Lowering sulfur diesel

Art Suchanek and Safa George, Criterion Catalysts & Technologies L.P., USA, Alexei Gabrielov and John Smegal, Shell Chemical Company, USA and Tom Remans, Shell Research and Technology Centre, the Netherlands, **evaluate the performance of a new catalyst which attempts to meet the severe specifications imposed by regulatory boards.**

The world's automobile manufacturers via the WorldWide Fuels Charter (WWFC) are pushing for 'zero sulfur' diesel fuels (ULSD), as well as many other potential specification changes. Most of the world is now focusing on sulfur removal while other WWFC specifications remain under study to determine future specified tolerance levels and implementation dates. However, refiners worldwide are wishing that none of these 'other' changes will ever materialise.

The refining industry has clearly directed its suppliers that it is short of capital, and more specifically to the technology and catalyst companies, 'Find us a catalyst solution.' Criterion Catalysts & Technologies L.P. has responded to the plea, investing significant time and money to develop superior products that can help refiners reach their goal to reduce capital investment.

The new Criterion CENTINEL catalysts are one such catalyst solution. This article highlights how existing units can be operated to achieve ULSD with these catalysts. It further presents a detailed description of the new catalysts compared to conventional catalyst performance.

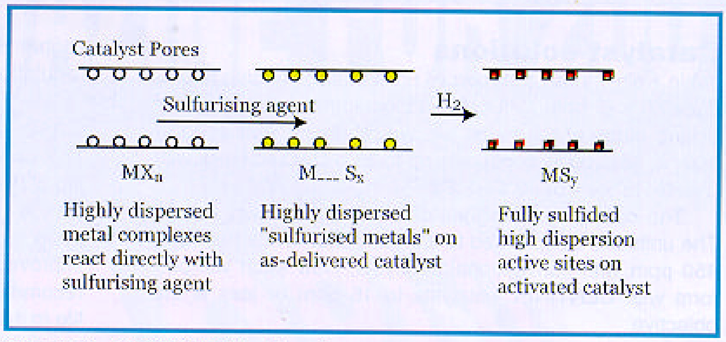

Figure 1. CENTINEL technology.

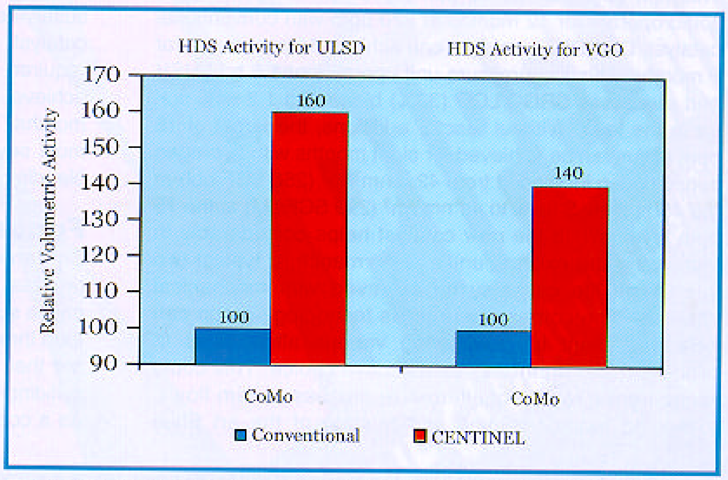

Figure 2. A new generation of catalysts for high quality fuels.

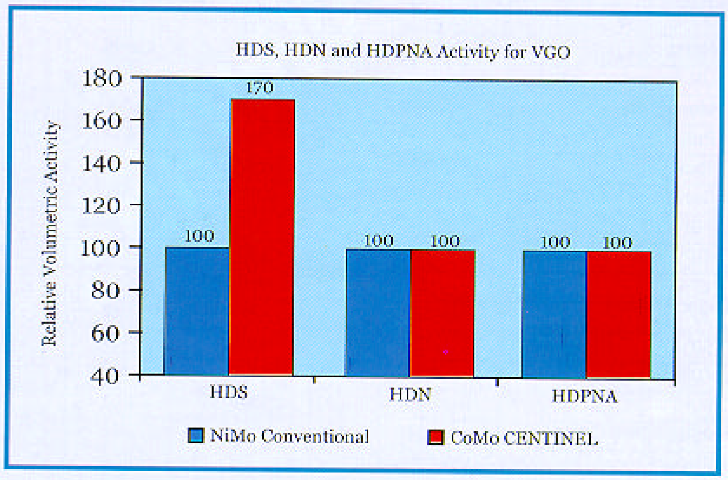

Figure 3. HDS, HDN and HDPNA activity for VGO.

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Table 1.Application of CENTINEL technology to achieve ULSD

					Operating conditions		Conventional catalysts			CENTINEL		
Case	Components	S,wt%	API	T95,˚C (˚F)	H_2pp	LHSV, h^{-1}	Sp, ppm	Cycle life, (mths)	CHC nm^3/nm^3	Sp ppm	Cycle life, (mths)	CHC, (mths)
One	SR/LCO 67/33	1.2	29	352 (665)	Low	1.5	400	18	42.4	180	16	51
						220	12	42.4	70	12	51	
									15	8	49	
Two	SR/LCO 90/10	1.0	36 (680)	360	High	2	400	24	39	200	24	3
						50	4	31	15	4	31	
					0.8	50	18	44	15	18	44	
Three	SRGO	0.5	39 (667)	360	Medium	1.9	50	18	25.4	50	30+	29
						10	8	23.7	10	18	27	

Catalyst solutions

Table 1 cites three commercial units that are aiming to produce 10 - 15 ppm sulfur diesel blending components. The boiling range of the feeds are typical diesel, that is 352 - 360 ˚C, 95% point, containing up to 33% cracked stock with a sulfur range from 0.4 - 1.2%.

The operating conditions of the units are also shown. The units are all operated to various sulfur levels from 50 - 450 ppm with conventional catalysts. How each will perform with CENTINEL catalysts to 15 ppm or less is the objective.

Case one

This unit operates at 400 ppm sulfur for 18 months and could operate for 12 months at 220 ppm with conventional catalyst. CENTINEL catalyst can achieve 15 ppm sulfur for 8 months. This low pressure unit operates at 1.5 h^{-1} LHSV and processes SRGO/LCO (33%) blend and 1.2 wt% sulfur in the feed. Without reactor additions, the target of 15 ppm sulfur can be achieved for eight months with hydrogen consumption increased from 42.4 nm^3/m^3 (250 SCF/bbl) at the 450 ppmw S level to 49 nm^3/m^3 (290 SCF/bbl) at the 15 ppm level. While the new catalyst helps considerably in increasing the existing unit's performance, a typical two year cycle life can only be achieved with mechanical changes. The company's process technology group can help this client in considering various alternatives in order to make the most cost effective choice. This could range from a review of alternative process stream flows, to adding reactor volume and/or state of the art Shell Global Solutions reactor internals, with potential future regulations in mind.

Case two

This concerned a 90/10 SR/LCO 1.0% sulfur feed operating at 2 h^{-1} LHSV and high pressure. This is a difficult task, yet the new technology can achieve 15 ppm with a 4 month cycle life. As in case one, while CENTINEL catalyst improves the performance of this unit, the authors would recommend additional reactor volume to increase catalyst life to 18 months.

Case three

This represents a typical European operation with a 0.5% sulfur feed operating to 50 ppm sulfur, with conventional catalyst at 1.9 h^{-1} LHSV and medium pressure. At the required 10 ppm sulfur, the conventional catalyst would achieve an eight month catalyst life and CENTINEL 18 months. This represents a viable catalyst solution for the most severe requirement of 10 ppm sulfur in the product blending stock.

Fundamentals of the technology

Conventional hydrotreating catalysts are manufactured by a process, during which metal precursors are impregnated onto a support material and are then converted to their oxide form through high temperature calcination. The metal oxides are then converted into the active sulfide phase through a sulfiding process, which takes place in the customer's unit. As a consequence of the calcination process where strong

Table 2. Performance of DC-2118 and the conventional catalyst, using feedstock 2

Number	1	2	3	4	5	6	7
Type	SRGO/CGO/LCO	SRGO/ICO	SRGO	SRGO/CGO	SRGO/LCO	SRGO	VGO/HCGO
Sulfur, wt%	0.67	0.53	1.80	1.83	1.25	1.46	2.89
Nitrogen, ppm	855	127	448	291	180	146	1130
UV Aromatics, (wt%)							
Mono	6.0	5.6	5.4	6.0	5.3	5.8	4.8
Poly	13.1	9.2	7.3	6.7	10.2	6.8	13.7
Total	19.1	14.8	12.7	12.6	15.5	12.5	18.5
Density at 15.6 C, g/cc	0.8726	0.8619	0.8667	0.8534	0.8686	0.8534	0.9390
TBP-GC - °C							
IBP	115	93	172	128	138	160	239
10%	201	213	252	202	222	238	350
30%	206	260	286	260	259	277	410
50%	285	284	314	294	283	310	431
70%	313	304	343	323	308	343	485
90%	351	329	383	365	346	382	530
95%	368	339	392	389	364	402	550
FBP	408	366	424	466	411	435	603

Notes: SRGO = straight run gas oil; CGO = coker gas oil; ICO = intermediate cycle oil; LCO = light cycle oil; VGO = vacuum gas oil

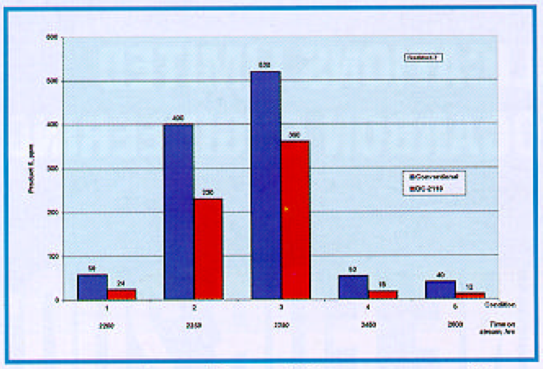

Figure 4. Product sulfur at different test conditions.

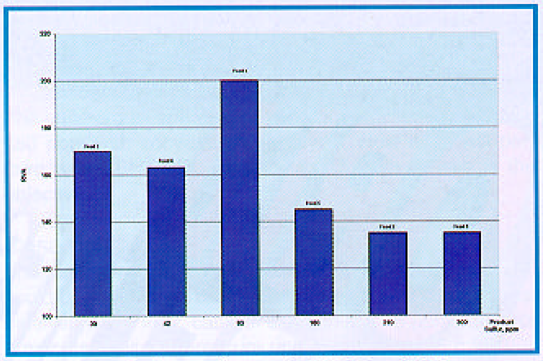

Figure 5. Relative volumetric HDS activities versus conventional catalyst using different feedstocks.

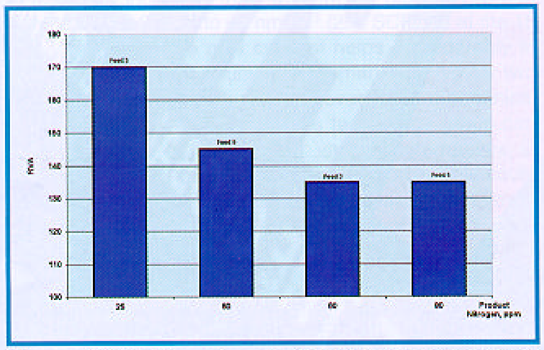

Figure 6. Relative volumetric HDS activities versus conventional catalyst using different feedstocks.

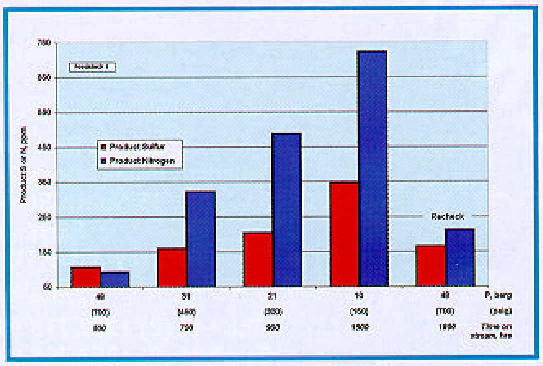

Figure 7. Pressure scout at constant temperature.

interactions are formed between the metal oxides and the support material, the Mo and Ni (Co) retain some of these metal-oxygen interactions and are not fully sulfided. In addition, some of the Ni(Co) become intercalated into the alumina support and are unavailable for dispersing onto the edges of the MoS_2 crystallites. These edge sites have been identified as the active sites in these catalysts.

As a result of the novel manufacturing process used for CENTINEL catalysts (Figure 1), metal complexes (MX_n) physically absorbed on the surface directly react with sulfur compounds to form highly dispersed metal sulfide species, $M{-}{-}{-}S_x$. These highly dispersed metal sulfide crystallites are 'locked in place' during the activation process. This results in the active sulfide phase of the catalyst: MS_y. As a result, all of the metals placed on the catalyst are fully sulfided while maintaining high dispersion and better metals utilisation than conventional catalysts.

Using x-ray photoelectron spectroscopy (XPS), the degree of sulfiding of the produced DN-3100 NiMo catalyst is seen to be nearly complete. All of the nickel in the CENTINEL catalyst is sulfided, as is half of the molybdenum. After treatment with H_2S, the XPS shows that the remainder of the molybdenum is now fully sulfided. On the other hand, XPS indicates that sulfiding of a conventional NiMo catalyst leaves a significant portion of the molybdenum and nickel unsulfided. Using high resolution transmission electron microscopy (HRTEM) to investigate the MoS_2 morphology of a conventional and CENTINEL NiMo catalyst confirms the high dispersion of the fully sulfided active sites on the latter, indicating less stacking overall (higher dispersion). This higher dispersion for the DN-3100 combined with the exclusive presence of the fully sulfided active sites provides the high activity performance.

Performance test results

Criterion's CENTINEL technology has resulted in new HDS catalysts that display step-out activity enhancements when compared to those prepared by conventional routes. These HDS activity improvements are illustrated in Figures 2 and 3 for both distillate and vacuum gas oil (VGO) service. The CoMo CENTINEL catalyst displays 60% higher relative volumetric activity for the production of <50 ppm sulfur diesel when compared to a conventional catalyst of equal metal content. When evaluated for VGO HDS service, a 40% higher volumetric activity is observed.

Figure 3 compares the performance of conventional NiMo catalyst with CoMo CENTINEL in a VGO/FCC pretreat type of operation. While providing 70% higher hydrodesulfurisation activity, the CENTINEL CoMo catalyst is as active in hydrodenitrogenation and aromatics saturation as the conventional NiMo catalyst. It is worth noting that conventional CoMo catalysts are typically 50 - 70% less active in HDN/HDA than their NiMo counterparts. It is believed that high HDN activity of CoMo CENTINEL also contributes to its high HDS performance by lowering the concentration of basic nitrogen molecules in the reaction zone.

The DC-2118 catalyst is Criterion's first CoMo catalyst to utilise the new technology. This catalyst is ideally suited for the production of ULSD products. Figure 4 compares the performance of DC-2118 and the conventional catalyst, using feedstock 2 (Table 2) at 2.5 - 3 months on stream. The test conditions varied as follows: LHSV from 1.0 - 3.4 h-1, pressure from 26 - 35 barg (380 - 500 psig), WABT from 335 - 349 °C. This data demonstrates that the DC-2118 CENTINEL catalyst has a significant advantage throughout all of the operating conditions investigated, with the greatest advantage observed upon going to the

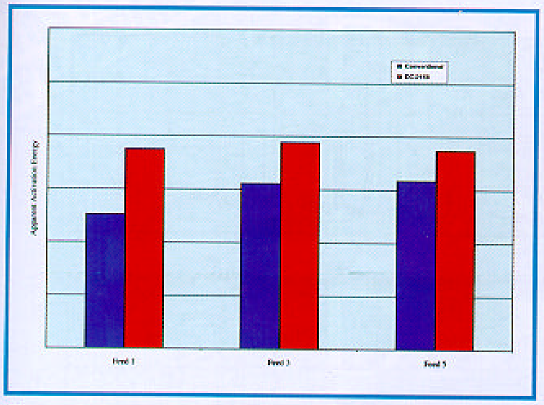

Figure 8. Apparent activation energies using different feedstocks.

lowest product sulfur concentrations. This data also shows that a 12 ppm sulfur slip can be achieved at 349 °C, 35 barg (500 psig) and 1h^{-1} LHSV, while conventional catalyst shows 40 ppm product sulfur at the same conditions. This is very important in terms of new future regulations, when refiners will be looking at 10 - 15 product sulfur levels.

The high activity of the DC-2118 as opposed to the CoMo catalyst for the production of low sulfur diesel is observed with a wide variety of feedstocks (Figure 5). The properties of these feeds are summarised in Table 2. The DC-2118 consistently shows a HDS relative volumetric activity improvement of 138 - 200%, depending on the type of feed and the degree of conversion obtained. This improvement translates into an 8 - 17 °C temperature advantage for DC-2118 to achieve the same sulfur conversion levels as the conventional catalyst. As can be seen from the data for feeds 3 and 5, the relative volumetric activity improvement increases with the degree of HDS conversion.

Although the focus for diesel is on sulfur, the product nitrogen content can become very important if further processing for cetane improvement is being considered. Hydrogenation of aromatics for cetane improvement utilises noble metal catalysts, which are very sensitive to nitrogen poisoning. The DC-2118, although optimised for high HDS activity, displays a very impressive HDN activity for a CoMo catalyst. This is demonstrated in Figure 6 for various feeds and conditions. As was observed for the HDS activity, the relative volumetric activity improvement increases with higher severity of operation (lower product nitrogen).

Figure 7 shows the effect of operating pressure on the HDS and HDN activity of the DC-2118 catalyst at constant temperature. This data demonstrates the wide applicability range of this catalyst for distillate HDS applications. The feed is a combination of SRGO/LCO/CGO in approximately equivalent proportion, and has the highest aromatics and total nitrogen contents of the diesel feeds tested. During the first 500 hours of operation at 48 barg (700 psig), the catalyst was under initial lineout conditions where activity was exceptionally high. After two months of operation at the reduced pressure, the activity loss did not exceed 20% relative to initial start-of-run activity (see recheck conditions). The catalyst has shown a good stable operation even at the extremely low pressure of 10.3 bar (150 psig). The results also show that the HDS activity is less responsive to the pressure variations than the HDN activity.


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Figure 8 shows the data derived from the Arrhenius plots for the DC-2118 and the conventional catalyst, which indicate a higher apparent activation energy for the former. This results in increasing relative HDS and HDN activities at higher temperatures and therefore higher conversions. This attribute makes the catalyst ideally suited for the production of <50 ppm sulfur diesel.

When desulfurising to high conversion levels, the most difficult sulfur molecules, typically referred to as refractive sulfur compounds, must be hydrotreated. These molecules are usually substituted dibenzothiophenes, in which the side chains are in such a position that imposes a steric hindrance for the direct (one-step) desulfurisation route. An example of this type of compound is 4,6-dimethyldibenzothiophene (4,6-DMDBT). Other, more bulky 4,6-dialkyl-dibenzothiophenes have been identified and were found to be even less reactive for HDS. Figure 9 shows feed and product sulfur distribution by individual components at 28 and 8 ppm product sulfur levels. The substituted dibenzothiophenes become the predominant sulfur containing compounds in the product, as opposed to the feedstock composition. In the given feed, 36 wt% of the total sulfur consists of substituted DBTs, a percentage that increases to 93 wt% in the 28 ppm S liquid product. In the 8 ppm S liquid product, 99% of the S is found to be in substituted DBTs. The concentration of dibenzothiophenes substantially decreases upon going from the 28 to the 8 ppm sulfur product, which indicates the high activity of DC-2118 catalyst and its ability to remove the refractive sulfur compounds to achieve ultra low sulfur product concentrations. For example, the amount of 4,6-DMDBT decreases from 60.6 ppm S in the feed to 3.9 ppm S in the 28 ppm S liquid product, with a further decrease to 1.0 ppm S in the 8 ppm S liquid product.

Cumulative sulfur distributions of the same liquid products can quantify the effect of a lower feed (or product) cut point (Figure 10). Both the 8 ppm S and the 28 ppm S liquid products have 0 ppm S in the 335 °C fraction, which in both cases constitutes 88% of the total liquid product. In the 28 ppm S liquid product, 10 ppm S is localised in the 352 °C fraction, which constitutes 93% of the total liquid product.

Overall, sulfur speciation clearly demonstrates that the highly active DC-2118 attacks all of the refractive sulfur compounds. It is therefore an ideal catalyst for ultra deep HDS, capable of reaching 10 ppm S in liquid product under commercially viable conditions.

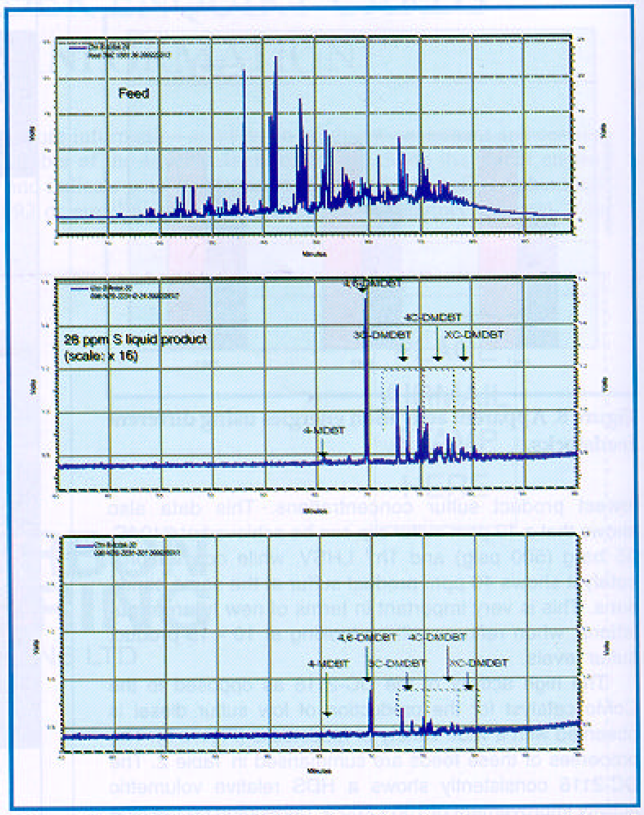

Figure 9. CENTINEL DC-2118: sulfur feed - versus 28 and 8 ppm(w) S in liquid product.

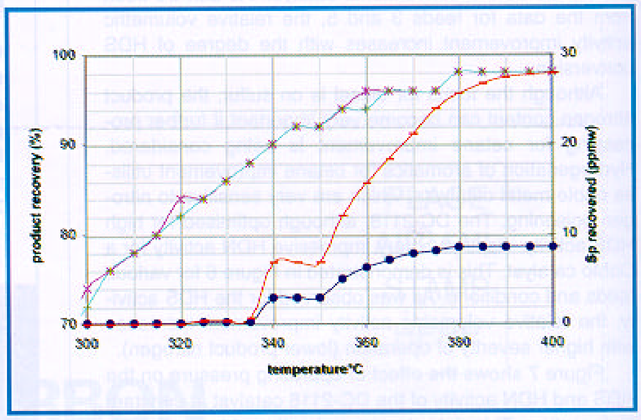

Figure 10. CENTINEL DC-2118: cumulative sulfur distribution and recovery versus boiling point.

Conclusion

Criterion Catalysts & Technologies L.P. is pleased to introduce a breakthrough development of products to help refiners meet their ULSD requirements. The cases above amply illustrate the step-out improvements in performance that can be expected with only a marginal increase in hydrogen consumption, associated with better removal of feedstock impurities.

The high activity of the CENTINEL DC-2118 catalyst is observed with a wide variety of diesel range feedstocks. Activity improvements of 38 - 100% over conventional catalysts are observed. Sulfur speciation analysis clearly shows that the DC-2118 is effective at desulfurising all of the refractive sulfur compounds present in diesel feeds and is therefore ideally suited for the production of ULSD.

Certain refiners may need to make capital investments in order to maintain an economically sound operational cycle life. The company's process technology group working with its SYN alliance partners, Shell Global Solutions and ABB Lummus, can help a refiner review the various alternatives available where such capital expenditure is required, in order to make the most cost effective choices.

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