Cat Tech®

CATnap™ Catalyst Passivation Process

An Alternative to Inert Entry

CATnapTM Catalyst Passivation Process

Cat Tech is pleased to present the CATnap® Catalyst Passivation Process - an exclusive, patented technique for unloading catalysts from petroleum processing units. CATnap technology passivates pyrophoric or self-heating catalysts by the application of a proprietary CATnap catalyst coating chemical. The catalysts' surfaces (and equipment surfaces) are coated with an organic film which retards oxygen penetration and reaction. The passivated catalyst can be unloaded under air, thus eliminating many of the hazards and expenses related to inert entry.

This passivating effect is demonstrated in Figure 1. The blue line shows the heat release of a spent Co/Mo catalyst as it is gradually heated in air to 400°C. The catalyst starts heating up at about 120°C when the metal sulphides begin to oxidize. A second reaction representing the carbon burn commences around 300°C. Once the catalyst is passivated by the CATnap process (red line), the catalyst is stable to about 300°C.

Application of the CATnap technology involves the injection and adsorption of a chemical inhibitor. Often, this procedure is a departure from the norm because the unit is partially cooled under oil. Although the details of the procedure must be customized for each application, a generalized procedure is outlined in Figure 2. Initially, the feed rate is reduced while the reactor starts cooling down. When the unit is below reaction temperatures, a carrier oil of prescribed viscosity and other properties is introduced to displace the normal process feed. Once the feed oil is flushed out, the carrier oil is put on total recycle and the CATnap catalyst coating chemical is injected. The unit is then cooled to a target temperature (typically 140 - 150°C). Oil flow is discontinued and the reactor is further cooled under flowing gas. At this point the unit may require evacuation or purging to reach permissible entry limits for H_2S, S_20, LEL, CO and $Ni(CO)_4$. The working area is then flushed with air and the catalyst is unloaded by conventional techniques.

The benefits of the CATnap process are clear: Improved Safety, Time Savings, Reduced Costs, and Intangibles. These are outlined on the following pages.

Clearly the most important feature of CATnap technology is that it eliminates the life threatening nature of working in a nitrogen atmosphere. In spite of this, reactor entry technicians (RETs) are outfitted with full life support equipment. Safety is further enhanced by handling passivated catalyst and minimizing the hazardous dust normally present with catalysts removal.

“Elimination of a hot H2 strip and cooling down with liquid circulation can significantly reduce shutdown time.”

Experience has shown that significant time can be saved with the CATnap process. Elimination of a hot H_2 strip and cooling down with liquid circulation can significantly reduce shutdown time. Also, the equipment and procedures used with CATnap technology can reduce the actual unloading time.

The time savings and other features can provide substantial cost savings. The expense of nitrogen for inert entry is significantly reduced or eliminated. Many associated costs, such as equipment rental and contract labour, are reduced due to the shortened turnaround time. Probably the most significant value to the refiner is having his unit back on stream quicker and minimizing production losses.

Intangible benefits are difficult to quantify but are, nevertheless, very important. Clearly, not having to deal with a life threatening environment increases morale, productivity, and quality. A cleaner, safer operation means less complications and distractions for all personnel.

Another important feature of CATnap technology is that the catalyst is fully regenerable. A variety of hydrotreating and hydrocracking catalysts have been tested and qualified through laboratory studies and commercial runs.

Cat Tech is proud to bring CATnap technology to the refining community. We feel if offers a major breakthrough in catalyst unloading technology and sets a new standard for safety in the industry.

CATNAP® PROCESS ADVANTAGES

SAFETY

- Non-life-threatening atmosphere for catalyst removal
- Suppresses self-heating or pyrophoric tendencies of catalysts
- Reduces hazard of handling, transportation, and storage
- Minimizes dust emissions
- Working in a dust-free environment

TIME SAVINGS

- Eliminates hot H_2 stripping step
- Faster cooling with liquid
- Reduced catalyst vacuuming time
- Eliminates time to clean/change bag filters

COST REDUCTION

Time value of unit (critical path)

- Reduces equipment rental time (crane, etc.)
- Reduces contract labour
- Eliminates energy cost for hot H_2 strip
- Reduces (eliminates) cost of nitrogen for inert entry
- Reduces environmental risk
- Reduces the possibility of accidents
- Reduces risk of adverse public relations in case of incident

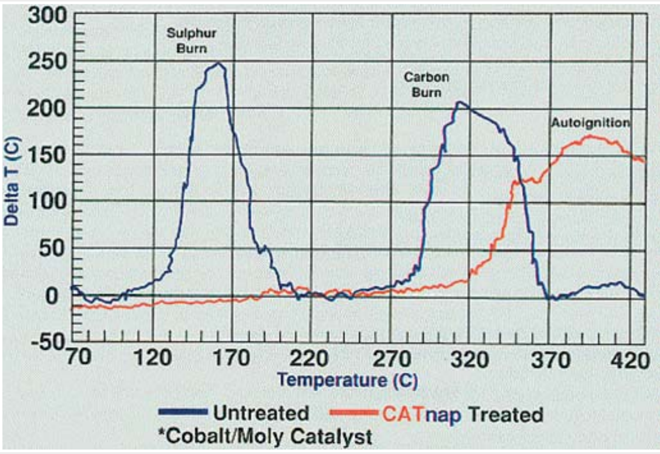
REGENERATION

- Catalysts are fully regenerate

INTANGIBLES

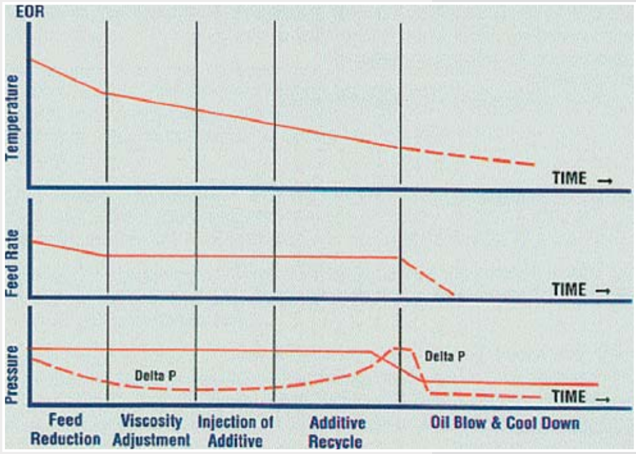
- Improved morale of reactor entry technicians, supervisors, and refinery personnel
- Improved quality and productivity - people concentrate on doing their job rather than the stress and worrying about working in an inert atmosphere
- Fewer distractions for refinery management
- Cleaner operations
- Allows refinery supervision to pursue other tasks

* figure 1



Catalyst treated by CATnap Catalyst Coating Chemical
Delta Temperature vs. Temperature*

* figure 2



CATnap Passivation Process
Application of CATnap

> Clearly, not having to deal with a life threatening environment increases morale, productivity, and quality.

Case Study

BAYERNOIL MILD HYDROCRACKER CATNAP APPLICATION

SUMMARY

On January 21st, Bayernoil, Neustadt successfully shut down the mild hydrocracker (MHC) using the CATnap catalyst passivation process applied by Cat Tech (Europe) Ltd. The CATnap technology was chosen as a means to reduce catalyst reactivity, eliminate dust problems, reduce shutdown time window and minimize potential volatile hydrocarbon (LEL) issues. This was the maiden catalyst replacement for this unit. With no history, there were many uncertainties with how the unit would respond during shutdown and unloading.

The application was a total success accomplishing all of the objectives. The unit was shut down one day quicker than it would have taken with the “conventional” procedure. There were no issues with reactive catalyst and toxic and pyrophoric dust was completely eliminated. The unit was LEL free after a normal pressure/depressure procedure. The catalyst was not unloaded under air which will be an option to accelerate the procedure and minimize nitrogen cost further for future applications.

INTRODUCTION

Bayernoil was the third refiner in Europe to apply the technology. CATnap is a process to chemically treat hydrotreating and hydrocracking catalyst so that they can be safely handled in air. This provides the potential to eliminate inert entry for catalyst removal from reactors, avoiding a dangerous operation and minimizing the cost of nitrogen for unloading.

Other benefits include reduced down time through shutting down the reactor without hot hydrogen stripping and better efficiencies in unloading. Dust particles adhere to the catalysts eliminating dust problems that can produce very toxic and pyrophoric material. Furthermore CATnap is an effective way to mitigate LEL problems in units with a history of high LEL.

The CATnap process involves applying an organic chemical during oil recirculation while cooling the unit. The chemical coats the catalyst surface with an organic film that retards oxygen penetration to the reactive metal sulfides in the catalyst pores. The carrier oil must have the proper balance between viscosity, pour point and flashpoint. The viscosity should be high enough to help the chemical provide a chemical barrier, but the pour point must be low enough to allow the catalyst to be free flowing at the catalyst removal temperatures. This was a bit of a challenge at Neustadt where the ambient temperature was -10 C and below in January. The IBP and flash point need to be sufficiently high to ensure no light hydrocarbons are left in the reactor which might be difficult to purge out and produce high LEL in the reactor.

APPLICATION

For the MHC, a middle distillate was chosen as the carrier oil. It had an IBP >200 C, pour point of -3 C, flash point of 85 C and viscosity of 3.4 cSt at 40 C. At 08:00 on January 21st the feed rate was reduced to 170 m3/hr and the temperatures began reducing at ~25 C/hr. After five hours the reactor inlet temperatures were around 300 C and the carrier oil was brought to the unit to flush out the normal feed oil. Samples were taken at the feed drum and fractionator bottoms and analyzed for viscosity and flash point to follow the flushing operation. After about seven hours of flushing, the unit was put on internal oil recycle.

The CATnap passivation chemical was injected over two hours. This was followed by five hours of oil circulation while continuing to cool the reactors. The inlet temperatures could only be reduced to ~130 C which was a bit higher than the target of 120 C. This was deemed to be acceptable and the bulk oil was pushed out with maximum hydrogen flow.

REACTOR COOLING AND GAS FREEING

This completes the application of the CATnap process. The de-oiling, depressuring and gas freeing are according to the normal procedures. It took about 24 hours to depressure the unit and get the reactor wall temperatures down to ~40 C. This was pretty much according to schedule. The anticipated timeline and the licensors recommended timeline/procedure are show in the figure below. By eliminating the diesel flush, heating and hot hydrogen strip, the CATnap procedure reduced the shutdown timeline by one day.

We went through ~7-8 pressure/depressure cycles with nitrogen to gas free the reactors. The pressure was increased to ~ 3 bars and depressured to ~ 0.6 bar. The hydrocarbon content was measured at the outlet of the second reactor. It was found to be 600 ppm. This would be equivalent to ~ 10% LEL. That is borderline acceptable, but gas samples at reactor outlets are always suspect. It was decided to open the reactors. The initial reading on the 1st reactor was 60 ppm hydrocarbon and gave 0% LEL on an explosivity meter. This was most encouraging. It is possible that additional time could have been saved by reducing the number of pressure/depressure cycles.

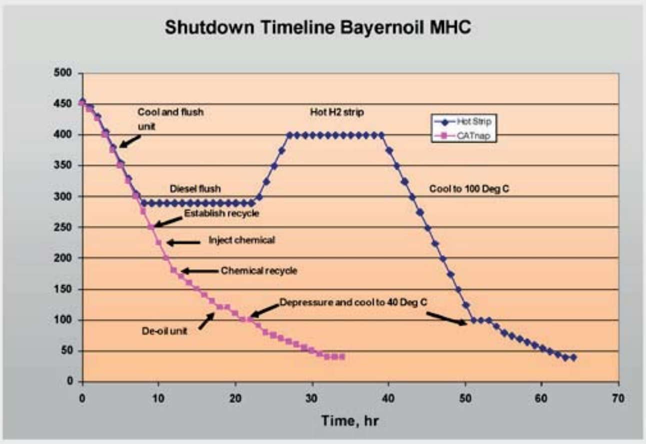
CATALYST REMOVAL

Bayernoil elected to unload the catalyst under nitrogen rather than air. Since the catalyst was primarily dumped the cost of nitrogen and the safety issues were not as severe as in vacuuming operations. We did not want to apply soda ash to the reactors and tray sections for passivation and cleaning. Our preference was to maintain the unit under nitrogen for unloading, cleaning and reloading.

The reactor was entered for tray removal. Many of the tray sections had double and triple nuts on the hold down bolts making their removal much more time consuming than planned. Catalyst was supposed to be unloaded by dumping through dump nozzles on each bed. There were some problems with free flowing Catalyst on bed 3 of the first reactor. This is probably a result from the catalyst being dense loaded and several unit upsets during the run cycle. The catalyst was very compacted. As a rule, CATnap will mitigate this problem. Hot hydrogen stripping will dry out these compacted pockets and cause them to cake worse. CATnap does not dry out the catalyst and provides some lubricity for free flowing.

CONCLUSIONS

Our actual CATnap application went very much according to plan. The timeline was achieved and the unit was LEL free. Catalyst was stable to air and there were no dust issues. The compacted catalyst unloading and tray work are not impacted by the CATnap technology and were subject to normal catalyst handling delays and problems; however, inert entry could have been eliminated and thereby reduced any timeline effects. Bayernoil will have a second CATnap application for our CHD unit in March 2011. This unit offers new challenges in that it does not have a feed drum for oil recycle and it has a documented history of serious LEL problems.



* figure 3

Shutdown Timeline Bayernoil MHC

IMPROVEMENTS

Although the application went very smoothly there are some lessons and improvements that can be applied in future applications:

- Oil sample analyses were misleading since the sample lines were not completely flushed before each sample was drawn. Good flushing in the future will speed up the carrier oil flushing step.
- Gas sampling at the reactor outlet appeared to give artificially high hydrocarbon analysis. Perhaps a better sampling point can be identified. This would expedite the gas freeing operation.
- Significant oil was found on the reactor trays. To ensure the possibility of draining, we drilled a couple of holes into each tray
- The tray sections were secured with multiple nuts on the studs. It is only necessary to hold the sections in place. This can be accomplished with a single nut. Additional nuts only increase the time required to install and uninstall the tray sections. This modification will be realized during the next catalyst exchange.
- We elected to unload and load the reactor under nitrogen. The catalyst proved to be totally stable. In the future, the catalyst could be unloaded in breathable air. In such an operation, the reactors would be purged with dehumidified air during unloading.
- Typically the trays are then power washed with soda ash and detergent. This will passivate the metallurgy and clean the trays in one operation. In our case the time required is less than cleaning without power washing. This allows the inspection and catalyst loading to be carried out under ambient air.

Cat Tech®

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