Catalyst & Technology News

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The Next Phase of ULSD

Cleaner Diesel – Global Trend

Over the last 6 years, global ULSD (Ultra Low Sulfur Diesel) legislation has promoted a steady improvement in diesel fuel quality. Adoption of Euro IV standards at the beginning of 2005 reduced sulfur levels in Europe (EU) to <50 ppm. More recently, many EU refiners have taken advantage of tax incentives to adopt the Euro V standard of <10 ppm sulfur well in advance of the legislated 2009 date. In 2006, the majority of North American refiners made significant investments to upgrade their distillate hydrotreating capabilities to meet <15 ppm sulfur standards. The trend does not stop there, with monthly press announcements indicating other countries establishing timetables for ULSD, including Mexico, Brazil, Russia, China and Australia.

Not only will the cleaner diesel reduce pollutants like sulfur dioxide by 97%, but the near-zero sulfur fuel will permit diesel vehicles to be equipped with modern pollution control equipment, much like gasoline-powered vehicles today. EPA estimates that implementation of the 2007 Highway Diesel Rule could reduce nitrogen oxide emissions by 2.6 million tons each year and soot or particulate matter by 100,000 tons a year in the US alone.

Collective ULSD Experience

With more than 100 cycles of ULSD experience over the last 6 years, Criterion has collected this operating knowledge and applied it to improve subsequent cycles. While many of the ULSD issues refiners encounter are obvious, some are often misunderstood given all of the priorities and economics governing day-to-day operations. The top 5 issues that refiners ask Criterion for assistance with are shown in Table 1on the next page.

TABLE 1

Common Issues Affecting ULSD Unit Performance

Issue	Impact on ULSD Unit/Refinery	Possible Solutions
Overtreating to 1-5 ppm Sulfur	Higher operating temperatures by 5-15°F (3-9°C) and subsequently shorter cycle life.	Utilize on-line analyzer and tank sulfur totalizer to operate as close as possible to the product release spec.
Feed quality – heavier endpoint or poor fractionation	Significant negative impact on operating temperature and cycle life.	Monitor individual component distillations to track source of offending stream. Better coordination with upstream units (Crude, FCC, Coker)
Feed quality – cracked feed content and quality	Good diesel margins provide a large incentive to avoid down-grading of cracked stocks. Significant negative impact on cycle length as operating temperatures and deactivation rates increase.	Short-term fix is to run units harder, ensuring that gas circulation rates and H_2 purity are maximized to minimize impact on catalyst deactivation rate. Long-term solution is to apply next generation catalyst like CENTINEL GOLD to improve overall cycle length.
Hydrogen consumption	High H_2 consumption can restrict ULSD unit or refinery throughput. Also may incur purchase of incremental H_2 from higher cost source that exceeds the value of the product upgrade.	Short-term solutions can be implemented by modifying process conditions to minimize aromatic saturation reactions, particular at SOR. A long-term solution could involve a catalyst change or use of multiple catalysts to maximize activity within a given H_2 constraint.
Optimization of more complex reactor operations	Multi-bed, multi-reactor systems can be more difficult to optimize. Operations staff can have difficulty in hitting targets without specific guidelines, and can "waste" catalyst performance if not properly balanced.	Clear guidelines are necessary to utilize quench systems and balance reactor temperatures to maximize HDS performance and minimize catalyst deactivation rates. Online algorithms can help establish operating criteria.

Addressing These New Challenges

Following customer feedback from early ULSD experiences in Europe, Criterion developed a second generation of catalysts to assist refiners with solving these problems. Two separate catalyst manufacturing technologies were developed to address the multitude of issues: ASCENT and CENTINEL GOLD. These next generation catalysts were commercialized in late 2004 and are now used extensively.

ASCENT Catalysts for Distillate (DHT) Service

There were 4 major drivers for development of the ASCENT catalysts for Distillate Service:

1. Maintain high ULSD performance comparable to CENTINEL products
2. Improve regenerability – Achieve >90% activity recovery with conventional regeneration techniques
3. Minimize H_2 consumption (for CoMo version)
4. Provide sulfiding flexibility – available for both in-situ and ex-situ presulfurization

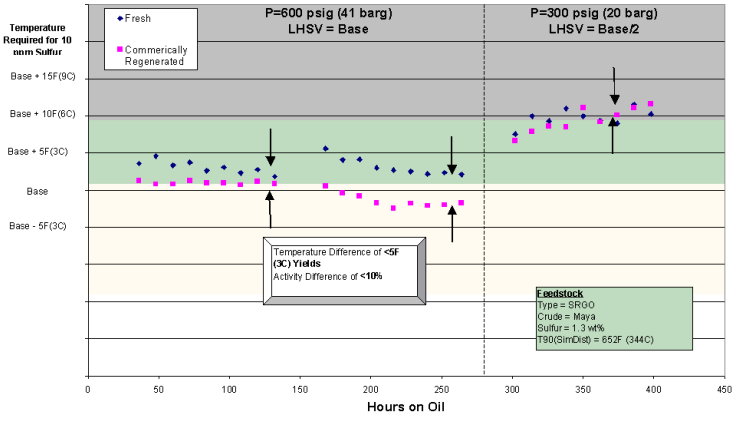
With nearly 40 sales of ASCENT DHT products, including CoMo DC-2531 and NiMo DN-3531, all of the described benefits have been proven in commercial operation[1]. Most recently, the commercial regenerability was demonstrated in the summer of 2006, with activity recovery >95% of fresh DC-2531 (Figure 1).

This capability will allow refiners to use substantial quantity of catalyst in subsequent ULSD cycles and provides for a more attractive reuse strategy.

[1] ERTC, 2005 "Catalyst Innovations to Increase Reliability and Value of ULSD Assets", Justin Swain: Criterion Catalysts & Technologies, Fareham, UK; Mattias Niklasson: Shell Raffinaderi AB Gothenburg; Wolfgang Wienken: Shell Deutschland Oil GmbH, Elbe Mineralolwerke

FIGURE 1

Comparison of Fresh and Commercially Regenerated DC-2531



CENTINEL GOLD Catalysts for Distillate (DHT) Service

There were 2 key drivers for development of the CENTINEL GOLD catalysts for ULSD Service:

1. Create market-leading ULSD performance in CoMo and NiMo catalysts representing a step-out improvement compared with CENTINEL products
2. Develop top-tier performance in CoMo and NiMo performance categories to permit options to balance with H_2 consumption needs

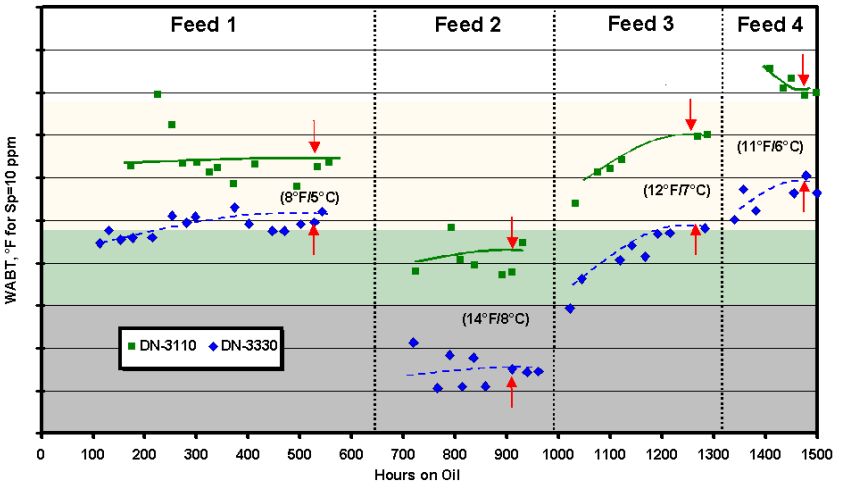
CENTINEL GOLD products have in commercial use since October 2004 and the first application is still in ULSD service. Since that time, more than 20 refiners around the world have chosen CENTINEL GOLD ULSD products to upgrade their catalyst system for several different reasons, including

1. Providing additional insurance in meeting very low sulfur targets
2. Extending their cycles
3. Maximizing profitability by increasing throughput via increased endpoints and/or increasing cracked stock content.

DN-3330 NiMo ULSD catalyst can provide a significant benefit over prior generation NiMo and CoMo ULSD catalysts, showing activity benefits of 8-25°F (5-15°C) over a range of applications. Examples of a few of these applications are shown in Figure 2 on the next page.

FIGURE 2

Performance Advantage of CENTINEL GOLD DN-3330



Feed	1	2	4	4
Crude Source	American	Middle Eastern	American	Synthetic
Blend	SRGO	70%SR/30%LCO	60%SR/40%LCO	40%SR/25%LCO/35%KGO
Feed Sulfur, wt%	1.65	1.85	1.52	1.44
Feed Nitrogen, wppm	240	340	560	1000
Feed D-2887 T90, °F(°C)	650 (343)	670 (355)	670 (355)	675 (357)
H_2 Pressure, psia(bara)	500 (35)	550 (38)	700 (48)	870 (60)

Distillate Hydrotreating Seminar

To learn about ASCENT and CENTINEL GOLD technologies and other future trends in ULSD catalyst developments, please consider attending the Distillate Hydrotreating Seminar on October 17-19 in Winston-Salem, North Carolina. This power-packed workshop will cover all aspects of distillate hydrotreating, including recent North American and European experiences with ULSD. Space is limited, so please enroll soon to reserve your place. For more information, check out Criterion University on www.criterioncatalysts.com.

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