ART Excels In ULSD Service: Update on Sulfur minimization by ART

ART first introduced the SmART Catalyst System® Series for ultra-low sulfur diesel (ULSD) in 2001. Since that time the technology has been widely accepted by the refining industry as top tier for ULSD. As detailed previously (Catalagram® 99, 2006), the SmART System is a staged catalyst system customized to meet individual refiners objectives with the performance of the system driven by ART’s DX™ Catalyst Platform.

ULSD production with the first SmART System began early in 2004 at a North American refinery processing a feed containing 40% of a high endpoint Light Cycle Oil (LCO). Since that time DX Catalyst Platform has been selected for over 35 ULSD applications as either stand-alone catalysts or as components in SmART System. The technology has been a great success since its introduction with millions of pounds installed in commercial units around the world. Several of the first refiners to utilize a SmART System are still enjoying benefits today, or have reloaded another SmART System based on the exceptional first cycle they received from the technology.

This article contains several case studies highlighting the performance of ART catalysts in a variety of ULSD units around the world. These are summarized in Table I.

Refiner A is an initial user of a SmART System in Asia Pacific. This refiner conducted in-house testing for their ULSD catalyst selection.
They requested catalyst samples from ART and a “market leading” domestic supplier. The DX Catalyst Platform tested as a substantially more active catalyst than the others in the program. As a result, ART was selected as the catalyst supplier for their unit, which started up in the last half of 2004. This refiner was completing a revamp, which involved the addition of a new reactor in front of an existing reactor. They decided to use fresh catalyst in the new lead reactor while keeping used ART catalyst in the lag reactor. The unit conditions are characterized by an inlet pressure of 930 psig and a LHSV of 0.7 hr⁻¹. The feed contains up to 40% cracked stocks, and the product sulfur has averaged 5 ppm. The unit ran for three years before the refiner decided to change out the “used” catalyst in the lag reactor with fresh catalyst from ART. The performance of the unit is summarized in Figure 1 and, as the figure depicts, stability has been exceptional.

Figure 2 shows data for Refiner B. This was another major Asia Pacific refiner using a SmART System. This refiner needed to produce 10 ppm sulfur diesel for two years in a newly revamped unit. The operating conditions for this unit are 770 psig inlet pressure with an LHSV around 0.7 hr⁻¹. The feed was a high end point, straight run diesel with typical sulfur content of 1.25 wt.%. This refiner was concerned with minimizing hydrogen consumption as hydrogen availability was limited at the refinery. This was a situation well suited for the flexibility of the SmART System to tune the hydrogen consumption/activity relationship. The optimum loading for this unit was 90% cobalt-molybdenum (CoMo) and 10% nickel-molybdenum (NiMo) catalyst. This design was expected to be significantly more active than an all CoMo loading and would consume the same amount of hydrogen as an all CoMo loading. The final selection of the SmART System was based on competitive pilot plant testing by the refiner.
About eight months into the ULSD portion of the cycle, the refiner significantly increased the operating severity and began producing very low sulfur diesel. Typically, 8 ppm is the recommended product sulfur target when producing <10 ppm ULSD. In the higher severity mode, the product sulfur was well below 8 ppm 85% of the time, whereas in the lower severity mode the product sulfur was below 8 ppm only 15% of the time. The higher severity led to a much higher deactivation rate and potentially jeopardized the two year cycle length. After discussions with the refiner, the severity was reduced and the two year cycle length was achieved.

ART was chosen for the second cycle which again was based on competitive testing and the outstanding performance demonstrated in the first cycle. The current system is performing very well.

Refiner C, another Asia Pacific refiner, selected ART catalysts for their ULSD unit based on the strong reference from the refiners mentioned above. This refiner needed to produce 8 ppm sulfur diesel for two years and hydrogen availability was not a constraint. The operating conditions included an inlet pressure of 850 psig and LHSV of 1.2 hr⁻¹. The feed was also a high endpoint, straight run diesel with a sulfur content of 1.8 wt.%. This was a more demanding operation than those discussed previously, and a required system designed for maximum activity. The catalyst loading in this case was 55% CoMo and 45% NiMo. The performance is summarized in Figure 3.

This unit met all performance targets during the two year cycle and has just been reloaded with a new SmART System.

Operating data for Refiner D is shown in Figure 4. This is a grassroots ULSD unit in Asia Pacific. ART was chosen to participate in this project because of the excellent performance of the SmART System from previous references in the region. ART worked closely with the refiner and engineering construction firm on the design basis for this project. A 30% CoMo and 70% NiMo SmART System was designed for this unit in order to deliver maximum activity. The operating conditions for this unit included an inlet pressure of 1130 psig and LHSV of 1.1 hr⁻¹. This unit also processes a straight run feed which has a relatively high level of nitrogen and an endpoint of 730°F (by D86).

The unit is running well and meeting all performance expectations with a somewhat lower than estimated deactivation rate, and is well on track to meet the targeted three-year cycle length.

Refiner E is another grassroots ULSD unit, which started up in the second quarter of 2006 in North America. ART worked with the licensor on the unit design and proposed a SmART System loading consisting of about 65% NiMo. This loading was designed for maximum activity as the design feed contained a high percentage of cracked stocks. The conditions of the unit included an inlet pressure of 1070 psig with an LHSV of 1.25 hr⁻¹. This refinery processes mostly sweet crudes, and the feed to the unit typically contains about 40% FCC LCO and coker LGO. The activity of the system has been extremely high, allowing this refiner
to operate at 20% over design charge rate. Figure 5 shows the performance for the cycle thus far, and it is evident from the figure that the catalyst stability has been excellent. In fact, the unit was designed for a 24-month cycle, but 48 months appears possible even at higher than design feed rates.

This unit also typically processes 10% kerosene with occasional increases to as much as 30%. As can be seen in Figure 5, the addition of kerosene to the feed has no negative impact on the activity of the system, and may even improve the performance. Notice how the WABT decreases when processing higher amounts of kerosene. This suggests that the increase in feed vaporization (decrease in H\textsubscript{2} pressure) is offset by the decrease in hard to treat, substituted dibenzothiophene sulfur species.

Figure 6 summarizes data from Refiner F in North America. This refiner had completed a project to revamp an existing hydrocracker to ULSD service. The objectives were to increase feed capacity from 30,000 to 45,000 BPSD, while ensuring the capability to process 50% or more LCO, as well as provide for cold flow improvement during the winter months. This refiner also wanted to minimize the hydrogen consumption so that feed rate could be maximized within make-up hydrogen constraints. Along with Süd Chemie, ART designed a dewaxing/ULSD catalyst system meeting the unit objectives. The unit started up successfully in the 2nd quarter of 2006 and processes both sweet and sour crude derived feeds in block operation. The feed is also comprised of 40-50 vol.% of a high endpoint LCO. The performance of the unit is summarized in Figure 6. The unit came on stream with higher than expected activity, and is well on its way to exceeding the target three year cycle length. Additional details on this unit can be found in Catalagram® 103, Spring 2008.
Refiner G is another grassroots unit which started up in the fourth quarter of 2006. The performance of this unit is summarized in Figure 7. ART again worked closely with the licensor on the new unit design and proposed a SmART System loading using 65% NiMo catalyst for maximum activity. The unit typically processes >70% LCO, including both LCO produced within the refinery and purchased externally. The initial deactivation rate of the unit was significantly higher than expected, and it was determined that this was due to lower H₂ partial pressure than design combined with lower H₂/Oil ratio. This can be seen in Figure 8 which shows the trend of reactor inlet pressure and the recycle hydrogen purity. Early in the cycle there were control issues and the inlet pressure showed a steady decline. The recycle hydrogen purity also decreased steadily and had periods where it fell dramatically. Once the H₂ partial pressure concerns were addressed, combined with better bed temperature management, the deactivation rate decreased significantly. The operation became much more consistent, and since that time the deactivation rate indicates that the unit will easily meet the expected 24-month cycle length.

Finally for Refiner H, Figure 9 summarizes the performance of a SmART System at a U.S. Gulf Coast refinery. This was another grassroots unit that started up in the Fall of 2006. SOR activity met expectations, and since that time the unit operating severity has steadily increased. The current feedrate is 22% over design and the feedstock endpoint has increased by 30-40°F. Typical unit conditions include 0.8 hr⁻¹ LHSV and 1300 psig inlet pressure, and, on average, the unit processes a feed containing 15% FCC LCO, 30% LCGO and 5% coker naphtha. At times the unit has processed as much as 80% cracked stocks in the feed, and still the product sulfur has averaged less than 6 ppm for the cycle. The target cycle length was 24 months, and the unit is currently on track for a 36-month cycle. Also shown in Figure 9 is the API uplift from the unit. From the chart, the API typically increases 6-10 numbers depending on the feedstock.

As this sampling of case studies demonstrates, the SmART System has been employed in a wide variety of ULSD applications around the world. The technology has been successfully operating over a broad range of operating conditions from low to high pressure with feeds ranging from straight run to 80% cracked stocks. In each application, all expectations have been met or exceeded, and in a number of cases ART catalyst has been selected for the second cycle based on the excellent performance. ADVANCED REFINING TECHNOLOGIES continues to develop higher performance products for ULSD as evidenced by the recent introduction of the newest DX™ Catalyst Platform, 420DX. The addition of this catalyst to the ULSD portfolio is an example of the commitment that ART will continue to deliver state-of-the-art technology for ULSD.