Chevron USA's Salt Lake City Refinery loaded their recently revamped ULSD unit in April 2006 with approximately 220,000 lbs of ART's SmART catalyst system™ consisting of 75% ART CDXi and 25% ART AT505. The unit commenced operation in May 2006. At the time of startup, the unit received hydrogen from several sources, and estimates put the hydrogen purity between 65% and 75% at the reactor inlet. Shortly after start up the unit began deactivating at a higher than expected rate, and it appeared that a catalyst change-out would be required by the end of the year. A summary of the performance experienced during this period is shown in Figure 43. The figure shows that the start of run WABT was 665-670°F, and the very high rate of deactivation is readily apparent.

To help understand the performance of this ULSD unit the refinery provided feedstock for use in the pilot plant program. The goal of the study was to evaluate the performance of the SmART system using Chevron, Salt Lake City feed and operating conditions, and to explore...
the impact of hydrogen partial pressure on catalyst activity and stability.

The initial phase of the pilot plant program utilized 100% hydrogen at unit conditions using lot retains of the catalyst loaded in the commercial unit. This showed that 628°F was required to achieve 7 ppm product sulfur. The Salt Lake City ULSD unit is not equipped with a recycle gas scrubber, and measurements indicated that there was about 2 mole% H₂S in the recycle gas stream. Simulating 2 mole% H₂S in the treatgas to the pilot plant resulted in a decrease in HDS activity, and it then required about 635°F to achieve 7 ppm sulfur.

The next phase of the testing was aimed at investigating the effects of hydrogen purity on performance. Chevron was interested in comparing the impact of 90% H₂ purity and 70% H₂ purity. As mentioned above, the purity at the start of the cycle was believed to be between 65-75%, and 90% represented the expected case after start up of a new hydrogen plant at the refinery. Since the pilot plant uses 100% hydrogen, the hydrogen purity effects were simulated by adjusting the pressure to match the hydrogen partial pressure corresponding to the desired hydrogen purities. Flash calculations were completed using the commercial unit feed and conditions to determine the H₂ pressure for both 90% and 70% H₂ purity cases. The 90% purity case operated at a hydrogen partial pressure of 612 psia while the 70% purity case was at a partial pressure of 480 psia.

The effects of lowering the hydrogen partial pressures representing the 90% and 70% purities had a significant effect on catalyst activity in ULSD service. Operating at 612 psia hydrogen resulted in an increase of WABT to achieve 7 ppm from 628°F to 642°F while the 480 psia hydrogen case required an increase in temperature to 657°F for 7 ppm sulfur. These results are summarized along with the 100% H₂ purity and H₂S effect in Figure 44.

The pilot plant protocol then called for 1000 hours of operation while maintaining 10 ppm sulfur in order to compare the effects of decreasing hydrogen purity on catalyst stability. The results of this are shown in Figure 45. The 90% purity system had a deactivation rate of about 6°F/month while the 70% system deactivated at about 17°F/month. These pilot plant runs are summarized Figure 45.

In September 2006 the Salt Lake City refinery brought their new hydrogen plant on line and this, combined with several other operational changes, increased the hydrogen purity of the treat gas to the ULSD unit to >95%. This resulted in a significant decrease in the rate of deactivation. The unit was experiencing 15°F/month deactivation on average, with periods as high as 30 °F/month prior to starting the hydrogen plant. The fouling rate decreased to about 5°F/month with the improved hydrogen purity. This part of the unit cycle is shown in Figure 46. These changes allowed the unit to run a full 12-month cycle before turning around.

Not surprisingly, the hydrogen purity of the treat gas also has a significant impact on the product color.
The color of the product degraded steadily as the catalyst deactivated, and after the aging step the ASTM color was significantly worst for the 70% H₂ case at <3.0 ASTM compared to 1.5 ASTM for the 90% hydrogen case. This compares with an ASTM color of around 1.0 for both cases prior to aging. Similarly, the HDN activity is severely affected. The product nitrogen increased from 1-2 ppm to 20 ppm during the aging test for the 70% purity case compared to a change of only 1 to 3 ppm for the 90% purity case. This demonstrates that lower H₂ purity results in a loss of HDS and HDN activity, degrades product color and increases the deactivation rate.

Chevron, Salt Lake turned the ULSD unit around in June 2007 and loaded a fresh SmART catalyst system. The unit has been operated at full capacity for several months without the same drastic start-of-run fouling rate observed on the previous run, due to operation with >95% pure hydrogen. The current deactivation rate is showing <5 °F/month.

Advanced Refining Technologies and Chevron worked closely together to troubleshoot the poor performance experienced in their newly revamped ULSD unit charged with a SmART Catalyst System. The pilot plant testing was able to prove that the high deactivation rate observed early in the cycle was completely the result of the low hydrogen partial pressure and not the catalyst. Based on the confidence developed in the pilot data, Salt Lake again chose to load the ART catalyst for the second run. This experience is a good demonstration of the importance of hydrogen partial pressure in ULSD applications. Maintaining good hydrogen partial pressure is extremely important for lower pressure ULSD units, and the data suggests that there is a hydrogen partial pressure "cliff" where lower purities cause a much greater than expected increase in fouling rate.