothiophene decreased significantly. The concentration of components boiling in the benzothiophene range changed little. This is consistent with the laboratory distillation results.

Some limitations are inherent in the simulation analysis. This is because the simulation represents the sulfur distribution as a relatively smooth curve as opposed to large contributions from several discrete components as is shown in Figure 8. However, the simulation matches the cumulative sulfur distribution closely and somewhat overstates the sulfur in the gasoline cutpoint boiling range. Therefore the conclusions reached from the simulation analysis are probably somewhat conservative.

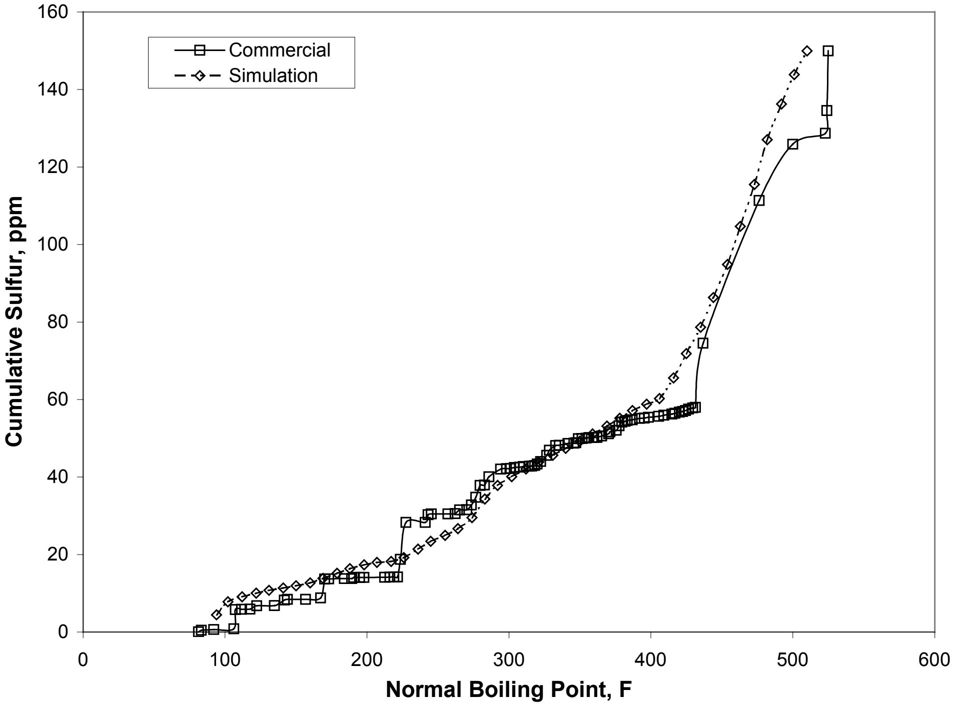

Figure 8: Sulfur versus Boiling Point Distribution for Commercial and Simulated Naphtha

For the LCO/Slurry fractionation section the reflux ratio was increased from approximately 0.05 to 0.15 mol/mol averaged at the top and bottom theoretical stage of the section. The theoretical stage count was also increased up by up to five theoretical stages from the base configuration. This is a much larger increase in stages relative to the typical commercial unit than was considered for the Naphtha/LCO section. However, it has the same relative impact in terms of overall vessel height.

The effect of additional stages and reflux on LCO composition is much more complex than for Naphtha. Part of this is because the method used to increase reflux also increases reflux in the Naphtha/LCO fractionation section. This increases the sulfur concentration in the front end of LCO at the same time as the sulfur concentration in the tail is being reduced. However, due to the complex sulfur distribution in the heavy tail of the LCO it is necessary to evaluate the multicomponent patterns of change in the region of the LCO product draw to determine the precise impact on sulfur species. This analysis is more typically used in the chemical industry but can be applied to refining columns when the distribution of individual species is of interest.

In general adding trays to the LCO fractionation section had more impact than might be anticipated with the extremely low reflux ratio in this section. However, the base tray count is very low. This is typical for FCC main fractionators which may have three to five actual trays in this service that operate at 50% efficiency or lower. Adding trays increased the overall sulfur concentration in the LCO by approximately 25 ppm at all reflux ratios. This increase is insignificant compared to the total LCO sulfur content of approximately 4100 ppm.

Increased reflux in the LCO fractionation section reduced bulk LCO sulfur content by approximately 15 ppm at all tray counts. Again, this change is insignificant compared to the total LCO sulfur content. However, as pointed out above some of the increase in sulfur comes at the front end of the LCO as higher sulfur naphtha "tail" species are dropped into the LCO replacing lower sulfur naphtha range material. The impact of trays and reflux on bulk sulfur are shown in Figure 9.

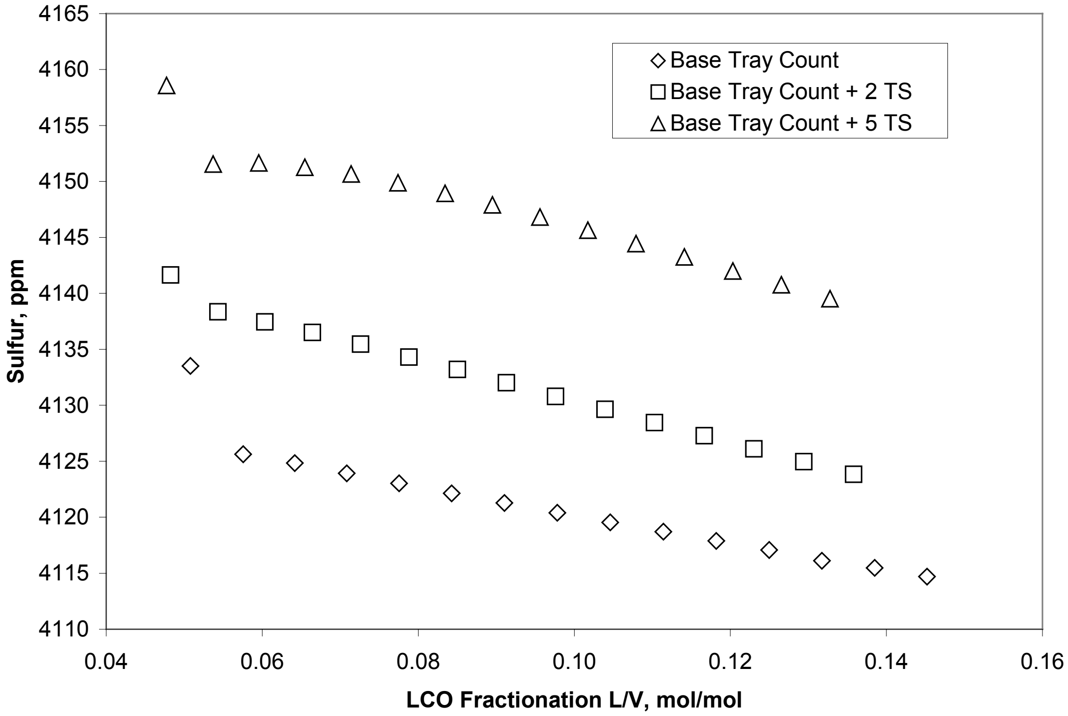

Figure 9: Impact of Reflux and Tray Count on FCC LCO Sulfur Content

As discussed earlier, this change is confusing but is due to the complex nature of the sulfur distribution in the LCO tail and the limitations of the approach used to simulate the sulfur distribution. To help clarify the impact we examined the impact of reflux and tray count on the sulfur contribution of individual pseudocomponents in the region of the LCO cutpoint (~675 °F). The sulfur contribution from components well below the cutpoint increased marginally with both increased tray count and reflux as shown in Figure 10. As expected, due to the extremely low initial tray count the first additional trays had the largest impact with the benefit from additional trays declining rapidly by the time five trays were added. The sulfur species in this boiling range (approximately 600 °F) contain a very low concentration of sterically hindered dibenzothiophenes,[7,11] therefore this increase does not necessarily make the LCO more difficult to hydrotreat.

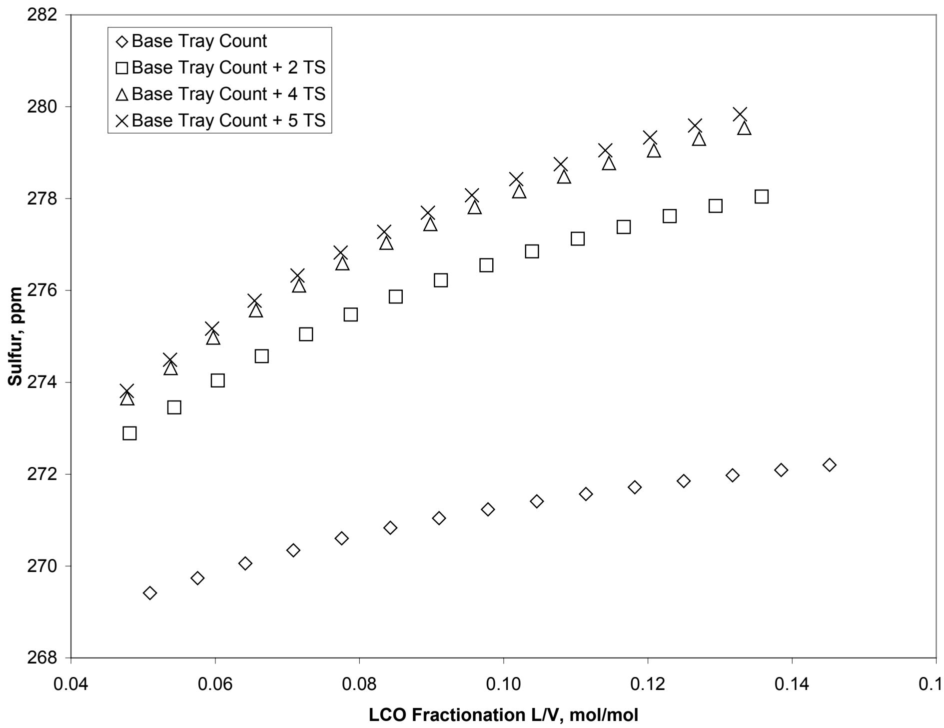

Figure 10: Impact of Reflux and Tray Count on Sulfur Contribution From NBP 604°F

For components near the cutpoint increased tray count slightly increased the LCO sulfur contribution as shown in Figure 11. Increased reflux had just the opposite effect. Again, this impact was small relative to the sulfur contribution from these species. For components lower in the C_2-substituted dibenzothiophene boiling range (~640 - 680 °F) increased reflux either slightly increased the sulfur contribution or had no impact. To significantly reduce the concentration of sulfur from these species will clearly require some reduction in LCO cutpoint.

For components above the cutpoint, the sulfur contribution declined for both increased reflux and additional trays (Figure 12), especially at higher tray counts. The sulfur species in this boiling range are predominantly C_3+ substituted dibenzothiophenes. As stated earlier these components have relatively low reaction rates for desulfurization. Therefore this reduction is positive. However, to significantly reduce the sterically hindered sulfur species present in the LCO it is necessary to substantially reduce the concentration of C_2-substituted dibenzothiophenes through undercutting the LCO.

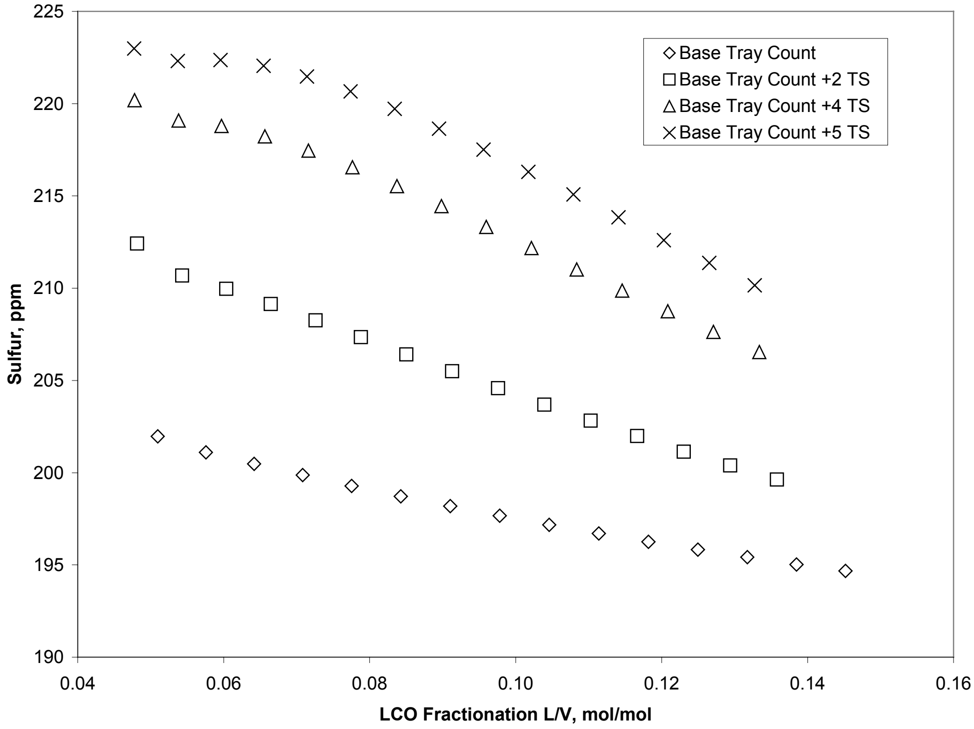

Figure 11: Impact of Reflux and Tray Count on Sulfur Contribution From NBP 671°F

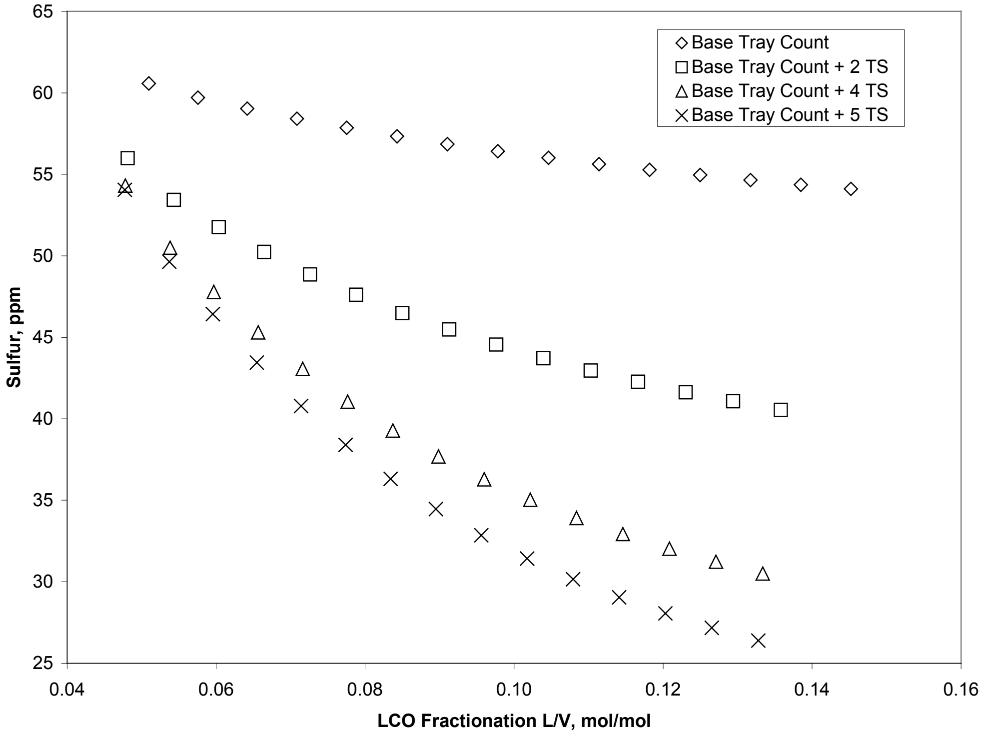

Figure 12: Impact of Reflux and Tray Count on Sulfur Contribution From NBP 696°F

The simulation results to date have represented the sulfur distribution in the FCC C_5^+ product utilizing overall sulfur content versus boiling point and the petroleum pseudocomponents typically used for refinery distillation simulations. This does not invalidate the results. In fact, the results so far are encouraging, especially with respect to naphtha. However, it may be possible to better understand the impact of fractionation improvements by more precisely representing the sulfur species of greatest interest. Future simulation work will attempt to do this. Also, future studies will explore potential commercial applications in greater detail.

Part 3: Field Test Run

As discussed earlier, planned field test runs could not be completed in time for publication. However, the results of the laboratory and simulation studies indicate that the approach originally planned for the test run - increasing reflux ratio with a constant tray count - has the greatest probability for improving the distribution of sulfur in the FCC Naphtha and LCO. These test runs will be completed at the earliest date possible and the results presented in future work.

Conclusions

The work presented clearly shows that given sufficient theoretical stages and reflux it is possible to reduce the hydrotreating requirements for FCC Naphtha to meet low sulfur gasoline specifications with little or no impact on yield or other qualities. It also shows that some degree of cutpoint reduction is necessary to achieve significant impact on LCO sulfur. The study clearly points to increased reflux as the preferred method for improving fractionation. However, it doesn't completely address the commercial viability of this approach. The work to date demonstrates promise but additional evaluation is necessary. Future simulation work will attempt to better define the mix of sulfur species present at the cut between the adjacent product streams and address what generic modifications might be possible for a commercial unit to take advantage of these results. The impact on main fractionator heat balance must also be addressed. High level heat available from the slurry pumparound will be reduced and more heat will have to be rejected at a lower level. The impact that this has on the FCC gas plant and other units that may be heat integrated with the FCC will vary between units. The commercial test runs planned for Step 3 of the experiment will provide additional valuable information as well as insight into the feasibility of this approach to meet new clean fuels specifications.

While general conclusions can be drawn, each FCC and refinery is different. Some refiners may be able to take advantage of fractionation improvements to reduce the cost of compliance with new clean fuels guidelines while others will not. What is clear is that it is important to consider the sulfur distribution in FCC main fractionator products during scope evaluation for FCC revamps.

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