Mid/Heavy FCC Gasoline treating
CDTECH

Since there was little need to desulfurize FCC gasoline previously, technology selection was quite limited. However, several licensors have recently entered the market with various approaches to sulfur reduction. Some schemes treat the full range catalytic naphtha (FRCN) as a single stream, while others separate the FRCN into various fractions to utilize advantages of narrow cut processing. Since nearly all of the projects, which are proceeding, are based on either conventional fixed bed HDS reactors or HDS by catalytic distillation, this paper will concentrate on comparison of those approaches.

Desulfurization of straight run naphtha (SRN) streams is not difficult and has been practiced commercially for many years. The typical application is used to prepare the straight run naphtha for feed to a reformer by reducing its sulfur content from a few hundred ppm to as low as 0.1 ppm. The technologies employed are considered “open art” and use conventional HDS catalyst in fixed bed reactors with very high hydrogen partial pressure. Catalyst life is fairly long because the SRN is a clean stream, which produces little or no coke in normal operation.

Desulfurization of full range catalytic naphtha (FRCN) is complicated by its olefinic nature. Typical FRCN contains 25 to 40% olefins and 0.1 to 0.5% diolefins. The olefins provide a large part of the octane in the FRCN. However, at desulfurization reaction conditions the olefins are easy to saturate with hydrogen, resulting in a high loss of octane in a nonselective process such as an SRN hydrotreater. The diolefins are very reactive and will combine with each other and with other olefins at ambient conditions to form oligomers (also called gums). Refiners normally add antioxidants or other additives to stabilize the FRCN and inhibit gum formation.

These gums also form on the HDS catalyst in fixed bed HDS reactors. Over time the gum converts to a hard, black substance called coke. The coke reduces catalyst activity by plugging catalyst pores and blocking access to the active catalyst sites. Increasing the reactor temperature can offset loss of catalyst activity, however this tends to reduce selectivity and increase octane loss. The octane loss may start at a low level at start-up, but it continually increases throughout the catalyst cycle length. Eventually, the temperature can no longer be increased due to physical constraints. At that point it is necessary to shut down the HDS unit and either regenerate the catalyst via steam/air burn or replace the catalyst with new. In situ regeneration will require extra equipment to conduct and control the catalyst regeneration, thus increasing the capital cost.

If the FRCN HDS unit is shut down for a few days to recover catalyst activity, what happens to the FCC? Since the FCC is often the biggest money maker in the refinery, it is not desirable to shut it down too. Therefore, it is necessary to have temporary intermediate storage in the tank farm for the FRCN while the HDS unit is out of service (Figure 1). When the HDS unit starts up, another feed pump plus spare will be required to transfer the stored FRCN from the tank farm back to the HDS unit where it will be co-fed with the normal FRCN production. That means that the HDS unit will require extra built-in capacity to handle the normal production plus the shut down makeup. So the extra tank, pumps and increased capacity all

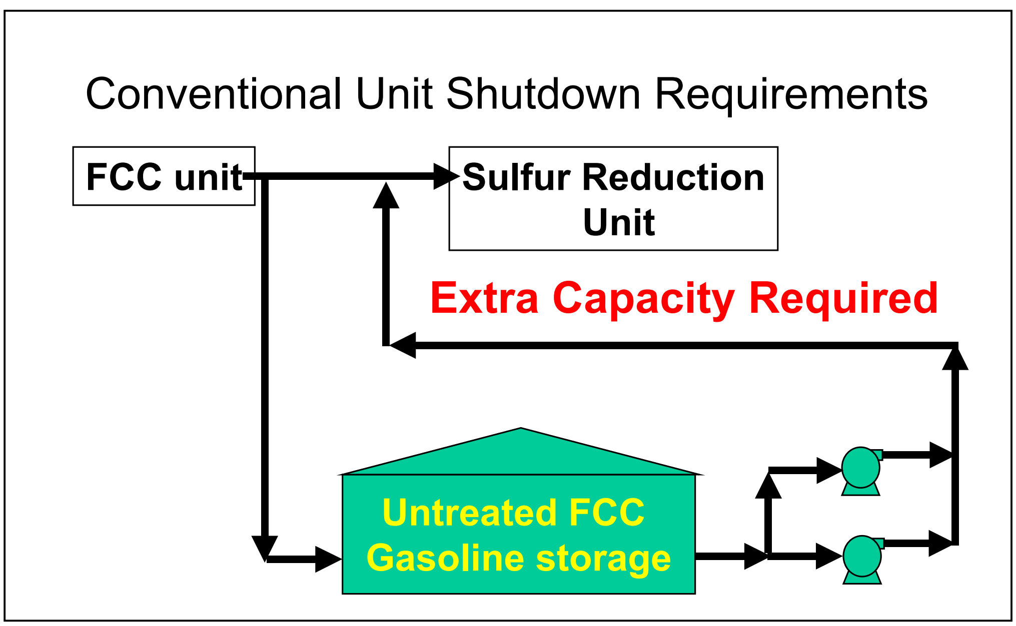

Figure 1

increase the capital cost as well. Another potential solution to this problem is to sell the high sulfur gasoline on the spot market at distress prices.

Initially, the fixed bed FRCN desulfurization technologies were offered without any pretreatment requirements. However, pretreatment has recently been added for selective hydrogenation (SHU) of diolefins prior to the HDS reactor in order to limit coke formation. This new step was added because the coke from diolefins limited the HDS reactor to fairly short cycle times. This approach typically utilizes hydrogenation catalyst in another fixed bed reactor. In order to reduce diolefins to very low levels, these fixed bed SHU's will actually saturate some of the lighter olefins resulting in octane loss before the gasoline even gets to the HDS reactor.

Although the hydrogenation reactor will reduce diolefins in the HDS reactor feed, it too is subject to fouling by oligomer sourced coke. So the hydrogenation reactor will also occasionally require catalyst regeneration or replacement. Even with this pretreatment requirement, the fixed bed HDS processes do not meet the FCC cycle requirement and will require mid-FCC cycle shutdown and regeneration or spare reactors loaded with additional catalyst.

At desulfurization conditions, the reactivity of the olefins is significantly higher than at ambient temperature. So, not only are they easy to saturate, but they can also form oligomers, although not as fast as diolefins can. So, even if the FRCN has been pretreated to remove diolefins, the formation of oligomers and therefor coke, has not been stopped. The fixed bed HDS catalyst will continue to lose activity with time due to coke formation, albeit at a lower pace than if using untreated FRCN feed.

In an effort to improve refinery profitability, refiners have been looking for ways to extend the on-stream time between major turn-arounds. Advancements in FCC design and maintenance techniques have made turn-around cycles of five years a standard in some refineries and a goal in others. In fact, some FCC gasoline sulfur reduction inquiries have indicated a requirement of five years continuous operation for selection criteria.

Fixed Bed Reactor Commercial Data

Figure 2 depicts catalyst activity for a fixed bed HDS unit treating mid-catalytic naphtha (MCN). This particular unit has a diolefin hydrogenation reactor upstream of the HDS reactor in order to maximize the cycle of the HDS catalyst. At start-of-run (SOR) the catalyst activity is representative of new catalyst. On the chart, EOR indicates the minimum required catalyst activity at end-of-run. In this unit the catalyst activity has dropped about halfway to the EOR level after 15 months of operation. It would appear that the unit would require a shutdown well before five years of operation.

If this reactor was processing a feed including the heavy catalytic naphtha, it is expected that the operating temperature would be increased in order to desulfurize the heavier more difficult sulfur compounds. At this higher temperature, it is likely that the oligomerization rate would be increased and that the catalyst cycle length would be even shorter.

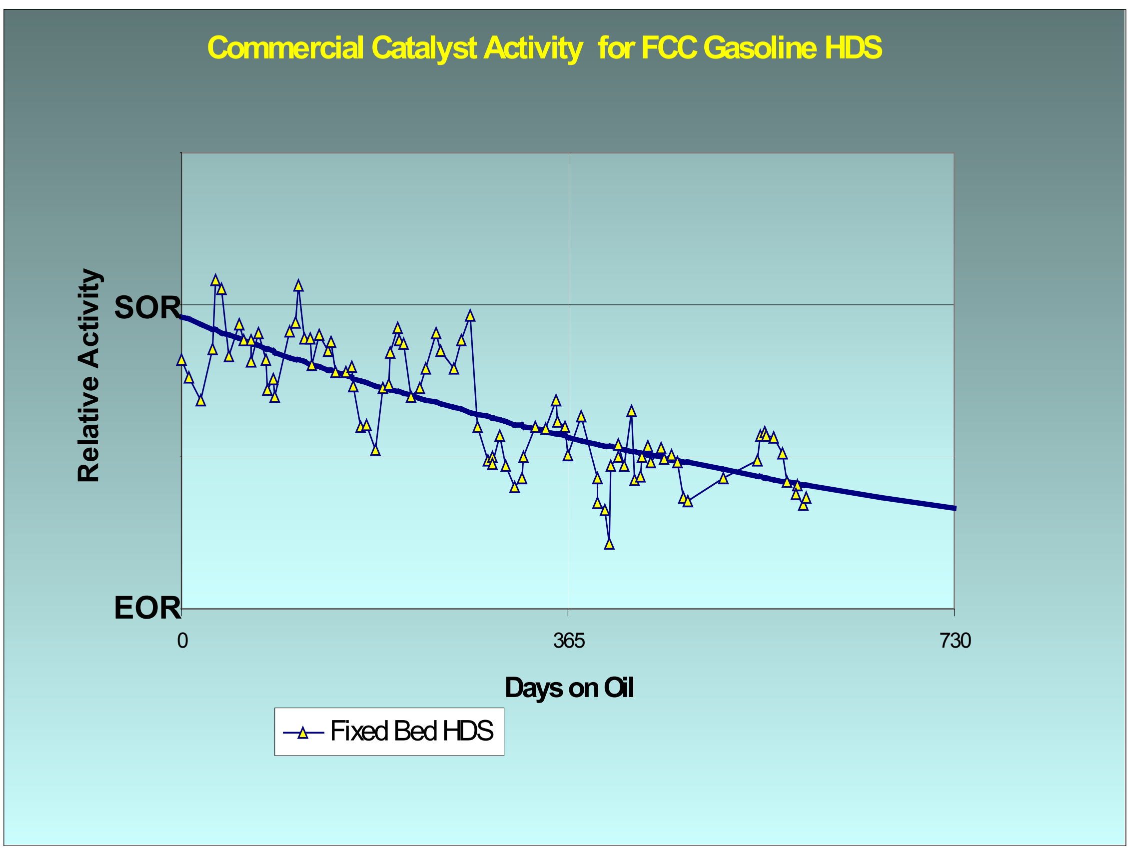

Figure 2

Catalytic Distillation Commercial Data

Shown in Figure 3 is the process scheme for the CD*HDS* unit at Motiva's Port Arthur, Texas refinery. This unit processes mid to heavy catalytic naphtha.

The HCN feeds the CD*HDS* unit via a feed preheat train (not shown) consisting of several exchangers maximizing heat integration within the unit. The feed enters the CD*HDS* column on flow control.

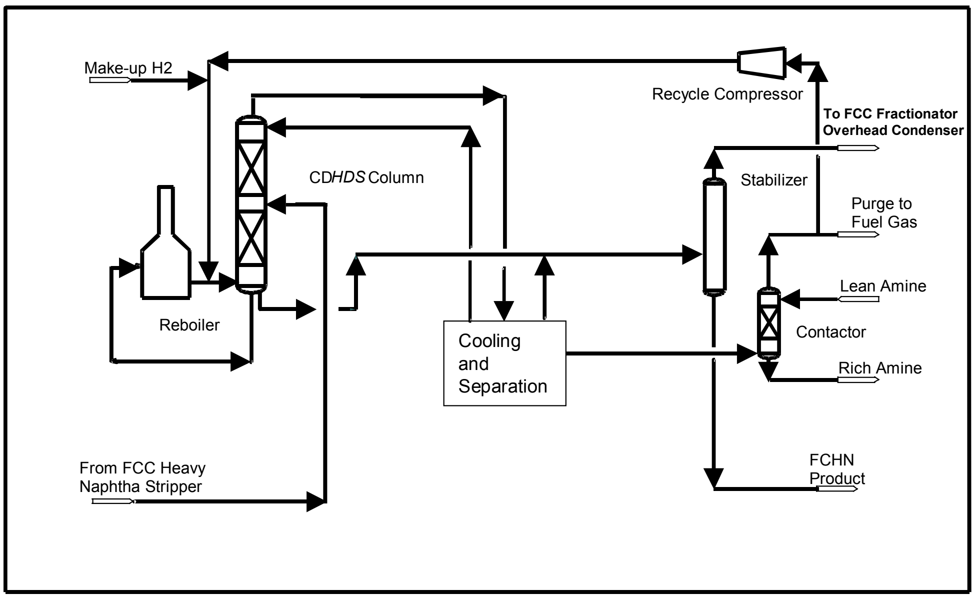

Figure 3

The CD*HDS* column contains the hydro-desulfurization catalyst embedded in structured distillation packing. This arrangement facilitates simultaneous distillation and hydrodesulfurization.

The conditions in the CD*HDS* column form a selective hydrodesulfurization environment in which the sulfur compounds will react with hydrogen to form hydrogen sulfide (H_2S) while preserving olefins. The greater portion of the desulfurized naphtha leaves with the overhead vapor.

Make-up hydrogen supplements the recycle hydrogen to provide the total hydrogen requirement.

The CD*HDS* column reboiler is a fuel gas fired heater. The overhead vapor from the CD*HDS* column is partially condensed and sent to an accumulator that operates at moderate temperature. A portion of the liquid from this drum is pumped back to the column as reflux while the remainder feeds the stabilizer. The vapor containing H_2S is routed to an amine contactor.

The sour vapor from the cooling and separation section is contacted with lean amine to remove H_2S. The vapor leaving the contactor is recycled back to the process by a recycle compressor on flow control. A purge is taken to fuel gas to control non-condensables in the process.

The function of the stabilizer is to remove hydrogen, H2S and light hydrocarbons from the desulfurized naphtha. The vent from the stabilizer is returned to the FCC Fractionator Overhead Condenser for reprocessing. The bottom stream from the stabilizer is the HDS naphtha product (FCHN) that is routed to offsite blending.

Unlike the previous example, the feedstock has no pretreating before entering the desulfurization reactor. The catalyst activity history of the CD*HDS* process is compared with the fixed bed performance in Figure 4. At fifteen months of operation, the CD*HDS* catalyst has used only 15% of its activity window. Extrapolation of the activity curve projects a cycle length of well over five years. This low rate of loss of catalyst activity demonstrates how catalytic distillation minimizes the impact of catalyst fouling on catalyst life. As a result, it is not necessary to shutdown for catalyst regeneration in the middle of an FCC cycle. This means considerable capital cost savings by elimination of temporary FCC gasoline storage and pumping facilities. The operating cost also stays low because the octane loss stays low throughout the FCC cycle, unlike conventional fixed bed reactors.

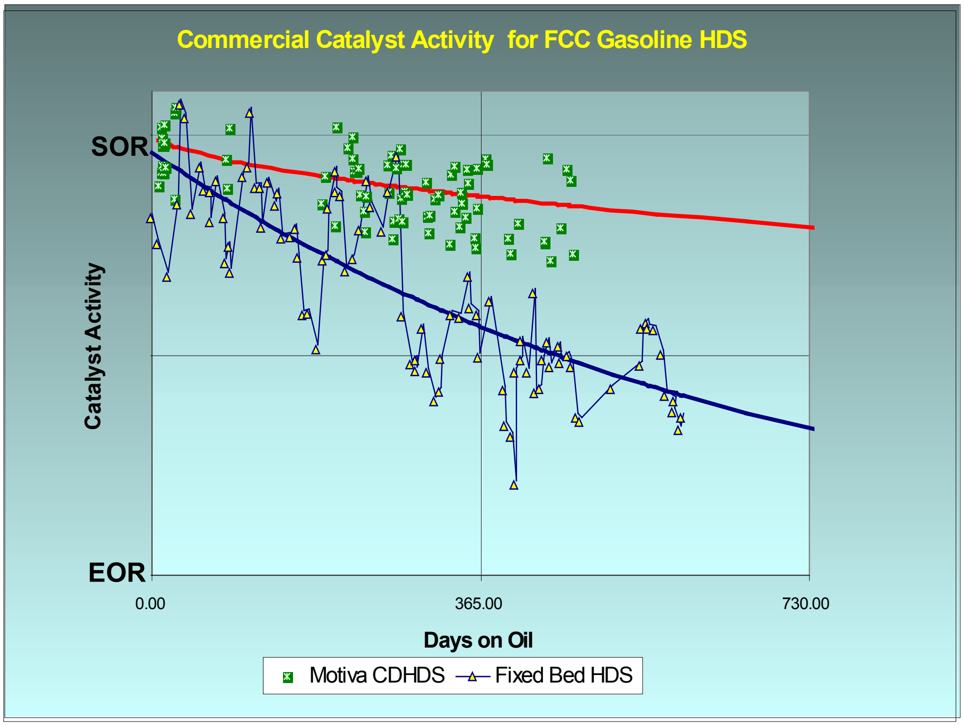

Figure 4

Mercaptans

Another important factor in desulfurization of FCC gasoline is the level of recombinant mercaptans in the product. When FCC gasoline is desulfurized in a fixed bed reactor, the reactor exit contains high levels of olefins and hydrogen sulfide. These components have a tendency to react with each other to form recombinant mercaptans at reactor exit conditions, thus increasing the product sulfur content to higher than the reactor exit. The only way to keep the sulfur level down in this unit was to increase the operating severity so than more olefins were saturated and therefor not available to react with the hydrogen sulfide. The net result is a very large loss in octane. Motiva had previous experience with a fixed bed HDS technology on the same feedstock now processed by the CD*HDS* unit. The results of that operation are depicted in Figure 5. High mercaptans are produced when the octane loss is minimized and high octane loss results when the sulfur content is reduced by saturation of olefins.

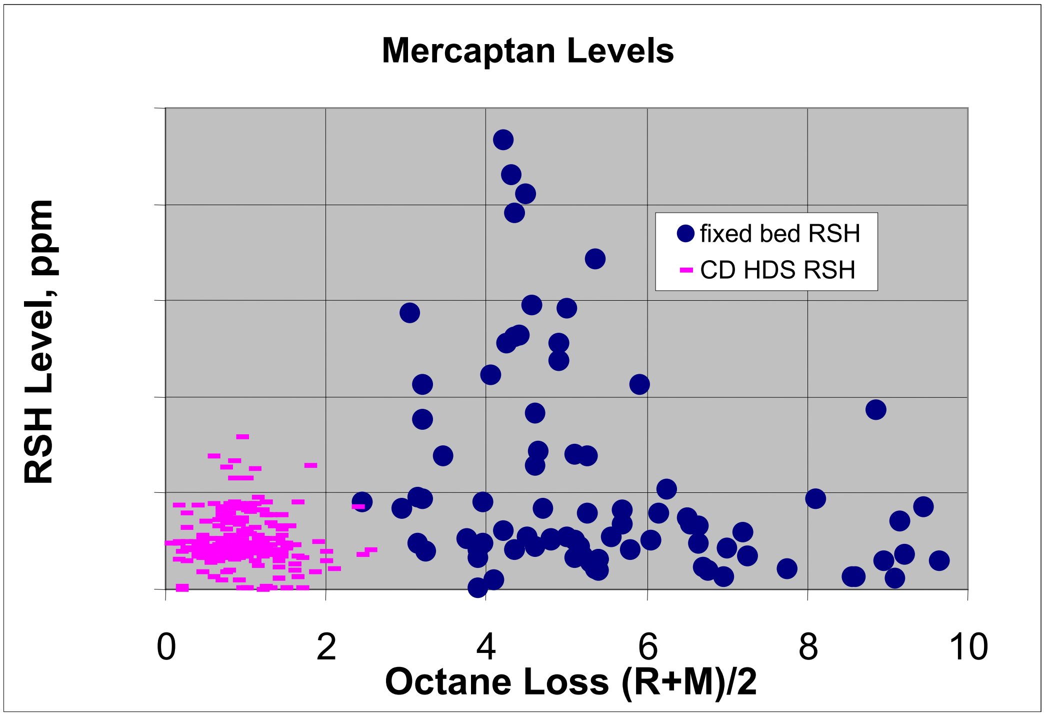

Figure 5

In the CD*HDS* process, the hydrogen sulfide exits the top of the reaction column at considerably lower temperature than for a fixed bed HDS reactor. As a result, the mercaptan formation is kept at a much lower level in the CD*HDS* than for the conventional technology.

FRCN Treating

CDTECH provides a complete technology package to treat FRCN for 10 ppm pool gasoline specification. In addition to using the CD*HDS* process for the heavy FCC gasoline, the CD*Hydro*® process is available for the light fraction. This process has already demonstrated seven years in this service with no detectable permanent loss of catalyst activity. So the complete FCC gasoline stream can be desulfurized while maintaining a five year FCC cycle using this combination of CDTECH processes.

Conclusions

Refiners are evaluating new technologies developed to reduce FCC gasoline sulfur content with minimum octane loss. They need the catalyst cycle in the gasoline HDS unit to be consistent with an FCC unit cycle length of five years. Fixed bed HDS processes will require mid-FCC cycle shutdowns to regenerate or replace catalyst. In addition, as they lose catalyst activity during the cycle, the octane loss will increase. Catalytic distillation extends catalyst cycle length to exceed five years. During this time, it keeps catalyst activity very high so that the average octane loss over the cycle is less than the fixed bed approach. It also reduces capital cost by eliminating the need for temporary FCC gasoline storage equipment and catalyst regeneration associated equipment. In addition, catalytic distillation minimizes the recombinant mercaptan problem experienced by fixed bed HDS technologies.