Balancing the Need for Low Sulfur FCC Products and Increasing FCC LCO Yields by Applying Advanced Technology for Cat Feed Hydrotreating

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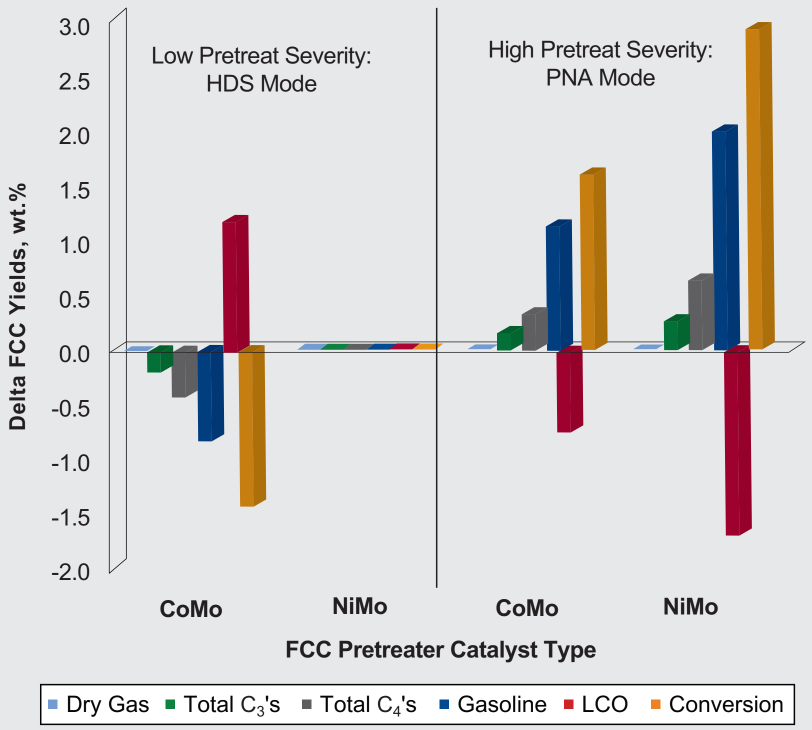
The benefits that hydrotreating fluidized catalytic cracking Unit (FCC) feed has on product yields and sulfur content were recognized some time ago and described in many earlier publications[2-5]. Recent regulatory demands and the drive towards clean fuels resulted in a renewed interest in FCC feed hydrotreating to facilitate compliance and satisfy the need for improved yields. To address these needs, Advanced Refining Technologies LLC (ART) introduced the ApART® Catalyst System for FCC pretreatment [6]. This technology was developed to provide significant increases in HDS conversion while at the same time providing significant upgrading of FCC feedstock quality and has been described in detail previously[7]. In essence, an ApART® Catalyst System is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each catalyst can be optimized to meet individual refiner's goals and constraints. ART has continued to develop a better understanding of the reac-

Figure 1
Impact of Pretreater Catalyst and Operating Severity



tions and kinetics involved in FCC pretreating, and through its relationship with Grace Davison Refining Technologies, a detailed understanding of the effects of hydrotreating on FCC unit performance. The complexity of combinations of catalyst design and operating conditions for both the FCC feed hydrotreater and the FCC unit continues to present a significant optimization opportunity for refiners to drive the combined operation to maximum product value.

It has been shown that both the hydrotreating catalyst system and the operating strategy for the FCC pretreater are critical to providing the highest quality feed for the FCC[8]. In general, NiMo based catalysts produce FCC feed with lower nitrogen and Poly Nuclear Aromatic (PNA) content than CoMo based catalysts. This shifts the FCC yields towards higher conversion at the expense of LCO production. The operating mode of the hydrotreater can also be used to improve the FCC feed. Driving the hydrotreater to remove more nitrogen and PNA's (so-called PNA mode of operation) results in an FCC feed which again shifts the FCC products toward more gasoline and LPG production. This is shown in Figure 1, which summarizes the delta FCC yield at constant coke yields from an Advanced Catalytic Cracking (ACE) pilot plant study comparing the effects of hydrotreating FCC feed over a CoMo and NiMo catalyst. The data clearly show that using a NiMo catalyst results in higher FCC conversion along with higher gasoline yield compared to a CoMo catalyst for both low and high FCC pretreat severity. (Higher dry gas noted at higher conversion and constant reactor temperature is an artifact of pilot testing and is not observed commercially.) The data also show the impact of pretreater operating severity. At high severity or PNA mode, there is a large increase in FCC conversion and corresponding increase in gasoline yield.

Of course, there are also significant differences in hydrogen consumption and pretreater cycle length for the different modes of operation, and these costs need to be balanced against the benefits of increased FCC conversion. This is described in more detail in other work[8].

The FCC catalyst formulation is also an important factor that can be tailored to shift FCC yields and help maximize profitability. Figure 2 summarizes pilot plant data demonstrating the impact on yields of different FCC catalysts using a constant FCC feed that was hydrotreated over a NiMo catalyst with the pretreater operating in PNA versus HDS modes. The data show that significant differences in FCC conversion and FCC product yields at constant coke yield can be affected by changes in FCC catalyst technologies.

Much of the work investigating the effects of FCC pretreating on FCC performance has emphasized gasoline production due to the prevailing economics of the time. The governmental mandate for ultra low sulfur diesel (ULSD) and the resulting increase in demand for these cleaner fuels prompted many refiners to increase LCO production from the FCC unit to maximize the mid-distillate pool. Several papers have explored ways to increase FCC LCO by adjusting FCC catalyst formulations and modifying FCC operation[9]. Understanding the effects that this increased LCO production has on downstream ULSD operation and options for dealing with it have been explored in detail[10]. Given the impact FCC pretreating has on the FCC performance just described, the pretreater clearly has a role to play in modifying the FCC product slate to meet increasing distillate demand.

In addition to changing economics, refiners are also looking at more stringent regulations on fuels which often serve as an outlet for FCC LCO. LCO is blended into wide variety of mid-distillate streams as summarized in Figure 3. It can be sent to a hydrocracker to make high quality jet and kerosene products, and if the refiner has the hydrotreating capacity available, it can be sent to a diesel hydrotreater to produce ULSD or sent to higher sulfur products like fuel oil. A portion of the LCO may also be used as cutter stock or blended for marine diesel. Sulfur specifications on many mid-distillate streams are expected to get more stringent, and Figure 4

Figure 2
Impact of FCC Catalysts on Performance

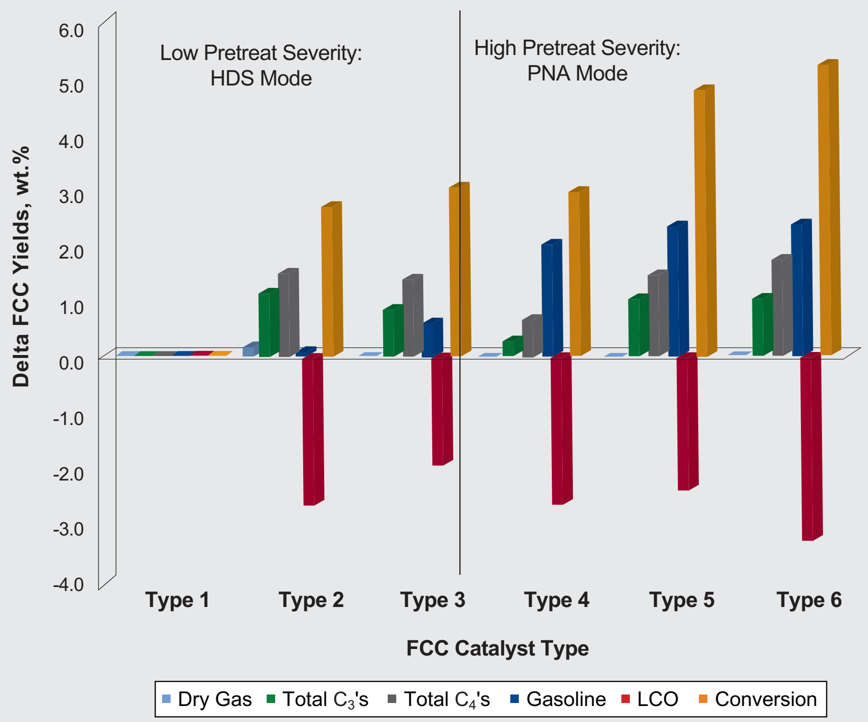


Figure 3
Outlets for FCC LCO

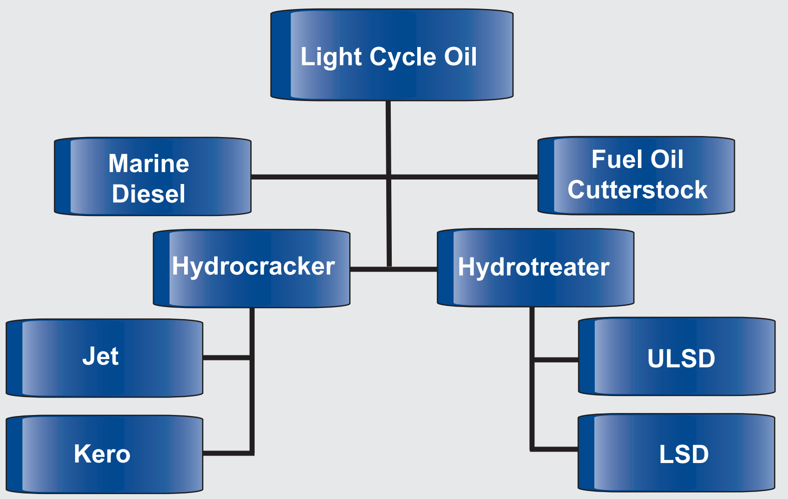


Figure 4
Proposed Sulfur Limits for Marine Diesel[1]

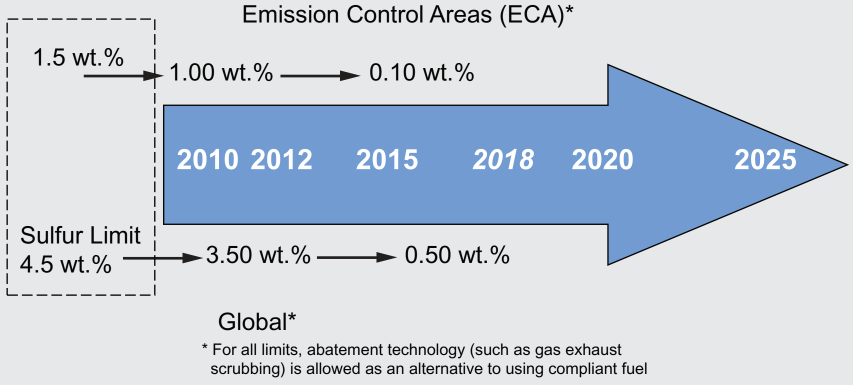
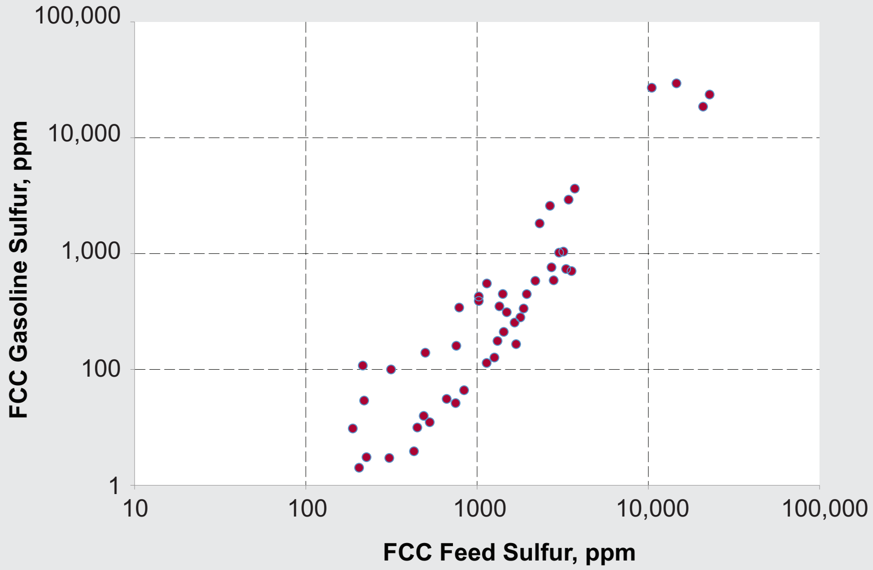


Figure 5
Relationship Between FCC Gasoline Sulfur and FCC Feed Sulfur



summarizes expectations for one such stream, marine diesel.

It is clear that FCC pretreating plays an important part in reducing the sulfur content of FCC products like gasoline and LCO. ART has completed many studies looking into the effects of hydrotreating on FCC performance and the quality of the FCC products. The work demonstrates that reducing the sulfur in FCC gasoline and LCO simply requires a reduction in the sulfur of the FCC feed by increasing the severity of the pretreater. Figure 5 shows the relationship between FCC feed sulfur and the resulting sulfur of the FCC gasoline. This data was generated using a variety of FCC feeds that had been hydrotreated over several types of catalysts and catalyst systems. As can be seen in the chart, there is a good correlation between FCC feed sulfur and the corresponding FCC gasoline sulfur. In this case, the sulfur content in the FCC gasoline is roughly 100 times less than the sulfur in the feed to the FCC.

As might be expected, a similar relationship exists between the sulfur in the FCC LCO and the FCC feed sulfur. An example of this relationship is shown in Figure 6. This chart shows that the LCO sulfur is roughly the same as the FCC feed sulfur. These rules of thumb are helpful when trying to estimate the impact of a change in the FCC pretreater and its effect on the FCC product sulfur levels.

Figure 6
Relationship Between LCO Sulfur and FCC Feed Sulfur

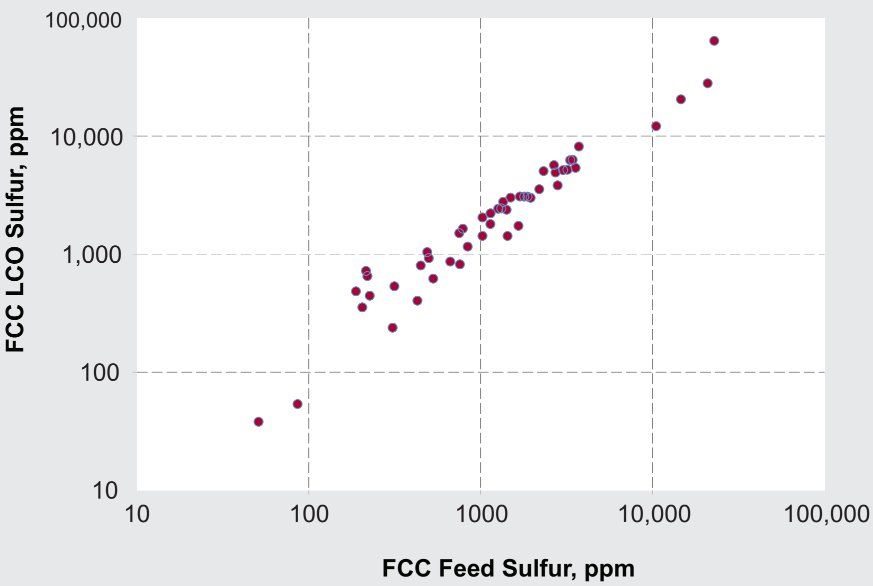
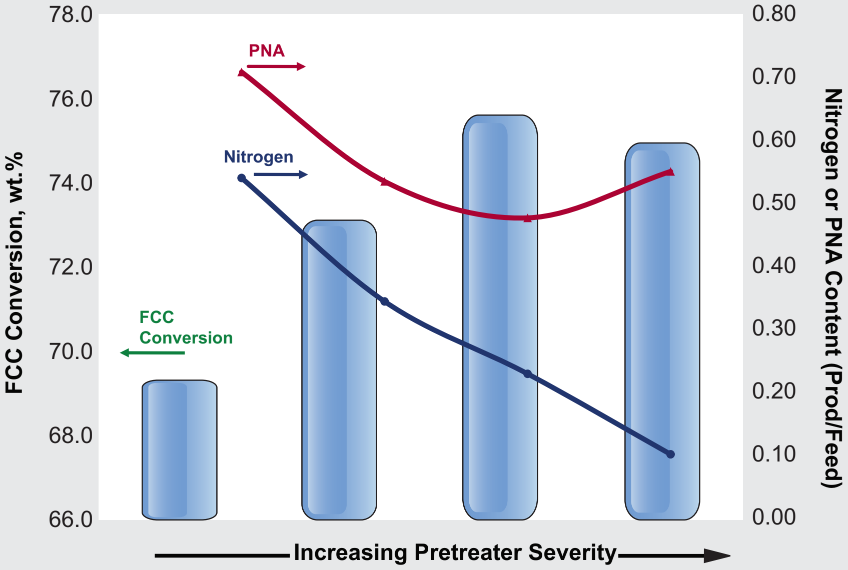


Figure 7
Pretreater PNA and Nitrogen Affect FCC Conversion



The balance of operating the FCC pretreater to meet increasing HDS requirements and increase LCO yield, requires an optimized catalyst system and changes to the pretreater operating strategy in order to provide lower sulfur FCC products and higher LCO yields when the market demands it.

As discussed previously, removing PNA's and nitrogen from the FCC feed improves FCC performance in terms of increased conversion and higher gasoline yield. Figure 7 summarizes FCC pilot plant data for several hydrotreated FCC feeds. The left axis shows the FCC conversion and the right axis shows the FCC feed quality depicted as a ratio of either product nitrogen content to feed nitrogen content or product PNA content to feed PNA content. Clearly, the PNA and nitrogen content of the FCC feed have a strong effect on FCC performance. At the highest pretreater severity, the FCC conversion actually decreases by about 1 wt.% relative to the previous severity in the chart. The decrease in FCC conversion coincides with an increase in PNA content from 0.48 to 0.55. Notice also that the conversion decreases despite the fact that the FCC feed nitrogen content is at the lowest level suggesting the PNA feed content has the larger impact on FCC conversion.

Figure 8 summarizes data from this same study which shows that as FCC conversion increases as a result of increasing pretreater severity, the gasoline yield increases and the LCO yield decreases. Can this effect be mitigated somewhat by the proper choice of catalyst system in the pretreater?

Another study was completed which investigated the impacts of the pretreater catalyst system on FCC performance. A range of catalyst systems were investigated ranging from 100% NiMo to a system which was predominantly CoMo catalyst. Figure 9 compares the gasoline and LCO yields as a function of the catalyst system at constant pretreater severity. The data indicate that adjusting the catalyst system does result in a shift in the FCC product yields. In this example, increasing the amount of CoMo catalyst tends to result in higher LCO yields and correspondingly lower gasoline yield. The data also suggests that there is an optimum catalyst system which can result in a maximum LCO yield.

As expected, the quality of the FCC products is also impacted by the catalyst system. Figure 10 shows the FCC gasoline and LCO product sulfur observed in the same study. As mentioned previously, there is a good correlation between FCC feed sulfur and the FCC product sulfur.

This same work also looked at the sulfur speciation for the FCC gasoline and LCO products. This is useful information if the LCO is subsequently fed to a hydrotreater. Figure 11 compares the yield of LCO and the amount of substituted dibenzothiophenes (hard sul-

Figure 8
FCC Conversion Affects Gasoline and LCO Yields

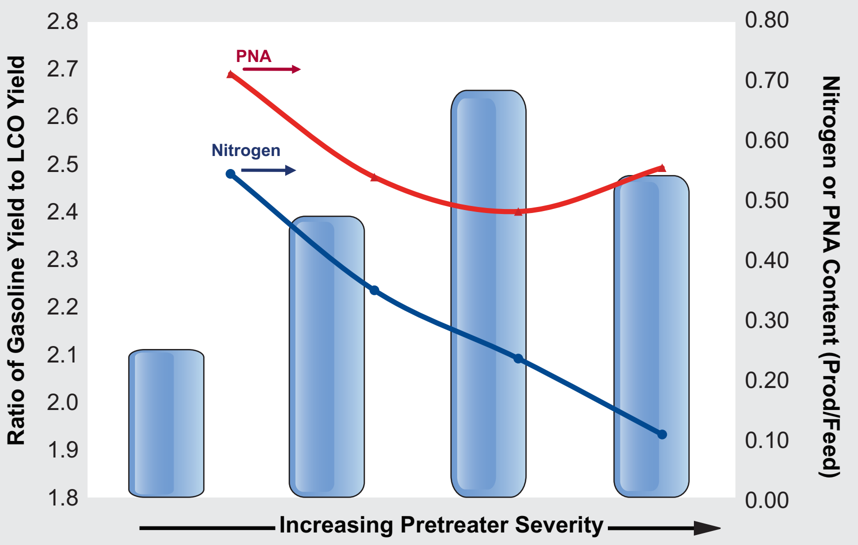
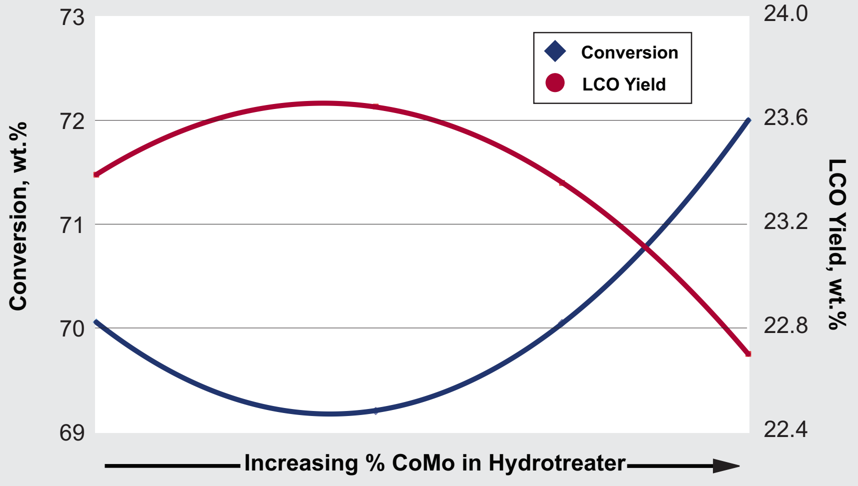


Figure 9
Pretreat Catalyst System Shifts FCC Yields



fur) remaining in the LCO as a function of the pretreater catalyst system. The total sulfur in the LCO decreases at a significantly faster rate than the hard sulfur concentration, but the amount of hard sulfur as a fraction of the total sulfur decreases at an even faster rate. Decreasing the total LCO sulfur by 25% lowers the hard sulfur concentration by over 35%. It also shows that as LCO sulfur decreases, the yields of LCO can shift assuming constant FCC operation. Simply cutting the LCO sulfur in half with additional pretreater severity can decreases the quantity of LCO by almost one percent in this case. Again, the data suggests there may be an optimum catalyst system which can provide the right balance between LCO yield and LCO sulfur content.

The LCO API gravity was also estimated from correlations using FCC feed gravity and FCC conversion since not enough LCO product is produced to measure density. The LCO API gravity gives a rough indication of the aromatic content and can also be useful for estimating hydrogen consumption if the LCO is being sent to a hydrotreating or hydrocracking operation. Figure 12 shows some general trends in LCO gravity as a function of FCC conversion and FCC feed API. There is a strong correlation between LCO API and the FCC severity. As FCC conversion increases to produce more gasoline, there is a negative impact on the LCO API indicating the LCO is becoming more aromatic. By increasing

Figure 10
FCC Gasoline and LCO Sulfur Trends with FCC Feed Sulfur

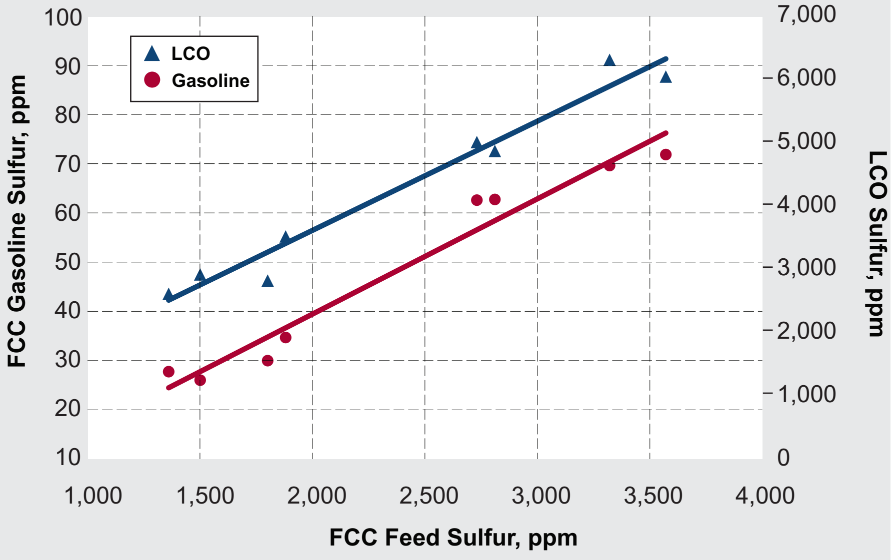


Figure 11
Impact of Pretreater Catalyst on LCO Yield and Sulfur Species

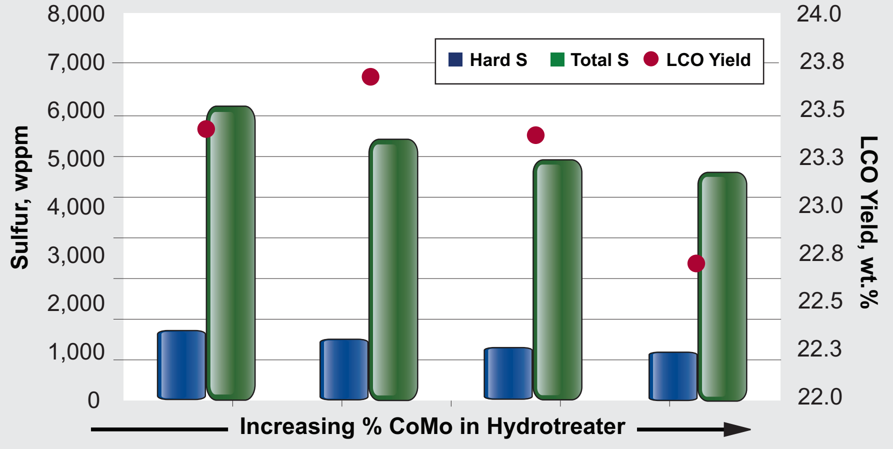


Figure 12
Impact of Pretreatment on FCC LCO API

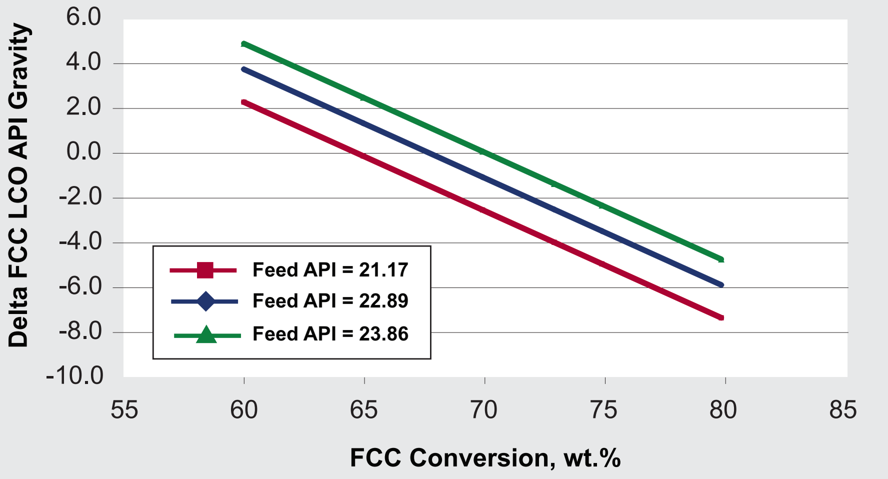
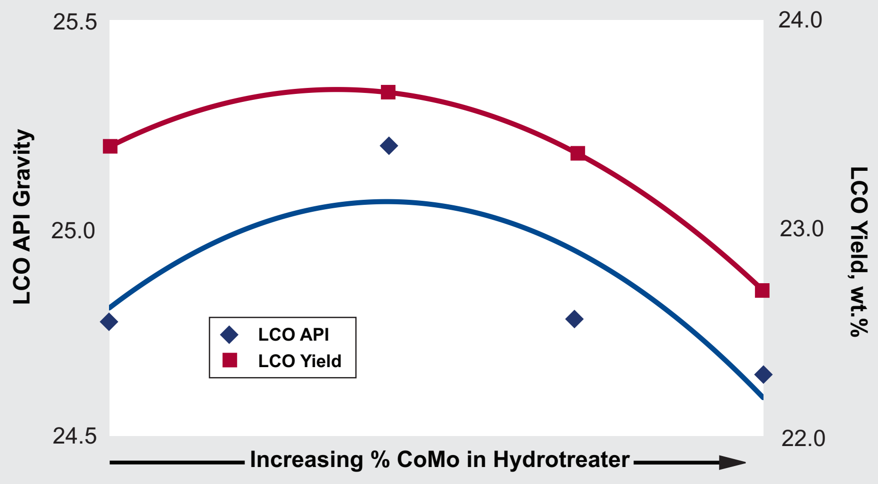


Figure 13
LCO Sulfur and Gravity Comparison



pretreater severity, the quality of the feed to the FCC improves (API gravity increases) and at constant FCC conversion levels on the chart, it is apparent that the LCO API increases along with FCC feed API, indicating that a better quality LCO can be produced.

Directionally decreasing the FCC to increase LCO production can increase the LCO API by as much as 5 numbers. This indicates there is an interesting interaction between the FCC pretreater operation and the quality of the FCC LCO. Increasing the severity of the pretreater will increase the FCC feed API and decrease the FCC feed sulfur and nitrogen. This can result in a higher quality LCO in terms of lower sulfur and higher API (higher cetane), but as alluded to earlier, this requires between 200-400 SCFB higher hydrogen consumption at the pretreater. The higher cost may be justified depending upon the margin of the finished product that contains the LCO.

These correlations were also used to assess the product quality in terms of aromatics or API in the study above. As a general rule when the FCC feed sulfur is decreased there is a corresponding decrease in LCO yield and a decrease in LCO API gravity. However, having to operate the pretreater at higher temperatures in order to lower the sulfur and improve the FCC feed API is not the only solution to improving product properties. Figure 13 compares several pretreater catalyst systems, and shows how an optimized

Figure 14
Comparing CoMo and NiMo Impact on LCO API

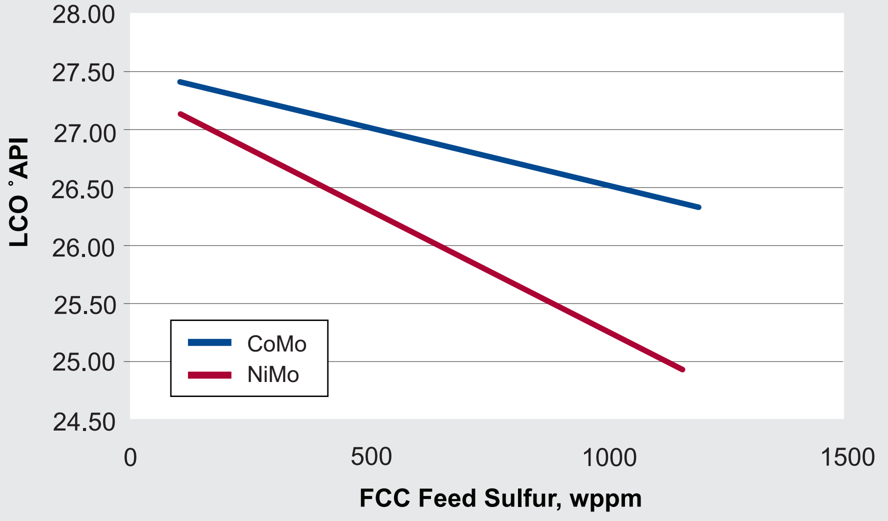
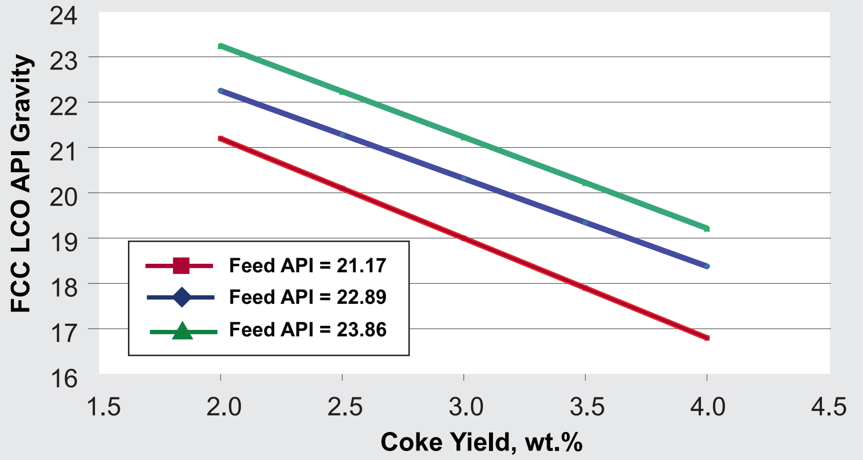


Figure 15
Changing FCC Operation



loading can not only produce a higher yield of LCO, but also one with the highest possible API gravity. In this case, there is a maximum LCO yield which is about one wt.% higher, and there is almost a one number improvement in the API of the LCO.

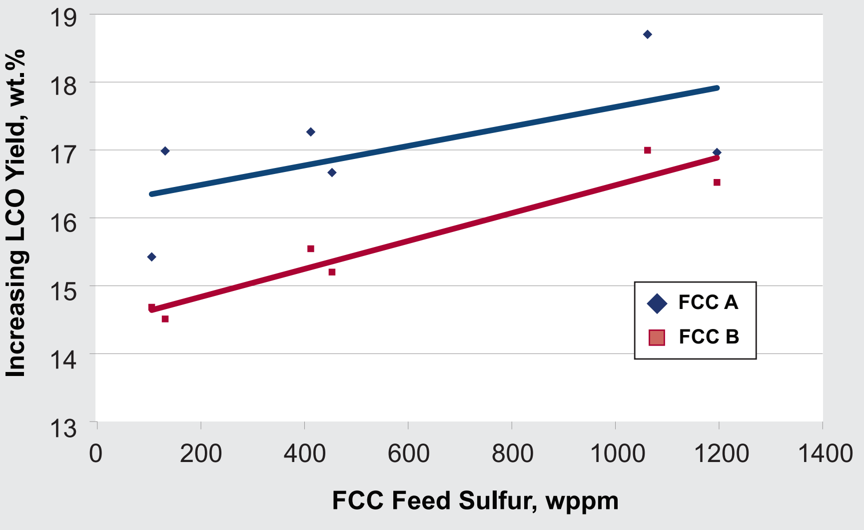
Figure 14 shows another example demonstrating the effects of FCC pretreater catalyst type on LCO quality. The chart compares how a CoMo and NiMo catalyst system can change the feed quality to the FCC and ultimately the LCO API gravity. Although the all CoMo system is producing the highest quality LCO in terms of API gravity, it is apparent that the all NiMo system is capable of nearly achieving the same quality at high pretreater severity. This is comparable to the PNA mode of operation mentioned above, and as indicated the pretreater cycle length will be shorter operating that way. This suggests that the tailoring of the FCC pretreater is important in order to gain the maximum flexibility.

Making changes to the FCC pretreater to operate in a different mode (HDS or PNA mode) also influences the resulting LCO product. Switching between HDS and PNA modes of operation can result in changes in the LCO API gravity. Figure 15 compares the same three FCC feedstocks as in Figure 12 but this time the data is plotted against FCC coke yield to represent changes in the FCC operation. So, both the pretreat catalyst system and the pretreater operation can influence LCO yield and quality.

In addition, the operation of the FCC changes the LCO yield and quality. This indicates that re-optimization of both the FCC and pretreater operation is required to ensure high yields of LCO and an overall profitable FCC yield slate.

Different pretreat catalyst systems can result in higher FCC bottoms yields if the FCC is not re-optimized as it shifts from maximum conversion to maximum LCO operations. Figure 16 is an example of comparing the LCO yield generated from two different FCC catalysts processing the same FCC feedstock. Switching FCC catalyst from A to B provides several percent higher LCO yield at the same FCC feed quality. This provides a means to offset higher bottoms yield which may occur from changes in the operation of the upstream pretreater to focus on increasing LCO yields. Hu et.al. showed that Grace Davison's MIDAS® catalysts and Olefins® Ultra ZSM-5 technologies are a profitable approach to minimize bottoms yield during maximum LCO operation.[9]

Figure 16
Changing FCC Catalyst



Conclusion

If the refiner's objective is to maximize the distillate pool it is important to understand the key relationships between FCC pretreat and FCCU operations and their corresponding catalyst systems. Both processes must be re-optimized as the refiner moves from gasoline to distillate production to ensure maximum profitability. All of the combinations presented show the need for refiners to follow an integrated approach to managing the catalysts and operation of the FCC pretreater and FCC units. Both FCC and hydroprocessing unit operations can be continuously optimized throughout the course of the hydrotreater run, to significantly increase refiner revenue.

Results from a variety of ACE studies using many different feeds and a variety of FCC pretreat catalyst systems indicate that the amount of sulfur in the FCC products is dictated primarily by the FCC feed sulfur. Furthermore, for hydrotreated FCC feeds, the distribution of sulfur in FCC products is independent of the type of FCC pretreat catalyst system employed and depends solely upon the amount of sulfur in the FCC feed. This work demonstrates that the ability to make a major impact on FCC yields is strongly influenced by the type of FCC pretreater catalyst system used in conjunction with the appropriate FCC catalyst. Simply making a change to one operation without consideration for the other can result in unexpected results and limited flexibility to produce the fuels needed for downstream blending or use.

Both the hydrotreating catalyst system and the operating strategy for the pretreater are critical to providing the highest quality feed for the FCC. Driving the hydrotreater to remove nitrogen and PNA's improves FCC product value when targeting gasoline production, but this needs to be balanced against the increased costs of higher hydrogen consumption and shorter cycle length that result from this mode of operation. Use of tailored ApART® catalyst systems can optimize the FCC in order to produce not only high quality feeds to the FCC but also low sulfur products resulting in less impact on downstream hydrotreating. This tailoring can also be beneficial if the FCC products are used directly without hydrotreating, as they can be driven towards lower sulfur and higher gravity products allowing the refiner to be able to blend these fuels directly. This creates a fuel pool that can also have higher cetane values due to the higher gravity.

The complex relationship between the FCC pretreater and the FCCU underscores the importance of working with a catalyst technology supplier that has the capabilities to understand the interplay between the hydrotreating performance of the FCC pretreater and the performance, yield structure and product sulfur distributions of the FCC. ART, and through its relationship with Grace Davison Refining Technologies, offers just such capabilities and delivers them through tailored ApART® catalyst systems to meet the refiner's specific FCC feed slate needs and FCC pretreat operation constraints.

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