Abstract

Government regulations limiting the sulphur content of gasoline are being introduced throughout the world, and the limits that are being set are generally being phased in over several years. In most refineries, the FCC process is the major contributor of sulphur to the refinery gasoline pool. Because of this, the ability to reduce the sulphur content of FCC gasoline with catalyst additives is increasingly becoming of interest.

FCC gasoline reduction additives are a relatively new technology, and there has been a lot of development in this field over the last 5 years. During this time, an increasing understanding has also been gained of the mechanisms that are involved.

This paper will introduce the current state of art in terms of the additive technologies being used in the refining industry. It will also explain in general terms the mechanisms that are believed to be contributing to the effectiveness of these materials. Commercial examples will be given in order to demonstrate how to best take advantage of these technologies.

Background

Current and future legislation worldwide is forcing refiners to lower the sulphur in gasoline to ever lower levels. In Europe and Japan, for example, gasoline sulphur is expected to be limited to 10ppm with the enactment of proposed regulations. In the United States, the refiner’s gasoline pool sulphur level is currently limited to an average of 30ppm. In Saudi Arabia, although current domestic levels are relatively high, these are being reduced and the Kingdom also finds itself producing gasoline with much lower sulphur for export. Other countries around the world generally aim to harmonize their fuel and emissions regulations with Europe. With few exceptions, the trend around the world appears to be towards the eventual requirement for the production of a sulphur free gasoline (defined as less than 10ppm).

Typically, between a third and a half of a refiner’s gasoline pool comes from the Fluid Catalytic Cracker Unit (FCCU) but this stream contributes the greatest part of the sulphur; it can be as much as 90%. It is therefore obvious to look first to the FCC when reducing sulphur in the gasoline pool.

A sulphur balance around the FCCU, Figure 1, shows that sulphur distributions can vary widely depending on the feed type and processing history [1]. Typically, up to 10% of the feed sulphur ends up in gasoline; however, some refiners report levels as high as 20%.
Options to reduce the sulphur in FCC gasoline include:

- Reduce the end point of the gasoline stream. This will put the sulphur into the LCO stream and can be removed by an LCO hydrotreater. Penalties of doing this include a reduction of gasoline yield, loss of MON and a detrimental effect on the LCO cetane number.

- FCC feed hydrotreating is an option but involves very high capital expenditure.

- FCC naphtha treating also involves significant investment in equipment and can reduce gasoline octane through olefin saturation.

- Selecting low sulphur feed stocks can force the refiner into purchasing more expensive feeds and reduce cracking margin.

- Use an FCC catalyst additive. This involves zero or near zero capital investment and can either be used to reduce gasoline sulphur to acceptable levels by themselves, or allow lower severity in treating and thus preserving octanes and increasing treater run lengths.

This paper will concentrate on the use of FCC catalyst additives to reduce FCC gasoline.
**Gasoline Sulphur Species**

Typical full range FCC gasoline has sulphur in the form of mercaptans, sulphides, disulphides, thiophenes and benzothiophenes. Some of these are easier to remove than others and the ability to catalytically reduce sulphur content in FCC gasoline is limited by the molecular species that are present. The following table presents how easy to crack each species is:

<table>
<thead>
<tr>
<th>Percent of total gasoline sulphur</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptans</td>
<td>5%</td>
</tr>
<tr>
<td>Sulphides</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Disulphides</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Thiophenes</td>
<td>78%</td>
</tr>
<tr>
<td>Benzothiophenes</td>
<td>13%</td>
</tr>
<tr>
<td>Other</td>
<td>4%</td>
</tr>
</tbody>
</table>

Table 1 – Cracking of Different Sulphur Species in a Typical FCC Gasoline

The first group have the following structure:

- **Mercaptans**: \( R – S – H \)
- **Sulphides**: \( R – S – R \)
- **Disulphides**: \( R – S – S – R \)

Table 2 – Light Sulphur Species

These are primarily in the lighter fraction of the gasoline stream and can be cracked very easily on active catalyst sites. The sulphur is mostly liberated as \( \text{H}_2\text{S} \).

The thiophenes have these structures:

![Thiophenes Diagram](image)

Figure 2 - Thiophenes
And the benzothiophenes:

These last are present in the heaviest fraction of FCC gasoline (in the boiling range of about 220°C) and are very stable molecules, not easily cracked; the quality of fractionation can have big impact on their concentration in gasoline.

Using catalyst additives, it is typically easy to achieve reduction levels of above 90% for mercaptans and sulphides, liberating the sulphur as H₂S. The reduction levels for thiophenes typically vary from 30% to 40%. The most difficult species to remove are the benzothiophenes found in the heaviest portion of the gasoline. The formation pathways of gasoline sulphur compounds are complex. The sulphur compounds in the feed are converted to mercaptans, thiophenes, alkyl thiophenes and benzothiophenes. These can be further cracked into H2S as gaseous phase and Coke as solid form. [3]
**Early Sulphur Reduction Additives**

The first gasoline sulphur reduction additives from Intercat were developments of its bottoms cracking additive which was found to often reduce gasoline sulphur as a side effect. The first product was designated LGS-150 and the following commercial data demonstrate typical effects of this product [4].

These data are from a trial in a large US refinery in 2001. At 14% additive concentration, a reduction in gasoline sulphur of approximately 25% was observed. Figure 4 summarises the results.

To eliminate any variation in feed sulphur or gasoline cut point, gasoline sulphur (in ppm) is divided by feed sulphur (in weight percent) and plotted against the gasoline 90% boiling point. The data are further split into 0% to 9% LGS-150 in the unit catalyst inventory (actually all at zero except for two points), between 9% and 13% LGS-150 and above 13% (between 13.5 and 14.3).

![Figure 4 – Commercial Data of LGS-150](image)

The reduction in gasoline sulphur can clearly be seen in these data. What was further encouraging was that towards the heavier end of the gasoline the effect is more marked, demonstrating LGS-150 was reducing the heavier sulphur molecules. Note that this effect can also be used to allow increased gasoline yield at constant sulphur, i.e. moving to the left from the blue to the green lines.

However these benefits were not seen at all locations. Below is a table showing the variability in response of different refineries to this product in early trials.

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Location</th>
<th>Unit Type</th>
<th>Gasoline Sulphur Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery A</td>
<td>Japan</td>
<td>Modified Kellogg</td>
<td>25 – 30%</td>
</tr>
<tr>
<td>Refinery B</td>
<td>Mid West USA</td>
<td>UOP SBS</td>
<td>24%</td>
</tr>
<tr>
<td>Refinery C</td>
<td>Northeast USA</td>
<td>UOP SBS</td>
<td>3 – 5%</td>
</tr>
<tr>
<td>Refinery E</td>
<td>Mid West USA</td>
<td>UOP SBS</td>
<td>16%</td>
</tr>
<tr>
<td>Refinery F</td>
<td>Greece</td>
<td>-</td>
<td>29%</td>
</tr>
</tbody>
</table>

Table 3 – LGS-150 Trials Summary
Sulphur Removal Mechanisms

Additives can provide the most convenient and simple means of reducing sulphur levels but a more sophisticated approach was required if additives were to be used at more locations. The effectiveness of additives varies considerably from unit to unit depending on the feed quality, catalyst activity and operating conditions, thus a protocol of laboratory testing and evaluation of additives became an important factor in successful application of this technology to determine the right type of additive and its concentration for each FCC Unit.

Intercat considers there to be three main mechanisms for the reduction of sulphur in gasoline, namely dilution, inhibition and cracking. Intercat has several gasoline sulphur reduction technologies available, each of which exploits these mechanisms to different degrees.

Mechanism 1 - Dilution

This mechanism is most effective at lower conversions. It works by increasing the gasoline yields, thereby decreasing the overall percentage of sulphur levels in the gasoline. The net effect is a reduction in gasoline sulphur by increasing the gasoline yield with low sulphur material.

Mechanism 2 – Inhibition of Sulphur Species Formation.

Most of the sulphur species found in the gasoline are formed during cracking; they are not present in the feed. Two of Intercat’s additives contain active matrix structures. These enhance cracking reactions and change the reaction pathways thus inhibiting the formation of sulphur species without affecting gasoline yields.

In this category are Intercat’s LGS-150 and LGS-500 [5] additives. These additives both contain active matrix alumina sites. LGA-150 was developed from Intercat’s bottoms cracking additive as described above. Being predominantly a matrix material, it has an open pore structure which allows easy access to large refractory molecules. As the alumina sites in the matrix material are milder than those found in “Y” zeolite of conventional FCC catalyst, dehydrogenation to coke and benzothiophenes is less dominant. The large, sulphur containing molecules have a chance to catalytically crack to more valuable products and less difficult sulphur compounds. This mechanism is seen as more of a prevention of thiophenes than cracking them.

A secondary effect is the active alumina sites allow cracking of sulphur compounds themselves, whether they are originally in the fresh feed or products of the selective matrix cracking of the largest feed molecules. The lower rate of coking also allows the full height of the reactor riser for secondary cracking.

Furthermore, simple sulphur dilution occurs as described above. As these additives contain active matrix, they crack heavy oils and produce gasoline through normal catalytic cracking mechanisms. Thus more low sulphur gasoline is produced and the overall concentration of sulphur drops.

Mechanism 3- Cracking of Sulphur Species

In this mechanism the sulphur species are cracked after they are formed. The sulphur removed is released as H2S along with the dry gas. Intercat’s LGS-300 series of gasoline sulphur reduction additives are capable of removing up to 40% sulphur over the full range of FCC gasoline. Unlike other additives, LGS-300 works almost exclusively by a cracking mechanism. Consequently, gasoline sulphur is capable of being reduced with less dependence on the underlying feed and operating conditions. LGS-300 has no conventional cracking activity but functions through a proprietary active metal catalyst for cracking the sulphur species once formed.

The suitability of an additive solution for gasoline sulphur reduction has been found to vary with the particular feed and operating conditions of the FCC unit. A summary of Intercat’s gasoline reduction additives and their mechanisms are summarise in figure 5.
Gasoline sulphur reactions are very complex and not completely understood. Research is continuing to establish these mechanisms. Intercat is also developing sulphur species specific additives and the effectiveness of this technology continues to improve.

**Commercial Experience of Recent Additives**

Gasoline sulphur reduction additives are widely applied in the refining industry. The results of some of the commercial trials carried out at Indian Oil Corporation Mathura Refinery are outlined below [2].

The refinery was required to meet the Euro III gasoline sulphur specification of 150 ppm, down from the previous level of 500 ppm.

IOC Mathura along with their support group, IOC R&D, conducted a laboratory evaluation of various gasoline sulphur reduction additives. Following an R&D recommendation, Intercat's LGS-300 gasoline sulphur reduction additive was initially selected. Subsequently, a second trial was carried out using Intercat’s LGS-550.

**Performance with LGS-300**

In figure 6, the ratio of gasoline to feed sulphur has been plotted against the 95% boiling point of the gasoline. The data separate well and indicate a 35% or better reduction in gasoline sulphur from the use of LGS-300 at an addition level of 10%.
Commercial Trial Results with LGS 550

Following the successful use of LGS-300 to reduce gasoline sulphur content, Mathura refinery decided to proceed with a trial of LGS-550. In order to determine the optimum concentration to use, IOC R&D centre carried out a laboratory performance evaluation of LGS-550, targeting a 40% reduction in gasoline sulphur. IOC R&D carried out MAT experiments of LGS additive at 10% and 15% along with base catalyst at refinery operating conditions. The additive and base catalysts were hydrothermally deactivated at 810°C/5hrs with 100% steam. The results are presented in table 4.

<table>
<thead>
<tr>
<th>Product (wt %)</th>
<th>Base Case</th>
<th>10% LGS-550</th>
<th>15% LGS-550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas</td>
<td>2.35</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>LPG</td>
<td>12.4</td>
<td>11.6</td>
<td>11.8</td>
</tr>
<tr>
<td>Gasoline</td>
<td>33.6</td>
<td>34.2</td>
<td>33.7</td>
</tr>
<tr>
<td>HN</td>
<td>9.5</td>
<td>9.7</td>
<td>9.6</td>
</tr>
<tr>
<td>LCO</td>
<td>27.9</td>
<td>28.6</td>
<td>28.7</td>
</tr>
<tr>
<td>TCO</td>
<td>37.4</td>
<td>38.2</td>
<td>38.3</td>
</tr>
<tr>
<td>CLO</td>
<td>11.0</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Coke</td>
<td>3.3</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Conversion (wt %) 216°C</td>
<td>61.1</td>
<td>61.1</td>
<td>61.0</td>
</tr>
<tr>
<td>Sulphur reduction at constant gasoline yields</td>
<td>20%</td>
<td>38%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 - Laboratory Performance Evaluation of the LGS 550 additive

Based on this experimental work, IOC R&D department recommended LGS-550 for use at a concentration of 16 wt% of total catalyst additions.

This trial followed on directly from the LGS-300 trial so no further base load was felt to be necessary and LGS 550 additions were commenced at the same 10% addition rate.

The sulphur reduction results for the LGS-550 are shown in figure 7 along with the base case and LGS-300 data.

The graph is plotted with feed sulphur as the X-axis and the gasoline sulphur ppm on the Y-axis to see the relative effect of LGS-550. There is marked improvement in reduction of the gasoline sulphur levels.
in the range of 30% - 45% and above at concentration levels of 10-12% LGS in the unit. The results clearly demonstrate the possibility of even more reduction with LGS 550 at the same feed sulphur levels.

**Feed Sulphur Effects on Additive Efficiency**

At another location, LGS-561 was used to reduce FCC gasoline sulphur. This refiner uses a variety of feed stocks with varying levels of sulphur. They found that higher sulphur feeds allowed greater levels of sulphur reduction in the gasoline. This is shown in table 5.

<table>
<thead>
<tr>
<th>Feed Sulphur, wt.%</th>
<th>Gasoline/Feed Sulphur Ratio</th>
<th>Gasoline Sulphur Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 - 0.7</td>
<td>6.3</td>
<td>10%</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>5.6</td>
<td>20%</td>
</tr>
<tr>
<td>1.0 - 1.3</td>
<td>4.2</td>
<td>40%</td>
</tr>
</tbody>
</table>

Table 5 – Feed Sulphur Increases Reduction
Conclusions

With ever increasing pressures on refiners to reduce levels of sulphur in gasoline, the use of catalyst additives in FCCU’s can offer a cost effective way to lessen the amount of gasoline range sulphur molecules produced in the reactor riser. This may be sufficient to meet gasoline pool sulphur levels or allow treatment units to run at lower severities reducing octane loss and increasing treater run lengths.

Early trials of gasoline sulphur reduction additives gave fair reductions of sulphur in some units but were found to be less effective in others. Recent trials have shown the benefits of offering a range of additives which use different mechanisms of reduction and the advantages of laboratory additive selection studies before use in the FCCU.

Experience shows that whilst some vendors have a “one size fits all” approach for sulphur reduction additives, Intercat believes that testing is essential to selecting the optimum formulation for each location. The laboratory testing protocols to do this are not simple and considerable development and effort are required to carry them out correctly. Intercat is pleased to provide this service without charge for its customers.

Gasoline sulphur reduction additives are being continually improved through extensive R&D at Intercat’s research laboratories and are leading to a range of additives to target specific species of sulphur molecules.

References:

[5] LGS-150 and LGS 500 Intercat data sheets