Question 37: To help manage fouling and pressure drop in a naphtha hydrotreater, do you rely on graded bed technologies or feed filtration (magnetic or other) or both? What is your experience with these options? What other means are being employed?

Olivier Le-Coz (Axens)

The countermeasures to pressure drop build-up in naphtha hydrotreaters units obviously depend on the cause of the fouling. The two main causes that we know in Naphtha HDT units of are corrosion particles usually coming from outside the battery limit and gums or coke. Axens addresses those two issues at design stage.

Corrosion particles are a potential problem and we indeed address that by implementing both feed filters and grading beds. Feed filters are specified as mechanical filtration devices, usually using metallic cartridges. We don’t have experience with magnetic filters.

As regards grading, Axens uses in its new unit's design or in catalyst replacement loading diagrams a wide range of products from inactive and high void fraction materials to lower void fraction and active products which can also address the removal of specific contaminants. Grading materials have proven to be efficient against particles in many cases. Grading arrangement can be studied on case-by-case basis and when relevant. Axens can propose arrangements of newer generation high void fractions and various pore size materials called CatTrap.

The gums and coke is a problem with units treating olefin and especially diolefins rich feeds from FCC or Coker Naphtha. The important considerations when designing a unit to treat such feedstocks are:

- avoid storing these materials but treat them directly from fractionation columns.

- foresee the injection of an antioxidant chemical if storing cannot be avoided.

- avoid hot spots in the heating system that would cause diolefins to polymerize, optimize the feed preheating scheme to avoid the use of a fired heater, or to reach the full vaporization point ahead of the heater.

But the most efficient way to stay away from gums pressure drop issues is to implement a selective hydrotreating reactor upfront the main HDT reactor. At low temperature and using a dedicated selective hydrotreating catalyst this pre-treatment reactors eliminates the diolefins without giving them a chance to coke further downstream in the process in the heater or at the top of the main and more active HDS catalyst which operates at higher temperature. Axens has been successfully applying this philosophy in many Coker Naphtha and FCC Gasoline (PrimeG) units. We have successfully revamped diolefins rich Naphtha HDT units with addition of a selective pre-treatment reactor, achieving a dramatic decrease of the downstream equipment fouling rate.

Ujjal Roy (Indian Oil Corporation)

We have much naphtha hydrotreaters (NHT) in our ten refineries, some operate with total straight run naphtha and others with cracked gasoline varying from 10% to 40% in feed. In many of the hydrotreaters, we have experienced run length limitations due to high-pressure drop-in reactors or pre-heat circuits while the catalyst was still active for continued operation. Depending upon the basic design, source of feedstock and its composition, we have feed filters (magnetic or cartridge or candle) in all NHT along with graded bed in few of them.

In one of our NHT processing 40% FCC gasoline, we have both magnetic feed filter and graded bed. But even in this unit, we have experienced pressure drop problem in CFEs due to caustic carry over from up-stream FCC unit. In another unit, where we have added graded bed 3 years back in addition to cartridge filter in feed, we have observed increased run length after addition of graded bed. In another unit, in which we have basket and cartridge filters in series but no graded bed, we had to do three skimmings in four years' operation. The feedstock for this unit is straight run naphtha comprising about 30% material transported from other refinery by tank wagon. We have, off late, replaced the transportation from tank wagon to pipeline and directionally there is improvement in pressure drop, perhaps due to reduction in oxygen and iron pick-up from tank wagon. In another unit, processing about 10% FCC gasoline, having both cartridge and magnetic filter but no graded bed, skimming had to be done five times in six years. The reasons for the high pressure drop as observed after opening of the reactor bed is found to be central hip created at catalyst top bed. This may be due to some design deficiency. In all our hydrotreaters where we are processing cracked gasoline, we directly route the gasoline to hydrotreater with provision of intermediate balancing tank. All these tanks are nitrogen blanketed. Also, in one of the refineries, we inject antioxidant stored in the tank.

General causes contributing to pressure drop in hydrotreaters are either iron scales or coke/polymers. Iron scales are carried with feed from up-stream equipment like tanks and piping. Magnetic and other filters would be helpful in arresting foulant coming from up-stream units and tanks. Coke and polymers come from CFEs and charge heaters. High olefin content in feed than design and dissolved oxygen picked up during storage will aggravate pressure drop. In some case, we have observed high sodium content in the crusts formed on top bed. The source of sodium is likely carry over from up-stream unit. We have taken additional operating measures in up-stream unit to arrest sodium carry over.

In many instances in hydrotreaters, we have observed spikes in Delta P after restart of compressor subsequent to its tripping. It is suggested by our licensor that this might be due to two phase flow at the start of the compressor carrying coke from CFEs and charge heater to reactor. To avoid two phase flow, they recommended to reduce reactor pressure considerably when starting the compressor and to increase the reactor pressure only when reactor attains 260°C and above.

Where we have coker naphtha in feed, in one of the hydrotreaters, multi-layer grading beds have been used. The selective hydrogenation upfront also acts as guard to hydrotreater.

Most of the pressure drop problems in hydrotreaters are unit specific and might have been overlooked in design stage. Preventive measures can only be determined through careful studying the problem over run length.

Brad Palmer (ConocoPhillips)

ConocoPhillips generally uses graded beds on all our hydrotreating units. Several units also have feed filters. The graded beds are usually adequate for all but the worst cases, in spite of precautions. We have experienced extreme cases of upstream corrosion that have forced us to occasionally skim reactors and clean preheat exchangers, in spite of precautions. The upstream problems were eventually corrected by alloy or chemicals, although we prefer to avoid too many chemicals in the naphtha feeds. The difficulty with iron sulfide in units is that the particles can be extremely small (< 1 micron), so filtration is not always effective. Filtration for the naphtha units is usually cartridge filters.

Another more frequent cause for fouling in our system is polymerization of cracked feed stocks. This is promoted by exposure of the feed (or any feed component) to oxygen in tankage but can also be caused by numerous other polymers initiating factors. Filtration is not often effective at removing the polymers, except for those gums already formed in tankage. Additional polymers form rapidly during preheat, downstream of any filtration. The polymers or gums will foul the preheat exchangers, fired heater and the reactors, if they make it that far. To manage polymers in a naphtha hydrotreater, we prefer to add antioxidant to the cracked stocks as they rundown to tankage and add anti-polymerants to stocks as they are feed to a unit. The chemicals help mitigate polymerization, but do not completely prevent it. We also make sure that the dry point of the feed is reached ahead of the fired charge heater to prevent polymer lay down in the heater, subsequent coking, and potential tube failure.

Erik Myers (Valero)

Valero uses the following key approaches:

1. Filter the feed

2. Aggressively use grading material as our naphtha hydrotreaters are not activity limited

3. Utilize mechanical solutions where they look to be effective, such as trash baskets or pressure drop reducing inlet trays.

A key operating area to focus on is avoiding two phase flow in the charge heater. Liquid in the charge heater can lead to coking which when thermally cycled will transfer this coke to the reactor. Similar transfers of iron scale can take place with upsets in any upstream fractionation towers or other equipment.

This topic was also covered in detail in last year’s Q&A (Gasoline question #35). I recommend referencing the transcripts from that review for more information.

At least one of our sites has had very good success with a chemical treatment program incorporating dispersant and antioxidant components to significantly extend the run length of the feed – effluent exchangers. Feed effluent exchanger fouling was also covered in depth as question #36 from the 2010

Q&A session. The 2010 answers for gasoline and FCC naphtha hydrotreating also provide good information on the impacts of olefins and feed gum and polymerization impacts.

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