FCC LCO has long been a common component of feed to diesel hydrotreaters. More recently, there has been greater interest in processing higher quantities of LCO due to economic considerations and to meet the market demand for ULSD products. LCO has a number of impacts both on the performance of the hydrotreater and on the resulting ULSD product properties. The extent of the impact depends upon a number of factors including the amount of LCO in the feed, and the catalyst used in the ULSD unit.¹

It is generally accepted that the addition of LCO to the diesel unit increases feed severity and requires an increase in reactor temperature in order to meet the
Figure 1
Impact of LCO Content on Hydrotreater Performance

![Figure 1](image1)

Figure 2
LCO Endpoint Effects Activity

![Figure 2](image2)

Product sulfur target. Figure 1 summarizes pilot plant data demonstrating this effect. The figure shows the required temperature increase relative to the straight run feed as a function of product sulfur for feeds containing 15 and 30% LCO. It is clear that even low levels of LCO impact catalyst activity. At lower severity (higher product sulfur) about 20°F higher temperature is required for 15% LCO, and this increases to 40°F higher temperature for 30% LCO relative to the straight run feed. The activity difference is even greater at lower product sulfur. For ULSD sulfur levels, about 45°F higher temperature is required for the 15% LCO feed and 70°F higher temperature for the 30% LCO blend.

In addition to the amount of LCO, the endpoint also has a significant influence on the reactivity of the feed. Figure 2 compares the performance of two 30% LCO blends relative to the straight run feed. The higher EP LCO has an endpoint of 780°F by D2887 compared to 749°F endpoint for the lower EP LCO. This difference corresponds to an additional 800 ppm of hard sulfur in the feed for the higher end point LCO in addition to a 15% increase in PNA’s. The LCO endpoint effects are apparent even when blended into the straight run feed. The higher endpoint feed requires about 20°F higher temperature relative to the lower endpoint feed at low severity, and nearly 30°F higher temperature for ULSD sulfur levels.

Processing LCO also has an impact on the product quality of the hydrotreated diesel. A significant problem relates to the aro-
matics content as LCO’s tend to have very high concentrations of naphthalene type aromatic species which have very low cetane numbers causing the LCO to have relatively low cetane. The high PNA content also has an impact on diesel product color. This becomes important as end of run (EOR) is approached since ULSD units processing LCO blends will have product go off color at a lower temperature relative to an SR feed.

A survey of commercial operating units shows there are a number of operating parameters which influence cetane improvement in a diesel hydrotreater, most notably hydrogen partial pressure, LHSV and feed API gravity (i.e. amount of LCO). Generally speaking, as LHSV decreases the potential cetane improvement increases.

Commercial ULSD experience has shown that for LHSV’s around 1 hr⁻¹ or less, cetane increases (as measured by cetane index, ASTM D-976) of about 10 numbers are achievable provided the H₂ pressure is high enough when processing LCO blends. At higher LHSV’s (greater than about 1.7 hr⁻¹) the potential cetane improvement decreases to about 4 numbers or less.

Not surprisingly, higher pressure units tend to achieve much larger cetane increases. It has been observed that the cetane uplift is typically less than 6 numbers when the unit pressure is less than 1000 Psig while the cetane uplift increases to 8-10 numbers as pressure increases beyond 1000 Psig. A more detailed discussion can be found in reference 2.

Figure 3 is a summary of commercial data from a ULSD unit using a SmART Catalyst System® which operates at about 1300 Psig and slightly under 1 LHSV. The feed blend varies from 100% cracked stocks to 100% straight run material. As the figure shows, the feed API gravity has a major effect on the cetane upgrade. At low feed API gravities (high LCO levels) the cetane index increase achieved in this unit is around 9 numbers compared to 6 numbers or less for low (or no) LCO included in the feed (higher feed API gravities).

As might be expected, there is a significant cost in hydrogen to achieving very high cetane increases from feeds containing LCO. Figure 4 shows how the H₂ consumption increases with increasing cetane uplift from the same commercial ULSD unit.
For cetane number increases of 5-8 numbers the H\textsubscript{2} consumption is consistent with the rule of thumb that H\textsubscript{2} consumption equals 100*\Delta cetane. Notice, however, that getting increases beyond the 8 numbers in this case come at a very large increase in H\textsubscript{2} consumption; at 9-9.5 numbers of cetane improvement the H\textsubscript{2} consumption is over 1200 SCFB, a 30% increase in H\textsubscript{2} consumption per incremental cetane number. This suggests there is a practical limit to the cetane improvement achievable for a given set of feed and operating conditions, and in this commercial example it looks to be about 8 numbers.

Another potential product quality issue when processing LCO containing feeds is the diesel color. It is generally accepted that the species responsible for color formation in distillates are polynuclear aromatic (PNA) molecules. Some of these PNAs are green/blue and fluorescent in color which is apparent even at very low concentrations. Certain nitrogen (and other polar) compounds have also been implicated as problems for distillate product color and product instability. Work conducted by Ma et.al.\textsuperscript{3} concluded that the specific species responsible for color degradation in diesel are anthracene, fluoranthene and their alkylated derivatives. Other work completed by Takatsuka et.al.\textsuperscript{4} showed that the color bodies responsible for diesel product color degradation were concentrated in the higher boiling points in the diesel (>480°F) suggesting that color can be improved by adjusting the diesel endpoint.

PNA's such as these are readily saturated to one and two ringed aromatics under typical diesel hydrotreating conditions at start of run (SOR), but as the temperature of the reactor increases towards EOR, an equilibrium constraint is reached whereby the reverse dehydrogenation reaction becomes more and more favorable. At some combination of ‘low’ hydrogen partial pressure and ‘high’ temperature, PNA’s actually begin to form (or reform) resulting in a degradation of the diesel product color.

Figure 5 summarizes data from a commercial ULSD unit using ART catalysts. The data show that the product color exceeded 2.5 ASTM, the pipeline color specification for diesel, at reactor outlet temperatures above 730°F. The feed to this unit contained 30-50% LCO and it was
operated at 1.0 LHSV and 850 Psig inlet pressure.

Figure 6 summarizes some pilot plant data which was generated as part of a larger color study on a sample of used CDXi, a premium CoMo catalyst for ULSD. The figure shows a comparison of the diesel product color achieved from a SR feed and a 30% LCO blend at 2100 SCFB H₂/Oil ratio and two pressures. The SR feed results in acceptable color over a wide range of temperatures for both pressures shown. The product from the LCO blend, on the other hand, goes off color (>2.5 ASTM) between 730-740°F at 800 Psig while at 1200 Psig the temperature can exceed 760°F before going off color. This clearly demonstrates the significant impact that H₂ partial pressure has on diesel product color when processing LCO containing feeds.

Processing LCO as part of the feed to a ULSD unit can be challenging since the quality, quantity and endpoint of LCO affect catalyst activity and product properties. These challenges can be overcome with proper choice of catalyst system and an understanding of the impact LCO has on both unit performance and ULSD product quality. Advanced Refining Technologies is well positioned to provide assistance on how best to maximize unit performance and to take advantage of opportunities to successfully process more LCO into ULSD.

References
2. G.Rosinski and C.Olsen, Catalagram 106, Fall 2009
3. X. Ma, et. al., Energy and Fuels, 10, pp 91-96 (1996)