



Catalysis

Part One of a Two-Part Series

The Challenging Chemistry of Ultra-Low-Sulfur Diesel

By **Salvatore Torrisi Jr.**, Criterion Catalysts & Technologies (Houston);
Tom Remans, Shell International Chemicals Research (Amsterdam);
Justin Swain, Criterion Catalysts & Technologies (Fareham, England)

The destiny of the diesel fuel sulfur specification is clear. Legislators around the world will push for “zero”-sulfur diesel fuel (ULSD) until it is a global reality. U.S. and Canadian legislation requires a 15-ppm sulfur maximum by 2006, and initial implementation of the 10-ppm maximum in the European Union is now set for 2005, with full compliance required in 2009. Thanks to tax incentives, 50-ppm sulfur diesel has already been introduced in a number of European markets, and a few European refiners are even producing 10-ppm sulfur diesel. Some Asia-Pacific countries, such as Japan and Korea, are also now formulating plans for ULSD implementation.

Laboratory studies and commercial results from some European refineries show that making the step from 50-ppm to 10-ppm sulfur can be at least as difficult as the step from 500-ppm to 50-ppm sulfur. This fact has led to many questions about how to cost-effectively produce ULSD.

In a two-part article, we will discuss the potential for advanced hydrotreating catalysts to provide a solution to many of these challenges. In part one, we will discuss the chemistry involved in producing ULSD and how it affects the refiner’s course of action. The second part of the series, which is scheduled to be published in the January/February 2003 issue of *World Refining*, will examine how new hydrotreating catalysts are being designed to more effectively exploit the ULSD chemistry and thus provide more cost-effective solutions to ULSD production.

General Sulfur Species in Diesel Feed

To meet the sulfur specification of ULSD, it is necessary to first understand the different types of sulfur compounds in diesel fuel and their relative reaction rates. Figure 1 depicts various sulfur compounds and their relative reaction rates as a function of boiling point.

In order to reduce sulfur levels below 500 ppm to meet ULSD specifications, it is necessary to remove the more-refractory, and therefore less-reactive, sulfur compounds based on multi-substituted dibenzothiophene (DBT). For a typical medium-pressure diesel hydrotreater, reducing product sulfur to 50 ppm can result in a more than 50% loss in achievable catalyst cycle length using conventional catalysts. In going one step further from 50- to 10-ppm sulfur, one would be pushing the boundaries of operation in units employing conventional catalysts, as this requires removal of the even less-reactive, more-complex, multi-substituted DBT and higher homologues.

In ultra-deep hydrodesulfurization (HDS) operation, the reactivity of a diesel feedstock depends on the relative amounts of less-reactive to more-reactive sulfur components present. The levels of these components, in turn, depend on the crude source, the degree of blending of cracked stocks, fluid catalytic cracker (FCC)/coker operation, and feed cutpoint. The boiling point of the feedstock, in particular the light-cycle oil (LCO) and coker gasoil content, has a significant impact on the required operating conditions for deep desulfurization.

As the boiling point of the feedstock increases, the concentration of the sterically hindered aromatic sulfur compounds increases as well. As the desired product sulfur in treated gasoil is reduced, sterically hindered compounds will have a more significant impact on the reactivity.¹

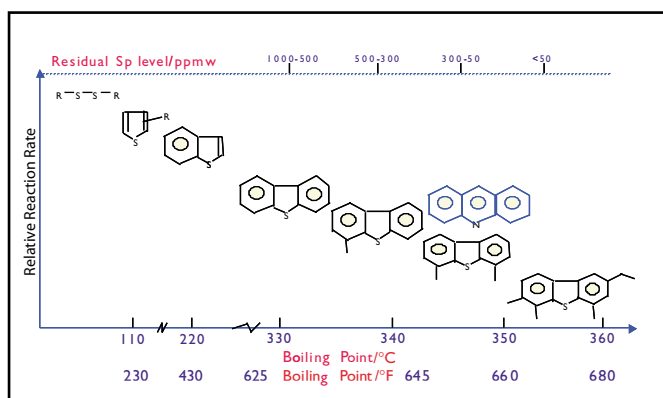


Figure 1. Reaction rates of various sulfur compounds as a function of boiling point. More stringent specifications lead to more involved chemistry.

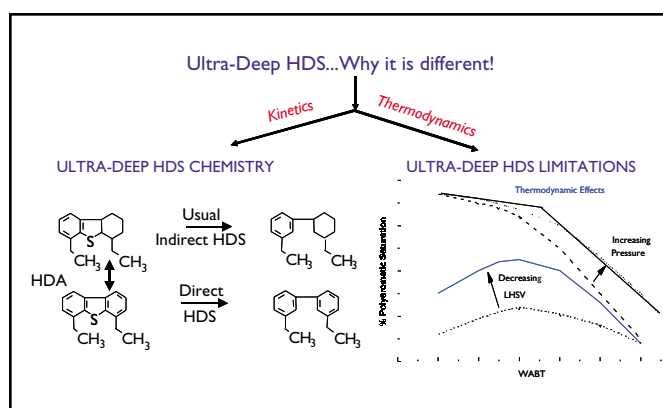


Figure 2. Mechanistic pathways of desulfurization reactions.

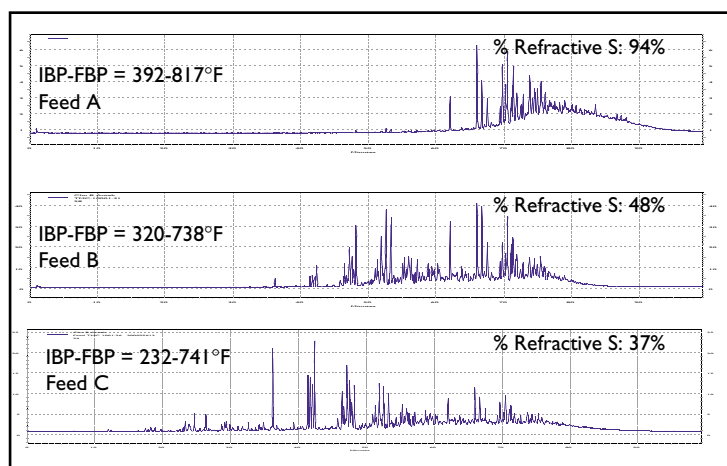


Figure 3. Percentage of refractive sulfur compounds in feed as a function of boiling point.

Removal of bulky basic nitrogen species is also a key element to efficient ULSD operation, as substances such as acridine (Figure 1) effectively compete for the same active sites as the sulfur molecules.²

Ultra-Deep HDS Reaction Mechanism

Making ultra-deep HDS chemistry happen effectively depends on both creating an environment for good kinetic response of the catalyst and steering the thermodynamics to ensure an economical window of operation. Desulfurization reactions can follow two mechanistic pathways, as shown in Figure 2 with a di-substituted DBT as the model sulfur compound.

The traditional mechanism features direct extraction of the sulfur, or hydrogenolysis (carbon-sulfur bond breakage), as the rate-determining step. This direct mechanism is favored on conventional catalysts when HDS is required down to product sulfur levels above 350 ppm. At this product sulfur level, all of the more-reactive sulfur compounds, up to and including non-substituted DBT, have been removed.

When a sulfur specification of 10 ppm or 50 ppm is to be met, then removal of the less-reactive and bulky di-substituted DBTs, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), is necessary. The concentration of these species increases with the refractory nature (sulfur, nitrogen, boiling point, percentage of cracked component) of the feed. These species are more effectively removed via the alternative hydrogenation-controlled mechanism (Figure 2). In order for the breakage of the carbon-sulfur bond to occur, saturation of one of the aromatic rings must first take place. This partial saturation changes the spatial configuration of the molecule, making the previously sterically hindered sulfur more accessible for effective adsorption on the active site and subsequent reaction. In this respect, the ultra-deep HDS mechanism is very similar to the traditional hydrodenitrogenation (HDN) mechanism, where pre-hydrogenation precedes hydrogenolysis.

Clearly the influence of the polyaromatic saturation equilibrium increases when producing 10- to

50-ppm sulfur diesel compared to 350- to 500-ppm sulfur diesel. This also explains why a higher-pressure existing hydrotreater can have more flexibility (greater temperature operating window) with a simple catalyst drop-in solution to meet lower sulfur specifications. When higher pressure is not an option, then the lower LHSV (liquid hourly space velocity) route must be followed.

Nitrogen removal follows a very similar reaction pathway, requiring a pre-hydrogenation step before heteroatom removal. It therefore competes with the hindered DMDBTs for active sites on the catalyst surface. Since nitrogen species, particularly basic nitrogen compounds, adsorb more strongly to that catalyst surface than sulfur species, near-complete removal of nitrogen is required when targeting sulfur levels <15 ppm. We discuss the importance of choosing a catalyst having this dual HDS/HDN functionality in subsequent sections.

Sulfur Compound Identification in Gasoil

Many sulfur species are present in the feed and product gasoil, and some of these are especially difficult to remove in the context of ULSD. The feedstocks shown in Table 1 represent a variety of feeds processed in Europe and in some North American refineries.

Feed A is an example of North Sea sweet straight-run gasoil (SRGO) that might appear to be the easiest to treat to ULSD because of its low sulfur content. However, note the unusual true boiling point (TBP) distillation that shows both a heavy tail and 90% of the feed boiling above 572°F (300°C).

Feed B is a typical full-range 80/20 SRGO/LCO blend derived from Arabian crude and is the most difficult feed in terms of sulfur and polyaromatic content. The presence of the LCO would suggest that this feed might be difficult to process to ULSD.

Feed C is a 70/30 SR/cracked blend derived from a Nigerian crude with a distillation typical of a full-range distillate feed.

A detailed sulfur analysis of the three feedstocks is shown in Figure 3 (page 25). From Figure 3, we could rank the feed reactiv-

TABLE 1. FEEDSTOCK ORIGIN AND PROPERTIES

Feed Origin Feed Type	Feed A SRGO	Feed B 80/20 SRGO/LCO	Feed C 70/30 SRGO/ VB+ LCO
Crude Origin	North Sea	Arabian	Nigerian
Density, °API	32.1	28.4	39.4
Sulfur, wt%	0.196	1.29	0.517
Total Nitrogen, wppm	200	200	145
Aromatics (IP 391), wt%			
Mono	14.1	17.2	18.2
Di	4.6	15.3	5.8
Pri +	3.8	2.1	0.9
Distillation (TBP), °F			
IBP	392	320	232
10	572	457	331
50	673	561	484
90	743	669	635
FBP	817	738	741

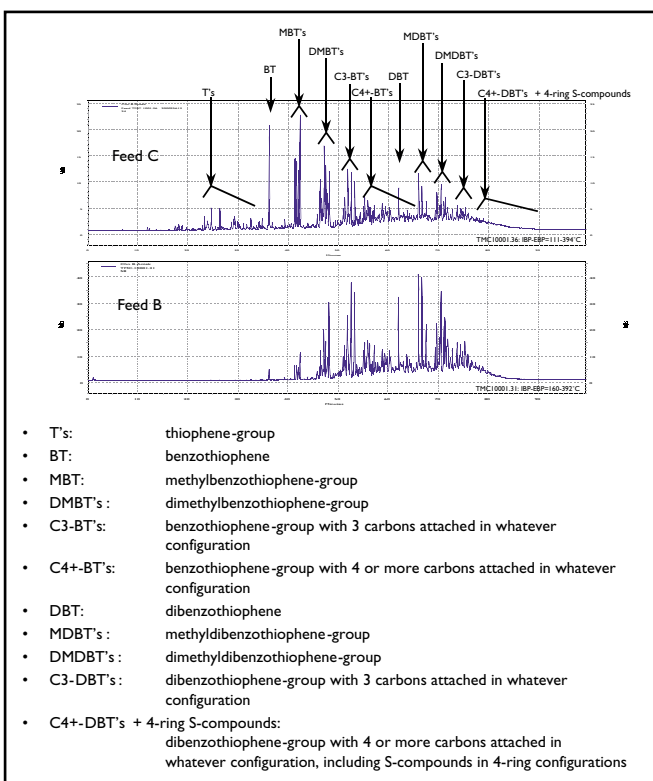


Figure 4. Compound identification in feed.

ity, from most to least reactive, as Feed C > Feed B > Feed A.

Feed A is characterized by having few or no sulfur species boiling below DBT. This is in line with its rather skewed TBP distillation showing 90% of the feed boiling above 572°F (300°C) and the heavy tail extending to a feed boiling point (FBP) of 817°F (436°C). The large concentration of bulky, multi-substituted, less-reactive sulfur species, as also evident by the large integrated area beneath the baseline, identifies this feed as one to be avoided when operating in ULSD mode. In fact, by characterizing refractive sulfur species as all those beyond DBT, then 94% of the sulfur in this feed is refractive.

Feed B, with its more typical diesel boiling range, is characterized by a more broad-ranging sulfur chromatogram of higher resolution. Note the smaller integrated area under the baseline, which indicates a broader range of sulfur species present. The amount of refractive sulfur in this feed was found to be 48%.

Finally, Feed C, with its wide boiling range, shows the largest distribution of sulfur species, with (correspondingly) the lowest concentration of the more difficult-to-remove sulfur compounds. This is evident by the high degree of peak resolution and the small integrated area under the baseline. The light front end of the feed skews the distribution to more easy-to-remove sulfur species, as is further evidenced by the lower amount of refractive sulfur (37%).

The detailed feed analysis of Feed C (compared with Feed B) revealed the identification of sulfur compounds as shown in Figure 4.

If Feed C is subsequently treated to <10 ppm Sulfur, the resultant distribution is as shown in Figure 5. From the product sulfur-speciation, one can observe the distinct peak of 4,6-DMDBT at the 645°F (340°C) boiling point, as well as the rest

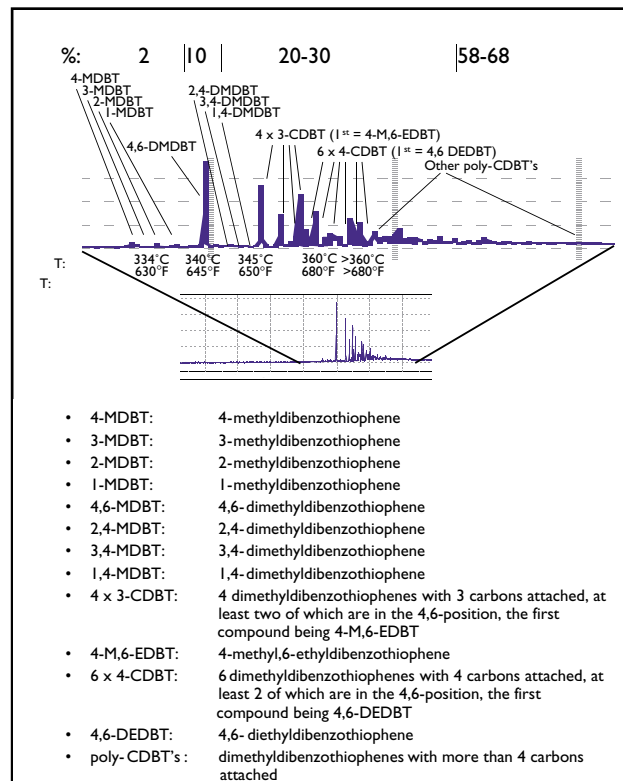


Figure 5. Compound identification in liquid product. X-CDBT = dibenzothiophene with X carbon atoms attached to the ring in unknown configuration.

of the unconverted substituted DBT beyond that boiling point.

Despite having the strongest peak in the chromatogram, 4,6-DMDBT accounts for only 10% of the sulfur remaining in this hydrotreated SRGO. The majority (up to 85%) of the sulfur is bound in the more-complex sulfur compounds extending all the way to what are termed poly-CDBTs (carbon dibenzothiophenes) whose reactivity is similar to or lower than that of 4,6-DMDBT. This distribution also illustrates why feed undercutting is such a powerful tool for meeting ULSD specifications.

Feedstock Effects on HDS

Having identified the different sulfur species present in the feed and product, we can look at the impact of these sulfur species on the “processability” of the different feeds to meet the ULSD specifications.

An investigation was made to study the reactivity of different feedstocks as the product sulfur specification moves from 300 ppm to 10 ppm. Figure 6 compares the reactivity in the ULSD regime of four feeds: three SRGOs and one 80/20 SRGO/LCO blend, each derived from different crudes. The data were generated by pilot plant processing of the feeds over a Criterion cobalt-molybdenum (CoMo) catalyst.

In terms of overall processability, the highest-sulfur feed (SRGO 1) has turned out to be the most difficult; it requires the highest weighted-average bed temperature (WABT) at each product sulfur level. However, when the feedstock reactivity ranking is defined in terms of temperature increase required to reach 30 ppm, then the order of most reactive to least reactive feed is: SRGO 2 > SRGO/LCO ~ SRGO 1 > SRGO 3.

Feedstock reactivity ranking changes very differently as the

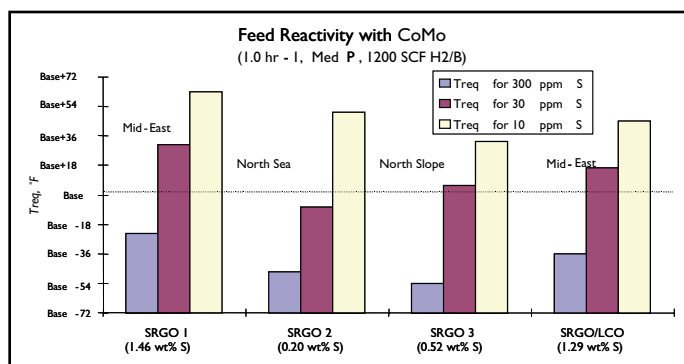


Figure 6. Temperature requirements (T_{req}) for low-sulfur diesel and ULSD.

shift from 30-ppm to 10-ppm product sulfur is considered. In this case the ranking becomes: SRGO 3 ~ SRGO/LCO > SRGO 1 > SRGO 2.

SRGO 2, despite being derived from the sweetest crude, proved to be the most difficult feed to hydrotreat from 300-ppm to 10-ppm sulfur. While a 35°F (20°C) increase in temperature was needed to go from 300-ppm to 30-ppm sulfur, a further 55°F (30°C) was required to go from 30 ppm to 10 ppm.

Effect of Reducing Endpoint

Based on the study so far, it can be seen that the more-difficult-to-remove sulfur species tend to be those substituted DBTs that start from 4,6-DMDBT at roughly the boiling point of 645°F (340°C). Especially if a sulfur level much lower than 50 ppm is desired, then the most-refractory sulfur compounds and higher-molecular-weight DBTs have to be reduced or removed.

One direct way to solve this problem is to reduce the cut point of the feed. Figure 7 (page 27) illustrates the impact of changes in feedstock properties, such as a decrease in T_{90} point through undercutting of the feed. This example illustrates that a reduction in T_{90} of 35°F (to 645°F) can exclude most of the difficult sulfur species and make it much easier to achieve ULSD. This comes at a substantial cost, as yield losses can range 10%–20% or higher depending on the particular feed. Each refiner's circumstance must be considered individually to evaluate the merits of endpoint reduction and subsequent economic impacts.

Importance of Nitrogen Removal to Produce ULSD

It is widely known that organo-nitrogen compounds inhibit HDS reactions, especially those involving the two-step conversion of refractory sulfur, like DMDBT. In particular, basic nitrogen species strongly adsorb to the catalyst surface and prevent some HDS reactions from proceeding unless the nitrogen compound is removed. Even non-basic nitrogen species having low adsorption constants, such as carbazole, are also known to react in the hydrotreating environment to form basic nitrogen. This will inhibit the effectiveness of HDS and add to the challenge of making ULSD.

Controlled experiments studying the effects of basic nitrogen on deep HDS of a gasoil stream were conducted to quantify the impact without interference from other variables. Two deeply desulfurized gasoils were mixed in different proportions, resulting in different basic nitrogen concentrations. The feed sulfur was then adjusted to a constant 2,000 ppm by adding DBT, which was selected because its reactivity would be sufficiently different from the low levels of refractory sulfur present in the deeply desulfurized feed.

Results presented in Figure 8 show that there is a marked dif-

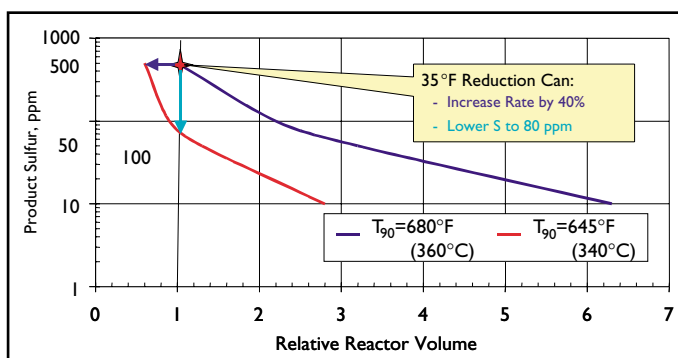


Figure 7. Relative reactor volume vs. feed T_{90} .

ference in the rate of sulfur removal between feeds containing 2 ppm and 18 ppm of basic nitrogen.¹ In part two of this article, we will discuss how the CENTINEL catalyst functionality has been modified to improve the HDN activity, which in turn enhances its ability to achieve ULSD levels of <10 ppm. ●

REFERENCES

1. Ee, C.S., Parthasarathi, R.S., and van den Brule, T. "Sulfur Species and Distribution in Gasoil," paper presented at a technical conference in Pusan, Korea, Oct. 18-19, 2001.
2. van Looij, F., van der Laan, P., Stork, W.H.J., DiCamillo, D.J., and Swain, J. "Key Parameters in Deep Hydrodesulfurization of Diesel Fuel," *App. Catal. A*, 170: 1-12, 1998.

ABOUT THE AUTHORS

Salvatore P. Torrisi Jr., clean-fuels technical specialist for Criterion Catalysts & Technologies, has responsibility for clean-fuels project coordination in the Americas. He joined the CRI International family in 1996, becoming lab manager with the Research & Commercial Development Group. More recently he has been involved with new-product market introduction, particularly with the application of CENTINEL catalysts.

Justin Swain joined Criterion in 1996 and is currently technical manager for distillate hydrotreating. Before joining Criterion, he worked at the Milford Haven Refinery in Wales, where he was responsible for operation and optimization of distillation and catalytic processes.

Tom Remans has been working for Shell since 1997 in R&D and technical service for refinery catalysts marketed by Criterion Catalysts & Technologies. He has worked extensively in the areas of distillate hydrodesulfurization, first-stage hydrocracking, and catalytic dewaxing.

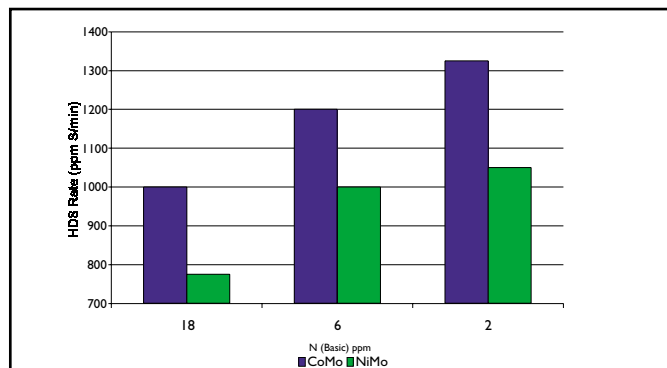


Figure 8. Inhibition of HDS activity by trace organo-nitrogen compounds.