The Era of ULSD – New Challenges and Opportunities for Hydrocracking Processes

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Introduction

Hydrocracking has long been recognized as an extremely robust and versatile conversion process in the petroleum refinery. Depending upon local market demand and refinery economics, hydrocrackers have been designed to produce primarily either naphtha or distillate products. For example, there are about 70 operating hydrocrackers in North America and roughly half of that conversion capacity is geared to the gasoline market. This situation is in contrast with Europe where hydrocrackers are mainly for middle distillate production. Nevertheless, many commercial hydrocrackers have the flexibility of switching from gasoline mode to distillate mode by adjusting operating parameters such as cracking conversion, liquid recycle rate, and cut points of the products or recycle. When in distillate mode operation, the qualities of hydrocracker distillate product (e.g. sulfur, smoke point, cetane number) are undoubtedly superior to those produced from other conversion units such as FCC.

The projected growth in distillate demand, the desire to push more feed, particularly heavier and cracked feed into the hydrocracker, and the drawing of more high quality liquid products have prompted refiners to reconfigure their operations, debottleneck existing hydrocrackers and install new reactors. As major hydrocracking catalyst suppliers, Criterion Catalysts & Technologies L.P. and Zeolyst International have been able to quickly contribute to the industry's needs by developing new catalysts with improved activity, stability, and product yields (Ref. 1).

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As we enter the era of ULSD, June 2006 for the United States, the first question asked by the refiner is "does my hydrocracker produce diesel with less than 10 ppmw sulfur?" Unfortunately, the answer is not always yes. Many hydrocrackers, which were able to easily surpass the sulfur specifications of earlier years, now fail to produce ULSD. It will be extremely costly to exclude hydrocracker distillates from the ULSD blending pool. Secondary processing of hydrocracker distillate to meet the new sulfur spec will not be an economical solution either.

Being supported by dedicated and experienced R&D teams, Criterion / Zeolyst has anticipated this problem and has recently commercialized several new hydrocracking catalysts with improved sulfur removal activity. In this paper, we will first discuss some of the technical issues faced in the production of ULSD in hydrocrackers and the catalytic solutions offered by Criterion / Zeolyst. The major part of this paper will be devoted to the operation of a hydrocracker in North America (Refiner A). Recent commercial data from this hydrocracker will be presented to demonstrate the benefits of installing these newly developed Criterion / Zeolyst catalysts with improved hydrodesulfurization (HDS) activity.

In addition to improving HDS activity, reducing reactor pressure drop will potentially improve hydrocracker profitability through higher feed rates, higher hydrogen partial pressure, extended cycle life, better yields and better product quality. The reduction of pressure drop can be achieved by installing newly developed and patented TX Trilobe shaped catalyst. The first set of commercial data from another North American hydrocracker (Refiner B) using this newly developed TX Trilobe shaped cracking catalysts will be presented.

Challenges of Producing ULSD from the Hydrocracker

The hydrocracking process can have several configurations (single stage, series flow or two stage with interstage ammonia removal). Regardless of the configuration, a key objective of the first stage in the operation is hydrotreating the feed to reduce its nitrogen content. The target nitrogen slip to the second cracking stage can range from less than one to over one hundred ppmw. This nitrogen slip target depends on the composition and type of cracking catalyst utilized (amorphous silica alumina or zeolite, base metal or noble metal). Different cracking catalysts have different tolerances to organic nitrogen poisoning. Typically, the target nitrogen slip is optimized to achieve a balanced cycle life between pretreat and cracking stages.

As indicated earlier, the hydrocracker could be a naphtha selective unit, an intermediate naphtha/jet unit or a maximum middle distillate selective unit. For a naphtha selective hydrocracker, the distillate product is mainly the fractionator bottoms bleed stream. For a naphtha/jet operation, an additional jet fuel sidecut will be drawn. The middle distillate selective unit will have several distillate draws: jet/kero, light/heavy diesel and fractionator bottoms bleed. Therefore, regardless of the type of hydrocracker, the challenge of ensuring that the sulfur level is below 10 ppmw for all the distillate products throughout entire hydrocracker cycle exists. Some hydrocrackers will have more difficulty in meeting the ULSD sulfur spec than others due to the differences in feed, catalysts, process conditions, operating severity and overall cracking conversion. The key factors affecting the sulfur content in distillate products are discussed below.

Process

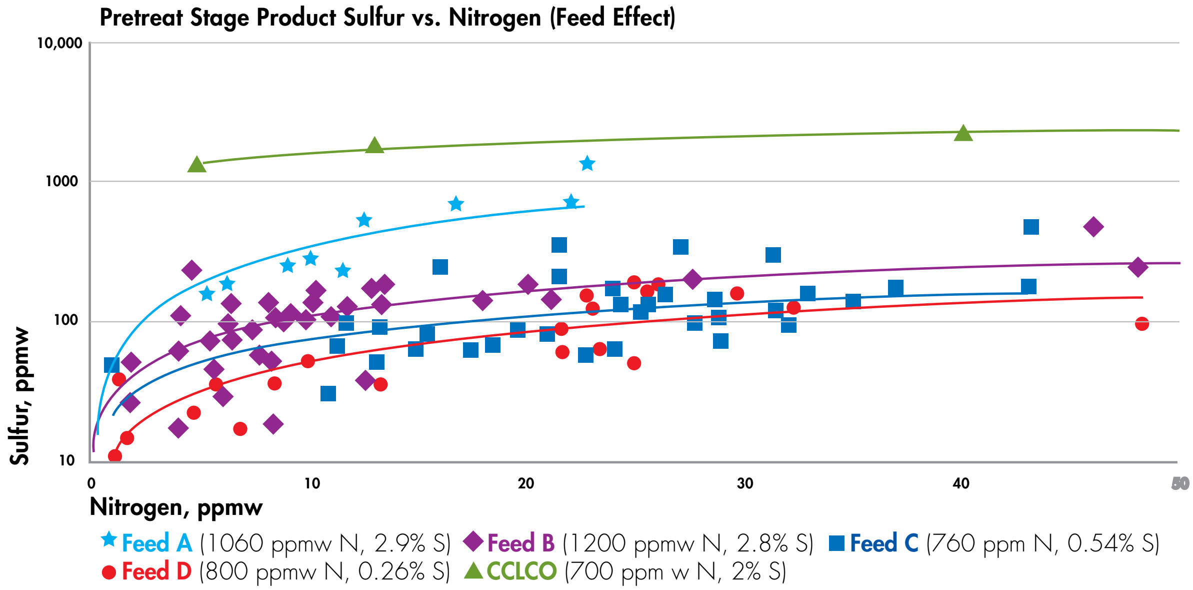
The main focus for hydrocracking catalyst development over the past decades had been to increase hydrodenitrification (HDN) for pretreat catalysts and improve liquid product yields and hydrocracking activities for cracking catalysts. The sulfur contents, in first stage effluent and second stage hydrocracker products, are resultant from attaining the desired target nitrogen slip and cracking conversion. More than 95% of sulfur in the feed typically will be removed in the first pretreat stage along with the nitrogen. The remaining sulfur must be converted, basically to extinction, in the cracking stage in order to keep sulfur in the distillate product below 10 ppmw. Therefore, as more sulfur slips into the cracking stage, it becomes more difficult for the hydrocracker to meet ULSD specification, unless a hydrocracking catalyst system with superior HDS activity is applied (Ref. 1).

Feedstocks

Figure 1 compares several sets of first stage effluent sulfur and nitrogen data, which were derived from various types of feed. Feeds A to C are straight run feeds arranged in a descending order according to their feed sulfur contents. Feed D is a synthetic feed. The amount of sulfur going into cracking stage for a given nitrogen slip depends not only on feed sulfur over nitrogen ratio but also on the relative reactivity of the sulfur and nitrogen molecules for that particular feed. The most problematic feed on the graph is the cat cracker LCO. Despite attaining less than 5 ppmw nitrogen slip, the sulfur content remains above 1000 ppmw. This feed will inevitably pose the greatest challenge for the hydrocracker to meet the ULSD spec. The synthetic feed (Feed D) is similar to Feed C in feed sulfur to nitrogen ratio therefore the effluent sulfur is also low for a given nitrogen slip. However, synthetic feeds are more difficult to hydrocrack than straight run feeds since they have already been severely processed (data not shown in the graph).

Figure 1

Pretreat Stage Product Sulfur versus Nitrogen (Feed Effect). Feeds A to C are straight run feeds and Feed D is a synthetic feed. The amount of sulfur going into cracking stage for a given nitrogen slip depends not only on feed sulfur over nitrogen ratio but also on the relative reactivity of the sulfur and nitrogen molecules for that particular feed. The most problematic feed on the graph is the cat cracker LCO. Despite attaining less than 5 ppmw nitrogen slip, the sulfur content remains above 1000 ppmw.



Catalyst Types

Another challenge for HDS and HDN reactions in the pretreat stage is related to catalyst formulations. It is well known that nickel-molybdenum (Ni/Mo) based catalysts are much more active for HDN than cobalt-molybdenum (Co/Mo) catalysts. However, the trend for HDS activity depends on reactor pressure. Figure 2 illustrates the catalyst effect on pretreat reactor product sulfur and nitrogen. For a given reactor temperature (T1), a much lower nitrogen slip can be achieved with Ni/Mo catalyst (Point A) than Co/Mo catalyst (Point B). However, for a given nitrogen slip, Co/Mo catalyst (Point C) results in lower product sulfur content than Ni/Mo catalyst (Point A). Of course, Point C requires a higher WABT (T2) than that of Point A (T1).

To keep sulfur low enough in the pretreat reactor effluent, the refiner may have to push target nitrogen slip lower than the optimum for Ni/Mo catalyst or apply a higher WABT for Co/Mo catalyst. A catalyst system must be selected to properly balance the needs of HDN and HDS activities for each potential application. If catalyst development efforts focus on improving HDN activity without paying attention to HDS activity, the cracking stage may not be active enough to cope with the higher sulfur slip. Therefore, it will be more difficult to meet the ULSD challenge. A new line of pretreat catalyst with enhanced HDS activity and comparable HDN activity to CENTINEL catalyst has been developed and commercialized based on proprietary ASCENT technology. More information on the technology can be found in Reference 2.

More stringent pretreat sulfur and nitrogen targets will impact hydrocracker cycle life. Under certain scenarios, the refiner will need to consider applying a sulfur slip target instead of the conventional nitrogen slip target. The absolute maximum sulfur content in pretreat reactor effluent to ensure < 10 ppmw sulfur in the final product depends on the process conditions, conversion level, and the type of cracking catalyst installed in the unit.

For hydrocracking catalyst, in 2004 Criterion/Zeolyst introduced a new high activity middle distillate selective catalyst with superior HDS activity, Z-3723 (Ref. 1). The higher HDS activity was achieved with an enhanced hydrogenation function. Figure 3 displays the hydrogenation activity, as expressed by the conversion of aromatics, for a range of hydrocracking catalysts currently available in the Criterion / Zeolyst's catalyst portfolio. Directionally, the catalyst with a higher cracking activity is more naphtha selective. Compared to its predecessor, Z-723, the new Z-3723 hydrocracking catalyst offers an increase in catalyst hydrogenation power (Figure 3). Products like Z-3723 are becoming critical in hydrocracking operations to meet the ULSD challenge.

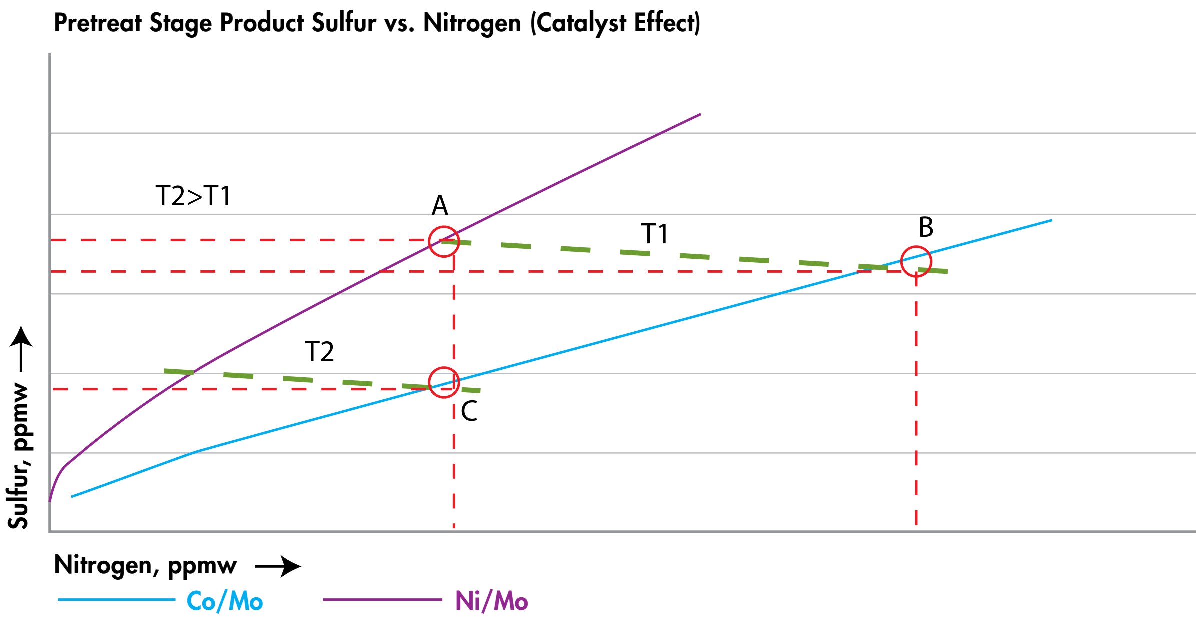


Figure 2

Pretreat Stage Product Sulfur versus Nitrogen (Catalyst Effect). For a given reactor temperature (Points A and B), a lower nitrogen slip can be achieved with Ni/Mo catalyst. However, for a given nitrogen slip (Points A and C), Co/Mo catalyst results in lower product sulfur content but requires a higher WABT.

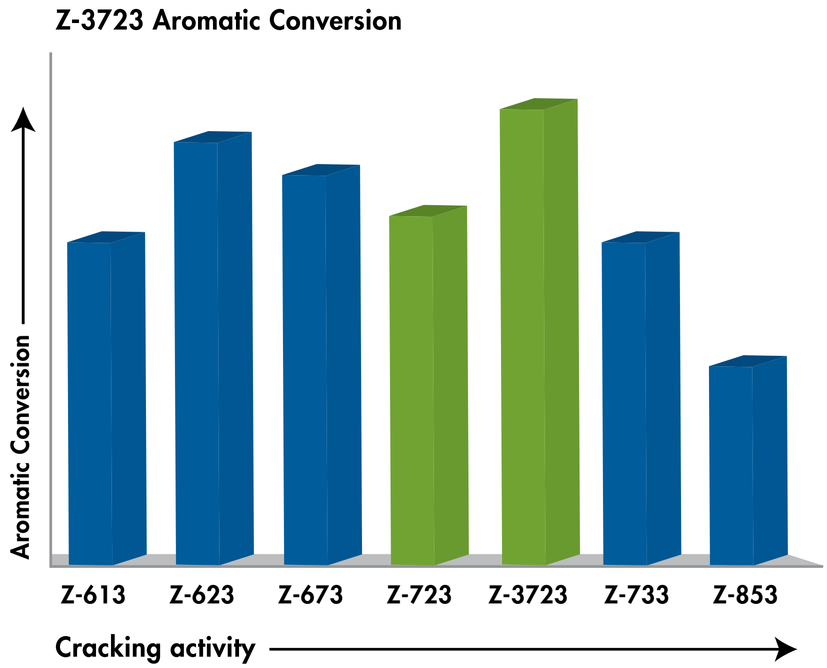


Figure 3

Aromatic Conversion of Z-3723 versus Current Cracking Catalysts in Zeolyst International Portfolio. The Z-3723 offers an improvement in hydrogenation activity (higher aromatic conversion). Because of the improved hydrogenation activity, Z-3723's HDS activity is 1.6 times greater than that of Z-723.

When the level of product sulfur drops below 50 ppmw, the majority of sulfur compounds are in the form of substituted dibenzothiophenes (e.g. dimethyl-dibenzothiophenes). The hydrogenation route is the preferred reaction mechanism for the HDS of these compounds (Ref. 3). Because of its improved hydrogenation activity, Z-3723's HDS activity is 1.6 times greater than that of Z-723 for comparable selectivity. The commercial performance of these two catalysts, Z-723 and Z-3723 at Refiner A's hydrocracker will be discussed in the next section.

Criterion / Zeolyst has further extended the advanced zeolite technology, catalyst formulation, and metals impregnation techniques employed for Z-3723 to other hydrocracking catalysts.

Review of Refiner A's Hydrocracker Operation

Refiner A's hydrocracker is a series flow unit (nitrogen removal in pretreat stage followed by cracking in second stage). The unit achieves a full conversion (>97% of fresh feed) with liquid recycle to the second stage. A simplified hydrocracker schematic diagram is presented in Figure 4. The hydrocracker feed is mainly a blend of light, medium and heavy vacuum gas oil derived from a sour crude. Table I highlights the properties of the feed.

As depicted in Figure 4, typical liquid products for Refiner A's hydrocracker are Light Naphtha (LN), Heavy Naphtha (HN), Jet (Jet A), Light Gas Oil (LGO), Heavy Gas Oil (HGO) plus a small amount of hydrocracker bleed. Both Jet A and LGO are blending components for the ULSD pool with a sulfur spec of <8 ppmw. The HGO will be routed to the distillate blending pool via a distillate hydrotreater (DHT). However, there is a great incentive to reduce the HGO total sulfur content to less than 10 ppmw so that this stream can be blended directly into distillate pool and thereby allowing the spare DHT capacity to be allocated for other more profitable feeds.

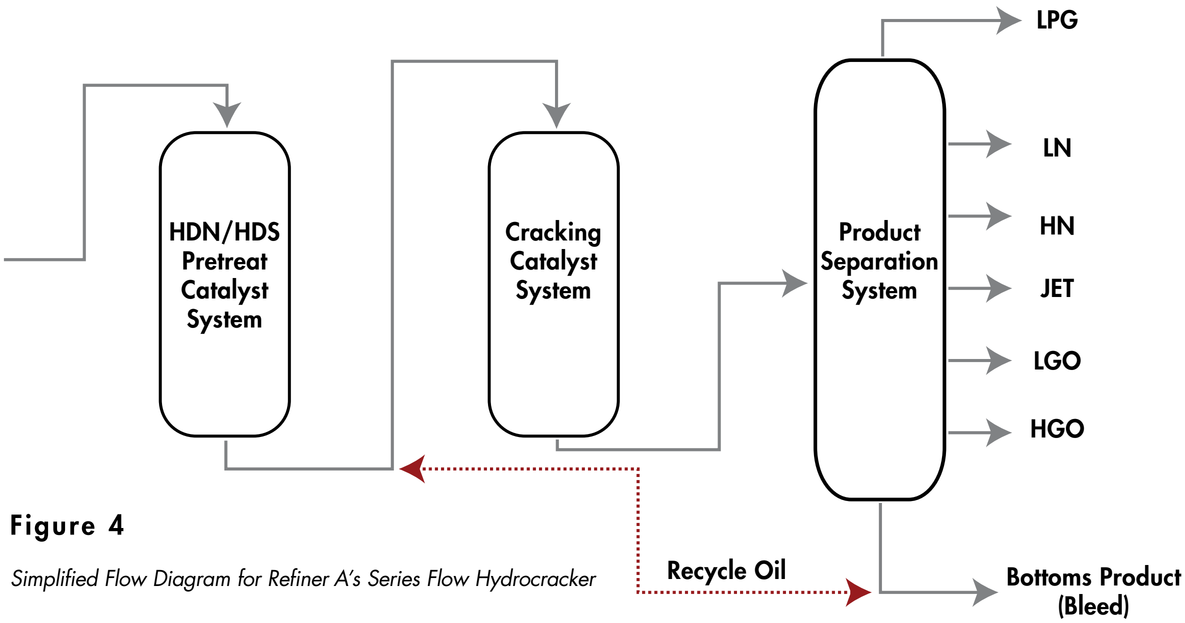


Figure 4

Simplified Flow Diagram for Refiner A's Series Flow Hydrocracker

Important economic drivers considered during the catalyst selection included cycle length, optimal hydrogen uptake, minimal LPG make, and maximum liquid yields. The previous cycle used Criterion CENTINEL DN-3100 and Zeolyst Z-723 as the main pretreat and cracking catalysts, respectively. The reactor WABT's are depicted in Figure 5 for DN-3100 and Figure 6 for Z-723. Both catalysts exceeded the cycle life projections by more than six months while meeting the target product properties.

The average sulfur contents for distillate products from the last cycle are plotted in Figure 7. In general, there was no noticeable deterioration in product sulfur throughout the cycle. As depicted in Figure 7, the average sulfur concentration of 3 ppmw for Jet A and 5 ppmw for LGO clearly met the < 8 ppmw ULSD target. The average sulfur in HGO was 12 ppmw. Therefore, this product still could not be blended into ULSD pool directly due to the > 8 ppmw sulfur content. Typically, the hydrocracker bleed stream is valued as cat cracker feed or straight run VGO. However, significant premium can be added to the bleed stream if sulfur level can be reduced further (preferably also < 8 ppmw). Therefore, one of the primary criteria in selecting the catalyst system for the current cycle was selection of a cracking catalyst with improved HDS activity.

Based on the commercial success of Z-3723 in another hydrocracker (Ref. 1), the Criterion CENTINEL GOLD product, DN-3300, and Z-3723 were installed for the current cycle. As shown in Figures 5 and 6, the start of run (SOR) activity data are very encouraging. DN-3300 is about 8° F more active than DN-3100 based on a similar feed and nitrogen slip. Although the primary catalyst development goal for Z-3723 was to enhance HDS activity, data also reveals about 10° F improvement in cracking activity after the initial stabilization period. With the assistance of the Criterion / Zeolyst hydrocracking tech service team, Refiner A continues to optimize the unit operation for maximum profitability.

Property	HCU FEED
°API	14.4-22.2
Sulfur, (%wt)	>1
Nitrogen, ppmw	>1000
TBP, %wt @ °F	
IBP	453
10%	606
30%	702
50%	775
70%	846
90%	943
FBP	1060

Table I

Refiner A's HCU Feedstock Properties.The hydrocracker feed is mainly a blend of light to heavy vacuum gas oil derived from a sour crude.

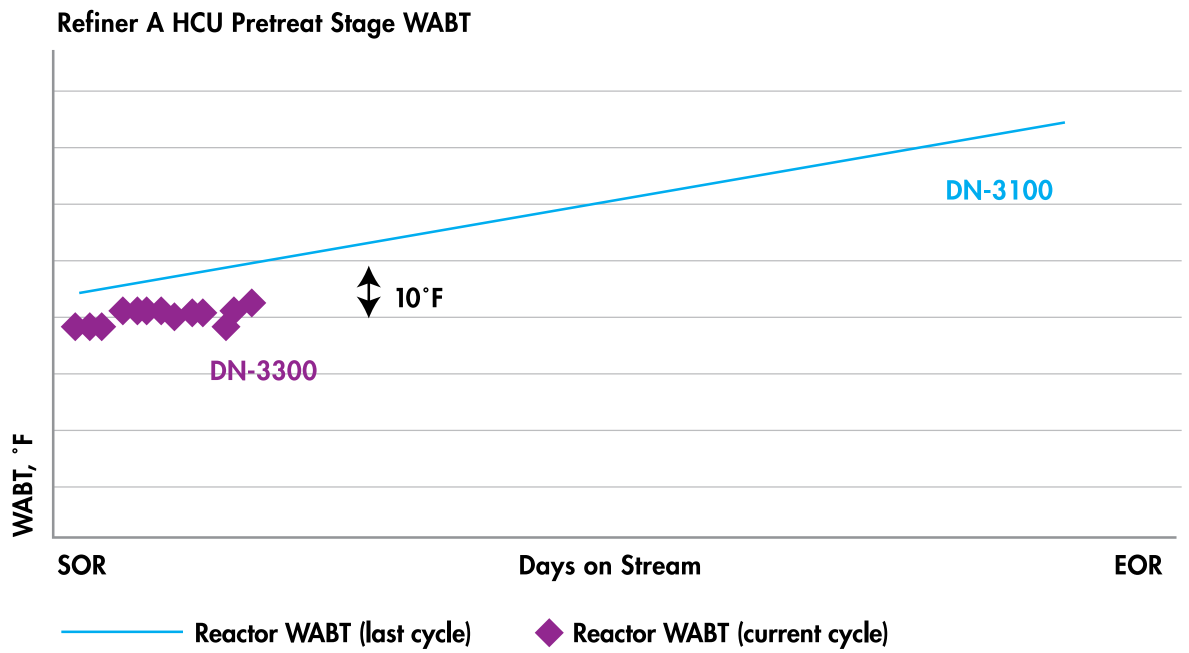


Figure 5

Comparison of Refiner A Pretreat Stage Catalyst Performance. *The SOR data shows the DN-3300 to be 8˚ F more active in HDN than DN-3100 after the initial stabilization period.*

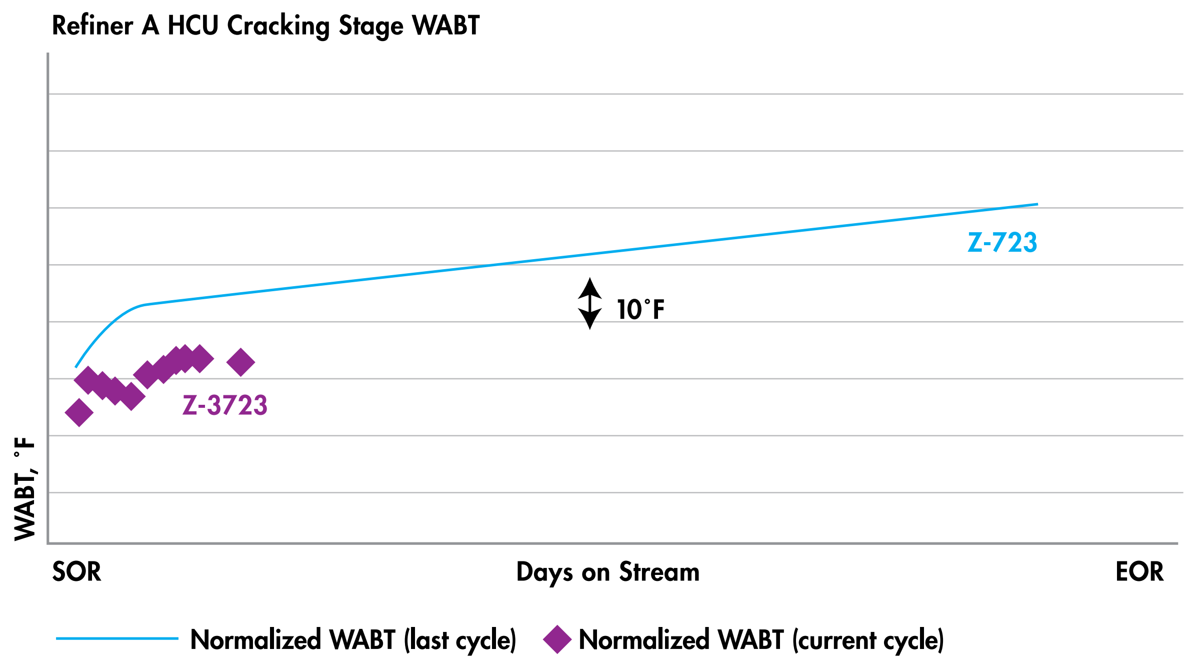


Figure 6

Comparison of Refiner A Cracking Stage Catalyst Performance. *The normalized WABT data at SOR show the Z-3723 is about 10˚ F more active than Z-723 in cracking after the initial stabilization period.*

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The initial sulfur data for distillate cuts from the current cycle are compared with those of the last cycle in Figure 7. Extremely low sulfur levels were observed for all the distillate components, including the bleed stream. Particularly, now the HGO stream can be blended to ULSD pool directly due to the < 8 ppmw sulfur. Moreover, there seems to be some reduction in LPG make (C4-) since start up of this cycle, providing additional economic benefit to the Refiner A.

Although the hydrocracker is only in the early part of the cycle, Refiner A has already initiated the catalyst selection process to identify an improved catalyst package for the next cycle. R&D programs have been defined and started at Criterion / Zeolyst's R&D facilities. Besides all the previously identified requirements such as higher activity, longer cycle length, optimal hydrogen uptake, minimal LPG makes, and maximum liquid yields, an additional goal of reduced reactor pressure drop was added.

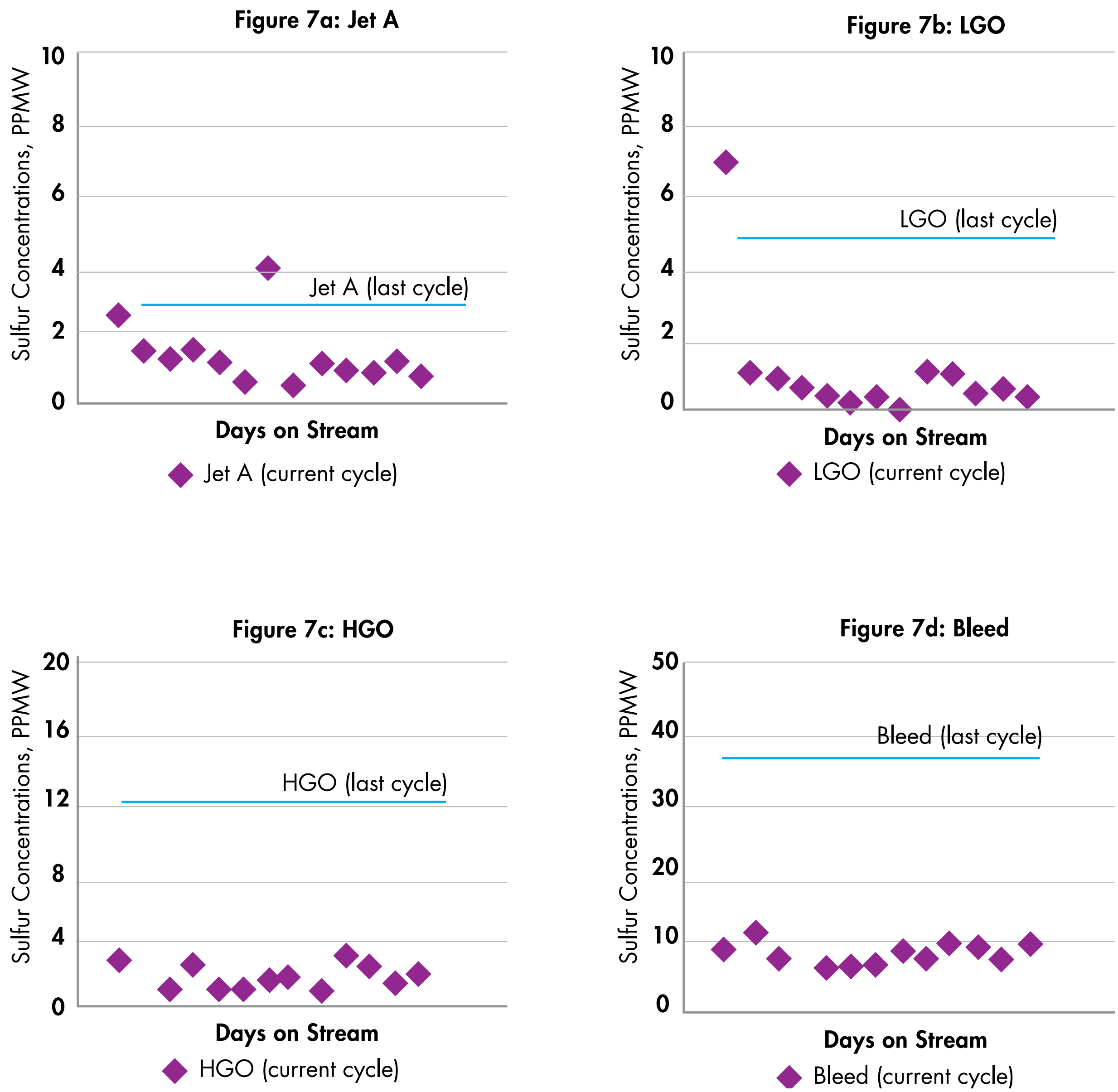

Figure 7

Refiner A HCU Distillate Product Sulfur Concentrations. *The average sulfur content of distillate products from last cycle using Z-723 catalyst clearly met the sulfur targets of < 8 ppmw for Jet and LGO, and < 50 PPMW for HGO. The initial SOR sulfur data for distillate cuts from the current cycle with Z-3723 exhibit even lower sulfur. Particularly, now the HGO stream can be blended to ULSD pool directly due to the < 8 ppmw sulfur.*

Commercial Performance Data for TX Shaped Catalysts

Lowering reactor pressure drop is always beneficial to hydrocracker operation, particularly, if it is a limiting factor for hydrocracker feed rate and cycle life. It also allows the hydrocracker to be operated under a higher gas to oil ratio and higher average hydrogen partial pressure. Both parameters are important for ULSD production. Therefore, pressure drop reduction is also one of the deliverables for the Refiner A's next catalyst changeout. This goal can be achieved by applying a cracking catalyst with the newly developed and patented TX Trilobe shape.

A detailed description of TX Trilobe shape can be found in Reference 1. Figure 8 gives a schematic comparison of regular TL and new TX Trilobes. The pressure drop reduction is due to the increase of interstitial void fraction between catalyst particles. Recently, the TX shape of cracking catalysts has been installed at Refiner B's hydrocracker.

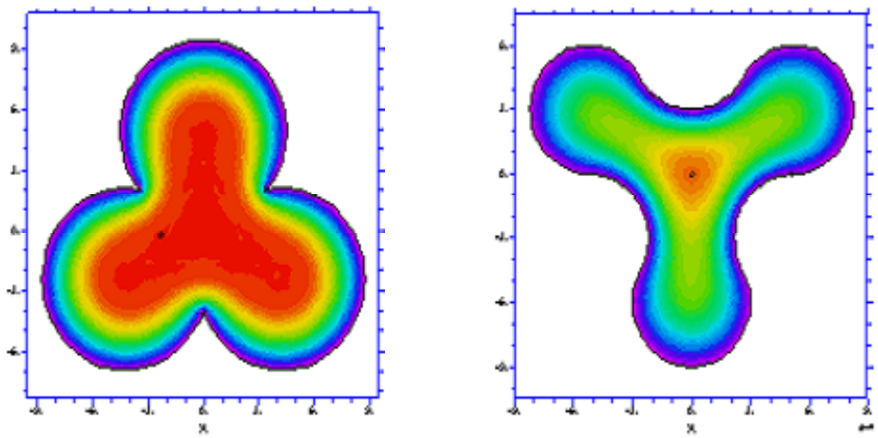

Figure 8

Cross Section of TL Trilobe Shape Compared to the New TX Trilobe Shape. *The TX Trilobe shape further reduces the diffusion path and simultaneously decreases pressure drop through a higher void fraction.*

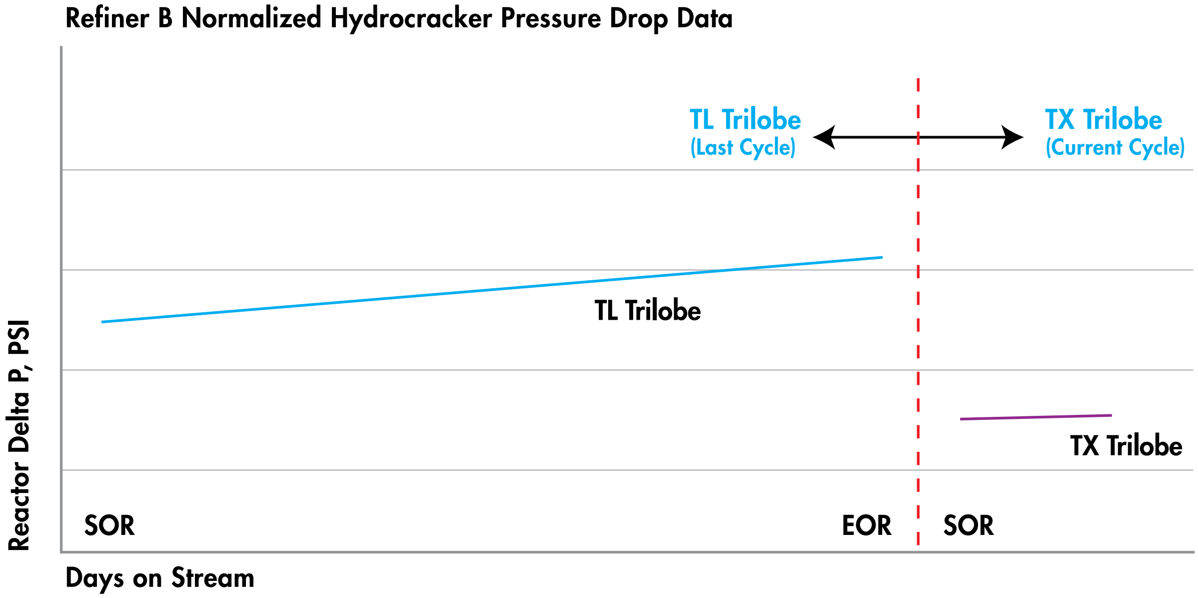

Figure 9

Refiner B Hydrocracker Pressure Drop Data Normalized to a Standard Feed Rate. *For the current cycle, 60% of total catalyst volume was replaced with TX Trilobe shaped catalyst. The start of run data shows 15 to 20% reduction in pressure drop.*

The pressure drop data from Refiner B is presented in Figure 9. It should be noted that the last shut down of Refiner B's hydrocracker was mainly due to reaching the reactor pressure drop constraint at the end of run. Therefore, in the current cycle, the cracking catalyst, which represented about 60% of the total catalyst volume, was replaced with TX Trilobe shaped catalyst. The pressure drop data normalized to a standard feed rate are plotted and compared in Figure 9 for these two cycles. The start of run data reveals about 15 to 20% reduction in pressure drop for TX Trilobe shaped catalyst. More commercial data from this application along with improved liquid product yields as the result of a shorter diffusion path will be published in the near future.

Conclusions

Hydrocrackers continue to be an excellent source of high quality diesel blending components. However, to meet the less than 10 ppmw sulfur specification for ULSD, refiners need to carefully select the best catalyst systems, closely monitor feed properties, and make timely adjustments to reactor conditions. In some instances, the sulfur specification could be the limiting factor for hydrocracker cycle life.

Criterion Catalysts & Technologies L.P. and Zeolyst International have successfully commercialized a series of new hydrocracking catalysts with enhanced characteristics to help refiners meet the ULSD challenge. For example, the Z-3723, a distillate selective hydrocracking catalyst, has been applied in Refiner A's hydrocracker and a significant reduction of sulfur in all distillate products has been achieved.

The commercial data from a hydrocracker using newly installed TX Trilobe shaped cracking catalysts was presented to demonstrate the reduction in pressure drop. Reduced pressure drop will improve hydrocracker profitability through higher feed rate, higher hydrogen partial pressure, extended cycle life, better yields, and better product quality. More performance data from TX application will be published in a separate paper.

In summary, the ever-changing regulations with even more stringent fuel specifications will continue to pose challenges to the refiners. However, with proper application of technologies, significant profit uplift opportunities can be realized. Criterion and Zeolyst will continue to work closely with the industry to address future issues and create value for refiners through the application of advanced catalytic solutions.

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