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XPRESS-CATALYST PRE-ACTIVATION TECHNOLOGY

COMMERCIAL APPLICATION IN HYDROCRACKING UNITS

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ABSTRACT

Two industrial cases in which catalyst pre-activation technology was applied in hydrocracking units are discussed. In the first application, only a partial catalyst load was pre-activated; and in-situ sulfiding was required to activate the remaining material. Nonetheless, the refiner was able to identify potential time savings achievable by having the entire catalyst load pre-activated. An evaluation of catalyst bed temperatures during in-situ sulfiding showed no exotherm in the pre-activated catalyst bed, proving that the pre-activated catalyst was not reacting with sulfur. In the second application, the full benefits of pre-activation technology were realized. Start-up of the unit was simple and smooth, without the use of sulfiding chemicals and without temperature holds. The catalyst performance clearly indicates the positive impact of homogeneous sulfiding. In both cases, pre-activated catalysts were supplied in a passivated condition, such that the refiners could load their reactors under normal atmosphere.

INTRODUCTION

Characterization studies of hydrotreating and hydrocracking catalysts, performed under working conditions, indicate that the included metals (Co, Ni, Mo and/or W) are active as metals sulfides¹. However, the catalyst is typically delivered to users in the refining and petrochemical industries with these metals in oxide form.

When manufactured, catalyst metals are in the form of highly dispersed MoO₃, CoO and/or NiO. Activation of the catalyst implies sulfiding of the metals prior to putting catalyst into service. Upon activation, finely dispersed MoO₃, CoO and/or NiO are converted into well-dispersed MoS₂ slabs with edges decorated with CoS_x and NiS_x.

However, the picture is not entirely clear. Hydrotreating catalysts form a dynamic system in which each component contributes to its structure. No clear agreement about the nature of the active catalyst phase has ever been established. In addition, no universally accepted methodology has ever been established to optimize the active phase of the catalyst.

Numerous studies have investigated the details of catalyst activation procedures. Variables including sulfiding gas composition, partial pressure of sulfur-containing species, heating schedule, final sulfiding temperature and various pretreatment procedures in inert gas or hydrogen before sulfiding have been discussed. Many authors report that sulfiding procedure strongly influences the performance of hydroprocessing catalyst. They emphasize the importance of fully sulfided structures for high activity, while noting that less desirable oxysulfides or incompletely sulfided species are formed at low sulfiding temperatures and after prereduction².

IN-SITU SULFIDING AND PRE-SULFURIZED CATALYST

Traditionally, catalyst sulfiding has been performed in-situ by adding a sulfur compound to the circulating gas, or by doping a refinery stream with a sulfur compound (e.g. dimethyl disulfide: DMDS) and circulating it through the catalyst bed. When in-situ sulfiding is performed, environmental precautions need to be taken. A separate injection system is required and significant manpower is engaged. Many sulfiding chemicals are toxic and volatile with vapor pressures of up to few hundred millibars at 20°C. For that reason, it is critical to minimize leakage of these compounds to the atmosphere. The flash point of DMDS (the most widely employed sulfiding agent) is 16°C, which categorizes this chemical as flammable. It must be stored and handled with special care. DMDS also has a strong irritating odor, which is readily detected throughout the area if spilled.

Other sulfiding agents, including polysulfides such as TNPS and TPS-54, have particular appeal due to their low vapor pressure at ambient temperature. However, polysulfides tend to leave carbon deposits on the catalyst via thermal decomposition. During decomposition, unsaturated hydrocarbons are formed. These unsaturates are very reactive, and have a tendency to polymerize leading to undesirable gum formation on the highly active fresh catalyst.

Another critical factor with respect to in-situ sulfiding is the time required to complete the procedure. The in-situ sulfiding procedures, recommended by catalyst vendors or the suppliers of sulfiding agents, are quite time-consuming. Their procedures involve several temperature holds for extended periods, and considerable liquid recycling to tankage. As product sulfur specifications for gasoline and diesel fuel become more restrictive in the next several years, the urgency to rapidly and consistently produce on-spec product will increase. Refiners will place increased value on a technique, which enables them to produce on-spec product in the shortest possible time.

Pre-sulfurizing technologies, which have been available on the market for many years, are an alternative to in-situ sulfiding. These pre-sulfurizing technologies pretreat the catalyst ex-situ by coating them with sulfur or a sulfur-containing compound. This step eliminates the need to handle the noxious chemicals at the plant. Sulfur coverage on the catalyst is typically more homogeneous due to the more uniform sulfur deposition at the ex-situ facility. However, catalyst activation must still be undertaken in the reactor, with many of the same drawbacks as conventional in-situ sulfiding. In addition, the sulfur compound used to coat the catalyst may wash from the catalyst surface and cause discoloration of the product. Product recycling at the end of catalyst activation, for up to 12 hours is often required to obtain on-spec product color.

In summary, in-situ sulfiding or the use of pre-sulfurized catalyst pose four main drawbacks for the user:

1. Incomplete and non-homogeneous sulfiding of active metals due to the poor flow distribution through catalyst bed and/or insufficient sulfiding temperature

When catalyst is sulfided in-situ, or presulfurized catalyst is activated in a reactor, total flow rate is typically lower than for normal operation. Given the design of recycle pumps and lines, feed recycle rates are typically not higher than 50-60 % of full capacity. In both cases, whether gas or liquid phase heat-up is applied, sulfiding reactions are occurring with lower mass flux. As a consequence, the contact between sulfiding reactants is poorer, leading to non-uniform and incomplete sulfiding of active metals. In addition, lower mass flow can lead to insufficient heat removal capacity to account for heat of reaction; and the risk of temperature runaway is increased.

Full conversion of catalyst metals from oxide to active sulfides forms is only theoretically achievable. However, sulfiding should be performed under operating variables that favor the highest conversion possible. While pressure is believed to play no significant role in sulfiding, temperature is a critical. Research work³ undertaken on conventional CoMo catalyst, reports that increasing the sulfiding temperature from 300 to 400 °C produces a major increase in the degree of sulfiding of molybdenum species. Activity measurements reported in this study for CoMo catalyst sulfided at increasing temperatures, confirmed progressive increase in the catalytic activity for model compound hydrodesulfurization.

As industrial in-situ sulfiding does not allow for the optimal temperature control and optimal heat release, final sulfiding step is usually set at 320 °C or lower, with the aim to prevent local overheating. The use of ebullated bed technology for catalyst pre-activation, however, allows for better removal of heat released at sulfiding reactions; therefore higher sulfiding temperatures can be applied.

2. Potential for damage to the catalyst structure during unit start-up

Catalysts are produced with high surface area and porosity, and high levels of metals dispersion. The loss of this area for adsorption and interaction of reactant molecules cannot be afforded. The uncontrolled high temperature that can accompany sulfiding reactions, particularly during highly exothermic gas phase sulfiding, can cause metals reduction and initiate metal sintering. Experimental temperature-programmed sulfiding studies suggest that in the presence of hydrogen, metal reduction is initiated at 343°C⁴.

3. Time requirement for sulfiding reactions

In order to eliminate the danger of metal reduction and agglomeration during the in-situ sulfiding or activation of pre-sulfurized catalyst, unit start-up requires temperature holds lasting from 2 to 12 hours, dependent on catalyst vendor's recommended procedures. Heat-up to required temperatures may also further delay operation. To ensure complete sulfiding, but to avoid high temperature excursions in the catalyst bed; the refiner is condemned to excessive delays during start-up. In large hydrocracking units, many of which are designed for gas-phase heat up, sulfiding may last several days. Extensive start-up time prolongs the downtime of these highly profitable units with economic uplift of

€20-80/tonne. Thus start-up time savings are critical. Producing on-spec product one day earlier will bring €300,000 product uplift to a medium size unit.

4. Pollution of user's environment by the sulfiding reactants

Hydrogen sulfide, released by decomposition of the sulfiding agent used for in-situ sulfiding, or released from coated pre-sulfurized catalyst, is employed in significant excess in the reactor system. H₂S reaches several volume percent of the rather large recycle gas volume during catalyst sulfiding. Sour gas, purged during and after sulfiding, needs to be treated in downstream units. Water, a byproduct of the sulfiding reactions, is drained at a high-pressure separator into wastewater collection systems. The wastewater is dangerous for operating staff as it contains dissolved hydrogen sulfide. When pre-sulfurized catalysts are used, large quantities of water are liberated in a short time when decomposition and sulfiding temperatures are reached. The water produced contains products from the decomposition of polysulfide or other sulfur compound used. These require special care when drained, as well as neutralization during downstream treatment.

XPRESS – CATALYST EX-SITU ACTIVATION TECHNOLOGY

The newest and most complete option for catalyst metal oxides conversion to active metal sulfides is ex-situ pre-sulfiding or pre-activation. XpresS, a patented technology, is the first and only widely available method to produce pre-activated catalyst for use in hydroprocessing. Knowing that good contact of reactants is the first condition for chemical reaction to occur and that more complete sulfiding is ensured at higher temperature, XpresS employs an ebullated bed design as the solution to meet both requirements. An ebullated bed is also employed for catalyst passivation, a post-treatment step, which enables pre-activated catalyst to be safely handled in air. Sulfiding is performed with hydrogen and hydrogen sulfide carried in nitrogen. No extraneous compounds are introduced to the reactor, thus avoiding the possibility of catalyst coking. In both the sulfiding and passivation reactors, the gases used for reaction also provide the means for bed expansion. Depending on catalyst shape and size, gas velocity is targeted to keep bed expansion in the range of 10-20%. Each reactor contains baffles to ensure that catalyst cannot short circuit through the reactors. Effective heat removal achieved in ebullated bed design maintains nearly isothermal operation throughout the sulfiding reactor. Catalyst is cooled in a water-jacketed cooler, thus avoiding contact with air that could bring moisture to catalyst.

Earlier papers presented by Tricat⁵⁻⁶ describe industrial cases where pre-activated catalysts were used in naphtha and diesel service. This work covers the applications in heavier service such as mild hydrocracking and high-pressure hydrocracking.

It is crucial for a refiner to minimize hydrocracker downtime, knowing that the economic uplift of a typical, large unit may be €50/mt or higher. To the contrary, hydrocracker start-ups are often time consuming, especially when catalyst activation takes place in gas phase. Gas phase sulfiding is practiced to avoid the risk of initial feed cracking, which can start over zeolitic catalysts before sulfiding is completed.

Published industrial examples⁷ show commercial hydrocracker start-ups with over 40 hours spent on sulfiding chemical injection. With a drying step and slow heat-up to

minimum pressuring temperature before injection of spiked feed is started, hydrocracker start-up can take as long as 3 days. In large catalyst beds, reactor temperature rise must be undertaken slowly. When sulfiding chemical injection starts, care needs to be taken that bottom of the bed is not exposed to temperatures above 230°C before H₂S breakthrough, in order to avoid active metal reduction. Reduction of the active metals on the catalyst is not an area of concern when pre-activated catalysts are used.

CATALYST EX-SITU ACTIVATION TECHNOLOGY APPLIED IN HYDROCRACKING UNITS

Two European refiners have recently employed XpresS technology to simplify and accelerate the start-up of their hydrocracking units, and to ensure homogeneous catalyst sulfiding. Both refineries were able to handle and load the pre-activated catalyst in air. Handling in air is often an important consideration for the refiner, due to safety considerations. Numerous accidents have occurred during inert loading, some even resulting in fatalities. Although pre-activated catalysts are classified as a self-heating inorganic solid (UN-3190), they can be easily stored, transported, and loaded into a reactor in ambient air. Care needs to be taken to avoid exposure to flowing air⁸ as this may lead to gradual heating. It is recommended to tightly close the bottom of the reactor and any side manway while loading the catalyst.

Case Study 1: Slovnaft Hydrocracker

During their spring 2002 turnaround, the Slovnaft (Slovakian National Oil company) refinery of Bratislava, Slovakia, contracted with Tricat to perform ex-situ regeneration followed by activation of their hydrocracking catalyst using TRICAT's XpresS technology. The catalysts employed in this unit operate in a high-pressure, single-stage hydrocracker consisting of one pretreater and two hydrocracking reactors. The unit feed is vacuum gas oil with a final boiling point of 560-570 °C. The main products are light and heavy naphtha, kerosene and diesel. The fractionator's bottom product is recycled in the unit. A steam reformer and a reformer provide the hydrogen with a purity of 97 vol%. The unit operates at 130 bars.

The cracking catalyst was first regenerated in TRICAT's regeneration plant prior to ex-situ activation in the adjacent XpresS facility. The pre-treating catalyst for the hydrocracker was also regenerated at TRICAT's facility.

Slovnaft's objective for their evaluation of XpresS was twofold:

- First and foremost, Slovnaft wanted risk-free hydrocracker start-up without any danger of catalyst damage.
- Slovnaft wanted to have homogeneously sulfided catalyst to maximize catalyst activity and cycle length.

For the turnaround, Slovnaft isolated the second hydrocracking reactor, which did not require regeneration. The catalysts from the pretreater and the first hydrocracking reactor were unloaded and delivered to the Tricat plant in Bitterfeld, Germany for regeneration and pre-sulfiding.

Due to time constraints, only a portion of the hydrocracking catalyst was pre-activated. Under the circumstances, in-situ sulfiding was required for the remaining quantity of hydrocracking catalyst that was delivered in the oxidic form after regeneration. Although the desired start-up time savings were not realized, the refiner was able to identify the delays that could have been avoided by employing pre-activated catalyst throughout the hydrocracking unit.

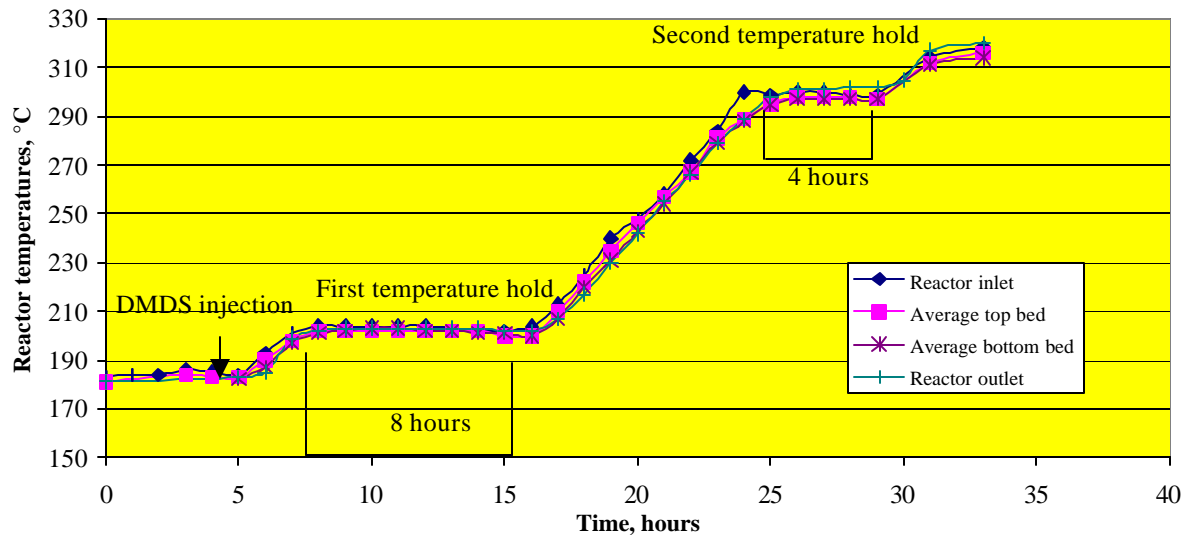
The pretreating reactor was loaded with regenerated, oxide form catalyst. In the hydrocracking reactor, the bottom part of the reactor was loaded with regenerated, oxide form hydrocracking catalyst. The pre-activated hydrocracking catalyst was placed on the top of the hydrocracking reactor.

All the catalysts were loaded in air. The catalyst-handling contractor applied exactly the same loading technique for the catalyst supplied in the oxide form as for the pre-activated catalyst. No reaction of the pre-activated catalyst was observed.

After catalyst loading, hydrogen was introduced to the reactor. The Slovnaft hydrocracker unit design allows for liquid phase in-situ sulfiding of the catalysts in the both pretreating and hydrocracking reactors. While the ability to perform the sulfiding in the liquid phase reduces the risk of severe exotherms, the time requirement is still extensive.

The DMDS injection began at a reactor inlet temperature of $\sim 180^{\circ}\text{C}$ as shown in Figure 1.

Figure 1 : Hydrocracking reactor temperature profiles



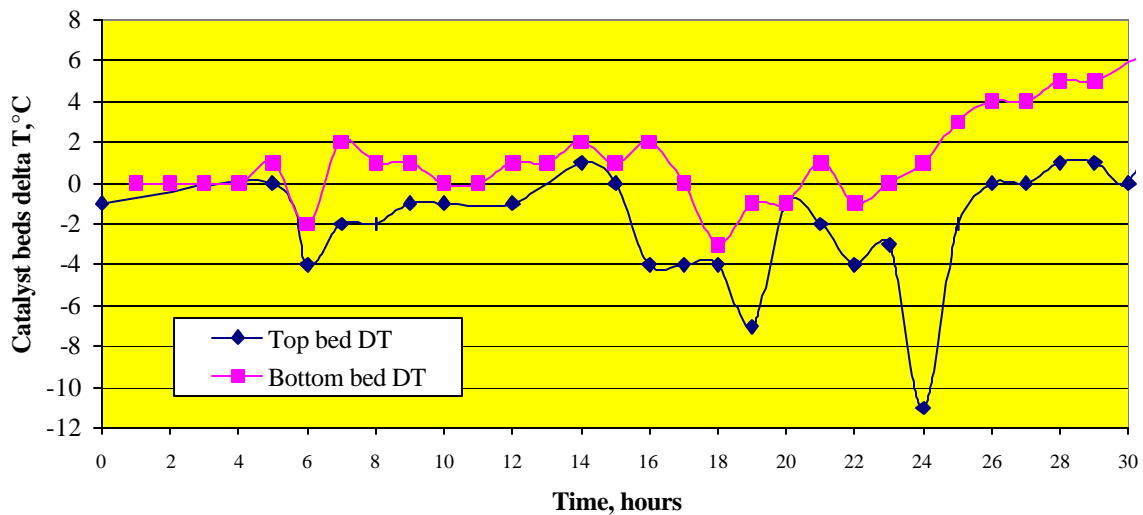
As per the in-situ sulfiding procedure established by the catalyst vendor, the first temperature hold for low temperature sulfiding required an 8-hour hold at 200°C . No exotherm was apparent at this temperature. The heat-up then continued until the next hold for high temperature sulfiding at 300°C . At this temperature, an exotherm appeared in the pretreating bed and in the bottom part of the hydrocracking reactor. No exotherm was observed in the reactor bed containing the pre-activated catalyst. Due to the exotherm appearance, a waiting time of 8 hours in the pretreatment reactor and 4 hours in

the hydrocracking reactor was needed. No noticeable delta T was detected in the top part of the reactor.

In Figure 2, delta T across the hydrocracking catalysts beds were plotted against sulfiding time. As noted above, the pre-activated catalyst showed no exotherm because the catalyst was not undergoing any conversion reactions since the metals were already in active sulfided form. While the exotherm was relatively small for the lower bed, it is clear that reactions were occurring to convert the metals from the oxidic to the sulfided form. During this reaction period, which persisted for several hours, the continuation of the reactor heat-up to normal operating conditions was delayed.

After 30 hours, the heating in the hydrocracking reactor was resumed toward start-of-run temperature.

Figure 2 : Top and bottom hydrocracker catalyst beds delta T

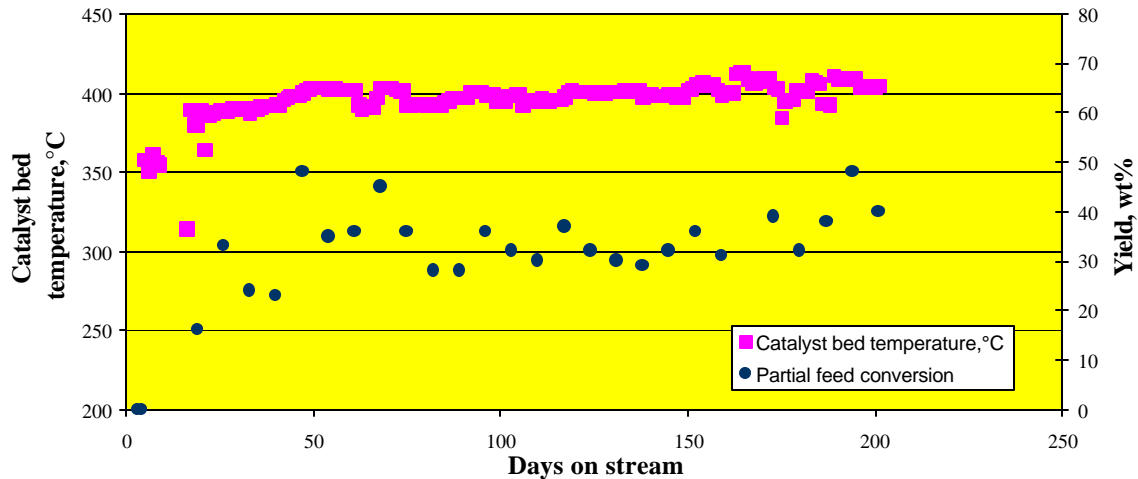


Improved sulfur distribution on the pre-activated portion of hydrocracking catalyst has likely led to catalyst activity optimization. Slovnaft is satisfied with the catalyst performances to date. In the first 6 months of the current cycle, yields and products quality are within expectation.

In Figure 3, catalyst bed temperatures and the conversion in the first hydrocracking reactor are plotted over time. Slovnaft has a sampling point after the first hydrocracking reactor such that they can monitor performance of the reactor. The desired level of partial feed conversion is occurring in the first hydrocracking reactor where pre-activated catalyst is loaded. Catalyst activity has shown little aging in the first half year of current cycle. Since lining out in the first 50 days of operation, operating temperature increases in the reactor have been made to increase severity. Little or no aging has been observed for the most recent 6-month period.

Currently, Slovnaft is expecting that the current cycle (with mainly second cycle catalyst) will continue longer than the previous run. Together with the potential start-up timesavings, the use of the pre-activation technology throughout the hydrocracker should significantly contribute to its economics. Slovnaft reports that daily economic uplift for this unit ranges from €220-340,000.

Figure 3 : First hydrocracking reactor catalyst activity indication



In the industrial cases described earlier ^{6,9}, activity improvements were shown when pre-activation technology was applied to catalysts used in gas oil and naphtha hydrodesulfurization service. Lower start-of-run temperature provided a larger operating window when using pre-activated catalysts in a low sulfur gas oil hydrotreater unit at Belgian Refining Corporation and naphtha hydrotreater at INA's Rijeka refinery in Croatia.

In summary, Slovnaft made the following conclusions about the application of XpresS pre-activated catalyst in their hydrocracker:

- The portion of the hydrocracking reactor loaded with pre-activated catalyst showed no exotherm at both sulfiding temperature plateaus during the injection of the sulfiding agent.
- The portion of the hydrocracking reactor containing only unsulfided catalyst showed an exotherm of 3-5 °C at the high temperature sulfiding plateau.
- Versus in-situ sulfiding, Slovnaft expects to obtain a timesaving of 12 hours in their next hydrocracker start-up through the use of pre-activated catalyst in the hydrocracker.
- A further benefit of a simplified start-up, which avoids the need for the injection of sulfiding compounds and more rapid production of on-spec product, is expected when pre-activated catalyst is employed throughout the hydrocracker train. Slovnaft will be closely observing the activity of pre-activated catalyst to quantify further benefits of its use.
- Considering only the time savings achievable through the elimination of temperature holds, Slovnaft estimates that the benefits of employing pre-activated catalyst are roughly €150,000. The actual benefits are likely to be greater due to improved catalyst activity.

Case Study 2: INA Diesel Hydrotreater / Mild Hydrocracker

XpresS technology was used to pre-activate fresh catalyst for the combined diesel hydrodesulfurization / mild hydrocracking unit (HDS/MHC) at INA Rijeka in Croatia. The unit consists of two reactors and can operate in two alternate modes: HDS or MHC. In the first mode, both reactors' catalysts are employed to hydrodesulfurize a mixture of straight run gas oil and light cycle oil. Most of the hydrodesulfurization reactions are occurring in the first reactor, with the second reactor providing hydrofinishing. The product is a low sulfur component for their commercial diesel pool.

In the MHC mode, the first reactor pretreats a vacuum gas oil feed, which is then cracked in the second (hydrocracking) reactor. Light naphtha, heavy naphtha and gas oil are separated in a fractionator. The bottoms product is an excellent desulfurized FCC feed. INA has also employed the unit in a customized, third mode as an FCC pretreater. In that case, both reactor catalysts desulfurize vacuum gas oil without cracking.

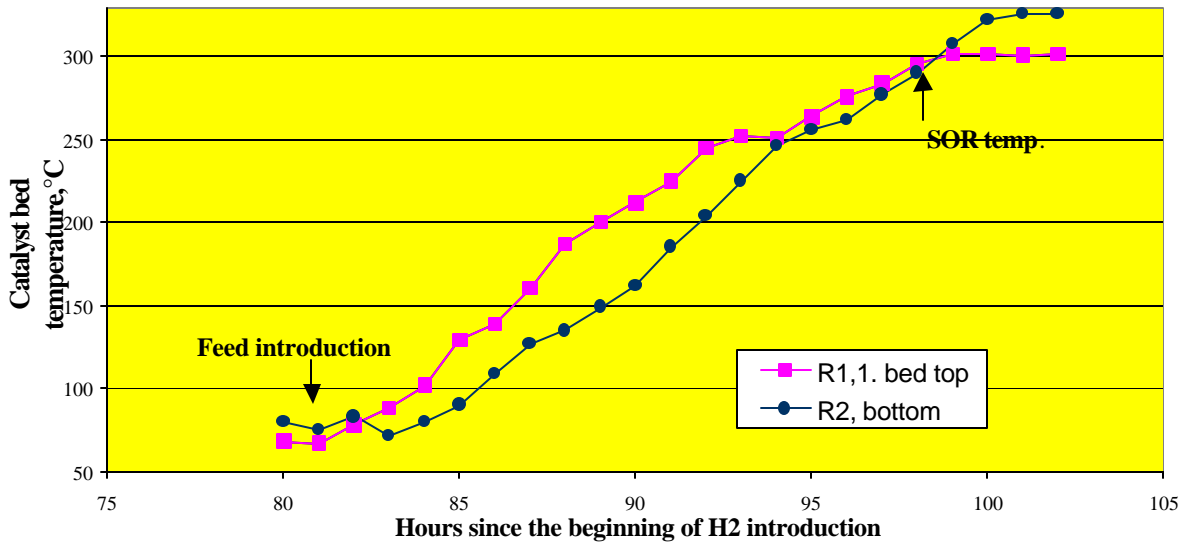
Different reactor inlet temperatures are applied in each mode. In all cases, the unit operating pressure is 57 bars. Hydrogen purity of the make-up gas is 80 vol%.

To comply with more stringent gas oil specifications during their 2002 turnaround, INA changed out the catalyst in the HDS/MHC unit. The product sulfur specifications for the diesel HDS operating mode were set to 50 ppm versus the 500 ppm target of the previous operating cycle. New generations of hydrodesulfurization and hydrocracking catalysts from the same supplier were put in service in order to meet the more stringent specifications. In the mild hydrocracking mode, the conversion target stayed the same. In conjunction with their decision to employ the latest generation catalysts, INA also chose to employ catalyst pre-activation using XpresS rather than the pre-sulfurization technology they employed in the previous start-up. 140 tonnes of fresh catalyst were shipped to Tricat in Germany for pre-activation. The pre-activated catalysts were dense-loaded at the refinery in air. No self-heating issues were observed for the catalyst during handling and loading.

The start-up was done in liquid phase. As the newly purchased fresh catalyst was already activated, the start-up was greatly simplified. No sulfiding agent was required on site. The heat-up rate was driven only by thermal limitations of the equipment. After the hydrogen introduction to the pre-sulfided catalyst at near ambient temperatures, an initial exotherm of 50°C quickly passed through the catalyst beds. This initial exotherm was expected, and is an indication of the reversal of the passivation step. It is harmless to the equipment and the catalyst since it initiates at very low (ambient) temperature, and rarely reaches temperatures much above 100°C. The heat created is easily removed when hydrogen recycle is established at this point. After the exotherm passed, light gas oil feed was introduced at 70°C and the heat-up to operating temperature was accomplished without temperature holds or other waiting time.

Figure 4 shows the unit heat-up rate.

Figure 4 : Temperatures of HDS/MHC reactors

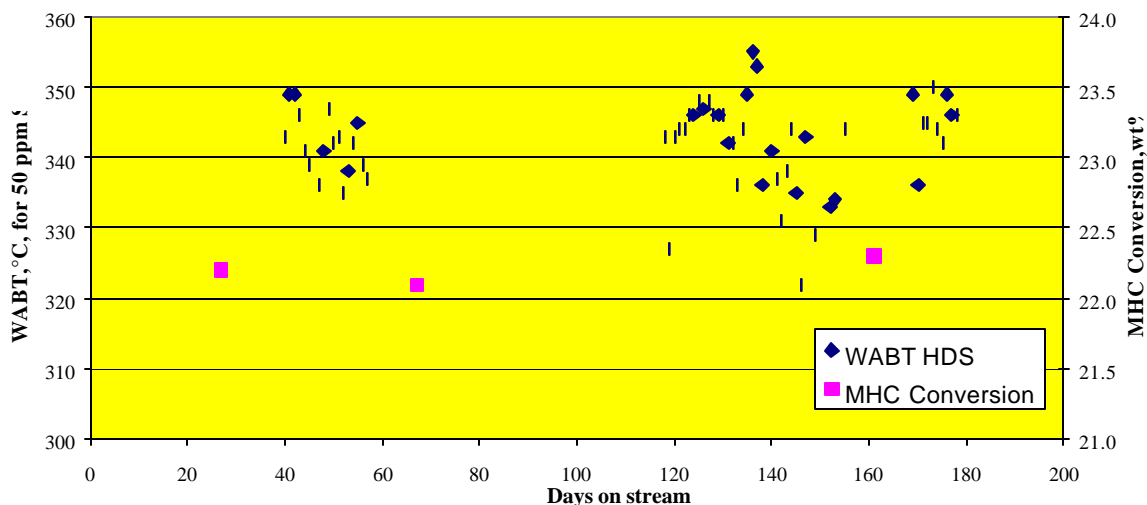


From the moment of feed introduction to start-of-run temperature, no temperature plateau was required and no sulfiding exotherm was observed. In INA's operation, heat-up rate was limited to 13°C/h, due to the furnace refractory drying requirement, and lasted 17 hours from the feed introduction to start-of-run temperature. In the previous start-up of unit performed with presulfurized catalyst, an additional 16 hours of waiting time was needed for temperature plateaus at two sulfiding temperatures.

At start-of-run temperature, initial analyses of product sulfur showed 30 ppm, which was lower than the desired specification. It took INA less than 17 hours from the moment of feed introduction at 70 °C to the moment when the required quality product was produced. The time could have been even shorter if furnace has not required a slow heat-up rate. The reactor inlet temperature was reduced of 10 °C in order to optimize the cycle length of the catalyst. A test-run performed later in the cycle confirmed high catalyst activity.

Since start-up, the unit has been running in both HDS and MHC mode in block operations. Catalyst activity in HDS mode has been monitored by plotting WABT temperature requirement for 50 ppm of sulfur versus time on stream. Figure 5 shows negligible catalyst deactivation rate over the six months since the beginning of cycle. Conversion during mild hydrocracking operating mode has been checked a few times during the current cycle, and has shown no change since start-up. A comparison of unit performance versus the previous cycle is not possible due to the change in catalyst and the significantly more severe product specifications in HDS mode. However, the performance of the catalysts is certainly meeting INA's requirements.

Figure 5 : WABT for 50 ppm S in Diesel HDS mode & MHC Conversion



In summary, INA concentrated their evaluation of XpresS by evaluating the benefits provided by pre-activated catalyst during start-up. Among the benefits INA observed were:

- The refinery enjoyed a much simpler, quicker and trouble-free start-up of their combined HDS/MHC unit.
- Relative to the procedure supplied by the catalyst vendor for start-up with pre-sulfurized catalysts, 16 hours of temperature holds were saved by employing pre-activated catalyst.
- Because the catalyst was delivered in active sulfide form, catalyst metals were not in a danger of reduction at any point during start-up. While this problem is not likely to appear with pre-sulfurized catalysts, it is a real concern during in-situ sulfiding.
- Hydrogen sulfide and acidic water formation were minimized, reducing impact on the environment in a densely populated and tourist-attractive area.
- The refinery completely avoided the use of sulfiding compounds.

CONCLUSIONS

XpresS pre-activated catalyst technology has been successfully applied in hydrocracking units. In both applications described here, pre-activated catalysts were loaded in air without any indication of catalyst self-heating during air exposure. Pre-activated catalyst showed no exothermic behavior throughout the temperature range of unit start-up.

In both applications, a direct comparison of the catalyst activity of the pre-activated catalysts with previous cycles was not possible, however in both applications, the refinery was satisfied with the catalyst activity observed.

In earlier applications of pre-activated catalyst, exceptional catalyst activity was observed. The activity benefit from ex-situ sulfiding is likely due to the more homogeneous sulfiding, which takes place in an ebullated bed versus an in-situ fixed bed operation. Higher catalyst activity should lead to longer cycle length. Along with the added benefit of shorter

hydrocracking unit start-ups, ex-situ activation is of critical importance due to high economic uplift of hydrocrackers.

When evaluating investment in catalysts, current cost analyses in refining incorporate a total performance concept. This approach includes detailed evaluation of each phase of catalyst usage, including cycle length, unit start-up duration, manpower utilization, and care for the environment. Pre-activated catalyst performs quite well in such evaluations.

References

1. "On the flexibility of the active phase in hydrotreating catalysts", Sonja Eijsbouts, *Applied Catalysis A: General* 158 (1997),53
2. "Catalysis", edited by John R. Anderson and al. *Science and Technology, Volume 11*, Springer, 1996
3. "Influence of the nature of the activation molecules on the catalytic activity", Silvy Prada at al, *Applied Catalysis*,46,1989,113
4. "Temperature-programmed sulfidation and oxidation of Ni-Mo/alumina catalyst and reaction with ammonia", Zeuthen, Per at al, *Applied Catalysis*,68 (1991),117
5. "Results from an Ex-situ pre-sulfiding Process", Daniel J. Neuman et al., *Petroleum Technology Quarterly*. Vol 3, Number 3. Autumn 1998
6. "A Case study in Catalyst Management for an Ultra-Low Sulfur Gas Oil Hydrotreater", Daniel Neuman at al., Presented at 5th European Refining Technology Conference, November 2000, Paris, France
7. "New presulfurized catalyst reduced exotherm potential in hydrocrackers", Blashka, Stephen, et al, *Oil&Gas Journal*, January 5,1998,36
8. "XpresS : The first true ex-situ pre-sulfiding process", Daniel J. Neuman et al., Presented at the 1998 NPRA Annual Meeting; March 15-17, 1998, San Francisco, California.
9. "XpresS pre-activation technology for exceptional hydroprocessing catalyst performance and unit start-up", J.Vukovic at al, *Petroleum Technology Quarterly* 19th/20th November 2002 at 7th European Refining Technology Conference, Paris, France