A wooden post stands on the left, with a clothesline extending from it. White laundry, including towels and sheets, is hanging on the line, secured with colorful clothespins. The background is a clear blue sky with a few wispy clouds. The text is overlaid on the center of the image.

**HOW
CLEAN
IS YOUR
FUEL?**

Maurice Korpelshoek and Kerry Rock, CDTECH, USA, explain how to produce and improve clean fuels with the latest technologies.

Since the early 1990s, refiners worldwide have made significant improvements to their refinery configurations in order to meet more stringent transportation fuel specifications. These new specifications were initially introduced in the US and Europe, and later adopted by other countries.

Some countries have only recently introduced new fuel specifications, while other parts of the world are still considering how to implement them.

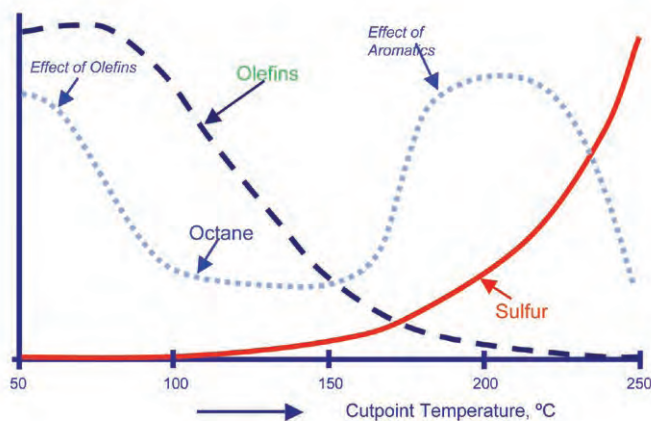


Figure 1. FCC gasoline properties.

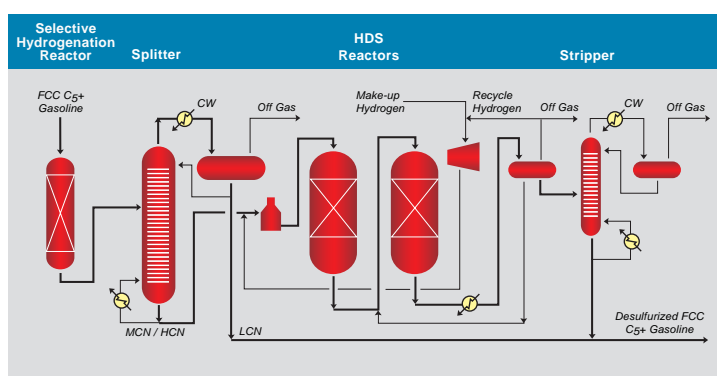


Figure 2. Conventional gasoline HDS process.

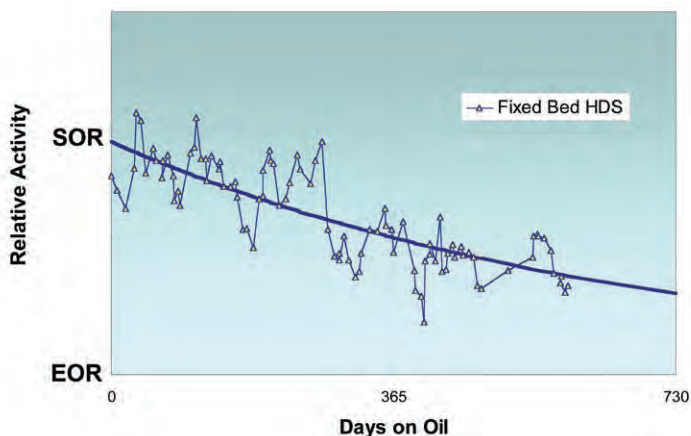


Figure 3. Commercial fixed bed catalyst activity for FCC gasoline HDS.

Refiners in these areas can benefit from the experience gained in the US and Europe because the technologies to produce clean fuels have improved considerably over the last decade.

Specifically for gasoline production, processes that reduce the sulfur content can often cause the loss of high octane components such as olefins, reducing the gasoline octane. Given the increasing requirement for high octane gasoline, the reduction in gasoline octane is undesirable. The refiner is then faced with a situation where other high octane blending components are required. Optimally, technologies applied to meet new fuel specifications should have a minimal impact on the

product octane value, and technologies applied to increase octane should efficiently use low cost feedstock.

FCC gasoline desulfurisation

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

Figure 1 shows the distribution of sulfur and olefins by distillation cut for a typical FCC gasoline, produced with 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 heaviest fraction, which is approximately 10% of the gasoline, contains approximately one third of the sulfur. Conversely, the olefins are concentrated in the light fraction while the heavy fraction has a low olefins content.

Therefore, the most logical approach is to fractionate the gasoline into light and heavy cuts. The light cut is treated to remove the mercaptan sulfur without saturating any of its high olefin content. The heavy cut is selectively hydrotreated to reduce its high sulfur content while minimising loss of the olefins contained in it.

Conventional hydrodesulfurisation (HDS)

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 290 – 340 °C at pressures of 20 - 35 barg. Under these conditions, significant quantities of light olefins are also hydrogenated. As a result, high octane loss occurs with conventional HDS treating of FCC gasoline.

Some conventional HDS processes experience recombination of olefins with hydrogen sulfide to form mercaptans as the reactor effluent cools down. As a result, the product still has a higher than desired sulfur level.

It may be possible to reduce recombination by saturating the olefins; however, this consumes excessive hydrogen and results in much higher octane loss. Another approach is to stifle mercaptan formation by using very high hydrogen circulation rates in order to dilute the H₂S and olefins. This has several drawbacks:

- The capital cost increases due to the much larger recycle compression requirements.
- The higher hydrogen partial pressure results in greater olefin saturation and octane loss.
- The gasoline HDS unit must be shut down in the event of a recycle compressor outage and cannot

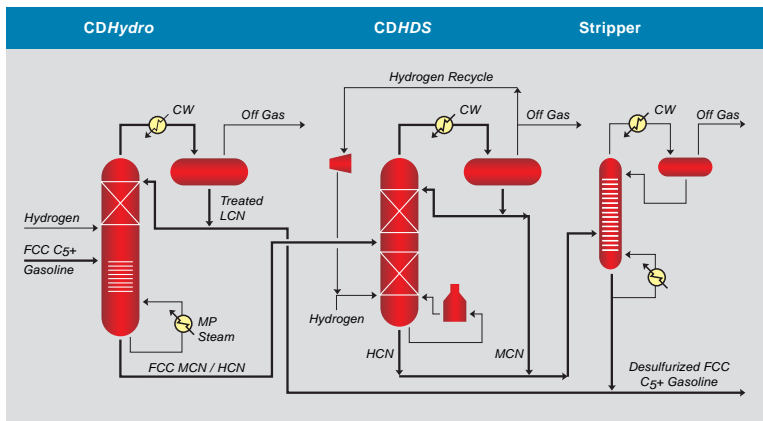


Figure 4. CDHydro/CDHDS process scheme.

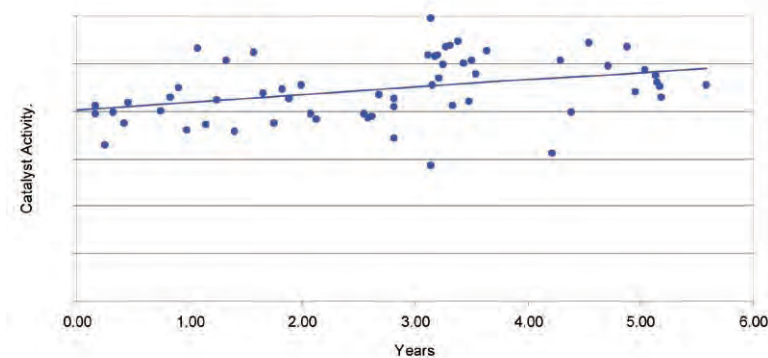


Figure 5. Catalyst activity for the Motiva Port Arthur CDHDS unit.

be run in a once through mode of operation. This is because the makeup hydrogen cannot sustain the high excess requirement for feed hydrogen critical to the operation of this vapour phase process.

Another important reaction is oligomerisation. A small portion of the olefins have two carbon double bonds. These 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 stabilise the FCC gasoline and inhibit gum formation in automotive fuel systems.

Gums also form on the HDS catalyst in fixed bed reactors. Over time, the gums convert to coke, which reduces catalyst activity by plugging catalyst pores and blocking access to active catalyst sites. This also increases pressure drop across the reactor bed. 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 feed pressure and temperature can no longer be increased due to physical constraints, at which point it is necessary to shut down the HDS unit and either regenerate the catalyst via steam/air burn or replace the catalyst with a new charge.

Normally, regenerated catalyst has less activity than new catalyst and the second cycle length will be significantly shorter than the first. As a result, most refiners replace with new catalyst rather than use regenerated catalyst. This effectively limits the fixed bed catalyst life to four years or less. Modern refinery practice is to keep the FCC unit onstream for five years,

and since fixed bed FCC naphtha treaters cannot meet this cycle length, an extra shutdown is required to change the fixed bed catalyst, reducing the refinery's profit margin.

Initially, fixed bed desulfurisation technologies were offered without any pretreatment requirements. However, pretreatment has recently been added to selectively hydrogenate diolefins prior to the HDS reactor. This additional step, which typically utilises hydrogenation catalyst in a fixed bed reactor, is required because coke from the diolefins limits the HDS reactor to short cycle times. In order to reduce diolefins to very low levels, these fixed bed selective hydrogenation units (SHU) actually saturate some of the lighter olefins, resulting in octane loss even before the gasoline reaches the HDS reactor.

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

Fixed bed reactor commercial data

Figure 3 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 to maximise the HDS catalyst cycle. 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 half way to the EOR level after 15 months of operation. It appears that the unit will require a shutdown well before four years of operation, especially since the activity decline rate will accelerate further. If this reactor processed a feed that included the heavy catalytic naphtha, the operating temperature would need to be increased in order to desulfurise the heavier, more difficult sulfur compounds. At this higher temperature, it is likely that the oligomerisation rate would increase and that the catalyst cycle length would be even shorter.

In an effort to improve refinery profitability, refiners have been looking for ways to extend the onstream time between major turnarounds. Advancements in FCC design and maintenance techniques have made turnaround cycles of five years a standard in some refineries and a goal in others. In fact, some FCC gasoline sulfur reduction enquiries have indicated a requirement of five years continuous operation as one of the selection criteria. A premature shutdown of the FCC unit, dictated by the run length of the FCC gasoline desulfurisation unit, would reduce profitability.

Catalytic distillation (CDHydro and CDHDS)

Most of the disadvantages related to the use of traditional fixed bed technologies in this service can be overcome by the use of catalytic distillation (CD). CD combines catalytic reaction and distillation functions in a single column operation. It can remove sulfur from FCC naphtha with less octane loss than other selective HDS processes because it simultaneously separates and hydrotreats the naphtha in three fractions. Each fraction is treated at its optimal severity, resulting in maximum sulfur removal with minimum olefin saturation. This ingenious approach takes advantage of what is shown in Figure 1: in the FCC naphtha, the light and medium cuts have higher olefin and lower sulfur content, while the heavy cut has the lowest olefin and highest sulfur content. Thus, highest severity is only applied to the heavy cut.

The CD approach also results in a reduction in capital cost by eliminating the need for a separate reactor and associated equipment. An unparalleled benefit of the CD operation is that it promotes extremely long catalyst life because the constant washing of the catalyst by reflux reduces oligomer fouling. CDTECH's process scheme is illustrated in Figure 4.

Full range FCC naphtha is fed to the CDHydro column, which fractionates the light naphtha overhead. In a reaction zone in the rectification section, mercaptan sulfur reacts with diolefins to produce heavier sulfur compounds, and the remaining diolefins are partially saturated to olefins by reaction with hydrogen. Bottoms from the CDHydro column, containing the reacted mercaptans, are fed to the CDHDS column where middle and heavy cat naphtha (MCN/HCN) are catalytically desulfurised in two separate reaction zones. HDS conditions are optimised for each fraction to achieve the desired sulfur reduction with minimal olefin saturation. The three desulfurised fractions can also be made available as separate product streams for further processing or blending. These processes have been fully commercialised on challenging feeds having both high olefin and high sulfur content. Long term actual plant experience has demonstrated robust operation and much longer catalyst life than fixed bed processes. The CDHydro process has demonstrated over 10 years of operation with no detectable permanent loss of catalyst activity. The CDHDS process has exceeded eight years of operation without the need for catalyst replacement.

Catalytic distillation commercial data

CDTECH's gasoline treating and desulfurisation processes are currently in operation in 28 refineries and another 14 units are under design and construction throughout the world. The cumulative licensed capacity is over 1.6 million bpd. The first CDHDS unit in gasoline service was brought onstream in 2000 at the Motiva Port Arthur refinery with a processing capacity of 12 000 bpd. The first CDHydro/CDHDS combination was brought onstream in 2000 at the Irving Oil refinery in Canada with a capacity of 60 000 bpd.

The catalyst activity history of the CDHDS process for the first catalyst cycle at Motiva Port Arthur is shown in Figure 5. The reaction rate constant is plotted relative to startup activity versus elapsed time since startup.

Even after six years of operation, the catalyst showed no detectable loss in catalyst activity, demonstrating how catalytic distillation minimises the impact of catalyst fouling on catalyst life. In fact, there is an upward trend with time. As a result, it is not necessary to shut down for catalyst regeneration in the middle of an FCC cycle. This means considerable capital cost savings by eliminating temporary FCC gasoline storage and pumping facilities. The operating severity stays low throughout the FCC cycle, unlike conventional fixed bed reactors.

Commercial operation of CDTECH's gasoline desulfurisation units over the last 10 years has demonstrated the following important features for refiners considering production of low sulfur gasoline.

Performance

The units are able to produce ultra low sulfur gasoline product with less than 10 ppm sulfur and over 99% desulfurisation levels while maintaining high yield and achieving low octane loss. Processing of partial and full range naphtha as well as naphtha from a resid FCC (RFCC) unit have been demonstrated with no restriction to gasoline with low olefins or low endpoint. All units continue to meet or exceed guarantees. They have also proven to be easier to operate than fixed bed reactors as they do not experience increase in pressure drop and do not require compensation for loss of activity over the life cycle. They are also very stable to run and do not require advanced process control to do so.

Flexibility

All units have demonstrated the ability to handle feedstock swings (e.g. large swings in boiling range, and sulfur and olefin content) through the full life cycle. Many licensees process 'opportunity' feedstocks, taking economic advantage of the light heavy crude differentials. The units can also produce HCN as a separate product for blending in the diesel pool to maximise ultra low sulfur diesel production.

Reliability

With a demonstrated catalyst life of almost eight years, the units can meet multiple FCC cycles without shutdowns, spare reactors, additional tankage, or extra run off capacity. Unlike fixed bed conventional HDS processes, they are not vulnerable to rotating equipment failure as they do not require a large hydrogen recycle compressor and can operate with hydrogen on a once through basis.

Conclusion

For refiners who have yet adapted to changing fuel specification requirements, challenging times are ahead with changing product demand and changing product specifications. While some refiners have already started projects to change their existing refinery configurations, others still have to perform process evaluations to investigate the modifications required. When performing these process evaluations, these refiners have an advantage since several refiners in North America and Europe have already built up experience with technologies that effectively treat gasoline to meet revised clean fuel specifications. 