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Maximising FCC Profitability with FCC Pretreater Performance A Proven Strategy for Maximum Aromatic Saturation

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Clark Refining and Marketing in Port Arthur, Texas, and Lyondell-Citgo Refining (LCR) in Houston, Texas, realised it was time to stop analysing it on paper and in the laboratories. In 1998, they finally started to reap the rewards of operating their commercial scale FCC feed hydrotreaters for maximum aromatic saturation. However, the problem with most paper studies and R&D efforts is that they generally do not come with commercial operating manuals.

It is well documented that operating the FCC feed hydrotreater with an objective for aromatic saturation improves the Fluid Catalytic Cracker (FCC) light product yields and economics. In many cases, yield improvement is obtained with no capital expenditure! Documented economic incentives have been in the range of $2-10 million USD/yr as long as additional makeup H2 is available and the FCC can actually take advantage of improved feedstock quality (increase cat/oil, increase conversion, etc). *If this operation is so beneficial, why hasn't every FCC feed hydrotreater adopted this strategy?*

Most refiners with a FCC feed hydrotreater have contemplated the aromatic saturation strategy. Even when the economic incentives appear to exist, there is a hesitancy to proceed with implementation due to a lack of clearly defined and proven operating practices. This article provides commercial feedback on a proven operating strategy for maximum aromatic saturation where cycle life and performance are optimised by practical application of the reaction chemistry and thermodynamics.

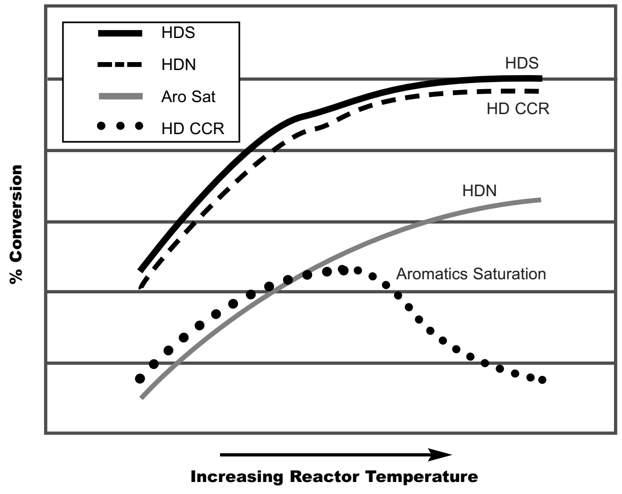
The Theory behind the Strategy

Definition of key operating parameters as they relate to FCC yield response is required in order to provide the foundation for the aromatic saturation strategy. In general, the FCC yield response is governed by feed quality as defined by the sulphur, nitrogen, carbon (CCR), metals, and aromatic species, as well as physical equipment limitations. Physical equipment limitations include air blower limits, catalyst circulation ability, heat balance, stack emissions requirements, etc. The FCC's response to changing sulphur, nitrogen, carbon, and metals is covered in detail in many publications and is not covered in this article. The FCC's response to feed aromatic.content is covered in general terms, as this will be the cornerstone of the operating strategy.

The following is a generalisation of the complex chemistry that occurs within the FCC. Hydrogen saturated species in FCC feed, like naphthenic and paraffinic structures, undergo cracking to lighter components in the FCC environment. Unsaturated aromatic species, like benzene, undergo very little cracking. Aromatic species exist as single or multiple ring structures, defined as mono, di, tri, and tetra aromatic.

Mono aromatic species will generally distribute in liquid products from the FCC, with a large percentage in the gasoline fraction. Di aromatic species distribute in all liquid products from the FCC, as well convert to coke on the FCC catalyst. Tri and Tetra aromatic species either convert to coke on catalyst or distribute in the Light Cycle Oil or heavier fraction from the FCC. Maximising FCC gasoline and lighter valuable products requires an understanding of how to maximise the conversion of multiple ring aromatic species (di+) to single (mono) aromatic

Figure 1:
Reactor Temperature vs. Conversion



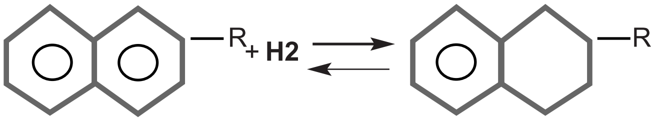
or saturated ring species in the FCC feed hydrotreater.

The starting point for developing an operating strategy for maximum aromatic saturation is to understand the kinetic and thermodynamic response for the removal of FCC feed contaminants. Figure 1 shows the generalised responses for the key FCC feed properties as reaction temperature is increased. The responses are set by the FCC feed hydrotreater severity (H2 partial pressure, space velocity, treat gas rate, and feedstock properties).

The kinetic and thermodynamic responses of sulphur, nitrogen, CCR, and metals removal are as one might logically expect. An increase in temperature results in conversion of these contaminants. The kinetic responses for these contaminants represent irreversible reactions.

The aromatic conversion curve has a different temperature response. The following generalised chemical equation represents the equilibrium limited or reversible reaction for aromatic saturation.

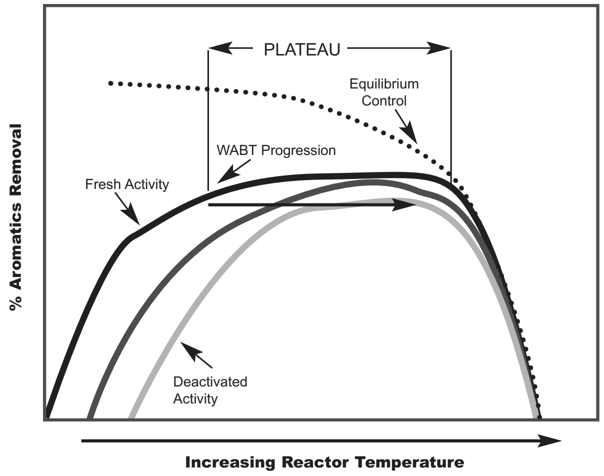
Eq. 1



The behavior has been modeled by Yui [1] by employing first order reversible kinetics. Figure 1 indicates that aromatic saturation will pass through a maximum as the reaction temperature is increased. The maximum is identified as the point where the net rate of aromatic saturation is zero due to offsetting effects of the forward and reverse reactions.

An understanding of the deactivation response is required for each of the key FCC feedstock properties throughout the FCC feed hydrotreater cycle. This information allows the operator to adjust the unit conditions to ensure that the FCC feed quality is optimised. The deactivated responses vary between hydrotreaters and must be individually determined. The preferred method is to obtain this information from the commercial operation, as pilot units may not take into account the actual flow distribution and temperature profiles within the commercial reactor. Obtaining reliable deactivation rate data from a commercial unit is difficult due to changing feedstock quality. This is where technical service supplied by Criterion Catalyst Co. becomes key in helping to remove the variability of feedstock and operating conditions. This normalisation method uses kinetic equations, process models, and in house developed correlations to provide feedback to the operator on the deactivated temperature response.

Figure 2: Aromatics Equilibrium as a Function of Catalyst Activity



Understanding how the aromatic saturation curve responds to catalyst deactivation is a critical element for the strategy for maximum aromatic saturation. Figure 2 provides a conceptual model of aromatic saturation as a function of both fresh and deactivated catalytic activity. Each curve has a "plateau" where maximum aromatic saturation will occur. The "plateau" is defined as the relatively flat area on either side of the maximum point. The left side represents the kinetically controlled area of the curve, where the right side represents the thermodynamic equilibrium controlled area. Fresh catalyst will have the highest aromatic removal maximum point, lowest operating temperature where the plateau begins, and the widest temperature range within the plateau. The response of this curve to deactivation will provide the foundation for the recommended temperature strategy.

Table 1

	Lyondell	Clark
FeedStocks	SRVGO/Coker GO	SRVGO/Coker GO
FeedRate MB/D	50	35
LHSV	.8	1.6
H2 Partial Pressure Bar (PSIG)	>69 (>1000)	<45 (< 650)
H2/Oil m3/m3 (Scf/bbl)	350 (2000)	210 (1200)

Translation of Theory into Practice

The theoretical foundation for the operating strategy for maximum aromatic saturation is provided above. Now is the time to translate theory into practice. Two US gulf coast refiners will detail their experience with converting FCC Feed hydrotreaters to maximum aromatic saturation.

Table 1 shows the operating conditions of the two units used as demonstration cases. The LCR hydrotreater is identified by moderate H2 pressure that represents the typical design that would consider the aromatic saturation strategy. Significant conversion of total and di+ aromatic species can occur at this H2 partial pressure (>35% and >55%, respectively). The Clark hydrotreater, on the other hand, represents a low H2 pressure operation. Units of this design have historically not considered this operating strategy. *Why?*

There is a paradigm that minimal aromatic saturation can occur at this H2 pressure. The reduction in total aromatic species "is" small (< 20%), however the reduction in di+ aromatic species can be as high as 40%! Remembering that conversion of di+ aromatic species to mono or saturated ring species results in higher FCC gasoline production, even low H2 pressure designs can have a large impact on FCC yields, as seen in Figure 3.

There is another paradigm that deactivation rates, at this H2 pressure, will cause “unreasonable” cycle lengths. The Clark unit actually had a longer cycle when utilising the operating strategy for maximum aromatic saturation compared to the previous sulphur removal strategy! The combined efforts of the Clark and Criterion staff have succeeded in shifting both of these paradigms at the Port Arthur refinery by marketing the commercial data and benefits among refinery personnel.

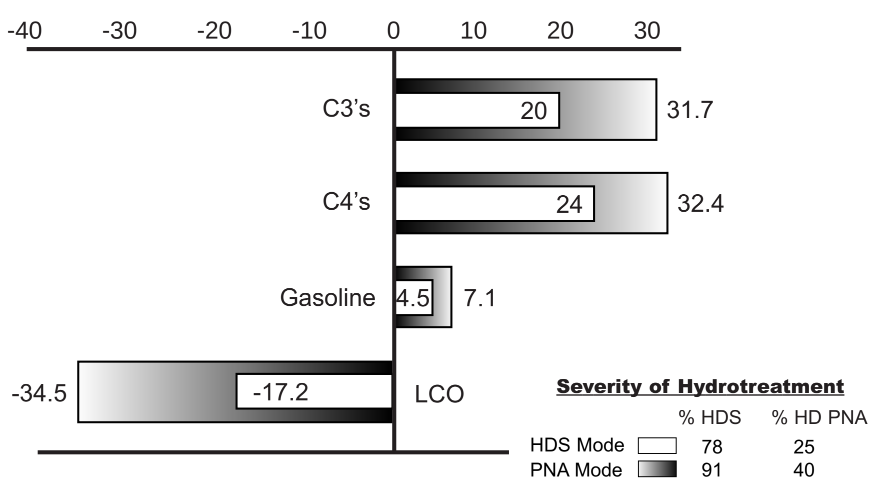


Figure 3: Impact Hydrotreatment on FCC Yields
H2 Partial Pressure 45 Bar (650 psig)
LV% Yield Shift (Base Condition is No Hydrotreatment)

There were several major hurdles that these refiners needed to overcome prior to conversion to the aromatic saturation strategy. The process engineers at the refineries needed to first “sell” the concepts and expected benefits to the operating personnel and management. A collaborative effort between Criterion and the refiners technical and operations staff was required to convince each refinery’s management about the safety, operability, and economic incentives of the operating strategy. With their management teams convinced on all issues, proper catalyst selection, detailed operating procedures and guidelines, analytical requirements, and operator training were required to ensure successful implementation.

Verification of Safety and Operability

The following list identifies major process impacts that were part of the safety and operability review. This list serves only as the starting point for evaluations.

Increased H2 Consumption: H2 consumption can increase by 15-40% depending on the historical start of run temperature requirement. Clark observed an increase of 38% when operating for maximum aromatic operation, which required the operation of a spare makeup H2 compressor. LCR observed an increase of 30%. If the increase in H2 consumption is greater than the amount of. H2 available, the feedrate needs to be decreased in order to hold unit pressure.

Increased Reactor Bed Exotherms: Evaluation of the expected bed exotherms and quench requirement are required to identify any safety and operability constraints.

Increased H2S Production in the Hydrotreater: At start of run conditions, H2S production can be higher than the previous sulphur removal strategy in the hydrotreater resulting in greater sulphur plant capacity or amine requirement.

Potential for Increased Ammonium Chloride and BiSulfide Corrosion: At start of run conditions, nitrogen and sulphur removal can be significantly higher. The increase in ammonia partial pressure in the mixed hydrocarbon phase, as well as ammonium bisulfide concentration in the water phase, can lead to an increased potential for salting and corrosion. A thorough evaluation of the water wash facilities and tube velocities needs to be completed.

Decreased Hydrotreater Catalyst Life: It is anticipated that the FCC feed hydrotreater cycle life decreases on the order of 15-50%. This is dependent on the unit operating conditions and the maximum allowable product sulphur. In addition to increased turnaround costs, safety and reliability issues related to increased turnarounds need to be part of the evaluation. The LCR conversion resulted in a 25% reduction in cycle life. For Clark, the new strategy resulted in a run that was actually longer.

Operational Impact at FCC: Do not automatically assume that reducing feed contaminant and aromatic content improves the economics at the FCC. Evaluations need to be rigorous and complete with respect to the expected FCC yield structure and equipment limitations. The following list identifies major potential FCC equipment limitations that may occur during the aromatic saturation strategy.

1. Impact of lower coke producing feed negatively impacts the heat balance.
2. Increased C3/C4 production exceeds Wet Gas Compressor and alkylation unit capacity.
3. Increased light product volume causes flooding in the main fractionator or other light ends towers.

Catalyst Selection

It is generally recognised that Nickel Molybdenum (NiMo) catalysts are superior to Cobalt Molybdenum (CoMo) catalysts (or their derivatives) for aromatic saturation and nitrogen removal. The Clark hydrotreater benefited from increased aromatic and nitrogen removal.by changing from a stacked bed of NiMo over CoMo to a 100% NiMo Criterion *DN200* catalyst system. LCR also selected *DN200* for their hydrotreater. LCR has utilised Criterion’s *DN200* catalyst for 2 consecutive cycles in the aromatic saturation mode. Clark recently reselected the *DN200* catalyst system for their second cycle.

A critical success factor for the aromatic saturation strategy is governed by obtaining the highest aromatic saturation and nitrogen activity catalyst in order to improve the “crackability” of the FCC Feed. Sulphur removal is actually a secondary requirement because sulphur does not significantly influence the valuable FCC light product yields. Sulphur removal only becomes an issue when the environmental requirements of the FCC regenerator, gasoline blendability, or physical H2S handling capabilities of the FCC are limiting. Desulphurisation (HDS) stability is the critical cycle life determinant. Sulphur removal activity generally limits the catalyst cycle due to higher deactivation rate compared to aromatic saturation activity. In over 38 FCC feed hydrotreaters, DN200 has provided “step out” commercial improvements in HDS stability on the order of 30-60% over industry benchmark catalysts like Criterion *424* and *411*. In the Clark low H2 pressure operation (< 45 bar, <650 psig H2 partial pressure), the unit experiences less than 1.4 C/mo (2.5 F/mo) HDS deactivation rate when utilising the aromatic saturation strategy. This allowed Clark to operate for an 18-month cycle, which was 50% longer than the previous cycle!

Operating Guidelines and Procedures

Determine the absolute maximum sulphur content of the FCC feed: This is a fundamental requirement. The definition of this boundary requires changing paradigms and allowing the limit to be set by:

1. FCC regenerator sulphur dioxide and nitrogen oxide requirements
2. Refinery gasoline, diesel, or fuel oil sulphur blending requirements
3. Physical FCC H2S removal capacity

Sulphur is not a critical factor in determining the FCC light product yields and its relationship with nitrogen removal should not be used as a basis for establishing this limit. Nitrogen and aromatic removal should be monitored individually and their respective impact on the FCC yields and economics should determine their limits. In the process of defining their sulphur limit, Clark identified that under the conditions above, their existing sulfur limit could be relaxed. When combined with the improved stability of DN200, the predicted (and observed) cycle life was longer utilising the aromatic saturation strategy compared to the previous sulphur removal strategy. The longer cycle life helped “sell” the concept to management.

Change of Operational Control Point and Temperature Strategy

Sulphur removal will no longer be a control point to adjust the reactor temperature, unless the product sulphur is above the established maximum limit. The operating strategy requires that reactor temperatures operate within the plateau of the aromatic saturation curve as soon as the catalyst has undergone a sufficient break in period. At the start of the cycle, the recommended operating procedure is to remove only the required sulphur for 4 weeks before increasing the reactor temperatures to the plateau.

The aromatic saturation kinetic and thermodynamic response is set by the H2 partial pressure of the unit at constant feed rate (space velocity). If the H2 partial pressure is maintained, the unit will achieve maximum aromatic saturation as long as all temperatures within the reactor are maintained within the plateau. This represents a more stable operation because daily adjustments are not necessary to maintain constant product sulphur. Only periodic increases in reactor temperature are required to counter the effect of catalyst deactivation on the aromatic saturation curve, as Figure 2 identifies. Clark and LCR have incorporated into their operating procedure a planned increase in operating temperature every 3 months.

Figure 4 shows the expected kinetic and thermodynamic response for di+ aromatic saturation for the Clark and LCR units as a function of the weighted average bed temperature (WABT). The WABT is calculated by the following equation WABT = Inlet Temp + 2/3 Reactor Delta T. H2 partial pressure and space velocity differences between the two units account for difference between the aromatic saturation curves. The Clark data represents the actual commercial unit response. The LCR data was measured in a pilot unit.

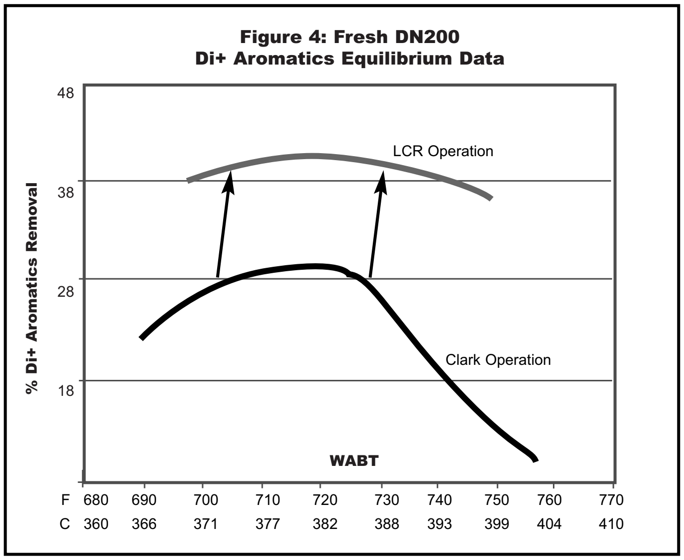


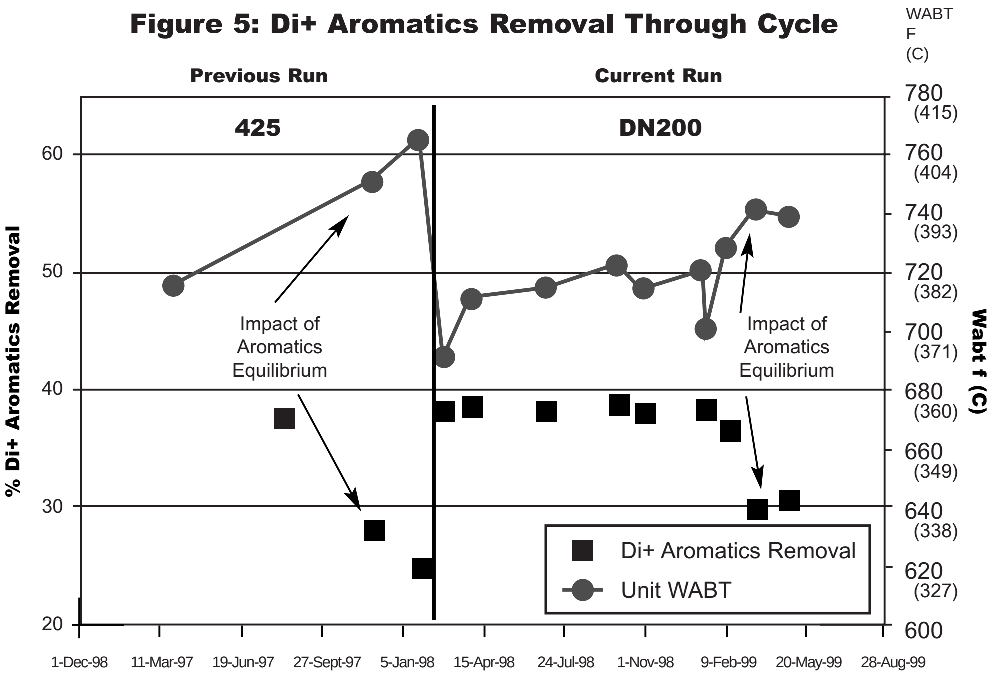
Figure 4: Fresh DN200 Di+ Aromatics Equilibrium Data

Aromatic saturation response curves generated in pilot units usually represent isothermal operation. However, commercial units operate adiabaticly which requires a translation of the pilot data. The WABT is used to correlate isothermal pilot result to adiabatic commercial operation for desulphurisation and denitrification reactions. The question is *“Can the WABT be used to control for aromatic saturation, given the implications of the reverse kinetics occurring at the higher reactor outlet temperature?”* The answer is yes as long as the outlet temperatures of the beds, and especially the last bed, are carefully monitored and are not allowed to operate above the temperature that corresponds to area beyond the right side of the plateau. This prevents production of aromatic species as the liquid leaves the hottest part of the bed.

Strategy and availability of quench are very important. If sufficient quench and heater capacity exists, equal bed outlet temperatures corresponding to the targeted WABT should be the objective during most of the run. As the product sulphur nears it’s maximum, the WABT should be increased such that the equal bed outlet temperatures correspond to the far right side of the plateau. The cycle can be extended if additional quench and heater availability exists by operating the front beds hotter than the final bed outlet temperature, which still remains within the plateau.

The Clark and LCR temperature strategy involves initially targeting a WABT that corresponds to the left side of the plateau on the aromatic response curve. Limitations on both units prevent all equal bed outlet temperature operation. However quench rates are optimised so that at least the back two outlet bed temperatures are equal. As the run progresses, the reactor WABT is slowly increased to counteract the effects of deactivation and ensure that the operation stays within thearomatic saturation plateau. Figure 2 identifies the reason for this strategy. As the catalyst deactivates, the left side of the plateau shifts to the right. If the WABT is held constant through the cycle, the operation will move away from maximum removal of aromatic species due to deactivation of the kinetically controlled portion of the curve. As the product sulphur approaches the maximum limit, the outlet temperature of the last bed will have crossed completely through the plateau and will correspond to the far right side. The temperature strategy has an advantage that relates to catalyst coking. By targeting the start of run WABT on left side (lowest temperature) of the plateau, catalyst coking is minimised compared to targeting the centre or right side of the plateau. The proposed operating strategy utilises an old hydrotreating rule of thumb, "coke no catalyst before it is time."

Figure 5: Di+ Aromatics Removal Through Cycle



Aromatic Removal Monitoring and Control

What method should be used to monitor aromatic removal? Monitoring of the speciated aromatic removal by utilising simple refinery analyses and process variables like H2 consumption have been considered, however it is the conclusion of the authors that nothing replaces the actual speciated aromatic analysis for monitoring and control of this strategy. The critical part of selecting the analytical method is that it identifies the aromatic species (mono, di, tri, tetra, etc). This requirement eliminates several simplistic refinery analyses such as aniline point, refractive index, or UOP K because these methods cannot differentiate aromatic species. Monitoring of H2 consumption does not provide effective aromatic removal determination because the consumption of hydrogen is also impacted by other reactions that are occurring. Any repeatable speciated aromatic method can be used provided the same method is consistently applied for initial equilibrium determination and monitoring. The two operations described in this article utilised a UV method.

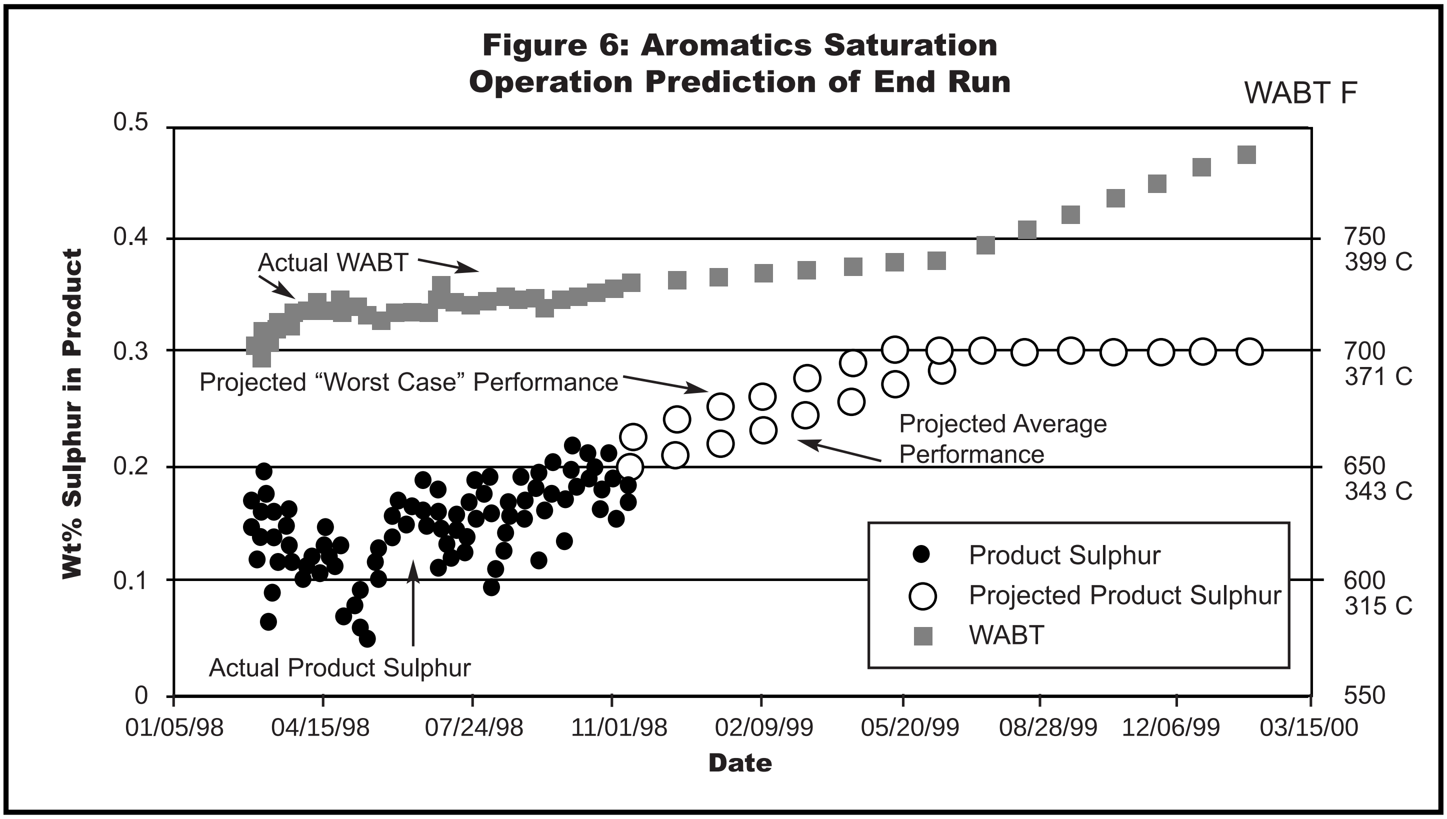
At what frequency should aromatic removal be monitored? The Clark operation relied on monthly analysis provided by Criterion Catalyst Co. in order to monitor the operation. If there was a significant change in feedstock, aniline point performance, or FCC yields, a non-routine sample was analysed for aromatic content to verify the observation. Monthly aromatic analysis was the measured variable utilised for unit control while simple refinery analyses provided performance indicators between samples. Figure 5 shows di+ aromatic removal and corresponding reactor temperature during the cycle for the Clark hydrotreater. The commercial data shows that the temperature strategy employed maintains relatively constant aromatic removal until the reactor temperature operates beyond the right side of the plateau where the di+ aromatic removal declines.

Personnel Training

A critical step in the implementation process is properly training all impacted personnel. This should include the operators, foremen, engineers from the FCC feed hydrotreater and the FCC, as well as planning personnel, and other refinery management. Clark utilised a "top down" training strategy for the operating personnel. Operating foremen were the first group provided with formal training. The training included a review of the theory, operating strategy and guidelines, expected unit impacts through the cycle, spreadsheet monitoring tools, and an exhaustive question and answer session. With the "buy in" of the foremen, head operators, followed by assistant operators, were provided with training. It is crucial that operations and management have bought into the concept and are willing to work through the transition period.

Predicting the End of Cycle

The theoretical end of cycle occurs when the product sulphur level exceeds the maximum limit, while still operating within the plateau. Most units still have the ability to meet product sulphur specifications for several months before the unit becomes temperature limited. End of run economics and planned turnaround dates will determine if the unit continues to



operate with sub optimal aromatic saturation.

In order to support the strategy, Criterion has developed a method of predicting when the product sulphur will reach the maximum limit. This method utilises the HDS deactivation rate determined through unit data normalisation and applies the data in a process model that projects future product sulphur. A graphical example of the quarterly prediction report for LCR is provided in Figure 6. The historical WABT and product sulphur is shown to identify where the unit has operated. A kinetic extrapolation forecasts product sulphur as the unit continues to deactivate for HDS. The "worst case" and average performance scenario show the sensitivity of the end of run prediction.

Conclusion

The aromatic saturation strategy is no longer a laboratory experiment. Clark Refining and Marking, Lyondell-Citgo Refining, and Criterion Catalyst Co. have developed commercially proven operating practices for maximum aromatic saturation that allow these refiners to reap long term economic benefits. Successfully operating for maximum aromatic saturation in a FCC feed hydrotreater requires that personnel translate the chemistry and thermodynamics into practical and proven operating practices.

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