Catalyst management for ultra low sulphur gasoil

By purchasing high quality regenerated catalyst rather than regenerating its own catalyst during turnaround, a Belgian refinery was able to reduce downtime from 12 days to six and also shorten startup with the XpresS presulphiding process

Constant Bruyninckx *Belgian Refining Corporation*
Daniel J Neuman Maarten van Vliet G Karl Semper *Tricat Companies*

Much of the discussion about diesel fuels in Europe centres on the 50ppm sulphur specification to be enacted in 2005. This figure may not be the ultimate lower limit in the world. Even further tightening appears likely in view of the recent proposed ruling by the US Environmental Protection Agency to limit sulphur to 15ppm. It remains to be seen whether Europe's 50ppm limit is tightened further.

In fact, many refiners are already profitably producing this ultra low sulphur product to meet market demand for this fuel. The City Diesel is marketed as a "green" product in several European markets (including Scandinavia and the UK), where market acceptance for this product is high.

Many refiners can produce this ultra low sulphur product in existing gasoil hydrotreaters. Although flexibility is reduced, proper choice of feedstock and the use of high activity cobalt molybdenum-base (CoMo) catalysts enable refiners to obtain acceptable (albeit shorter) cycle lengths on these units. Belgian Refining Corporation (BRC) has found that producing the ultra low sulphur city diesel can be a profitable operating scheme in the company's current operation.

Given the extreme cost pressures in today's refining industry, the use of these high activity catalysts for multiple cycles after regeneration is preferred. Fortunately, refiners have found that most of the modern catalysts currently available can be regenerated and used in a subsequent cycle with little loss in activity or cycle length during the subsequent cycle.

Another major issue refiners must address when producing city diesel is the length of hydrotreater turnarounds. Refiners often turnaround these hydrotreaters more frequently than other process units. As a result, much of the remainder of the refinery continues operating during the hydrotreater shutdown. Tankage and blending limitations make it imperative that the hydrotreater should operate in order to produce ultra low sulphur diesel. Any action the refiner can take to shorten the shutdown will improve the refinery's profitability.

BRC has been producing ultra low sulphur diesel in its HDS-2 unit intermittently since the early 1990s. When producing city diesel, the company lightens and sweetens the feed to ensure that it is able to produce product sulphur levels below 50ppm. At other times, a more sour light gasoil is processed in HDS-2 to produce diesel that meets current specs, and also a heavy gasoil for the home heating oil market is desulphurised. At times, this multifunctional hydrotreater also processes VGO for sale to other refiners as cat cracker feed.

By mid-1999, the HDS-2 catalyst was approaching end-of-cycle conditions. It was initially intended to regenerate and pre-sulphurise the catalyst during the turnaround and reuse it for another cycle. The current (CoMo) catalyst had been regenerated twice previously during turnarounds of this unit.

Minimising downtime

Tricat was contacted by BRC to quote services for the upcoming turnaround. The main goals were to minimise downtime on the unit and to ensure that catalyst activity for the subsequent cycle would be sufficient to produce city diesel on a frequent basis.

Tricat evaluated the quality of the catalyst installed for the current cycle, and determined that unit performance could be greatly enhanced by avoiding the use of the current catalyst for a fourth cycle. Instead, Tricat offered to supply once-regenerated CoMo catalyst containing predominantly the same catalyst type. The properties of the once-regenerated catalyst are shown in Table 1.

Upon dumping the unit, analysis showed the catalyst had deteriorated further during the current cycle. These data are also shown in the table. Since BRC could not identify any use for this catalyst in less severe services, the spent catalyst was discarded.

Had arrangements not been made to purchase once-regenerated catalyst from Tricat, few options would have been available – BRC would have had to spend considerable operating capital to purchase fresh catalyst, or accept the substandard catalyst after regeneration for reuse.

Another benefit obtained through this strategy is that the regenerated catalyst purchased from Tricat could be sulphided (discussion below) and delivered to the refinery prior to the unit shutdown.

During the previous turnaround, the unit remained out of service while the catalyst was shipped to be regenerated and sulphurised. During this turnaround, the same team was employed to unload the spent catalyst and reload the

Catalyst properties

	Post-3rd cycle Lab-regenerated June 1999	Tricat-supplied Once regenerated June 1999
Surface area, m^2/g	161	202
Crush strength, lb/mm	8.2	8.8
CBD, g/l	NA	788
Carbon, wt%	0.10	0.30
Sulphur, wt%	0.84	0.76
Contaminant metals, wt%		
Vanadium	0.37	0.06
Sodium	0.35	0.13
Silicon	1.5	1.5
Iron	0.05	0.17

Table 1

> "The process is the first to produce a truly sulphided catalyst. The catalyst is treated using H_2S in an ebullating bed to ensure that each catalyst pellet is uniformly sulphided. The sulphided catalyst is then stabilised in a second ebullating bed reactor, where treatment with a gas stream . . . enables it to be handled in air"

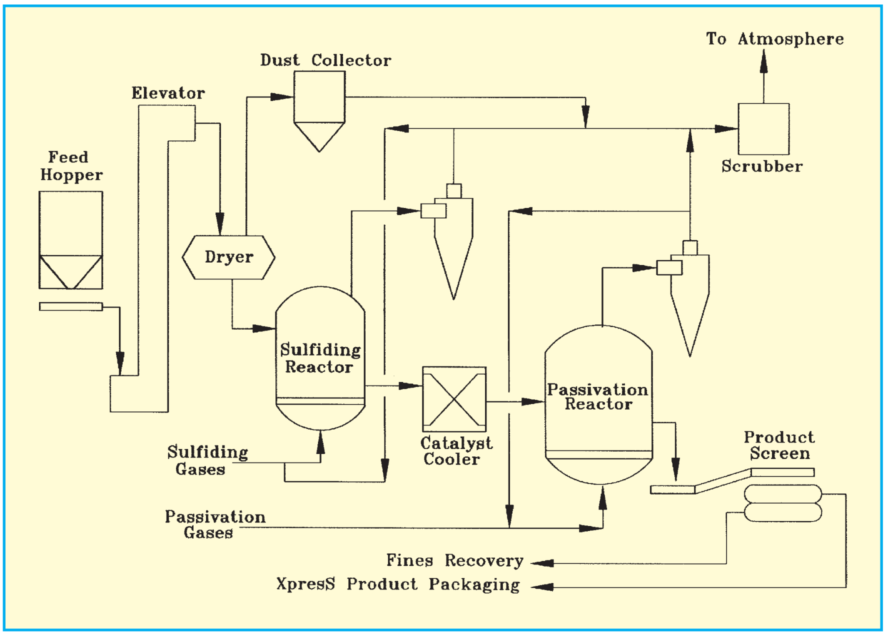

Figure 1 *The Tricat XpresS pre-sulphiding process*

replacement lot without delay. Six days were saved through the use of this strategy. During the previous turnaround, 12 days elapsed between the commencement of catalyst unloading until the unit was reloaded with catalyst and "buttoned-up". This turnaround required only six days.

XpresS pre-sulphiding

XpresS pre-sulphiding was introduced by Tricat at its Bitterfeld plant, in Germany, in 1997[Neuman, D J et al – (1) XpresS: The first true ex-situ pre-sulfiding process; NPRA annual meeting, San Francisco, 15-17 March 1998. (2) Results from an ex-situ presulphiding process; *Petroleum Technology Quarterly*, Autumn 1998].

The process is the first to produce a truly sulphided catalyst. The catalyst is treated using H_2S in an ebullating bed to ensure that each catalyst pellet is uniformly sulphided. The sulphided catalyst is then stabilised in a second ebullating bed reactor, where treatment with a gas stream renders the product odourless, and enables it to be handled in air. A schematic of the plant is shown in Figure 1.

By employing a completely pre-sulphided catalyst, refiners avoid many problems associated with in-situ sulphiding or activation of catalysts sulphurised using older technologies. The benefits of true ex-situ sulphiding provided by XpresS are summarised as:

Homogeneously sulphided, odour-free catalyst. As noted above, the XpresS product is sulphided and passivated in successive ebullating beds. The process ensures uniform sulphur distribution and stabilisation. Older sulphurised catalysts have a significant hydrocarbon odour.

No external sulphur supply or addition system required. Sulphiding compounds can be quite odorous and can cause significant concerns both in the refinery and the surrounding community. Failure of the sulphur addition system, which is used infrequently, can lead to irreversible damage to the catalyst during sulphiding.

Greatly reduced startup time. In-situ sulphiding requires several temperature holds to allow exotherms to pass during activation. XpresS pre-sulphided catalysts exhibit a single minor exotherm during initial heat-up.

No water liberation during startup. In-situ sulphiding liberates water from the catalyst. This water must be carefully monitored to ensure that no damage to the catalyst ensues.

Sulphurised catalysts also liberate water, but XpresS pre-sulphided catalysts do not.

XpresS startup

The once-regenerated and XpresS sulphided catalyst was loaded into BRC's HDS-2 unit using a combination of sock and dense loading techniques. After evacuating the unit and purging with nitrogen, hydrogen circulation was established at a temperature of 40°C. Immediately, a small temperature wave passed through the unit. Within 1.5 hours, this wave had passed through the unit, with a maximum temperature rise of about 60°C (Figure 2).

The exothermic reaction observed is part of the final re-sulphiding step of the passivated catalyst. No sulphur (in the form of H_2S) was observed in the recycle gas during this exotherm. Thus, the catalyst was not giving up any of its sulphur and is not at risk for reduction with hydrogen.

The remainder of the reactor heat-up proceeded without any observable exotherm. No water was noted in the separator. Both of these factors are clear indicators that no sulphiding reactions are occurring during heatup.

Reactor heat-up to normal feed-in temperature of 230°C was completed

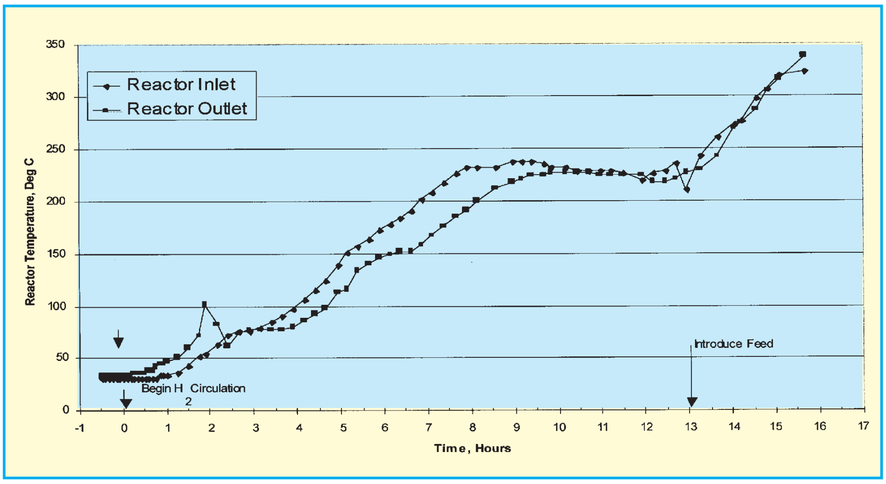

Figure 2 *XpresS startup temperature profile at Belgian Refining's HDS-2 unit, June 1999*

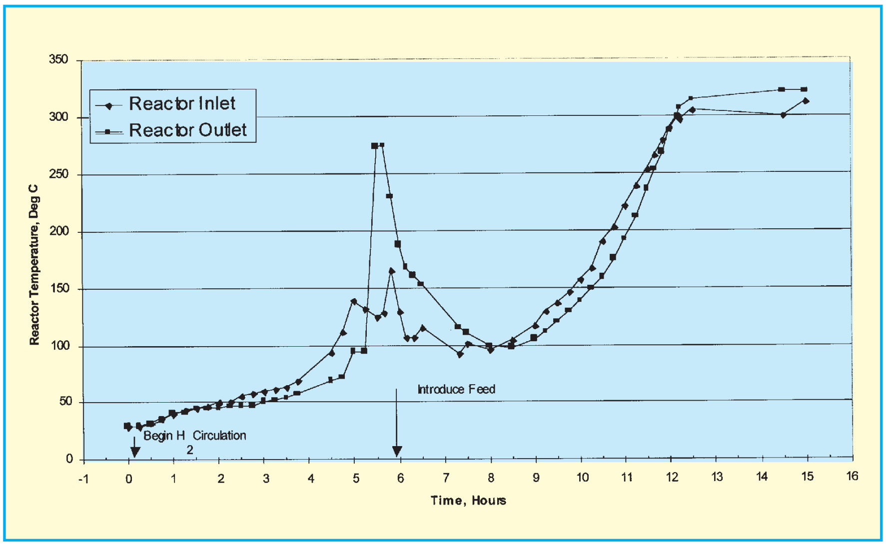

***Figure 3** Pre-sulphurised catalyst startup temperature profile at HDS-2, April 1997*

within eight hours. Tricat generally recommends a feed wetting step at lower temperatures during startup to ensure proper feed distribution. However, this unit has clearly shown no feed distribution problems throughout its operation.

By contrast, the previous startup of this unit at BRC in 1997 employed a mix of sulphurised catalysts. A sizable exotherm was observed when the reactor inlet temperature exceeded 100°C. The temperature rise across the reactor approached 200°C to a maximum temperature of nearly 300°C at the bed outlet (Figure 3).

Large amounts of H_2S were liberated from the catalyst, such that H_2S concentration in the recycle gas loop exceeded 7 vol%. The refinery was forced to wait several hours until this temperature wave passed before resuming reactor heatup. It was also critical that no H_2S was scrubbed from the unit during this event, otherwise reduction of the catalyst metals could occur due to the high temperatures reached in part of the bed.

This type of event can be mitigated for in-situ sulphiding or for sulphurised catalysts if feed to the unit is established at a low temperature. The feed acts as a heat sink to limit the reactor exotherms observed during the sulphiding reactions. However, this requires that large quantities of feed are recycled through tankage.

The liquid phase heatup is also quite time-consuming, particularly when sulphiding in-situ, when several temperature holds are required to ensure that sulphiding is completed. XpresS pre-sulphided catalyst requires no temperature holds such that heatup can be completed more quickly and feed recycling is kept to a minimum.

During the sulphiding steps, hydrogen is consumed as the metal oxide sites on the catalyst are converted to metal sulphides.

During the 1997 startup, BRC had difficulty maintaining hydrogen pressure. Low hydrogen pressure can lead to coking of the catalyst, particularly at the later stages of the sulphiding steps.

Significant water formation was also observed throughout the exothermic activation, and significant attention by operating staff was required to ensure that excessive water levels in the high pressure separator were avoided.

HDS-2 unit performance

	Previous cycle	Current cycle
Days on stream	48	99
Reactor WABT, °C	340	329
Hydrogen partial pressure, bar	30.5	31.9
LHSV	1.95	1.68
Light gasoil feed properties		
Density, g/cc	0.873	0.878
Sulphur, wt%	1.22	1.22
Distillation, °C		
5%	232	258
50%	316	318
95%	378	374
Product sulphur, wt%	0.18	0.20
Normalised temperature, °C to achieve 500ppm sulphur	347	340

Table 2

Despite the problems encountered during the startup with the sulphurised catalyst, the heatup time was only marginally longer than required for the XpresS pre-sulphided catalyst. By contrast, in-situ sulphiding would be expected to take at least one full shift longer for this type of unit where sulphiding is performed in the liquid phase.

For gas phase units, especially hydrocracking units containing sizeable catalyst quantities, pre-sulphided catalyst can save several days of start-up time [Blashka et al, New presulfurized catalyst reduces exotherm potential in hydrocrackers; *Oil & Gas Journal*, 5 Jan 1998].

Despite the fact that the startup time was nearly the same for the XpresS pre-sulphided catalyst as for the sulphurised material, it is clear that the XpresS catalyst startup was simpler. No concerns about high temperature exotherms, no H_2S liberation, and no water formation arose during the XpresS startup.

Catalyst performance

The current cycle for HDS-2 began in mid-1999. Since then, BRC has regularly alternated feed to the unit. A sour light gasoil feed, employed to manufacture conventional low sulphur diesel (less than 500ppm sulphur), is alternated with a sweeter, lighter feed to produce city diesel.

During the current run, city diesel has been produced from the lighter feed in about two-thirds of the time.

The conventional sour feed contains just over 1 wt% sulphur while the light sweet feed typically contains 0.1 to 0.8 wt% sulphur. Despite the sweeter feed properties, operating severity on the hydrotreater must be raised to produce city diesel. At times, a higher sulphur product (up to 2000ppm S) has been produced for the home heating oil market while employing the conventional feed.

The previous cycle for HDS-2 began in May 1997, and continued for just over two years. During this cycle, BRC processed a light gasoil over two-thirds of the time. The gasoil typically contained just under 1 per cent sulphur. Product sulphur levels varied widely in the earlier part of the run as the company frequently produced heating oil by reducing severity of the hydrotreater operation.

During the latter portion of the run product sulphur levels stabilised at or near 500ppm. The ultra low sulphur diesel product was also produced from the lighter sweeter feed about 30 per cent of the time during this cycle.

During the operation of HDS-2, BRC takes "snapshots" of unit performance at regular intervals. These evaluations include complete operating conditions of the unit, along with analyses of the feed and product. These data are stored in a database, which is then used to trend unit performance.

Table 2 examines two of these snapshots. One was taken in late 1997 during the second month of the previous cycle. The second was taken during the current cycle in late 1999, albeit nearly two months later in the cycle. These two periods were chosen because of the similarity of the feed properties and operating conditions between the cycles. In both cases, heating oil product was being produced.

At nearly identical product sulphur levels, the current cycle was operating at 11°C lower temperature.

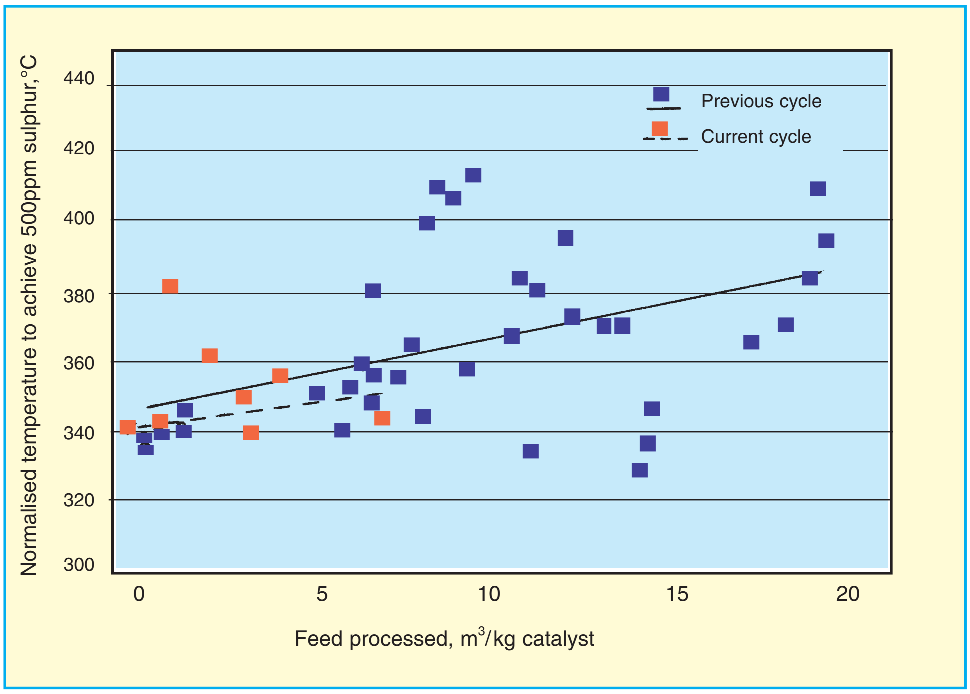

***Figure 4** Catalyst deactivation rate*

A first order rate constant is employed to normalise data to constant product sulphur levels (500ppm). Although these data lie far outside this level, the equation did adjust the temperatures to higher levels to achieve this sulphur level. The normalised temperature difference between these two data points shrinks somewhat to 7°C, which remains quite a significant improvement in activity.

At the time of writing, the current cycle has completed nearly 11 months. A comparison of the deactivation rates for the two operating cycles is shown in Figure 4. This plot compares the normalised temperature requirement to achieve 500ppm sulphur in the product with the conventional sour light gasoil as a function of the volume of feed processed through the unit per kg of catalyst loaded.

Comparatively few data points are available for the current run, since the vast majority of the run has processed the lighter feed to make city diesel. These data are not normalised because the product sulphur levels are too far below 500ppm to make the normalisation reasonable.

Nonetheless, the data clearly show improved activity for the catalyst employed during this cycle versus the previous cycle. Similar to the snapshot of data shown in Table 2, the trendline shows that the catalyst employed in the current cycle is about 7°C more active than the previous cycle. The stability of the catalyst tracks the performance during the previous cycle.

The improved activity for the current cycle can be attributed to several factors. Probably the most significant factor is the quality of the regenerated catalyst employed during this cycle. As noted earlier, the catalyst employed during the current cycle is the same type employed during the previous cycle. The current cycle, however, is employing once-regenerated catalyst while the catalyst employed during the previous cycle had been twice regenerated.

The impact of the novel XpresS catalyst pre-sulphiding procedure on the activity of the current catalyst is also likely playing a role in the improved catalyst performance. Recall that the catalyst from the previous cycle was sulphurised using older technologies. Both the older sulphurising technologies provide substantial benefits versus in-situ sulphiding.

These benefits arise mainly from the assurance that sulphur is uniformly distributed across the entire catalyst bed to ensure that all the metals sites become fully sulphided during startup. The XpresS process, however, can yield even further activity improvements versus sulphurised catalysts.

Tricat's patented process employs a novel passivation step, which enables the catalyst to be handled in air. During startup, the catalyst is returned to its fully active state.

It has been noted in the literature that the steps undertaken in the XpresS process, followed by reactivation during commercial start-up, will enhance catalyst activity versus conventional in-situ sulphiding [Brown V M et al – (1) The effect of passivation on the activity of sulfided Mo and Co-Mo hydrodesulpherization catalysts; *Catalysis Today*, vol 10, 1991. (2) The effect of passivation on the activity and structure of sulfided hydrotreating catalysts; *Journal of Catalysis*, vol 144, 1993].

The reason(s) for the activity enhancement are not clearly understood; however, current speculation is that the sulphiding/passivation/reactivation cycle may reduce interaction between the active metals and the catalyst support.

Conclusion

By utilising available once-regenerated catalyst rather than regenerating the catalyst already in use, the turnaround on a critical hydrotreater in the refinery was considerably shortened. The use of the XpresS pre-sulphiding process further aided in minimising downtime, and ensured the highest catalyst activity possible.

BRC is producing ultra low sulphur city diesel on a more frequent basis to meet market demand, and is obtaining acceptable cycle length. The current cycle, which is approaching one year, should continue at least for several additional months. The company is planning to repeat the strategy of buying pre-sulphided once-regenerated catalyst for the next cycle.

***Constant Bruyninckx** is manager of technical service with Belgian Refining Corporation, Antwerp, Belgium.*
***Daniel J Neuman** is vice president, Tricat Industries Inc, Baltimore, Maryland, USA.*
***Maarten van Vliet** is regional sales manager, and **G Karl Semper** plant manager, with Tricat GmbH, Bitterfeld, Germany.*