EXPERIENCES IN MAXIMIZING PERFORMANCE OF ULSD UNITS

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ABSTRACT

Refiners in the US and Europe, as well as many other countries, have been producing ULSD for at least 3 years. While some problems were encountered in the transition to ULSD, the vast majority of these new ULSD units and unit revamps have performed as well or better than expected. As these units reach the end of their first cycle, it's worthwhile to review their operating experiences and investigate opportunities to further optimize performance.

One area of significant progress in the past 3 years is in understanding the chemistry of hydroprocessing for ULSD. It turns out that there are more significant differences in the desulfurization chemistry for these units than can be accurately understood by using average bed temperature and basic kinetics. What is needed is a look inside the reactor in order to develop an understanding of the discrete reactions taking place. Albemarle has developed a methodology and a model to accomplish just that. This technology, designated STAX®, predicts the required catalyst functionality for each section of the reactor based on key parameters for the particular ULSD unit. The result is a catalyst system design which delivers maximum performance within the constraints of the unit and objectives of the refiner.

In this paper we review the development of the concepts and methods for STAX® technology. Commercial experience, where the STAX® design techniques have been successfully applied, will also be discussed.

I INTRODUCTION

A mandated reduction of the sulfur content of on-road diesel to a maximum of 15 ppm went into effect in the United States in June 2006. Over the last several years, refiners have struggled to find low-cost strategies to meet these stringent specifications. Options include revamping existing diesel units, construction of grass-roots facilities or a combination of these approaches. A vast majority, about 70%, opted to revamp existing diesel units, while the others opted for adding grass-roots capacity. Most refiners no longer have the excess capacity to rerun or blend off-specification products. Ultra-low sulfur diesel (ULSD) has to be produced correctly the first time or the refinery's economics will suffer. Sulfur contamination or unit malperformance cannot be tolerated.

For most of the history of hydrotreating, a single catalyst loaded in a single unit was sufficient to provide the expected level of performance. There were exceptions, such as fixed bed resid or grading to deal with contaminants, but for the majority of applications the single catalyst system approach worked well. As the demands placed on hydrotreating units have increased and the requirements for hydrotreated product have become more stringent, the opportunity for a more skilful approach to catalyst system design has become apparent.

The traditional approach to understanding the chemistry of hydroprocessing is to analyze feed and product properties, measure average reactor temperature (WABT) and use kinetic expressions to analyze unit performance. Obviously this approach only provides an average view of how the unit is operating. In recent years more sophisticated sulfur and nitrogen specific analysis as well as inter-bed temperature measurements have given more insight into unit performance. Still, the information is not detailed enough to fully understand the reactions taking place inside the unit.

Albemarle has developed a model that describes the chemistry within a ULSD reactor as occurring in distinct reaction zones. A design tool, based on this model, predicts the required catalyst functionality for each reaction zone based on key parameters for the particular ULSD unit being modeled. The result is a catalyst system design, called STAX®, which delivers maximum performance within the constraints of the unit and objectives of the refiner.

In this paper we review the development of the concepts and methods for the reaction zone based model and catalyst system design tool. Commercial experience, where the design techniques have been successfully applied, will also be discussed.

II ULSD REACTOR ZONE MODEL

Fully understanding the chemistry of hydroprocessing inside the reactor is key to designing a catalyst system for maximum performance. The problem, of course, as shown in Figure 1, is that there are many independent variables changing at every position in the reactor. The chemistry taking place at any position both affects and is affected by these variables.

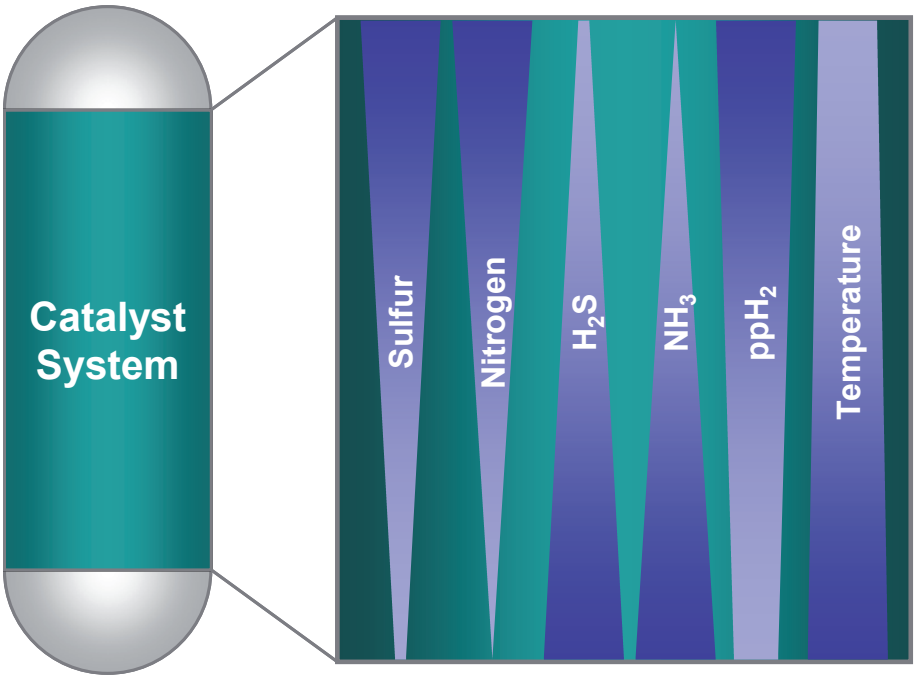

Figure 1: Conditions in a typical hydroprocessing unit

No two slices of the reactor along the vertical axis have exactly the same reaction environment and this means that the best catalyst for optimizing system performance could be different at each point. In addition, the particular species of sulfur and nitrogen are also changing as a function of position in the reactor.

As an example, consider the case of ULSD and a conceptual reaction zone model with three zones. Figure 2 shows this case graphically. Although the zones are shown as being equal in volume, in fact the size and position of each zone will vary as a function of feedstock properties, operating conditions and process objectives.

	Zone 1	Zone 2	Zone 3
Sulfur content	High	Medium	Low
Nitrogen content	High	Medium – Low	Very Low
Polynuclear Aromatics	High	Medium – Low	Zero
H_2S in Gas	0 – Medium	High	Highest
NH_3 in Gas	0 – Medium	Medium	High
H_2 in Gas	High	Medium	Medium – Low
Main HDS Reaction	Direct	Mainly Direct	Hydrogenation
Main HDS Inhibitor	H_2S	Organic Nitrogen	–
HDS Reaction Rate	Fast	Slow	Fast

Figure 2: Reactor zone model

Each of the 3 zones in this example has dramatically different reaction conditions which affect catalyst performance. In zone 1 the primary reaction occurring is (direct route) HDS. The rate of desulfurization is fast and sulfur content drops rapidly. At the same time hydrogen is consumed so ppH_2 is reduced and ppH_2S increases, the latter creating some inhibition. As the rate of direct route HDS slows, the feedstock moves into zone 2. In zone 2 the focus of reaction chemistry shifts from removal of sulfur to removal of nitrogen – organic nitrogen being the main inhibitor to increased HDS reaction rate. Zone 2 ends when organic nitrogen has been almost completely removed. At this point the feedstock enters zone 3 and hydrogenation route HDS picks up speed. Even though ppH_2 is at it's lowest in zone 3, the catalyst is operating in a nitrogen free environment. In this environment, the rate of hydrogenation of aromatics – including the aromatic rings of sterically hindered dibenzothiophene molecules – increases. Finally the feedstock exits the reactor as ULSD.

It should be clear from the three zone model above that understanding where reaction conditions change, presents an opportunity to improve system performance. Rather than an average level of performance from a single catalyst across all zones, an optimized catalyst system can be designed using catalysts which perform well in a particular regime. Of course this is much easier said than done, as it requires a detailed understanding of the conditions at each point in the reactor as well as the sulfur and nitrogen species present. Using new analytical methods and small scale testing equipment it is now possible to see into the reactor and develop models based on those observations. Albemarle has developed technology to track changes in sulfur, nitrogen and aromatics by slice along the vertical axis of a laboratory reactor. This approach allows us to follow the concentration of bulk sulfur and nitrogen through the reactor as well as analyze samples using GCxGC to segregate heteroatoms by structure. Figure 3 shows the change in sulfur content and sulfur type as measured in one of these tests.

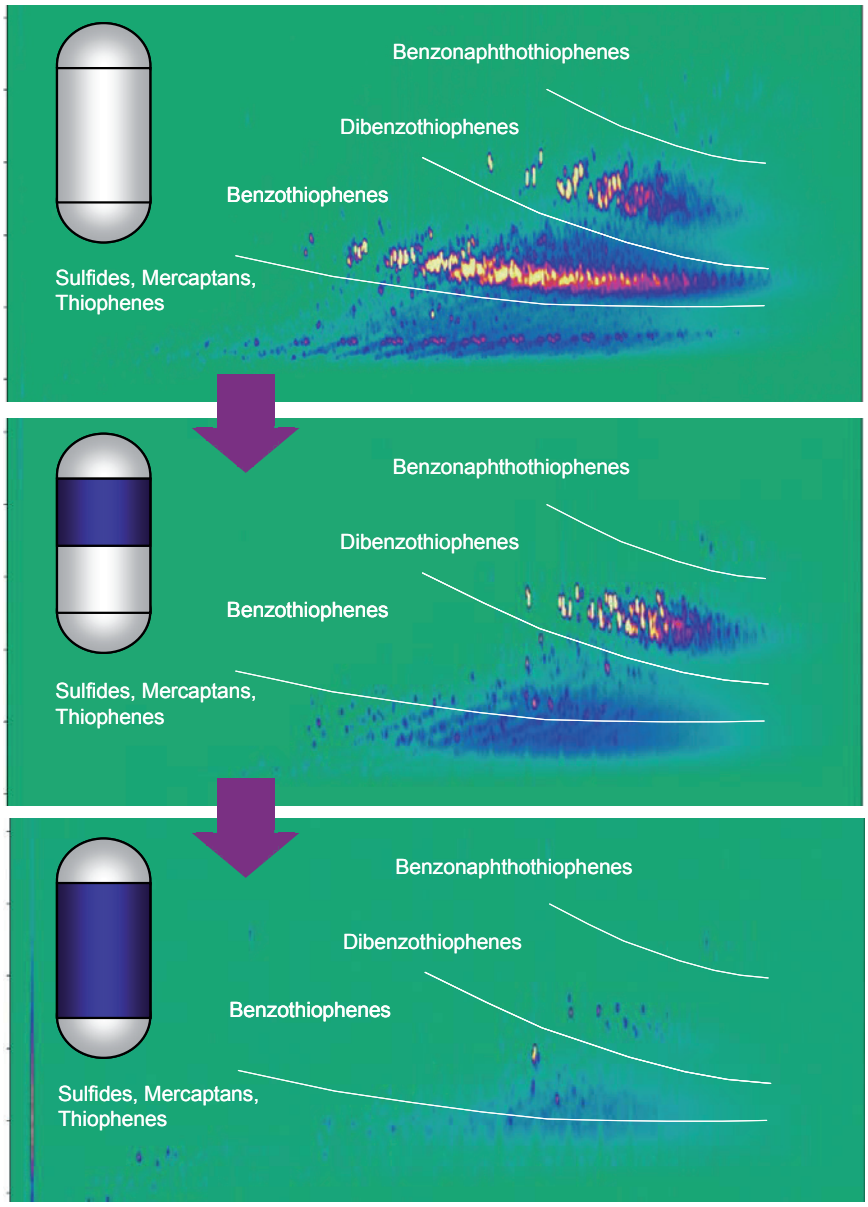

Figure 3: Removal of sulfur species throughout ULSD unit

III INTRODUCING STAX®

The reactor zone concept is powerful but to be of practical use a model is needed to define both the position and depth of each reaction zone. The insights into reaction chemistry as a function of reaction zones have enabled Albemarle to develop a model that forecasts the performance of ULSD units with high accuracy. Compared to models based on inlet and outlet conditions, this new model allows optimization of multiple catalysts within the reactor based on functionality. This catalyst system design technology, called STAX®, provides a powerful tool to deliver maximum performance from a ULSD unit.

The essence of STAX® is the ability to design a catalyst system which balances the capabilities of the unit and the objectives of the refiner. Using a proprietary model, catalyst selection and catalyst system design are made according to reaction chemistry and process condi-

tions in each part of the reactor. This allows the catalyst system to be much more accurately tuned to meet performance and process objectives than previously possible. Below are just a few of the possibilities to use STAX® technology to achieve refinery targets.

- Maximum HDS with constrained hydrogen consumption
- Maximum cetane uplift up to hydrogen limit
- Maximum cycle length while minimizing fill cost
- Maximum cycle length at specific S target
- Simultaneous sulfur and volume gain target

Varying layers of hydroprocessing catalyst has been practiced for decades so it is important to discriminate between these stacked beds and STAX® technology. The purpose of a stacked bed system is to enhance HDS or HDN in a unit by applying more or less CoMo or NiMo catalyst. The performance of the stacked system is an average of the individual HDS and HDN activities of the catalysts in the system. Contrast that functionality with STAX® technology where the performance of the STAX® catalyst system can be better than the performance of any of the catalysts in the system either individually or on average.

As will be discussed later, STAX® technology has already been introduced in several commercial units with an observable benefit in performance and ability to meet process objectives. In addition, both Albemarle and our customers have been able to confirm the benefit of STAX® technology in the laboratory. An example of the latter is shown in Figure 4. In this test a STAX® system was compared to a system with 100% KF 767 in ULSD service. KF 767 is a very active CoMo catalyst specifically designed for higher pressure ULSD units. The refiner was currently using KF 767 and pleased with the performance but needed to double the throughput of the unit while still producing ULSD with a reasonable cycle length. One option was simply to build a new reactor to double the catalyst volume and continue to use KF 767. As an alternate approach, Albemarle suggested a test to determine if a STAX® system could achieve the same result in the existing unit. Process conditions were moderate at 60 bar (870 psi) ppH_2 and 1.28/hr LHSV for the existing unit and 0.64/hr LHSV for a unit with double the catalyst volume. Temperature and H_2/oil were varied to judge system robustness.

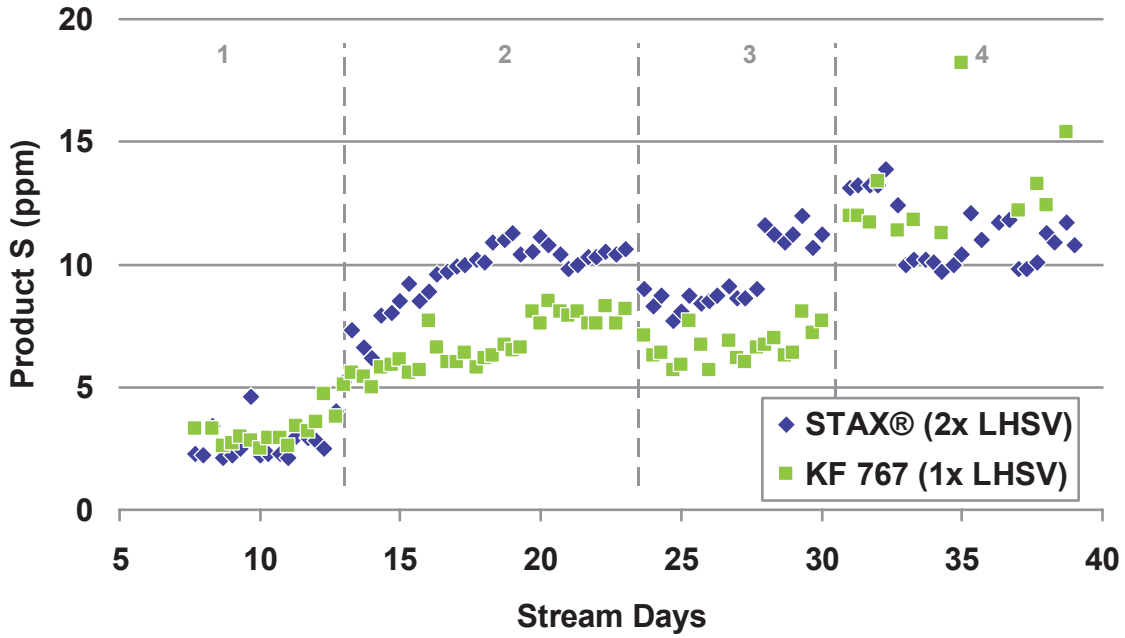

Figure 4: STAX® pilot plant test results

As can be seen in Figure 4, the performance of the STAX® and KF 767 systems are quite similar in sulfur removal. Since the STAX® system is operating at double the space velocity of the KF 767 system it is easy to see that RVA HDS is near 200 for the STAX® system.

A second example that illustrates the concept of STAX® is a series of pilot plant tests with a CoMo STARS™/ Nebula™ catalyst system for production of ULSD. The position of the Nebula™ catalyst in the reactor was varied between top, middle and bottom. The results are shown in Figure 5 for two pressure levels, 45 bar (650 psi) and 90 bar (1300 psi). Note that the sulfur scale is relative so the absolute levels are different for the two pressure levels. At moderate pressure (45 bar) an inverse relationship exists between the position of the Nebula™ catalyst in the reactor and product sulfur. Placing the Nebula™ catalyst in a lower position leads to higher product sulfur. At higher pressure (90 bar) it is clear that the reverse trend is observed, i.e. product sulfur decreases as Nebula™ is moved towards the bottom of the reactor. The explanation, based on the reactor zone model, is straightforward. At 90 bar the bottom of the reactor is operating in Zone 3. The Nebula™ catalyst is very effective as a zone 3 catalyst due to its superior hydrogenation activity. As a result the performance of the whole reactor improves as Nebula™ is placed at a lower position in the reactor.

At 45 bar the situation is quite different. Since the hydrogen partial pressure is less, the rate of HDN is dramatically lower than at 90 bar. It is the performance of the catalysts in Zones 1 and 2 that determine if there exists a nitrogen free Zone 3 and its size. By placing the Nebula™ catalyst in the top of the reactor a considerable boost is obtained in removal of organic nitrogen because of the higher ppH_2. The result is the creation of a small but existent nitrogen free zone in the bottom of the reactor that leads to an acceleration of HDS reactions. Placing the Nebula™ catalyst lower in the reactor reduces the HDN performance of Zones 1 and 2, causing the gradual disappearance of Zone 3 in the bottom of the reactor. As shown in Figure 5, product sulfur goes up as Nebula™ is moved lower in the reactor, exactly the opposite to what is observed at higher pressure.

This example demonstrates that through the use of STAX® technology a catalyst loading can be designed that optimizes unit performance for ULSD production within the conditions and constraints of the DHT unit.

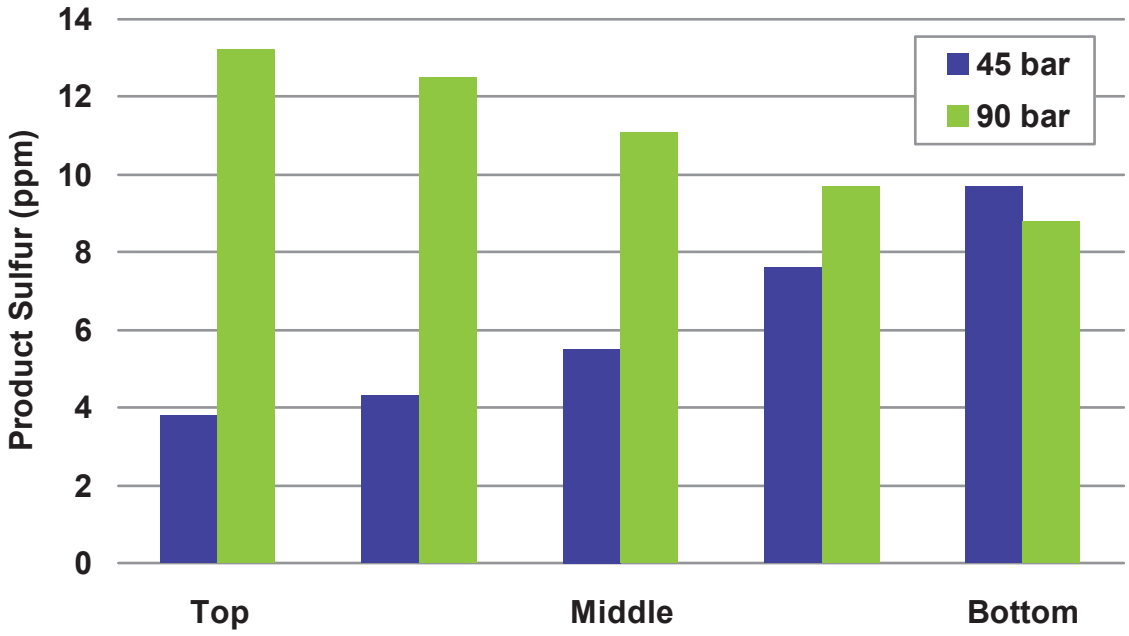

Figure 5: Sulfur of STAX® as a function of Nebula™ position in the reactor

IV COMMERCIAL EXPERIENCES WITH STAX®

Commercial units have been using catalyst system designs based on the concepts of STAX® technology for several years. The performance of these units demonstrates that STAX® is an effective way to optimize operation of the ULSD unit to achieve multiple objectives.

Commercial Example 1: Higher HDS activity with no additional hydrogen consumption

Obtaining higher HDS performance with minimal additional hydrogen consumption is one of the most appealing cases for STAX®. One of the first commercial applications was designed with this objective in mind. The unit, formerly a high pressure hydrocracker, was being revamped to produce ULSD. Being high pressure, the unit was capable of producing ULSD with either CoMo or NiMo catalyst. The benefit of STAX® is the ability to achieve the HDS activity of a NiMo catalyst system with the hydrogen consumption of CoMo catalyst system.

Pilot plant testing to simulate the unit was conducted prior to the unit start-up. This testing proved that the STAX® concepts were valid. At the time of this application there was no model capable of predicting and optimizing a STAX® catalyst system design. Therefore, pilot plant data was used to design a system with improved HDS activity. The unit was loaded with a STAX® catalyst system and Figure 6 shows the performance and stability of the catalyst system.

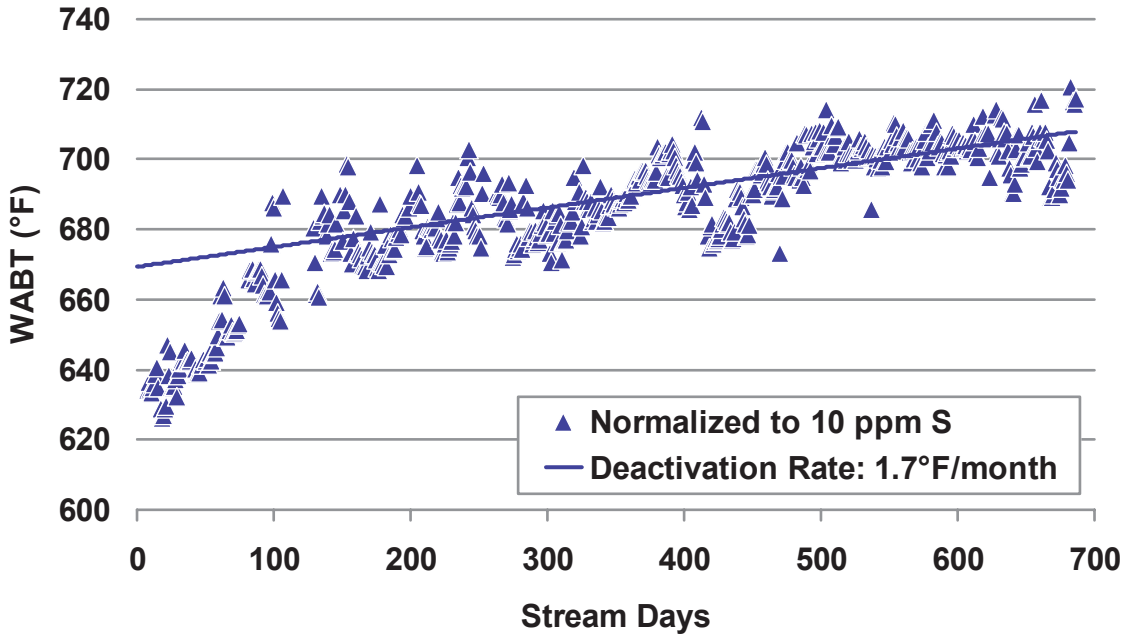

Figure 6: STAX® Commercial Example 1 normalized temperature for 10 ppm S

As can be seen, the deactivation rate for the catalyst system is modest, at less than 2°F/month. Hydrogen consumption met expectations. Future runs in the unit will benefit from improved catalyst system design owing to the development of a simulation model for STAX® technology.

Commercial Example 2: ULSD and aromatic saturation to a hydrogen limit

Many refiners in California were producing CARB diesel for years before EPA ULSD was mandated. It is the aromatic limits in the CARB diesel specifications, rather than sulfur limits, which typically controlled the required process conditions, feedstock selection and catalyst system. As a consequence, when EPA ULSD was introduced in 2006, the existing CARB diesel hydrotreaters were often capable of producing EPA ULSD and in some cases ULSD meeting both EPA and CARB specifications.

One California refinery desired to increase both throughput and cracked feedstock content to their CARB diesel hydrotreater while producing EPA ULSD. The unit had been using a conventional NiMo catalyst to produce CARB diesel. The catalyst system performed well enough for production of CARB diesel but the lower sulfur limit of EPA ULSD would have resulted in short cycles. Increasing throughput to the desired level while producing ULSD would have reduced cycle length even more – to the range of 6-8 months. Addition of cracked distillate was not practical at all using the existing catalyst system while producing ULSD.

The customer and Albemarle discussed strategies to produce ULSD in the unit with a reasonable cycle length of 12-18 months. A catalyst system using STAX® technology and Nebula™ catalyst was proposed as a way to achieve both higher throughput and cracked feed addition without loss of cycle length and without capital investment. Model forecasts predicted 15-18 month cycles with a STAX® system using 20% Nebula™ to produce 7 ppm sulfur diesel.

Cond.	WABT (°F)	LHSV	Sulfur (ppm)		Aromatics (wt%)		H_2 Cons. (SCFB)	
			STARS	STAX®	STARS	STAX®	STARS	STAX®
1	655	Base	6	3	25.3	22.3	363	412
2	651	Base	27	8	28.0	25.4	319	362
3	666	+25%	18	5	27.9	25.1	317	364
4	673	+25%	8	3	27.1	24.2	328	377
5	673	+25% / +45%	8	8	27.2	26.6	326	336

Table 1: Commercial example 2 pilot plant test results

The STAX® catalyst system was compared to a STARS™ catalyst system with KF 767 and KF 848 in an extensive pilot plant test program. The results of this test are shown in Table 1. In condition 5 both systems were operated to produce 8 ppm sulfur product. The STAX® system was able to be operated at over 15% higher throughput than the STARS™ catalyst system, at equal product sulfur. Hydrogen consumption was virtually identical for the 2 systems. The impressive performance of the STAX® catalyst system in the pilot plant convinced the customer to install it in their commercial unit.

Throughout the run, unit operating temperature was normalized to the projection basis using kinetic models. The weighted average bed temperature needed to produce 7 ppm product sulfur was calculated. Figure 7 shows a plot of the normalized temperature for the first 300 days of the commercial trial.

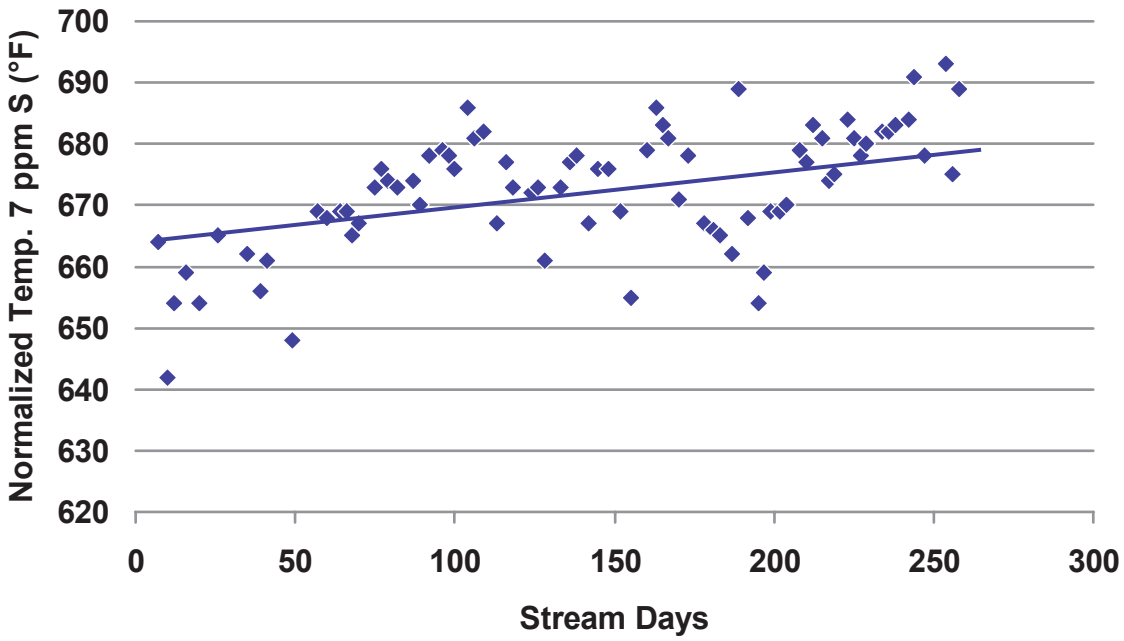

Figure 7: Normalized WABT from commercial run

After an initial break-in period of approximately 60 days, the start-of-run (SOR) WABT stabilized at 670°F (354°C). This SOR WABT is in good agreement with the pilot plant study prediction. Operations and process control teams at the refinery worked hard to minimize over-treating in order to maximize the run length. Product sulfur averaged 7 ppm and typically varied between 5 ppm and 10 ppm with minimal excursions below 5 ppm product sulfur. These excursions are usually caused by a reduction in the sulfur and nitrogen content of the feed due to a change in crude slate. Deactivation rate was a modest 1.8°F/month, meeting run length projections.

For the next cycle, the customer was interested in processing coker distillate in the unit. Albemarle concluded that in order to increase the unit feed rate with incremental coker distillate the quantity of Nebula™ in the current STAX® system should be increased. A second pilot plant test was conducted, comparing the current Nebula™ quantity (STAX® System 1) with a system containing additional Nebula™ (STAX® System 2). Three different feeds were investigated: SRGO, SRGO+6% coker distillate and SRGO+11% coker distillate. The pilot unit was operated to target the current product sulfur of the unit, 7 ppm.

Feed	WABT (°F)	Sulfur (ppm)		Aromatics (wt%)		H_2 Consumption (SCFB)	
		STAX® 1	STAX® 2	STAX® 1	STAX® 2	STAX® 1	STAX® 2
SRGO	669	7	6	27.0	26.2	346	359
6% Coker	676	10	8	27.9	27.0	333	348
11% Coker	687	8	6	28.1	27.2	351	367

Table 2: Pilot Plant Test Results with blends including coker distillate

The results of the pilot plant study are summarized in Table 2. Increasing the quantity of Nebula™ in the STAX® system 2 resulted in ~2 ppm lower product sulfur. The STAX® catalyst system with higher Nebula content™ had only marginally higher hydrogen consumption. The results of the pilot study were used with the Albemarle kinetic model to predict cycle length at a constant product sulfur level of 8 ppm. The effect of incremental coker distillate quantity on the projected cycle length is shown in Figure 8.

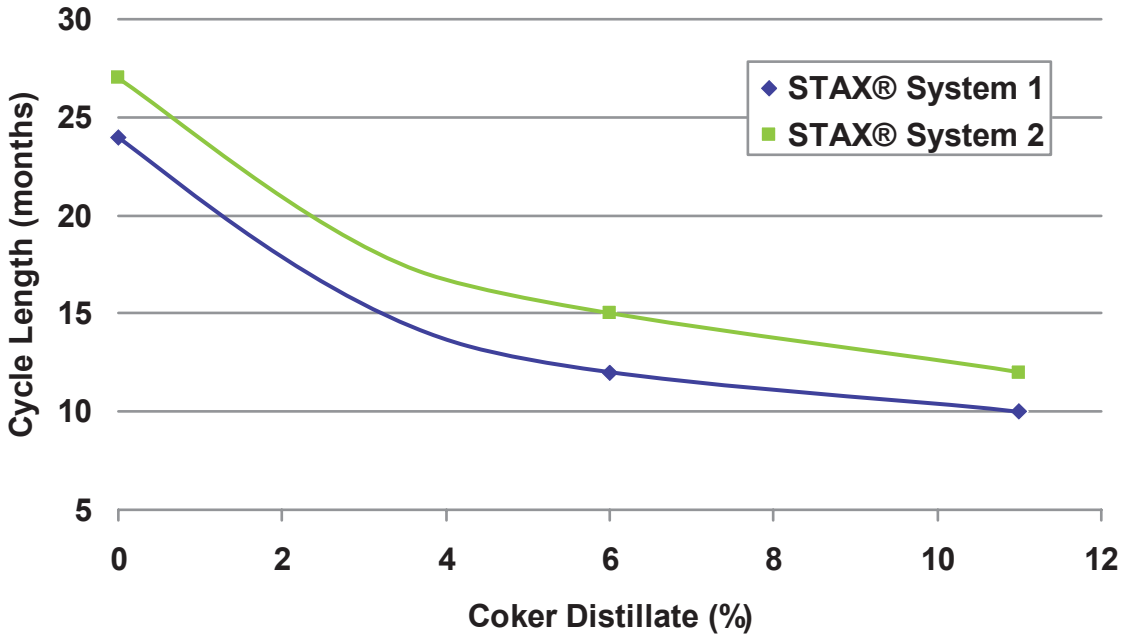

Figure 8: Effect of incremental coker distillate quality on cycle length

The refinery investigated the economics of adding 6-12% light coker distillate to the feed while meeting a one-year minimum catalyst life. The results from the case studies for this evaluation and economic analysis are illustrated in Table 3. All cases are evaluated for the STAX® system 2 catalyst design.

Case	Base	6% CGO	12% CGO
Feed	100% SRGO	SRGO+6% CGO	SRGO+12% CGO
Cycle Length	Base	0.63 x Base	0.5 x Base
Cost of Shorter Cycle	—	$0.17 / bbl	$0.29 / bbl
Gain from CGO	—	$0.82 / bbl	$1.64 / bbl
Payout	—	46 days	25 days

Table 3: Economic evaluation

The economic results were favorable for feeding higher levels of LCGO during the next catalyst run, despite the shorter cycle lengths, and the refinery decided to purchase the STAX® system with higher Nebula™ content. The projections for the STAX® catalyst system met the minimum required catalyst life while processing a higher percentage of LCGO. The economic benefits of processing LCGO far outweighed the additional catalyst and turnaround costs, even with a one-year catalyst life. Incremental catalyst cost and turnaround expense is recovered in three to six weeks, depending upon the quantity of LCGO processed.

Commercial Example 3: ULSD with more cracked feedstock

The refiner in this example was using a single catalyst system to produce ULSD. Processing additional cracked feedstock was very economically attractive so the refiner desired to

improve upon the existing catalyst system. Hydrogen availability was adequate for the current situation but hydrogen consumption needed to be controlled in the future case with more cracked feedstock in order to maintain catalyst stability.

Albemarle concluded that this case would be a good application for STAX® technology in order to increase system activity while controlling hydrogen consumption. Because reactor volume was limited, Nebula™ was included in this STAX® system. Pilot plant testing was conducted to compare the performance of a catalyst system with KF 767, a CoMo STARS™ catalyst to a STAX® system. The results of this test are shown in Table 4.

Feed	Feed Nitrogen (ppm)	Product Sulfur (ppm)		RVA HDS	Hydrogen Cons. (SCFB)	
		KF 767	STAX®		KF 767	STAX®
1	86	8.5	4.5	131	349	477
2	480	46.5	**10.1**	203	169	**251**
2	480	**10.0**	3.8	152	**202**	292

Table 4: Pilot Plant Comparison of STAX® and KF 767 Systems for ULSD

As can be seen, the activity of the STAX® system is much higher than the system with 100% KF 767. The very large difference in activity is due in part to the presence of Nebula™ but the quantity and positioning of Nebula in the catalyst system are equally important. One important characteristic of many STAX® applications is to gain a large activity benefit without a commensurate increase in hydrogen consumption. It's important to compare hydrogen consumption at equal product sulfur when comparing catalyst systems. As highlighted in Table 4, comparing hydrogen consumption for both systems at 10 ppm product sulfur indicates about 20% higher consumption for the STAX® system. While certainly significant, this level of increased consumption was manageable for the refiner and relatively modest given the substantial increase in catalyst system activity. The refiner chose to load the STAX® system. Performance of the system through the first 20 months of operation has met expectations as shown in Figure 9.

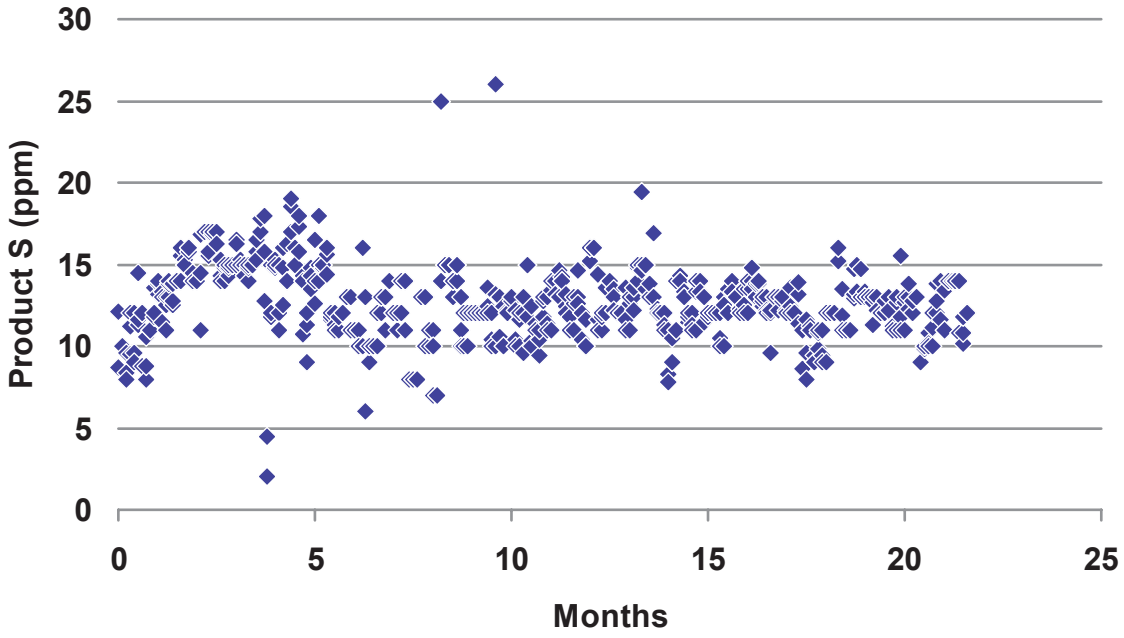

Figure 9: Performance of STAX® Commercial Example 3

V CONCLUSIONS

There is much performance to be gained by understanding the chemistry and kinetics of hydroprocessing reactions at every position in the reactor. Until recently, the tools to develop such a detailed understanding of the hydroprocessing unit were not available or were too expensive. With STAX® technology and the models which support it, Albemarle has opened a new arena for maximizing catalyst performance.

The concepts behind STAX® are well proven in both the laboratory and commercially. Although initially focused on ULSD, we expect STAX® applications to expand as the design tools are developed and tuned. Application of STAX® technology to other hydroprocessing units, such as hydrocracker pretreatment and FCC feed pretreatment are expected in the near future.