GT-BTX PluS®
Reduce Sulfur - Preserve Octane Value - Produce Petrochemicals
FCC Naphtha – Sulfur, Octane, and Petrochemicals

Introduction
Sulfur reduction in fluid catalytic cracking (FCC) gasoline is an interesting, important topic to refiners. Most worldwide specifications require sulfur to be reduced to very low levels. Traditional technologies use selective hydrodesulfurization, which results in an objectionable octane loss in the gasoline. GT-BTX PluS® technology is the best solution to address sulfur removal, while retaining olefins from undesired saturation by hydrogenation.

Many refiners recover propylene from the light ends of the FCC, but they are less aware of the commercial process to recover aromatics or other products from the FCC Naphtha stream. GT-BTX PluS® enables recovery of aromatics, as well as an intermediate stream that is easily convertible into petrochemical-grade propylene.

Sulfur
Sulfur reduction is a problem for many refiners. It is an onerous requirement to stay in business, yet there is no economic benefit gained. However, projects to accomplish sulfur reduction can be an opportunity to take advantage of innovative process technology to produce valuable petrochemicals that are otherwise missed.

Tier 3 (U.S.), Euro 5 (Europe, Middle East), and/or other similar regulations around the world are requiring the reduction of the sulfur content in finished gasoline to <10 ppm. FCC Naphtha is the dominant source of gasoline sulfur, and as a result, methods are developed to pre-treat the FCC feed or post-treat the FCC gasoline. The techniques for sulfur removal depend on the type of sulfur molecule. Mercaptans are easily removed by conversion to disulfides and extracted, or by mild hydrotreating. Sulﬁdes are relatively easy to remove by hydrotreating, and thiophenes are removed by more severe hydrotreating. As the sulfur requirement decreases to lower levels, nearly all of the incremental sulfur removed is of the thiophenic type, which requires more severe hydrotreating and results in unintended olefin saturation with commensurate octane loss. Each olefin molecule converted to the corresponding paraffin will lose approximately 20 octane numbers.
Figure 1 provides details about the distribution of sulfur and olefin species in FCC gasoline. Mercaptans are the dominant species in the lighter fraction, and thiophenes are dominant in the heavier cuts. Olefins are highest in the light fraction and lowest in the heavy fraction. Sulfur removal from the light cut is the easiest, and the heaviest fraction has hardly any olefins to matter in hydodesulfurization. However, there are significant thiophenic sulfur and olefinic hydrocarbons boiling in the mid-cut naphtha, which are the problem. The mid-cut is most susceptible to olefin saturation and octane loss via hydodesulfurization, when going to the new lower levels required.

**Figure 1:** Sulfur and Olefins distribution by boiling point
Another representation of this effect is shown in Figure 2. Note the olefins and sulfur components in the mid-cut naphtha boiling range, nominally covering the C₆-C₉ components.

**Figure 2:** FCC Gasoline – Olefins/Sulfur/RON Distribution
Conventional sulfur removal processes for FCC gasoline use hydrodesulfurization, in a scheme shown in Figure 3. The selective hydrogenation unit doesn’t remove sulfur, but simply shifts some species into the higher boiling fraction. The cut, which must have sulfur removed, also contains a large quantity of olefins that get saturated.

Similar to aromatics, the most difficult sulfur species to be removed by HDS are the thiophenic type, which are ring-shaped components. The novel method presented here is extraction of the sulfur along with the aromatics in the patented GT-BTX Plus® process using extractive distillation. The olefins are rejected from the aromatics as well as the sulfur, allowing the extract stream to be desulfurized even to 1 ppm with insignificant saturation of the hydrocarbons.

FCC Naphtha HDS units often include a selective hydrogenation unit (SHU), which selectively hydrogenates di-olefins, isomerizes olefins, and alkylates olefinic components with mercaptans into heavier disulfide compounds. This can be used in conjunction with GT-BTX Plus®. The heavier disulfides along with the extracted thiophenes combine together with the heavy-cracked naphtha for eventual desulfurization in the HDS reactor.
GT-BTX PluS® Process

In GTC’s design, we add a MCN draw (70-150º) from the naphtha splitter to feed into the GT-BTX PluS® process. This extractive distillation process uses the proprietary TECHTIV® DS solvent, which selectively increases the boiling point of thiophenic sulfur and aromatic components over the olefins and paraffins. This allows them to be rejected into a raffinate stream. The raffinate is greatly reduced in sulfur and aromatics. The extract, with aromatic and sulfur components, combines with the HCN (including the olefin-alkylated sulfides and disulfides) which then feeds the more severe HDS to achieve ULS gasoline.

The other advantage to the GT-BTX PluS® process is that olefins and H2S no longer co-exist in a hydrodesulfurization environment. Therefore, we avoid the chance of recombinant sulfur production, as is the case with the traditional FCC Naphtha hydrotreatment. Figure 3 below summarizes the GT-BTX PluS® process scheme.

Figure 4: GT-BTX PluS® scheme for FCC gasoline desulfurization
Octane
The obvious value proposition of GT-BTX PluS® is preservation of octane. Octane-barrel (bbl) costs are increasing. According to a recent report “Understanding Octane Value in America” by ADI Analytics’ Uday Turaga and Tyler Wilson, the value of an octane-bbl has risen significantly in recent years, presently in the range of $2.50-$3.50/bbl. Some of the reasons for the increase in octane-bbl costs are higher use of paraffinic crude oils having low octane, and higher compression automobile motors that require higher octane values. There is also a phase down on allowable aromatics in the gasoline pool, which otherwise would create more octane-bbls. The GT-BTX PluS® economics are still reliable, even with octane-bbl cost below $1.00.

In order to hydrotreat the thiophenic sulfur from FCC gasoline to <10 ppm, there will be olefin saturation resulting in an octane loss of 2-4 or more numbers.

![Figure 5: Dependence of the loss of octane number on the level of hydrosulfurization in HDS section of Prime G based on data by Axens](image)

At $3.00 per octane-bbl, a typical desulfurization unit would lose $20 million per year, for each drop in octane number. Selective HDS catalysts have undoubtedly improved over the years, but all of these will still saturate a significant amount of the olefins with commensurate octane loss, when going to the ultra-low sulfur gasoline.
Petrochemicals

Aromatics are being phased down in motor gasoline, but there is a continued demand for BTX in the petrochemical sector. GT-BTX PluS® automatically produces high quality aromatics after the HDS section and is rich in toluene, xylenes, and C9 aromatics, which can all be converted into paraxylene.

Additionally, this process creates a new stream, rich in olefins, but essentially void of sulfur and aromatics. The olefinic-rich raffinate from the GT-BTX PluS® process can go to any of three dispositions, each one having higher value than with the traditional processing scheme:

1) Process in a fixed-bed aromatization unit to generate additional aromatics. The C4 and C5 fractions from the FCC can also go to this unit.

2) Recycle to the FCC unit to re-crack into mainly propylene, or use a segregated unit such as Gasolfin™ to re-crack into propylene and butylenes.

3) Blend into gasoline as a low-sulfur, low-benzene fraction having higher octane value than from traditional systems.

The refiner should not destroy these in order to reduce the sulfur.

Figure 6: GT-BTX PluS® for Petrochemical Production
Application

Removal of aromatics and sulfur from cracked gasoline cannot be easily done with liquid-liquid extraction because of objectionable internal recycles of the olefins, and problems with phase separation. Instead, GT-BTX Plus® uses extractive distillation with the proprietary TECHTIV® DS solvent. TECHTIV® DS is stable and non-reactive with the unsaturated components, capable to operate with feed impurities, environmentally acceptable, and performs well across a wide boiling range of feed, thus providing the highest level of sulfur removal, with simultaneous rejection of olefins.

Figure 7: Liquid-Liquid Extraction vs Extractive Distillation system for extraction of sulfur with rejection of olefinic species. Objectionable recycles and phase separation problems occur with LLE.

Figure 8: An expanded rendition of the flow scheme
CAPEX and OPEX for a 1 MM ton per annum unit is:

<table>
<thead>
<tr>
<th>GT-BTX PluS®</th>
<th>1 MMTPA Unit, USGC Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX</td>
<td>23.0 MMUS$</td>
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<tr>
<td>OPEX</td>
<td>3.0 MMUS$</td>
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**Case Study**

At the beginning of 2016, a 400 KTA GT-BTX PluS® unit started up in Dongying, China. This unit was added as a drop-in to the scheme with an existing FCC gasoline HDS unit. After the addition of the GT-BTX PluS® unit, octane loss was reduced from 4.0 to 0.6; final gasoline sulfur content was reduced from the level of 600 ppm to 2-7 ppm; and H₂ consumption was reduced by 60%.

![Figure 9: GT-BTX PluS® unit in Dongying, China](image)
The GT-BTX PluS® configuration is quite simple. In this case, there were only three fractionating columns added, with re-use of the existing hydrodesulfurization reactor. Other schemes are also possible to conveniently retrofit. In the grassroots case, one may avoid the selective HDS section altogether and use a stand-alone GT-BTX PluS®.

![Diagram of GT-BTX PluS® configuration]

**Summary**

Removing sulfur from gasoline does not have to be a drain on refinery profitability. The key is to extract the sulfur species first, then hydrotreat only the extract. This way, the olefinic fraction does not go to hydrotreatment, which would cause substantial octane loss. The hydrotreated extract is an excellent feedstock for paraxylene production. The olefinic raffinate can go to simple aromatization to produce more aromatics; be cracked to produce propylene; or be blended into gasoline with very little change in octane value.

*Reduce sulfur. Preserve octane value. Produce petrochemicals.*
Engineered to Innovate

Richard Kolodziej PE, Joseph C. Gentry PE, and Sachin Joshi

GT-BTX Plus: Reduce Sulfur—Preserve Octane Value—Produce Petrochemicals

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