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## AM-07-41 Cracked Feed Protection for Hydrotreating Catalysts

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## **Cracked Feed Protection for Hydrotreating Catalysts**

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Refiners can reap significant operating profits by processing cracked and heavy feedstocks such as coker naphtha and light cycle oil (LCO). However, after catalyst change outs on hydrotreating (HDS) units, catalyst manufacturers recommend that only straight run feed should be used for at least the first three days of the new cycle. This delay in processing cracked feeds has several potential costs including:

- Lost profits from processing cracked and heavy feeds.
- Storage costs for the straight run feed required at start up.
- Storage costs for the cracked feed that must be held for processing later.

Cracked feeds tend to be highly reactive compared to straight run feeds since they contain significant quantities of olefins and poly-nuclear aromatics. When exposed to the hyperactive catalytic sites that exist on freshly sulfided catalysts, the unsaturated components of cracked stocks can form coke and gums that are readily deposited on the catalyst surface. Such deposits will block the catalyst's pores and active sites, leading to a permanent loss of catalyst activity and a reduction in the cycle length of the bed.

To avoid the adverse effects of cracked feeds at start up, catalyst manufacturers typically recommend a break-in period of at least three days using only straight run feed. By running only less reactive straight run feed, a small amount of coke will form on the catalyst surface, gradually reducing the hyperactivity of the catalyst. Once catalyst activity has stabilized, cracked feeds can be introduced to the unit without the risk of premature coke and gum formation.

Eurecat has developed an ex-situ treatment that allows the introduction of cracked or heavy feeds without the recommended three day delay. This process, called Totsucat<sup>®</sup> CFP, combines the Totsucat pre-activation process with an additional step to protect the catalyst from the harmful effects of cracked feed. Totsucat CFP is a carefully controlled procedure that gently tempers catalyst activity following sulfiding.

Catalysts treated with Totsucat CFP are fully sulfided and activated prior to loading. Their activity, however, will mimic a catalyst that has already been conditioned with straight run feed. Cracked and heavy feedstocks can be gradually introduced during the first hours of start up without causing permanent damage to the catalyst. Coke and gum deposits will be minimized since the catalyst activity has been carefully stabilized following activation.

## Totsucat<sup>®</sup> Catalyst Activation Process

Eurecat's patented Totsucat<sup>®</sup> sulfiding process takes catalyst pre-activation further than any other sulfiding techniques available. Unlike presulfurization techniques such as Sulficat<sup>®</sup> and actiCAT<sup>®</sup>, Totsucat treated catalysts are delivered to the hydrotreating unit totally activated and ready to work immediately. With Totsucat, the uncertainty of incomplete activation is eliminated and start up time is dramatically reduced. The advantages of the Totsucat process include:

- Load-and-Go reactor start ups. The catalyst is fully sulfided and activated and does not require any additional sulfiding agents or complex activation procedures.
- No exotherms since the sulfiding step is completed in Eurecat's equipment.
- No need for additional hydrogen at start up.
- Minimal sour water formation during start up.
- No odors.
- Negligible amounts of H<sub>2</sub>S are released during reactor heat up, protecting sulfur sensitive units downstream and avoiding the need to flare undesirable by-products.
- Concerns related to the handling of presulfiding chemicals are avoided.

Starting a unit with Totsucat treated catalysts is similar to a restart after an emergency shutdown. The loaded reactor needs only to be heated up to the start of run temperature. Time consuming drying steps, holding steps, or tests to determine  $H_2S$  levels are not required. Start up time is reduced to a few hours while start up risks are minimized. The catalyst bed will achieve peak performance since sulfiding and activation is controlled at very precise conditions.

Totsucat is particularly useful for:

- Critical path units where lost production time is costly.
- Units with temperature limits where effective sulfiding is difficult to achieve.
- Refineries with limited hydrogen supplies.
- HDS units run in parallel or series where only one unit is taken down while the other is still operating.
- Units that cannot tolerate H<sub>2</sub>S breakthrough.
- Units that utilize gas-phase start up, increasing the risk of catastrophic exotherms during in-situ sulfiding.
- Units where the use of sulfiding chemicals is undesirable or uneconomical.

Totsucat pre-activation has become the sulfiding process of choice for numerous refineries throughout the world. Totsucat CFP combines the convenience of Totsucat with protection from cracked feeds, ensuring long term reactor performance irrespective of when cracked feeds are introduced to the unit.

## Case Study

A naphtha hydrotreater (NHT) located in a Gulf Coast refinery is now on its third cycle using Totsucat CFP to pre-activate the catalyst. The unit processes 35,000 BPD of feed consisting of approximately 20% coker naphtha. The refiner's experience shows that using Totsucat CFP pre-activated catalysts provides a normal run length equivalent to what they would experience if the catalyst was broken in with only straight run feed for three days.

Figure 1 shows the reactor temperature for the unit during the last three full cycles. The first run, defined as "In-situ with Break In", utilized a catalyst that was sulfided in-situ and then fed only straight run for three days. For the second and third cycles, the reactor

was loaded with Totsucat CFP treated catalysts and started up with a mixture of cracked feed and straight run. Both Totsucat CFP runs showed steady performance throughout the run. The catalyst bed was dense loaded for the first Totsucat CFP run, providing an extended cycle time. The other two cycles were sock loaded.

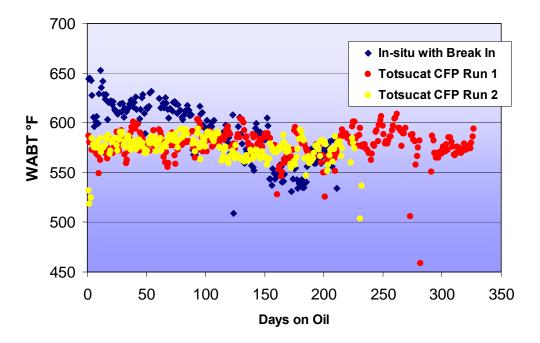


Figure 1 – Reactor Temperature (WABT)

Figure 2 denotes the temperature difference across the reactor during each cycle. On average, Totsucat CFP provided a lower temperature gradient across the bed.

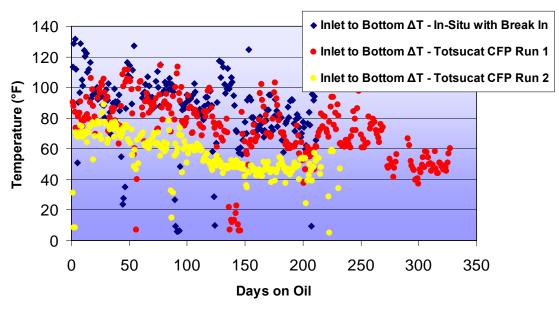


Figure 2 – Inlet to Bottom  $\Delta T$ 

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Figure 3 shows that the amount of coker naphtha fed to the unit during each run was comparable. The refiner is now on their third run in this unit using Totsucat CFP and plans to continue the use of CFP for the foreseeable future.

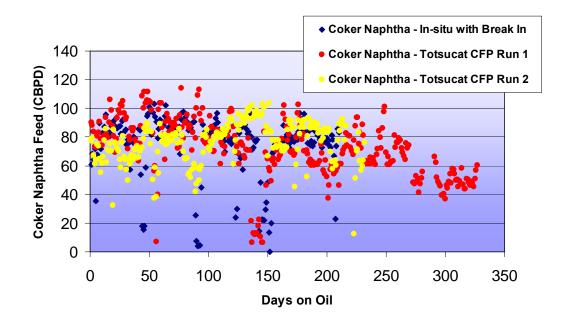


Figure 3 – Coker Naphtha Feed Rate