

Factors Influencing ULSD Product Color



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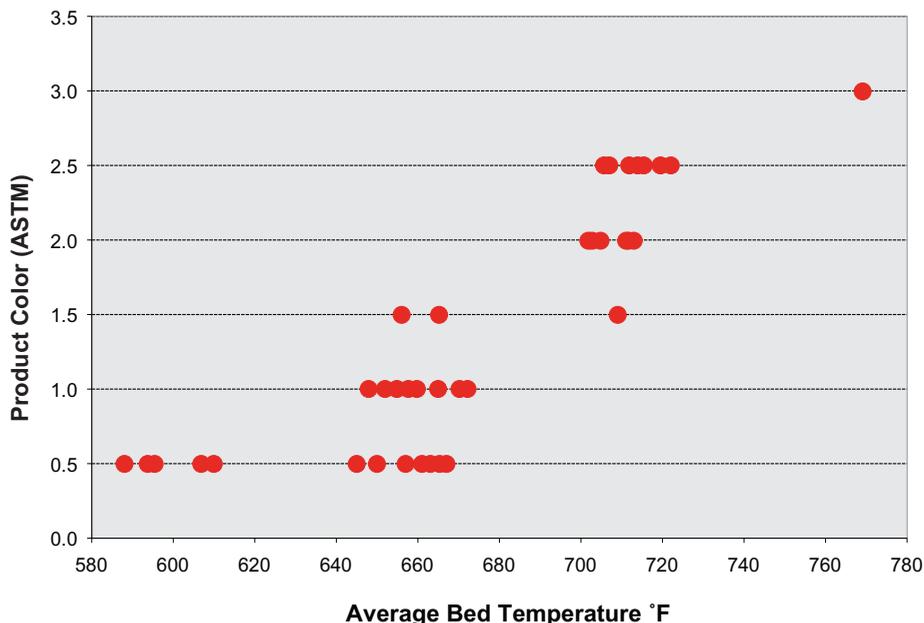
Product color is a common concern for refiners with a number of petroleum products including kerosene, jet fuel, diesel fuel and lube base oils. With the introduction of ultra low sulfur diesel (ULSD) the issue of diesel product color has become more of an issue as the typical ULSD unit cycle length may now be limited by color degradation of the product. Refiners have been uncertain about end of run (EOR) reactor outlet temperatures with expectations in the range of 710-760°F. The typical ULSD unit has a deactivation rate in the range of 2-3°F/month so an increase in EOR temperature of 10-20°F has a significant impact on a refiner's planning and economics.

Figure 1 summarizes data from a commercial ULSD unit using ART catalysts. The data shows that in this case

the product color exceeded 2.5 ASTM, the pipeline color specification for diesel, at a reactor outlet temperature above 730°F. The feed to this unit contained 30% LCO and it was operated at 1.0 LHSV and 850 psig inlet pressure.

It is well known that the color of distillate products is affected by the reaction conditions in the hydrotreater, especially temperature and hydrogen partial pressure. As (outlet) temperature increases and/or hydrogen partial pressure decreases, the product color degrades. It is also generally accepted that the species responsible for color formation in distillates are polynuclear aromatic (PNA) molecules. Some of these PNA's are green/blue and fluorescent in color which is apparent even at very low concentrations of these species. Certain nitrogen (and other polar)

Figure 1
ULSD Product Color Using a SmART Catalyst System™



compounds have also been implicated as problems for distillate product color and product instability. These species can polymerize to form condensed aromatic structures which tend to be green to yellow/brown in color and can also form sediment via oxidation and free radical reactions.⁽¹⁾ Work conducted by Ma et.al.⁽²⁾ concluded that the specific species responsible for color degradation are anthracene, fluoranthene and their alkylated derivatives. These are both three ringed aromatic structures and are shown in Figure 2.

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 may be reached whereby the reverse dehydrogenation reaction becomes more favorable. At some combination of low hydrogen partial pressure and high temperature the dehydrogenation reaction predominates and PNA's begin to form resulting in a degradation of the color of the diesel product. Other work completed by Takatsuka et.al.^(3,4) showed that the color bod-

ies responsible for diesel product color degradation were concentrated in the higher boiling points in the diesel (>480°F). This suggests that color can be improved by adjusting the diesel endpoint. They also suggest that the color bodies responsible for color formation in desulfurized diesel are newly formed PNA structures from desulfurized aromatic compounds.

To learn more about color degradation in ULSD, ART completed a pilot plant study which investigated diesel prod-

uct color over a wide range of operating conditions. The study utilized spent ART CDXi, a premium high activity CoMo catalyst for ULSD. The sample of spent catalyst had been in commercial diesel service for well over a year and had a carbon content of 10.9 wt.%. The testing program included straight run (SR) diesels, a 30 vol.% LCO blend and a 30 vol.% light coker gas oil (LCGO) blend. The properties of all the feeds are listed in Table I. The test was designed to examine the effects of H₂ partial pressure, H₂/Oil ratio and temperature on ULSD product color. H₂ partial pressure varied from 300-1150 psi and the H₂/Oil ratio covered the range of 700-2100 scfb.

Figure 3 shows how the diesel product color changes with temperature and pressure for the straight run feed (SR #1). Not surprisingly, pressure clearly has a significant impact. At the lowest operating pressure, which corresponds to 300-350 psi H₂ pressure, the product color exceeds 2.5 ASTM at a temperature greater than 740-750°F. Doubling the unit pressure to 800 psig allows the temperature to increase to 780°F before the product color reaches 2.5 ASTM, and at even higher pressures the product color is well below 2.5 ASTM for all practical temperatures encountered in ULSD processing. At these con-

Figure 2
Primary Fluorescence Species in Hydrotreated Diesel (Ref 2)

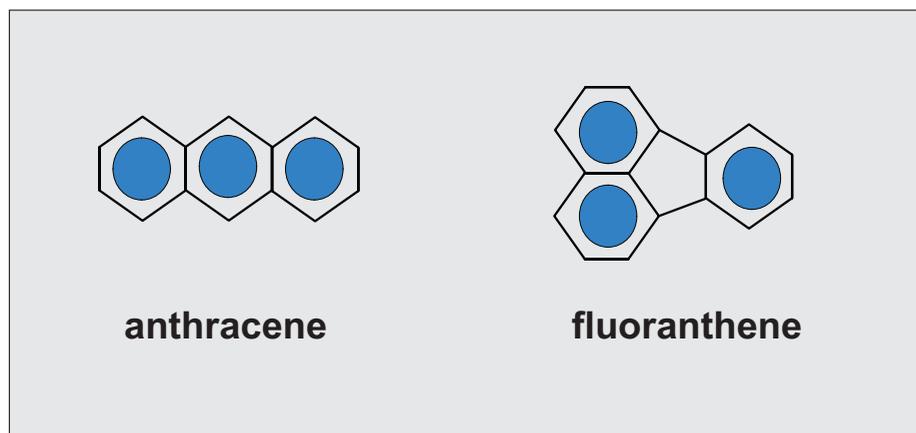


Table I
Feedstock Properties

	SR #1	SR #1/LCO	SR #2	SR #2/LCGO
°API	33.27	27.73	34.44	33.63
Sulfur, wt.%	0.68	0.93	1.12	1.34
Nitrogen, wppm	120	293	127	249
Total Aromatics, vol. %	31.5	40.0	27.3	30.1
PNA's (2-ring+), vol. %	10.7	21.9	9.5	10.8
ASTM Color	L3.5	L6.5	L2.0	L5.5
Distillation (D2887), °F				
IBP	275	265	222	238
10%	454	439	477	437
50%	580	565	613	579
90%	600	703	681	667
FBP	837	841	740	754

Figure 3
Product Color Improves with Pressure

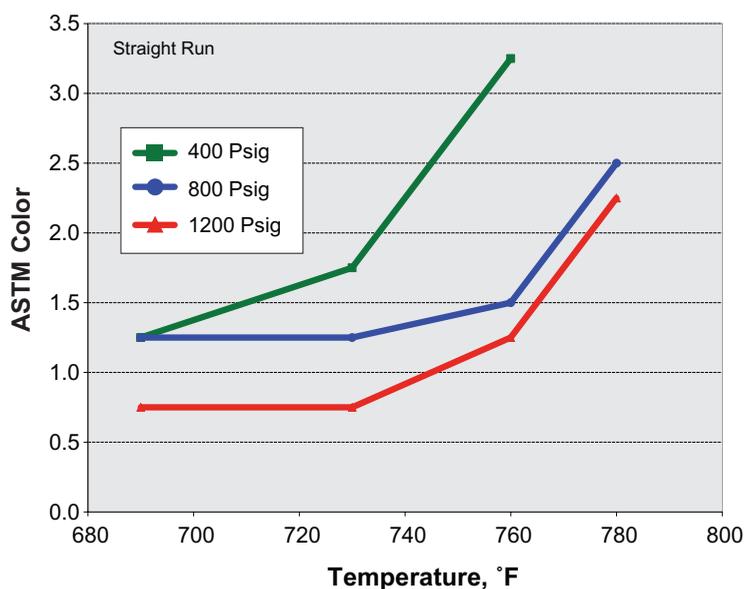
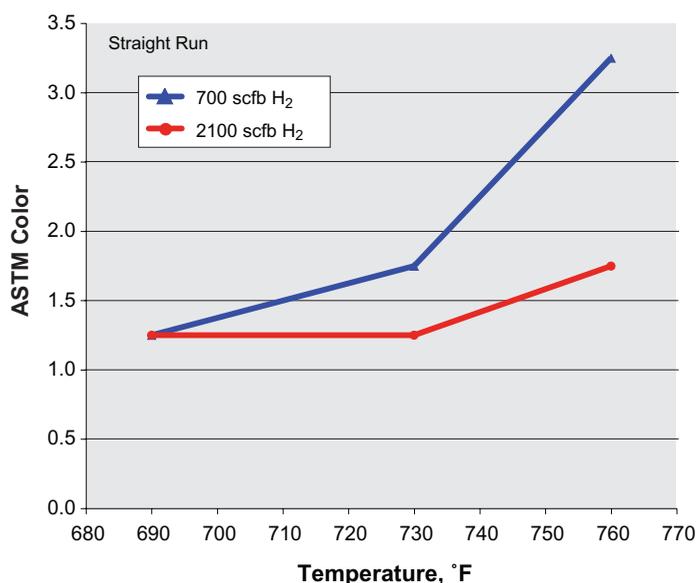


Figure 4
Product Color Improvement with Increased H₂/Oil Ratio



ditions the H₂ partial pressure increases by a factor of about 3.4 going from 400 psig up to 1200 psig total pressure for temperatures around 750°F.

The data in Figure 3 were generated at the low end of H₂/Oil ratios investigated. Figure 4 shows the effect of increasing the H₂/Oil ratio at 400 psig on the SR #1 feed. At this low pressure, the H₂/Oil ratio has a significant impact on product color. The data show that the temperature can be increased from 745°F to well above 760°F before product color exceeds 2.5 ASTM. At 400 psig total pressure and 760°F, changing the H₂/Oil ratio from 700 to 2100 scfb results in a 10% increase in H₂ partial pressure which appears to be enough to keep the reaction environment on the favorable side of the hydrogenation-dehydrogenation equilibrium curve. At higher operating pressures the impact of increasing the H₂/Oil ratio is reduced when processing the SR feed, but still has a positive effect on suppressing product color.

As might be expected, adding LCO to the ULSD unit feed makes the product color situation worse. Figure 5 compares the product color for the SR feed and the 30% LCO feed at 2100 scfb H₂/Oil ratio and two pressures. The SR feed results in acceptable color over the wide range of temperatures for both pressures shown. This compares

with the 30% LCO feed which goes off color at about 730-740°F at 800 psig; and at 1200 psig the temperature can exceed 760°F before reaching 2.5 ASTM color. This data demonstrates the significant impact that pressure has on diesel product color when processing feeds that contain LCO.

Figure 6 demonstrates the effects of the H₂/Oil ratio on product color when processing the 30% LCO feed. It shows the temperature at which the color reaches 2.5 ASTM as a function of H₂/Oil ratio for both 800 and 1200 psig total pressure. The temperature increases by about 25°F when the H₂/Oil ratio is increased from 700 to 2100 scfb. That range of H₂ rates corresponds to an increase in hydrogen partial pressure of 5-10%

The pilot plant program also investigated the effects of a coker derived material on ULSD product color. Figure 7 compares the product color for the second SR feed and a 30% LCGO/70% SR #2 blend at 800 psig. The data indicates that the feed containing LCGO behaves similarly to the SR feed. In both cases the outlet temperature can exceed 780°F before product color approaches the ASTM 2.5 level. This is not surprising when comparing the properties of the two feeds. The aromatics level, and in particular the PNA concentrations, are essentially the same for the SR and the coker blend. Compare this with the LCO blend shown in Table I where the PNA's are twice that of the SR or LCGO feeds.

As mentioned previously, it is generally accepted that product color is related to PNA's, and earlier work has concluded that specific three-ringed aromatics are responsible for color degradation in diesel. Figure 8 shows a comparison of the product PNA's (three-ring aromatics) and diesel product color for all the feeds and conditions of the study. It is readily apparent that the PNA's correlate reasonably well with product color.

Figure 5
Comparison of Product Color for SR and 30% LCO

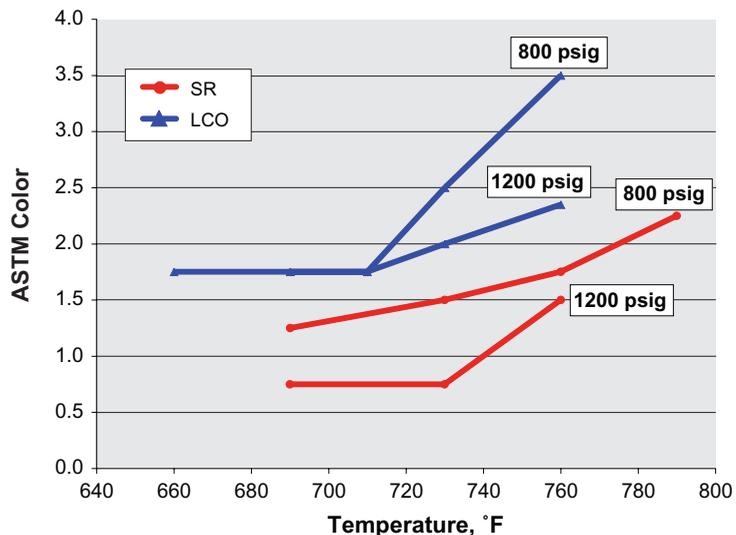


Figure 6
Effects of H₂/Oil Ratio on Product Color for 30% LCO

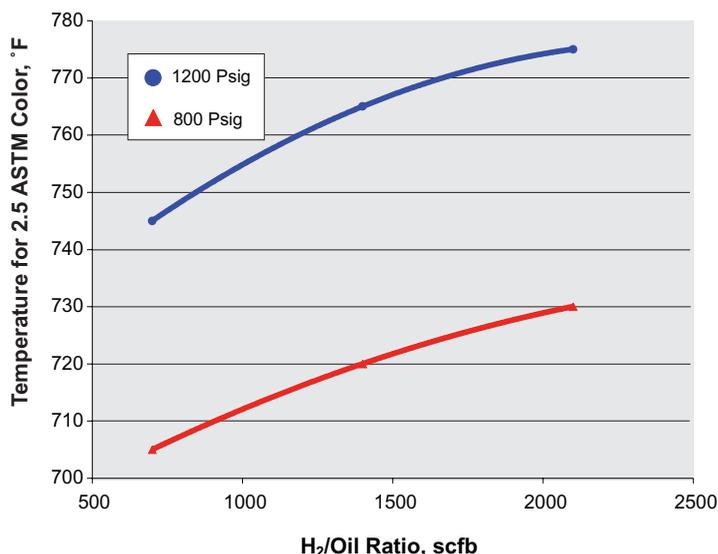
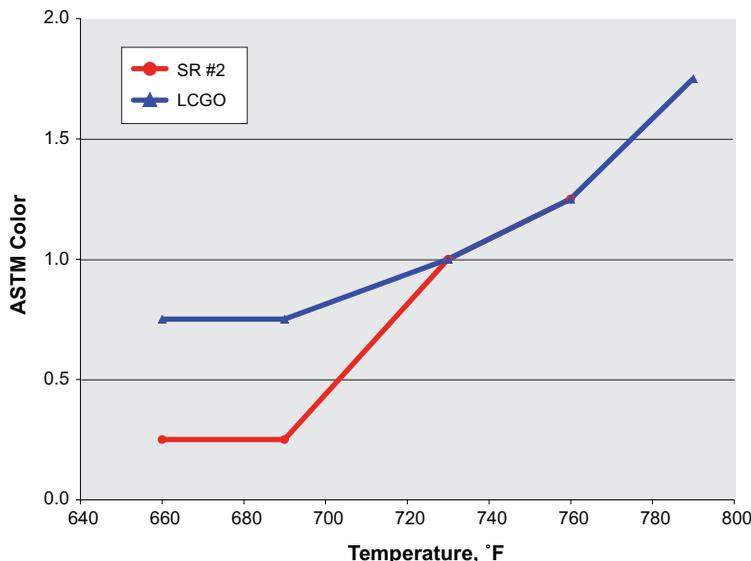


Figure 7
Product Color Comparison for LCGO and SR



From these data it is clear that hydrogenation of PNA's is key to maintaining acceptable product color in ULSD. This suggests a couple of approaches that allow an increase in EOR outlet temperatures and thereby increase the ULSD unit cycle length.

One approach which has been put to commercial practice is to increase quench to the bottom bed of the hydrotreater. This accomplishes two things which are important to maintaining a good environment for hydrogenation of PNA's. It reduces the outlet temperature and helps to increase the outlet hydrogen partial pressure relative to no or lower amounts of quench.

This, of course, requires that the upper beds of the hydrotreater be run at higher WABT's in order to maintain the required HDS conversion. This means that the furnace must have sufficient capacity to achieve the higher inlet temperatures. Operating in this manner offers the potential to add an additional 10-20°F on to the cycle length depending on the unit capabilities (furnace, quench capacity).

Another approach, which may be implemented with the one just discussed, involves adjusting the feed to the unit. The data from this work shows the significant impact LCO

Figure 8
3+ Ring Aromatics Correlate with Diesel Product Color

