Improve ULSD investment return

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Criterion Catalysts & Technologies, USA, examine new
technologies that enhance ultra low sulfur diesel strategy.

Over the past decade, the role of distillate fuels hydrotreating has evolved extensively due to legislated reductions in diesel sulfur specifications around the world. Table 1 provides a summary of global diesel fuel regulations until 2010. In the next few years, it is anticipated that the majority of nations will require ultra low sulfur diesel (ULSD) with a maximum sulfur level of 10 - 15 ppm for all onroad applications, and will require significant reductions in the sulfur cap for offroad diesel applications (maximum of 10 - 500 ppm).

Given the severity of operating change needed to make diesel fuel with 10 ppm sulfur, there have been many concerns and discussions regarding the best solutions for producing this new fuel. Substantial information has been published on this subject over the last few years to help refiners navigate the many issues and options. Understandably, much of the attention thus far has focused on the front end of the issue, i.e. how to approach the investment decision, and (particularly) how to minimise the capital investment needed to make ULSD. Several articles have provided good direction on the range of options for controlling capital investment and reducing the risk of incurring a stranded investment.[1-6]

Additionally, catalyst manufacturers have expended considerable resources on rapidly advancing catalyst performance, and now better understand the variables affecting catalyst selection for ULSD. This effort has been critical, as it is likely to create the greatest leverage for controlling capital investment for ULSD production. Over the past few years, the industry has seen an increase of approximately 50% in the activity of top tier catalysts. Criterion Catalysts & Technologies' discovery of a new catalyst manufacturing process, which led to its CENTINEL catalyst line, has boosted the capabilities of existing distillate hydrotreaters, and has thereby provided refiners with additional investment options. The quick acceptance of this new catalyst technology demonstrates the importance to refiners of better catalyst performance (Figure 1). Through further technological advances, Criterion expects to commercialise a new generation of CENTINEL catalysts by the end of 2003, aimed at helping refiners to develop more robust ULSD strategies (Figure 2).

Table 1. Legislated, proposed and voluntary sulfur levels in diesel fuels show continued direction towards ultra low sulfur targets

Region	Year	Onroad (ppm)	Offroad (ppm)
EU	2005	50/10*	> 500
	2008 - 2009	10*	10*
USA and Canada	2006	15	> 500
	2007	15	500*
	2010	15*	15*
Japan	2004	50*	> 500
North and South Korea	2006	50	> 500
Australia	2006	50	> 500

Proposed or voluntary.

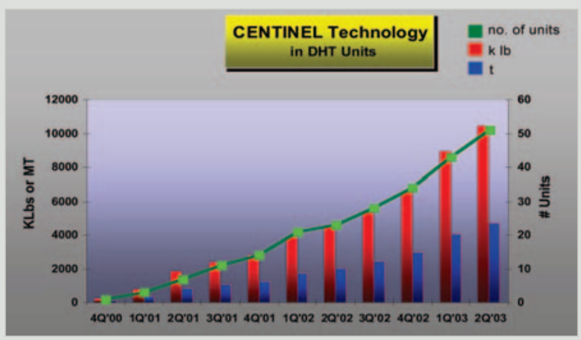

Figure 1. Rapid growth in CENTINEL catalyst usage confirms value of reliable top performance.

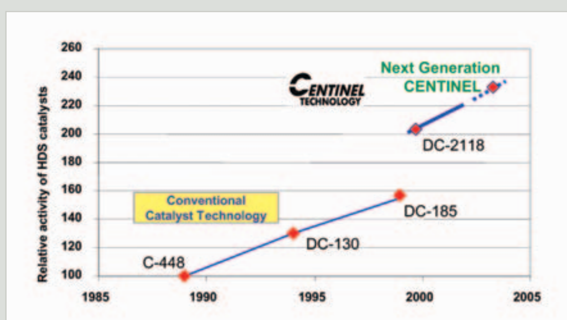

Figure 2. Catalyst advancements provide greater ULSD strategy flexibility.

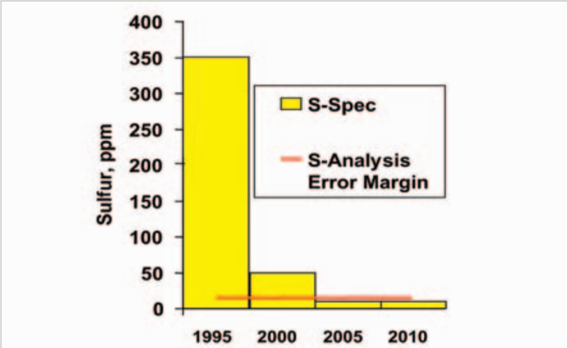

Figure 3. The disappearing gap between sulfur specifications and analysis error margin means that consistently reliable operation is essential.

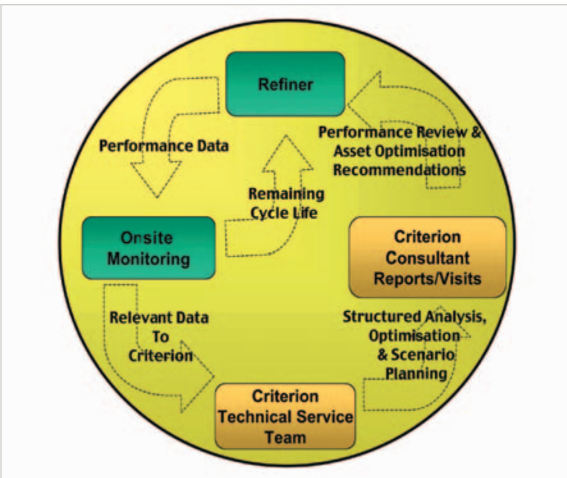

Figure 4. Achieving reliable ULSD production requires better monitoring and decision analysis.

The capital investment decision, and the corresponding unit design and operating strategy decisions, are immediate, critical issues. However, as refiners plan their ULSD strategies, they should not overlook the importance of what can happen once the hydrotreater is required to run in ULSD mode. Refiners also need to consider the post project requirements to ensure reliable, consistent operation, and to make the most of their new investments in this unforgiving environment. In the past, the distillate hydrotreater was often viewed as a simple hydroprocessing 'utility unit' with comfortable operating cycles and margins for error. Operational errors were common, but at lower severity and higher product sulfur specifications, often went undetected. Regenerated or older generation catalysts were frequently acceptable choices, but those days are now gone. In the future, reliable production of ULSD will be essential for smooth refinery operation, and there will be little or no room for error. Much more attention will need to be focused on the operation if costly product downgrades are to be prevented. With reactor sizes and catalyst volumes increasing, refiners will become even more concerned with optimising lifecycle investment, and this at a time when refinery staff numbers have dwindled and the demands on the remaining staff have increased. ULSD strategies that do not address these ongoing operational issues have a critical gap.

Dependable, cost effective operation

Producing ULSD reliably and cost effectively requires more than a good unit design, high performance catalyst and sufficient hydrogen supply. Constant attention to feed quality, reactor conditions, accuracy of laboratory analyses and catalyst performance are essential for good results. For example, a 10 - 20 ppm error variation in the product sulfur measurement did not cause any major issues when product sulfur specifications were 350 ppm or even 50 ppm. However, this amount of variation becomes a real problem when the product specification is 10 - 15 ppm (Figure 3). Similarly, with 50 - 350 ppm sulfur targets, small exchanger leaks or slight catalyst bed channelling would not be alarming. This is no longer the case with a 10 ppm target.

So what options do refiners have to optimise their daily ULSD operation? The obvious choice is to turn to their staff to monitor the operating variables and results; to develop the tools needed to effectively analyse the operation; and to carry out the analyses. However, the staff resources of many refineries are not sufficient to deal with this increased workload, nor are there the laboratory facilities or finances readily available to develop the monitoring and analytical tools. To improve the situation, refiners can purchase one of the available software packages that analyse a hydrotreater's performance. This approach can reduce the workload for the refinery's staff. However, as these software packages are neither 'tuned' to specific catalyst, nor to the characteristics of a specific unit, the output is mainly useful for general guidance, and not for unit performance optimisation, indepth troubleshooting, or detailed scenario planning. The next option could be to seek help from the catalyst supplier or process licensor, but unfortunately they have not been equipped to provide this capability. Generally, the transfer of the relevant information from the refiner to the supplier has been tedious and time consuming, and as a result it has been difficult to catch problems early. Attacking the issue by placing the supplier's personnel at the refinery is not a viable answer. Under severe cost cutting pressures, refiners are often unwilling to bear the costs of these extra resources. Likewise, shrinking margins leave no room for suppliers to add more resources.

In order to respond to this developing problem, Criterion has created a technical support system that can efficiently deliver the analyses needed to make good decisions about the ULSD operation. This system is built upon the same successful principles as CATSCAN®; the performance monitoring and modelling system for petrochemical applications, which was developed by Pavilion Technologies, Inc. and CRI Catalyst Company, Criterion's sister company. The system's structure provides refinery staff with tools for making fast, approximate evaluations of the ULSD operation, and delivers information that Criterion needs to make indepth analyses of the operation (Figure 4). With this system, the refiner can make better decisions as to how to respond to changing feed quality, product quality and product demand, and can easily evaluate turnaround timing options. Importantly, unit performance problems can be detected sooner, enabling faster resolution to prevent unwanted, irreversible consequences. Finally, the system's design provides Criterion with the means to analyse ULSD operation routinely, and recommends ways to use the assets more effectively. All of these benefits are possible, while at the same time reducing the amount of effort invested by refinery staff. The following casestudies are two examples of how this new technical support system has been used to increase the value of the refiner's investment.

Casestudy one

While using CENTINEL DC-2118 to produce low sulfur diesel, a European refiner's hydrotreater experienced a series of emergency shutdowns. A critical element of the operation was to hydrotreat the maximum amount of light cat cycle oil (LCCO) to meet the full diesel demand. The significant number of abrupt shutdowns caused serious doubts as to the hydrotreater's ability to reach the targeted turnaround date. Reducing the amount of LCCO feed to extend run time would have been very costly. On the other hand, an early turnaround, particularly one with little notice, would require premium payments.

Actions

Unit performance evaluation

Using its process monitoring tools, Criterion determined that the DC-2118's deactivation rate had not increased after the series of shutdowns. However, they had caused step changes in the catalyst's activity, leading to higher reactor temperatures to meet the product target properties. This meant that the unit would not be able to run to the target date at maximum LCCO feed rate.

Economics/planning options evaluation

Working together, Criterion and the refiner's process engineering and economics/planning groups defined the economic model for the hydrotreater. Using additional capabilities in Criterion's Technical Services' monitoring programme, the margin impact was calculated as a function of LCCO feed rate downgrade and remaining cycle life.

Results

Through proactive unit monitoring and analysis, including a clear understanding of unit/refinery economics, the customer was able to make the most profitable decision, weighing the trade off between unit margins, LCCO downgrade and operating costs, for unit shutdown and catalyst replacement (Figure 5).

Casestudy two

Over the past six years, Criterion and Shell Global Solutions have worked closely with a refiner in the former Soviet Union to upgrade its diesel hydrotreater. As with many refineries, this location wanted to achieve lower sulfur levels, without having to invest in a new unit. The challenge was to define the most cost effective upgrade for each stage of the market opportunity. Table 2 summarises the progression of unit improvements and the resulting demonstrated unit capability.

Actions

Unit performance evaluation

Beginning in 1996, ongoing unit assessments were conducted for each cycle, using Criterion's performance monitoring and modelling system to define the optimum upgrades to achieve the product targets for the next cycle. As the sulfur targets reached levels beyond standalone catalyst solutions, Criterion and Shell Global Solutions developed cost effective packages combining new reactor internals and high performance catalysts.

Upgrade implementation

Over the initial two cycles, straightforward catalyst upgrades succeeded in reducing sulfur levels to 500 ppm, and then to 350 ppm.

In 2001, new reactor internals were needed to make the significant step change to 50 ppm maximum sulfur. These changes were implemented at the same time as a normal catalyst replacement. As a result of the significant perfor-

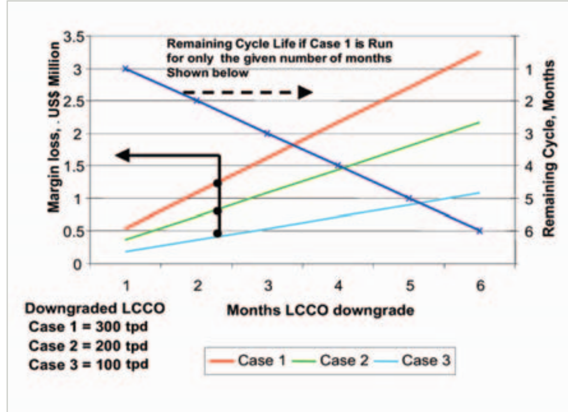

Figure 5. Decision options for a ULSD unit.

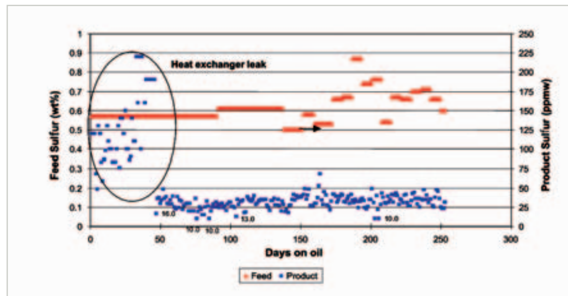

Figure 6. Consistent performance in low sulfur diesel operation.

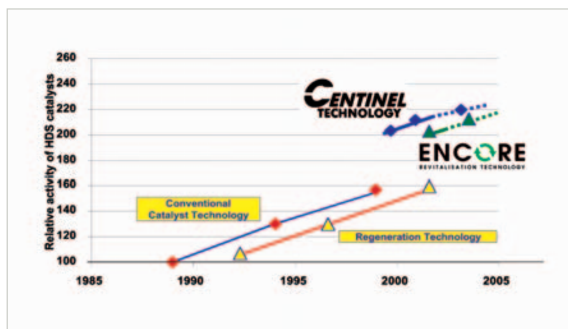

Figure 7. ENCORE technology reverses coke deactivation and metals agglomeration to recapture fresh catalyst activity.

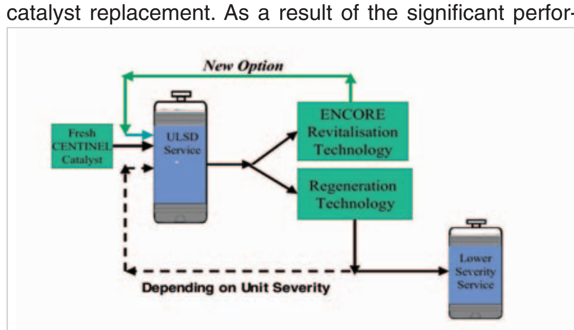

Figure 8. Refiners have a new option with ENCORE that improves catalyst lifecycle economics.

Table 2. Process unit progression to ULSD

	Year			
	1997	**1998**	**2001**	**2003**
Product sulfur (ppmw)	500	350	50	10
Criterion Catalysts & Technologies	C-448	DC-185/DC-130 C-448	DC-2118/DC-185 DC-130/C-448	DC-2118
Shell Global Solutions			Two new top, high dispersion (HP) tray sets	One new top, high dispersion (HP) tray set

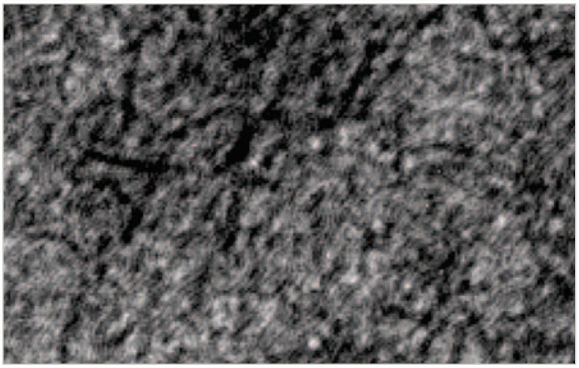

Figure 9. Fresh DC-2118, highly dispersed MoS_2.

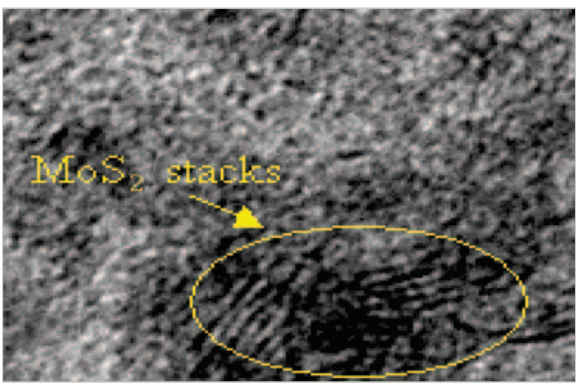

Figure 10. Regenerated DC-2118, multi stacked MoS_2 slabs.

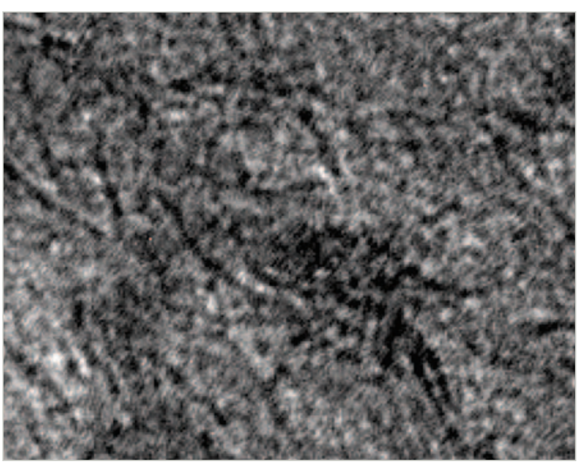

Figure 11. ENCORE DC-2118, highly dispersed MoS_2.

mance boost provided by the new internals, only a partial fill of new catalyst was required to meet the run length target.

Further reactor internal improvements were implemented in 2003, along with upgrading to a full load of CENTINEL DC-2118 catalyst. These changes enabled the unit to produce ULSD (10 ppm sulfur).

Results

Capital savings

Capital savings were maximised using existing process equipment and catalysts in an optimal configuration.

Reliable operation

At the start of the current cycle, Criterion's evaluations indicated that the unit should have been achieving much lower product sulfur levels than indicated in the laboratory analyses (Figure 6). Criterion and the refiner conducted a root cause analysis and identified the problem as a leaking feed/effluent exchanger. The revamped unit is currently running at design feed rate and producing < 50 ppm and < 10 ppm sulfur product.

Managing catalyst lifecycle economics

Another key issue that each ULSD strategy should address is catalyst lifecycle management. Maximising the catalyst lifecycle has been an important part of a refiner's efforts to control expenses. Given the significant increases in catalyst volume requirements for ULSD, this will become an even more important issue. In the past, refineries often regenerated their distillate hydrotreating catalyst and reused it in the distillate hydrotreater for at least a second cycle. Alternatively, they sometimes regenerated high performance catalysts from a 'clean' service, such as a hydrocracker pretreater, and then cascaded it into the distillate hydrotreater. With the higher diesel sulfur specifications and older catalyst technologies, refineries could extend the catalyst's lifecycle via regeneration, without jeopardising either product quality or run length targets. In the future, most ULSD units will require the most active catalyst to ensure reliable product specifications and reasonable run lengths. Current regeneration technologies do not recover a sufficient portion of the activity of the newest generation catalysts for ULSD service. Will refineries then have to resort to using fresh catalyst for every cycle in their ULSD unit? A new technology, recently invented by Criterion, is expected to provide another option for their ULSD catalyst requirements.

Revitalisation technology

Since the advent of the ex-situ regeneration of hydroprocessing catalysts over 25 years ago, refineries have grown accustomed to regenerating and reusing spent catalysts. This approach has become part of the catalyst lifecycle economics for many hydroprocessing applications. Catalyst deactivation is primarily the result of three mechanisms: coking, metals agglomeration and poisoning. Ex-situ regeneration is a well established process for reversing coke deactivation. Regeneration techniques have continually improved over the years to keep pace with conventional catalyst advancements. However, the recent step change in ULSD catalyst technology presented a unique challenge for the recovery of the catalyst's activity. Many of the latest generation ULSD catalysts, including CENTINEL, achieve their high activity through new manufacturing techniques, producing a greater number of highly dispersed active sites. Use of the catalyst in hydroprocessing applications, as well as the regeneration process itself, can cause metals agglomeration that decreases the number of active sites. Ex-situ regeneration processes cannot reverse the agglomeration. In order to overcome this problem, Criterion has invented ENCORE™ revitalisation technology to reconstitute the original chemistry and metals dispersion that gives CENTINEL catalysts their level of performance (Figure 7). This technology provides startup and onstream performance comparable to the original fresh catalyst. As this technique does not remove catalyst poisons, ENCORE is most effective on relatively uncontaminated catalysts, such as result from ULSD service.

ENCORE technology provides a supplemental option for CENTINEL customers wishing to reuse their catalyst (Figure 8). Special oxidative regeneration of CENTINEL catalysts can still provide recovery of activity levels that either matches or exceeds previous generation conventional catalysts. This recovery method may be the preferred choice for catalysts cascaded to less severe duties or shorter scheduled cycles. However, if maximum recovery of activity is required, ENCORE revitalisation is the answer, as it typically recovers more than 95% of fresh HDS activity for ULSD service.

In order to achieve very high levels of activity and stability, catalysts developed for ULSD service greatly rely on having the catalytic metals well dispersed throughout the porous alumina support. Criterion's CENTINEL manufacturing process has eliminated almost all of the metal 'stacking' that occurs with older manufacturing techniques. Figures 9 - 11 represent typical transmission electron microscopy (TEM) micrographs of DC-2118 catalyst particles in three forms: fresh, regenerated and ENCORE revitalised. The dark lines in these micrographs are active molybdenum sulfide (MoS_2) slabs, present on the alumina support of the catalyst. The fresh catalyst shows an excellent, uniform, metal dispersion, represented by predominantly single dark lines. Parallel dark lines are stacked MoS_2 slabs, which are an indication of metals agglomeration and consequent lower activity than single MoS_2 slabs. The regenerated catalyst shows many occurrences of multi layer MoS_2 stacks. The ENCORE revitalised catalyst has much fewer multi stacked slabs than the regenerated catalyst. In fact, it looks very much like the fresh catalyst, providing further evidence of ENCORE's ability to reverse metals agglomeration and restore the original CENTINEL catalyst active sites.

ENCORE's typical performance advantage over regeneration is illustrated in Figure 12. The feedstock for this set of tests was a blend of 55% straight run and 45% light cycle gas oils, with a sulfur content of 1.83 wt%. The performance of fresh CENTINEL and fresh conventional catalysts are included to complete the picture. At a sulfur product of 10 ppm, the revitalised CENTINEL catalyst is only 1 ˚C less active than fresh CENTINEL, and approximately 6 ˚C more active than the regenerated CENTINEL catalyst.

ENCORE revitalised DC-2118 also compares favourably with fresh DC-2118 when treating straight run gas oil (Figure 13). The catalyst's desulfurisation activity has been restored to essentially fresh by the revitalisation process.

ENCORE revitalisation technology has clearly demonstrated its effectiveness in restoring fresh catalyst performance for Criterion's DC-2118 catalyst in commercial ULSD service. Refiners now have two catalyst options for squeezing maximum value out of their CENTINEL catalyst. Firstly, new regeneration techniques can reverse coke deactivation and provide sufficient activity recovery to permit reuse in less demanding applications. Secondly, ENCORE revitalisation can reverse metals agglomeration and restore the original fresh catalyst surface chemistry to permit reuse in very demanding ULSD applications. With either choice, fresh catalyst purchase costs and spent catalyst disposal costs are avoided, and the refiner thereby improves the overall catalyst lifecycle economics.

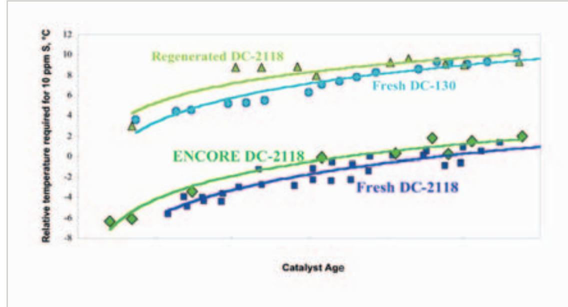

Figure 12. ENCORE achieves superior results.

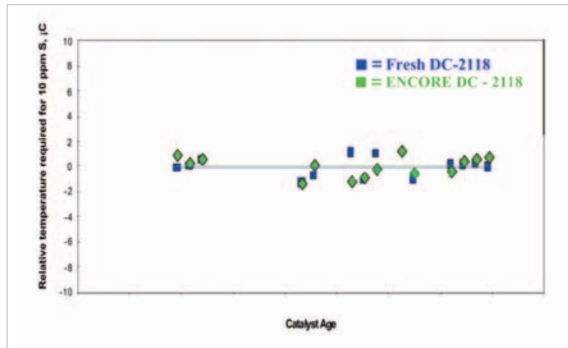

Figure 13. ENCORE provides fresh catalyst performance in ULSD.

The total picture

It is logical that ULSD planning efforts focus on investment issues and project execution at this stage. However, in order to avoid regrets about the investment choices at a later date, the ULSD strategy also needs to address management of the ULSD operation in the long term. In addition to its catalyst development efforts, Criterion has created new technologies and tools to assist with the ongoing operation. Incorporating such advancements in the ULSD strategy will generate more reliable, cost effective results, and will help to achieve the investment goals.

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