

Producing Low Sulfur Gasoline Reliably

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Introduction

Refiners in North America and Europe are making progress toward reduction of sulfur in the gasoline pool to meet upcoming fuels standards. Several FCC gasoline desulfurization plants are now in operation meeting current requirements with additional projects underway to meet even lower sulfur specifications in the near future. Unfortunately, refiners are discovering that some of the new HDS units will cause problems with the operation of their FCC units. This is because conventional fixed bed FCC gasoline HDS units are unable to run throughout the complete operating cycle of a modern FCC unit without having to shut down for regeneration or replacement of catalyst. As a result, the refiner must either have a very expensive FCC shutdown or spend significant capital cost in addition to the HDS investment to correct the problem.

Technology from CDTECH can prevent this problem without additional capital cost and give the refiner a reliable operation that will not interrupt the operation of the FCC unit for catalyst problems.

Background

Reduction of sulfur in FCC gasoline involves converting the contained sulfur to hydrogen sulfide in most available processes. This is done by reaction with hydrogen in the presence of a hydrotreating catalyst such as CoMo. However, other reactions can occur due to the presence of olefinic compounds in the feed.

The distribution of sulfur and olefins by distillation cut is shown in Figure 1 for a typical FCC gasoline with 1300 ppm of total sulfur, representing untreated FCC feed. The light ends are very low in sulfur (primarily mercaptans), while the heavy ends are very high (primarily thiophenes and benzothiophenes). The last fraction is about 10% of the gasoline and contains about one third of the sulfur. The olefins are concentrated in the light fraction with low olefin content in the heavy fraction.

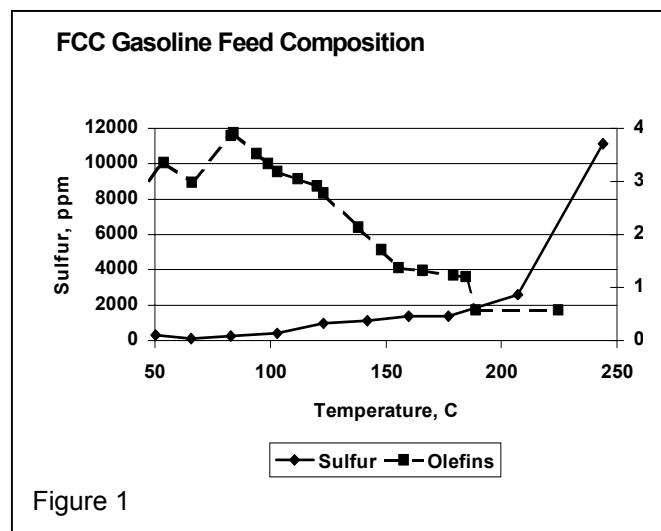


Figure 1

A common approach is to fractionate the gasoline into light and heavy cuts. The light cut is treated to remove the mercaptans without saturating any of its high olefin content. The heavy cut is hydrotreated to reduce its high sulfur content.

Conventional Hydrodesulfurization

The conventional approach to removing sulfur by hydrotreating is shown in Figure 2. The heavy cut of the FCC gasoline is heated and sent to a hydrotreating reactor where sulfur-containing compounds are converted to hydrogen sulfide and hydrocarbons in a highly exothermic, moderate pressure, fixed bed catalytic reactor. Typical fixed bed reactors operate with a temperature range of 550°F to 650°F at pressures of 300 to 500 psig. Under these conditions, significant quantities of light olefins are also hydrogenated. As a result, high loss of octane occurs with conventional HDS treating of FCC gasoline.

Conventional Gasoline HDS Process

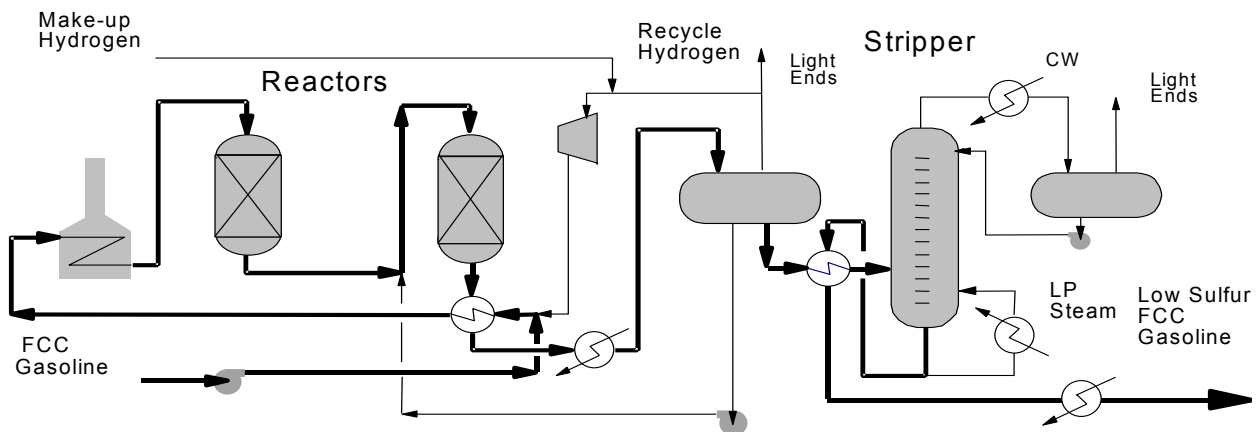


Figure 2

Some conventional hydrodesulfurization processes experience recombination of olefins with hydrogen sulfide to form mercaptans as the reactor effluent cools down. As a result, the product will still have a higher sulfur level than desired. It may be possible to reduce the recombination by saturating olefins, however this will consume excessive hydrogen and result in much higher octane loss. Another approach is to retard mercaptan formation by using very high hydrogen circulation in order to dilute the H₂S and olefins. This solution has the drawback of increasing capital cost due to much larger recycle compression requirements. Another disadvantage is that the higher hydrogen partial pressure will also result in greater olefin saturation and octane loss. This approach also has the problem that the unit must be shut down in the event of a recycle compressor outage. This is because the make-up hydrogen by itself is not sufficient to run the unit.

The other reaction of importance is oligomerization. A small portion of the olefins has two carbon double bonds and these are called diolefins. 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 FCC gasoline and inhibit gum formation in automotive fuel systems.

These gums also form on the HDS catalyst in fixed bed 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 accelerate the rate of catalyst fouling and activity loss. 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. In situ regeneration also requires environmental permits that are increasingly more difficult to obtain.

If the 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 FCC gasoline while the HDS unit is out of service (Figure 3).

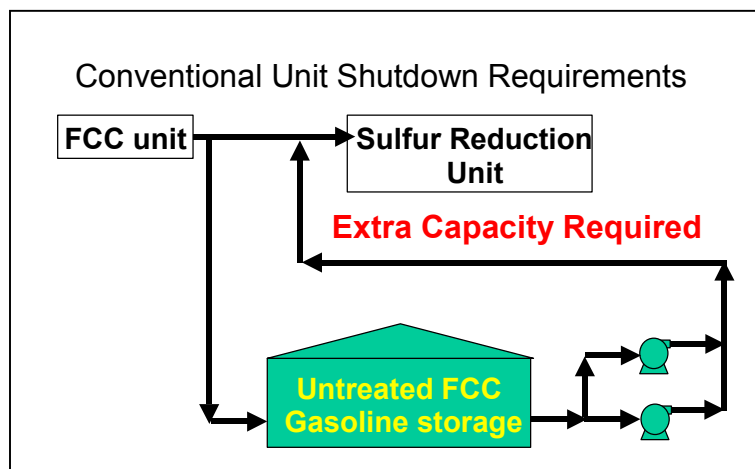


Figure 3

When the HDS unit starts up, another feed pump plus spare will be required to transfer the stored gasoline from the tank farm back to the HDS unit where it will be co-fed with the normal 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 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. It will be very difficult to sell this gasoline once the sulfur level is pushed to future low specifications.

Initially, the fixed bed 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 SHUs 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. One commercial SHU installation had a cycle time so short that it was necessary to add a second, parallel reactor to keep the unit in operation. 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 feed has been pretreated to remove diolefins, the formation of oligomers and therefore 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 feed.

Fixed Bed Reactor Commercial Data

Figure 4 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.

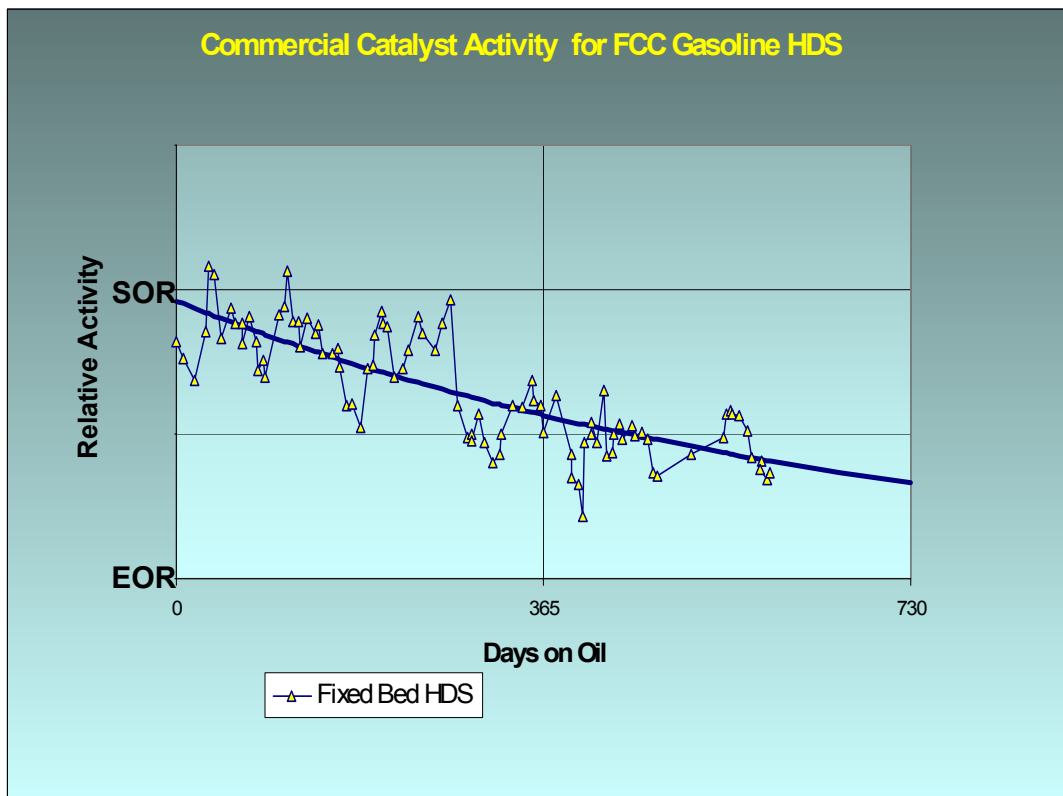


Figure 4

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.

Catalytic Distillation Commercial Data

Shown in Figure 5 is the process scheme for the refinery CDHDS units at Motiva at Port Arthur, Texas, Irving Oil in New Brunswick and ChevronTexaco at Pembroke UK. This unit processes mid to heavy catalytic naphtha. The Heavy FCC gasoline feeds the CDHDS unit via a feed preheat train (not shown) consisting of several exchangers maximizing heat integration within the unit.

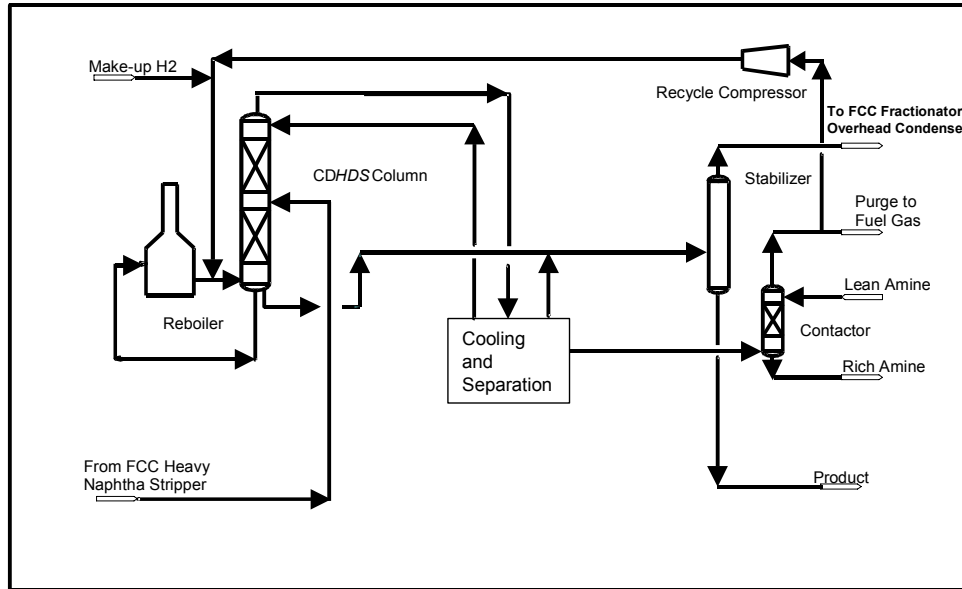


Figure 5

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

The conditions in the CDHDS column form a selective hydrodesulfurization environment in which the sulfur compounds will react with hydrogen to form hydrogen sulfide (H₂S) while preserving olefins. The greater portion of the desulfurized naphtha leaves with the overhead vapor.

The sour vapor from the cooling and separation section is contacted with lean amine to remove H₂S. 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.

Unlike the previous example, the feedstock has no pretreating before entering the desulfurization reactor. The catalyst activity history of the CDHDS process is shown for the three commercial units in Figure 6. The reaction rate constant is

plotted relative to start-up activity versus elapsed time since start-up. For the two units, which have run for over two years, there is no detectable decay in rate constant. The data in the period between 800 to 900 days was not meaningful due to malfunction of equipment external to the CDHDS column. 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.

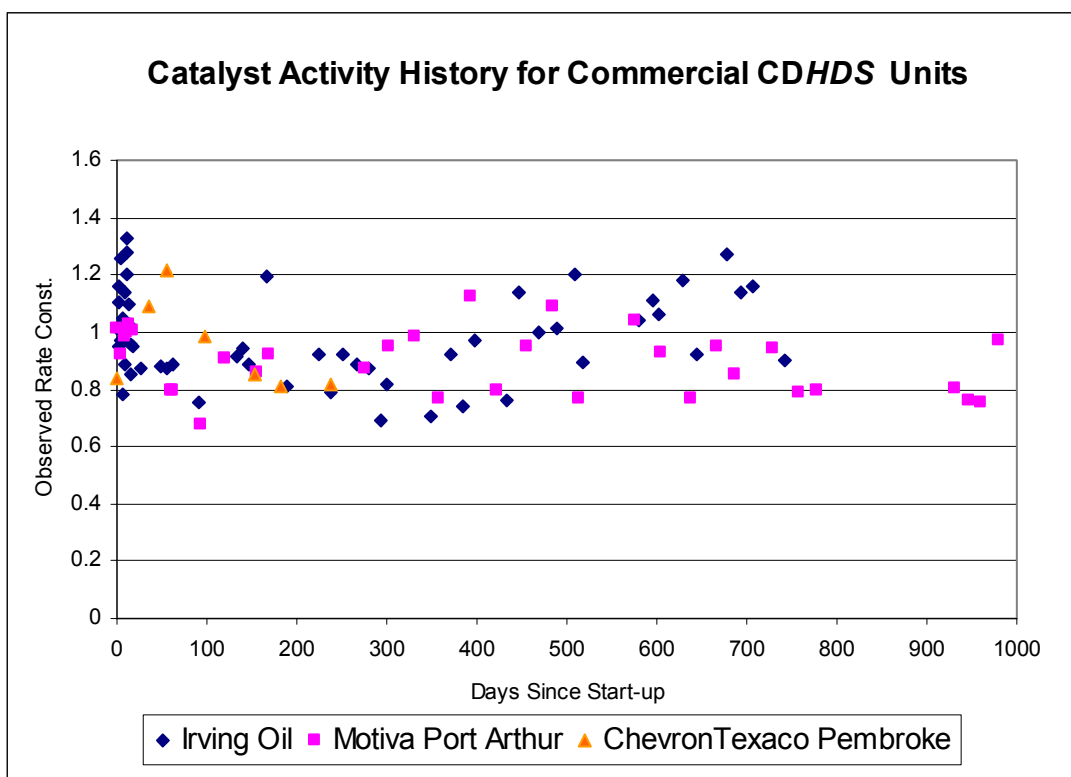


Figure 6

Mercaptans

Mercaptans have a boiling point that is roughly equivalent to a hydrocarbon with three more carbons than the olefin, which formed the mercaptan. As a result, the mercaptans are fairly easy to separate from the corresponding olefins by distillation. In the CDHDS process, desulfurized mid-range gasoline exits the top of the reaction column with considerably lower mercaptan content than typical for a fixed bed reactor. The heavy gasoline, which leaves the bottom of the CDHDS column, has virtually no mercaptans since there is very little H₂S. As a result, the

mercaptan formation is kept at a much lower level in the CDHDS process without additional measures.

Since the CDHDS process does not require the high hydrogen concentration to minimize mercaptans, it is able to operate at hydrogen recycle rates, which are much lower than the fixed bed processes. As a result, in the case of a recycle compressor outage, it is not necessary to shut down the HDS unit. This is because the unit can continue to operate on once through hydrogen, which would not be feasible for the fixed bed processes.

Full Range FCC Gasoline Treating

CDTECH provides a complete technology package to treat FCC gasoline for 10 ppm pool gasoline specification. The full range gasoline is fed to the CDHydro column, which separates the light and heavy gasoline cuts. The CDHydro process removes the mercaptans to lower levels than can be achieved via caustic treating and actually increases the octane by olefin isomerization. The isomerization achieves higher conversion than can be done in fixed bed SHU reactors, because it is performed at much lower temperature, which favors improved equilibrium conversion. In combination with the CDHDS process for the heavy FCC gasoline, the CDHydro[®] process provides complete treatment of the FCC gasoline with reliable, long catalyst life. This process has already demonstrated Eight years in this service with no detectable permanent loss of catalyst activity. So the complete FCC gasoline stream can be desulfurized while maintaining or exceeding 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. The catalyst cycle length for CDTECH catalytic distillation technologies easily align with five year FCC operating cycles. 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.

Commercial performance to date indicates cycle lengths may extend beyond five years. Ultimately our goal is to achieve 2 FCC operating cycles for each load of CD catalysts. Eliminating the need for temporary FCC gasoline storage equipment and catalyst regeneration associated equipment reduces capital cost. In addition, catalytic distillation minimizes the recombinant mercaptan problem experienced by fixed bed HDS technologies.