A Look at Gasoline Sulfur Reduction Additives in FCC Operations

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Refcomm Galveston 2016
Drivers for Low Sulfur Additive

- Worldwide legislative drive for air quality improvements require modifications in fuel quality

- 90% of gasoline sulfur is derived from FCC gasoline

- Tier III coming in 2017-2020
  - 10 ppm gasoline sulfur

- BASF has developed and commercialized - Low Sulfur Additive (LSA) and NaphthaClean® (catalyst formulation) for improved FCC gasoline sulfur reduction
### Global Sulfur Standards

<table>
<thead>
<tr>
<th>Region</th>
<th>Sulfur Standard (ppm)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada</td>
<td>10 ppm</td>
<td>2017</td>
</tr>
<tr>
<td>EU</td>
<td>10 ppm</td>
<td>2009</td>
</tr>
<tr>
<td>Japan</td>
<td>10 ppm</td>
<td>2008</td>
</tr>
<tr>
<td>Russia</td>
<td>10 ppm</td>
<td>2016</td>
</tr>
<tr>
<td>China</td>
<td>10 ppm</td>
<td>2018</td>
</tr>
<tr>
<td>S. Africa</td>
<td>10 ppm</td>
<td>2017</td>
</tr>
<tr>
<td>US</td>
<td>10 ppm</td>
<td>2017</td>
</tr>
<tr>
<td>India</td>
<td>150 ppm</td>
<td>2010</td>
</tr>
<tr>
<td>Brazil</td>
<td>50 ppm</td>
<td>2014</td>
</tr>
<tr>
<td>Thailand</td>
<td>50 ppm</td>
<td>2012</td>
</tr>
</tbody>
</table>

In 2011,
- Two countries/regions at 10 ppm
- US at 30 ppm
- 3 at 150 ppm, 2 at 500 ppm, 1 at 1000 ppm
According to EPA, 108 refineries will be impacted.

- 40 refineries are either:
  - Meeting 10 ppm Sulfur Level
  - Will purchase credits to comply
  - Operating changes will be made to eliminate the need for credits

- 67 refineries are able to comply with modifications to their existing equipment - can occur in 2 yrs

- Only 1 refinery will require the installation of a new gasoline hydrotreater to comply - can be installed in 3 yrs
Existing Sulfur Treatment Options
US FCC Units

- None: 15%
- Feed pre-treat: 16%
- Gasoline post-treat: 35%
- Both: 34%
Refinery Feed S

Feed S vs Gasoline S

% OF REFINERIES

0% 5% 10% 15% 20% 25% 30% 35% 40%

FEED SULFUR WT%

0-0.25 0.25-0.5 0.5-0.75 0.75-1 1-1.5 1.5-2 >2

GASOLINE SULFUR - TOTAL (PPMW)

0 500 1000 1500 2000 2500 3000 3500 4000

FEED SULFUR WT%

0 0.5 1 1.5 2 2.5 3 3.5
Tight Oil Impacts

- Tight oils typically have lower sulfur than conventional crudes, along with other contaminants

<table>
<thead>
<tr>
<th>VGO cut properties</th>
<th>TX Shale</th>
<th>Bakken Core</th>
<th>WTI</th>
<th>Maya Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity</td>
<td>31.9</td>
<td>24.5</td>
<td>26.3</td>
<td>21</td>
</tr>
<tr>
<td>Sulfur wt%</td>
<td>0.18</td>
<td>0.27</td>
<td>0.46</td>
<td>2.05</td>
</tr>
<tr>
<td>Acidity mg KOH/g</td>
<td>0.049</td>
<td>0.053</td>
<td>0.095</td>
<td>0.085</td>
</tr>
<tr>
<td>Nitrogen wt%</td>
<td>0.01</td>
<td>0.11</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>Refractive index 67C</td>
<td>1.4588</td>
<td>1.4824</td>
<td>1.4759</td>
<td>1.498</td>
</tr>
<tr>
<td>Nickel ppm</td>
<td>0.09</td>
<td>0.47</td>
<td>0</td>
<td>0.64</td>
</tr>
<tr>
<td>Vanadium ppm</td>
<td>0.08</td>
<td>0.14</td>
<td>0</td>
<td>4.48</td>
</tr>
<tr>
<td>Con Carbon wt%</td>
<td>0.03</td>
<td>0.68</td>
<td>0.01</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Source: Shackleford, Hydrocarbon Processing Sept 2014
Sulfur Reduction Technologies Overview
FCC Gasoline Sulfur Reduction Options

- **Hydrotreating**
- **Cutpoint adjustment**
- **Catalyst technology**
- **Sulfur credit$**
FCC Gasoline Sulfur Reduction Options

- CFHTs reduce FCC feed sulfur by 70-90%
- FCC gasoline from CFHT'ed feed is typically 200-500 ppm sulfur
- High severity can reduce this to 75-100 ppm
- Higher severity means operating more in poly nuclear aromatic mode (PNA)
- Removes nitrogen and improves FCC performance
- High severity may mean catalyst life of only 1-2 years
FCC Gasoline Sulfur Reduction Options

- LSA/Naphthaclean may be used on a spot basis or in conjunction with other measures to reduce gasoline sulfur to the post-treater
- Could help avoid a capital investment / octane loss / hydrogen limitations
FCC Gasoline Sulfur Reduction Options

- EPA estimates that in 2009, 22% of refineries undercut to distillate
- 2018 estimate is 68% as result of Tier 3
- FCC gasoline volume estimated to drop 16%
- With the benefit of a 50% reduction in FCC gasoline sulfur
- Coincides with predictions for increased diesel demand
FCC Gasoline Sulfur Reduction Options

- Revamps of post-treaters are likely to be the source of most investment to meet Tier 3.
- Can achieve up to 99% sulfur removal, depending on naphtha sulfur content.
- In high naphtha sulfur content cases, post-treating might not be enough.
- Octane loss can be significant at high severity.
- Hydrogen requirements are not linear with sulfur reduction.
%FCC feed sulfur re-distributed to products

### Non-hydrotreated feed

<table>
<thead>
<tr>
<th>Sulfur Distribution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Light gases</td>
<td>40-50%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>5-15%</td>
</tr>
<tr>
<td>Bottoms+LCO</td>
<td>40-50%</td>
</tr>
<tr>
<td>Coke</td>
<td>5-10%</td>
</tr>
</tbody>
</table>

### Hydrotreated feed

<table>
<thead>
<tr>
<th>Sulfur Distribution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Light gases</td>
<td>30-50%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>2-10%</td>
</tr>
<tr>
<td>Bottoms+LCO</td>
<td>30-50%</td>
</tr>
<tr>
<td>Coke</td>
<td>15-30%</td>
</tr>
</tbody>
</table>

However, 90% of naphtha pool sulfur comes from the FCC.
Development of BASF’s Low Sulfur Additive

- Sulfur speciation method developed for understanding sulfur reduction chemistry

- Reactive compounds (mercaptans, sulfides, disulfides) are cracked to H₂S

- Refractory compounds (thiophenes, alkyl thiophenes, benzothiophenes) remain in FCC gasoline

- Compounds like dibenzothiophenes (DBT) and substituted DBT’s remain in the LCO and bottoms fractions
Feed sulfur compounds

Typical contribution of sulfur compounds in gasoline cut:

- Saturates: 6%
- Thiophene: 5%
- Alkyl Thiophenes: 65%
- Tetra hydrothiophene: 3%
- Benzothiophene: 21%

Typical Contribution of S Compounds in Naphtha Cut

- Saturates: Good conversion
- Thiophene: Reasonable conversion
- Alkyl Thiophenes: Minimal conversion
Gasoline Sulfur Distribution Concentration in Back End Due to Benzo-thiophenes
R&D Testing to Develop & Improve Gasoline Sulfur Reduction

Develop an additive with best gasoline sulfur reduction performance
## Sulfur Speciation Tool Used for Sulfur Reduction Additive Development

<table>
<thead>
<tr>
<th>S species</th>
<th>Base ECAT S (wppm)</th>
<th>LSA S (wppm)</th>
<th>S reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon disulfide</td>
<td>0.8</td>
<td>0.5</td>
<td>38</td>
</tr>
<tr>
<td>Ethylmethyl sulfide</td>
<td>0.3</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>0.6</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>n-hexyl mercaptan</td>
<td>0.5</td>
<td>0.3</td>
<td>40</td>
</tr>
<tr>
<td>Thiophene</td>
<td>27.0</td>
<td>15.4</td>
<td>43</td>
</tr>
<tr>
<td>2-methyl Thiophene</td>
<td>25.8</td>
<td>14.6</td>
<td>43</td>
</tr>
<tr>
<td>3-methyl Thiophene</td>
<td>34.7</td>
<td>17.7</td>
<td>49</td>
</tr>
<tr>
<td>Tetrahydro Thiophene</td>
<td>12.1</td>
<td>5.4</td>
<td>55</td>
</tr>
<tr>
<td>2-methyltetrahydro Thiophene</td>
<td>6.8</td>
<td>2.4</td>
<td>65</td>
</tr>
<tr>
<td>2-ethyl Thiophene</td>
<td>6.9</td>
<td>3.8</td>
<td>45</td>
</tr>
<tr>
<td>2,5-dimethyl Thiophene</td>
<td>7.9</td>
<td>4.7</td>
<td>40</td>
</tr>
<tr>
<td>3-ethyl Thiophene</td>
<td>20.5</td>
<td>10.3</td>
<td>50</td>
</tr>
<tr>
<td>2,3-dimethyl Thiophene</td>
<td>18.3</td>
<td>10.0</td>
<td>45</td>
</tr>
<tr>
<td>3,4-dimethyl Thiophene</td>
<td>9.6</td>
<td>4.7</td>
<td>51</td>
</tr>
<tr>
<td>C3s Thiophene</td>
<td>51.6</td>
<td>26.7</td>
<td>48</td>
</tr>
<tr>
<td>C4s Thiophene</td>
<td>40.6</td>
<td>19.1</td>
<td>53</td>
</tr>
<tr>
<td>Benzothiophene</td>
<td>133.8</td>
<td>114.3</td>
<td>14</td>
</tr>
<tr>
<td><strong>Gasoline S (wppm)</strong></td>
<td><strong>411.3</strong></td>
<td><strong>255.9</strong></td>
<td><strong>38</strong></td>
</tr>
</tbody>
</table>
BASF’s Low Sulfur Reduction
FCC Catalyst and Additive Technologies

- Two types of technologies for gasoline sulfur technology:
  - Zinc based: focused on coking sulfur containing compounds
  - Vanadium based: focused on cracking sulfur containing compounds

- Both are built upon BASF’s in-situ catalyst platforms

- Maximize H-Transfer of additive

- Catalyst base allows BASF technology to achieve maximum volume and value expansion

- Both technologies are available as both:
  - FCC catalyst solution – NaphthaClean
  - FCC additive – LSA (Low Sulfur Additive)

- BASF will work with the refiner to determine the best fit for the individual refiner’s needs
Opportunities to use FCC Catalyst and Additive Technologies

- Octane preservation through by-passing a portion of light gasoline
- During turnaround of Post Treatment or Pre Treatment Unit
- Improved flexibility of crude selection
- Reducing severity of existing equipment
- Reduced hydrogen availability
- Can be used on an ongoing basis or on a spot basis
Considerations for using FCC Catalyst and Additive Technologies

- 15-25% of LSA can reduce gasoline sulfur by 20-40%

- Level of gasoline sulfur reduction is impacted by:
  - Sulfur speciation (impacted by feed hydrotreating and crude)
  - Operating conditions
  - FCC catalyst

- Value of sulfur credits

- Effects on H2S and/or SOX emission handling

- Value of octane retention

- Value of turning down severity of hydrotreating equipment
Commercial Example #1: Naphthaclean reduces gasoline sulfur across the range.
Commercial Example #1: Naphthaclean reduces gasoline sulfur by >20%
Commercial Example #2: LSA reduces gasoline sulfur by 35%
BASF’s NaphthaClean and LSA can cost effectively remove sulfur from gasoline

- Gasoline sulfur reduction strategy based on existing refinery configuration, expectations in capital projects, and existing sulfur credits
- Cutpoint change is a good method for a quick fix, but must take into account product values (diesel vs. gasoline)
- Hydrotreating (pre- and post-) have tremendous benefits, but watch out for octane impacts
- FCC catalyst technology solutions can be tailored based on refinery needs and constraints
  - Expectations for 20-40% reduction in gasoline sulfur
  - LSA maximizes volume expansion as its based on BASF’s in-situ based catalyst
  - Proven, experienced technology for removing sulfur from gasoline