FCC gasoline Treating Issues and Experience

CDTECH

Introduction

Reduced levels of VOC and ozone in Los Angeles have demonstrated the recent success of gasoline reformulation in the U.S. The EPA has issued regulations for further emissions reductions to be implemented in 2004 through 2007. European Union regulations are now in place requiring gasoline with less than 150 ppm sulfur in 2000 and less than 50 ppm in 2005. Specifications of less than 10 ppm are in consideration for 2008. In 1999, Germany and the UK are promoting early production of gasoline at 50 ppm sulfur in 2001 and less than 10 ppm in 2003. Similar actions are being discussed in other areas of the world. This paper discusses the implementation of gasoline sulfur reduction in refineries and highlights some of the issues that refiners will face while trying to make these changes.

European and US EPA regulators continue to push auto manufacturers to increase gasoline mileage in new vehicles while achieving even lower emissions. The auto manufacturers claim they have done all that can be done to improve mileage without improvements in gasoline composition. Specifically, the sulfur content must be reduced significantly to achieve the required efficiency and emissions. As a result, the new gasoline regulations issued by EPA in 1999 will limit 100% of the gasoline pool to less than 30 ppm sulfur by 2007. This specification will be phased in starting in 2004, targeting large refineries and the most polluted areas first.

However, further sulfur reductions are expected. The World-Wide Fuel Charter has published proposed gasoline specifications for “Sulfur Free Gasoline,” which is currently interpreted as 5 – 10 ppm maximum. In conjunction with the European move toward less than 10 ppm sulfur, it is anticipated that similar regulations will be adopted in the U.S. prior to 2010.

Refinery Changes Required For Sulfur Reduction

Nearly all the sulfur (85-99%) in the typical refinery gasoline pool comes from FCC gasoline with a small amount coming from light straight run and coker gasolines. As a result, FCC gasoline is the natural place to focus on sulfur reduction. The sulfur content of FCC gasoline is a function of the sulfur type and level in the FCC feedstock. Typical FCC gasoline sulfur ranges from 1000 to 2000 ppm. This can be reduced considerably by hydrotreating the FCC feed, although this is a capital cost intensive solution. In addition, FCC feed hydrodesulfurization (HDS) by itself will likely not be sufficient when specifications for very low sulfur gasoline become effective. It will still be necessary to desulfurize the FCC gasoline to achieve the <30 ppm pool specification.

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, while the heavy ends are very high. 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. Thus, the gasoline could be fractionated by removing the heavy cut to reduce sulfur by one third. Unfortunately, the heavy ends cannot be blended into middle distillate cuts due to the high sulfur content. They could be hydrotreated to remove sulfur and blended to middle distillate, or blended directly to fuel oil or cutter stock, but these options normally represent a significant downgrade in value relative to gasoline. Usually, removal of the high sulfur heavy ends from gasoline will not reduce sulfur enough to meet the requirement of <30 ppm.

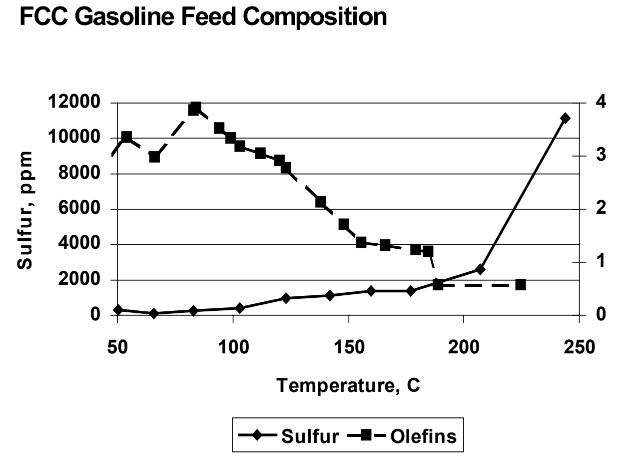

Figure 1

Another approach is to hydrotreat the complete FCC gasoline stream. Conventional hydrotreating technology at moderate pressure can be used for sulfur reduction. Unfortunately, at the temperature required for high sulfur conversion (>90%), there is considerable loss of octane. A typical distribution of octane is depicted in Figure 2. The higher octane contributions are concentrated in the front end (olefins) and the back end (aromatics). The light olefins are easily saturated at the conditions necessary for desulfurization of the heavy ends. With conventional hydrotreating at 90% desulfurization, octane losses exceeding 10 research and 3 motor can occur.

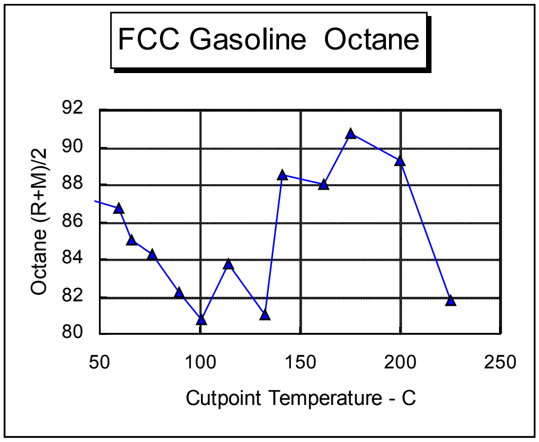

Figure 2

Another disadvantage of this method is the large hydrogen consumption incurred by olefin saturation. Hydrogen is in short supply in most refineries and hydrogen conservation will impact selection of the processing scheme.

An alternate strategy is to remove light cat naphtha (LCN) from the gasoline prior to hydrotreating. This reduces the olefin and octane loss and reduces hydrogen consumption. The resulting stream is then used to produce TAME and heavier ethers or is blended into the pool. However, when the pool sulfur specification drops below 30 ppm, it will be necessary to remove sulfur from the LCN as well as the heavier FCC gasoline. Most of the sulfur content of the LCN is mercaptan. The recognized method for treating mercaptans has long been caustic treating. This process is very effective for converting mercaptans to disulfides and has been used primarily for its ability to reduce the corrosiveness of the mercaptans in FCC gasoline. An additional step is required to remove the disulfide byproduct from the gasoline. This is accomplished by extracting the disulfides and regenerating of the caustic for recycle to the mercaptan reaction step.

The extraction works very well for light feeds such as C_4s where the primary sulfur compound is methyl mercaptan. However, for heavier hydrocarbons such as C_5/C_6, the disulfide byproduct is more difficult to extract. Refiners' experience with extractive caustic treatment of LCN indicates that only up to 90% of the disulfides are removed, depending on the boiling range of the feedstock and the design of the caustic treatment system. When gasoline sulfur specifications are 30 ppm or less, the residual disulfides from extractive caustic treatment will be a significant contributor to the total and will necessitate additional sulfur reduction in the heavier FCC gasoline in order to achieve pool specifications. This higher HDS requirement will result in additional octane loss due to higher severity requirements.

Some refiners plan to fractionate FCC gasoline downstream of a caustic treater prior to desulfurization of the resulting fractions. This is a bad idea for several reasons which have been demonstrated by Pemex in its refineries at Salina Cruz and Tula Mexico. Both of these refineries have FCC gasoline fractionators which separate a C5 fraction to send to downstream TAME units. The FCC gasoline is first sweetened by caustic treatment prior to being sent to the fractionator. Both refineries experience all three of the following operating problems.

1) Caustic carry over

The caustic treatment unit is occasionally upset by abrupt changes in feed rate due to changes in the upstream FCC unit. As a result, small quantities of aqueous caustic solution are carried into the treated FCC gasoline and enter the fractionation column. In the column, part of the water is evaporated and solid caustic deposits on the trays and the reboiler of the column. As caustic deposits build up, the trays become fouled and pressure drop begins to build. Eventually the column begins to flood and has to be shut down for cleaning. Pumping clean water into the reflux line can help dissolve the deposits and allow the column to operate again. However, the partially removed deposits form again and ultimately the column must be opened for manual cleaning. The reboiler also becomes fouled with solid caustic and must be cleaned. The cycle for column cleaning is about every two months.

Note: Part of the caustic solution goes out the bottom of the column with the remainder of the FCC gasoline. This does not cause a problem for Pemex currently. However, in the future, when they will desulfurize the FCC gasoline, it will cause problems. The sodium will react with the support material of the catalyst (alumina) and eventually destroy it, rendering the catalyst inactive.

2) Disulfide decomposition

The caustic treatment unit converts the mercaptans to disulfides. Each disulfide molecule is formed from two different mercaptans that were in the untreated gasoline. There are many different, complex disulfide products. The problem is that the disulfides become unstable at 150°C and break apart into mercaptans and some hydrogen disulfide. These conditions can exist at the surface of the reboiler tubes. The hydrogen sulfide is stripped overhead along with water that was dissolved in the FCC gasoline. In the overhead system, the water is condensed and absorbs the hydrogen sulfide. The resulting solution corrodes the condenser and other overhead components. Condenser tubes require plugging frequently and eventually replacement.

3) Peroxide Formation

In the caustic treatment unit, spent caustic is regenerated by exposure to the oxygen contained in air. The treated gasoline contains dissolved oxygen, which reacts with olefins to form peroxides. In the gasoline fractionator, the peroxides and olefins react to form polymers. The polymers tend to foul heat transfer surfaces such as the fractionator condenser. In the downstream Pemex TAME units, the polymers also foul the etherification catalyst, reducing its life.

Conventional Hydrodesulfurization:

The conventional approach to removing sulfur by hydrotreating is shown in Figure 3. 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. Two stages are normally used with different catalysts and different conditions to reduce fouling due to oligomer formation. The conditions in the second reactor are normally set to achieve hydrodesulfurization of the heavy sulfur compounds such as benzothiophene. Typical fixed bed reactors operate with a temperature range of 300ºF to 350ºF at pressures of 27 to 35 barg. 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

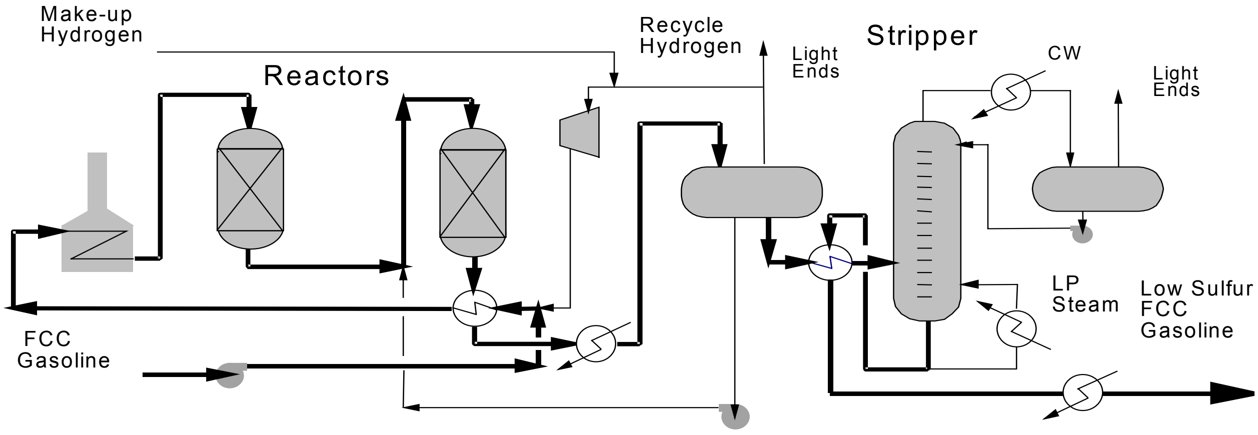

Figure 3

Some conventional hydrodesulfurization processes experience recombination of olefins with hydrogen sulfide 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 cut the heavy FCC gasoline out and hydrotreat it separately; a costly solution.

In order to minimize octane loss, the ideal process scheme would be to fractionate the FCC gasoline into various cuts and then to treat each cut according to its composition. For example, the fractionation could produce three gasoline cuts; LCN, MCN and HCN (Figure 4). The LCN contains a high olefin level and its sulfur content is nearly all mercaptans. This fraction could be hydrotreated at very mild conditions because this will minimize olefin saturation and the mercaptans do not need high temperature to desulfurize. The MCN contains thiophene, alky-thiophenes and mercaptans. It has lower olefin content than the LCN and requires medium severity HDS conditions to remove sulfur compounds while minimizing olefin saturation. The HCN is characterized by high concentrations of benzothiophene and alky-benzothiophenes while the olefin level is very low. It requires high severity to desulfurize the highly refractory benzothiophenes and there is little olefin to saturate. Although this scheme provides the desired goals of high HDS with minimal olefin saturation, it will be capital cost intensive with two distillation columns and three HDS units. It does however, set a performance standard for development of new technologies.

Optimized FCC Gasoline HDS
With Conventional Technology

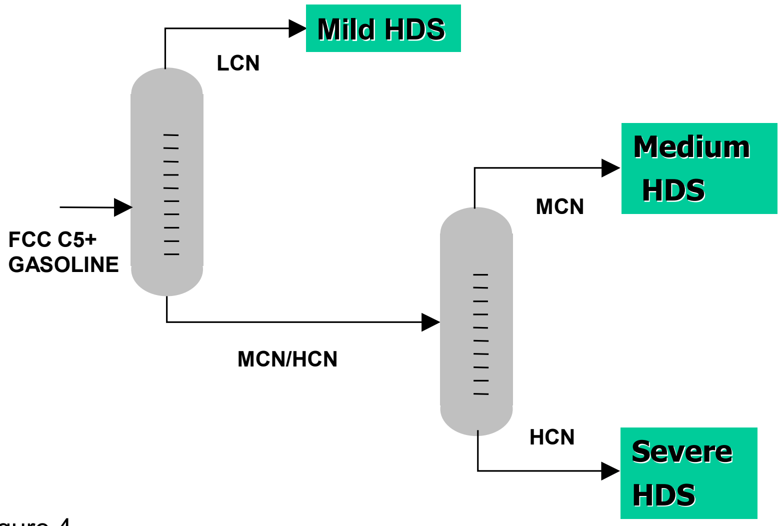

Figure 4

Conclusions

Reduction of sulfur to very low levels in FCC gasoline will be required in the near future to meet auto emissions regulations. Desulfurization of FCC gasoline with minimum octane loss is very difficult with conventional technologies. Advanced technologies are required by refiners to reliably reduce FCC gasoline sulfur with minimum octane loss and minimum operating problems.