CHEMICAL SOLUTIONS FOR TODAY’S FCCU CHALLENGES

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Overview

FCCU Challenges

Cases
- Slurry Fouling Control
- Nickel Passivation

Other FCC Treatments

Conclusions
FCC Challenges

Processing of heavier feeds with increased Nitrogen, Metals and Salt content leads to:

- Corrosion
- Main Fractionator Top NH4Cl Fouling
- Catalyst Issues
- High Decant Oil Ash Content
- Slurry System Fouling
- High Coke and H2 Generation
- Other
Slurry Fouling

Impacts:
- Inadequate cooling/heat exchange
- Poor product recovery
- Hydraulic limitations
- Throughput limitations
- Cleaning/Maintenance Costs
- Safety/Reliability
Slurry Fouling Mechanism

- Condensation of aromatic fouling precursors to condensed/fused aromatic networks that can no longer stay dissolved in the slurry and fall out.

- Coking in main fractionator bottom caused by high bottom temperature and poor liquid distribution of the slurry return.

- Excessive catalyst fines carry-over from reactor can cause deposition in exchangers.

- Low liquid velocity can accelerate fouling rate. Maintain velocities in piping > 1m/s, in exchanger tubes >2m/s.
Stream Analysis - determination of catalyst fines content, PNA content, metals, solids, carbon content.

Stream Characterization - determines slurry stream’s tendency to foul. Quantifies aliphatic and aromatic content.

Deposit Analysis - Extremely important in diagnosis. Quantifies amount of organic vs inorganic foulant.

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>MARCH</th>
<th>JANUARY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, ppm</td>
<td>97</td>
<td>170</td>
</tr>
<tr>
<td>Cu/Fe, ppm</td>
<td>0.13/6.7</td>
<td>0.11/12.0</td>
</tr>
<tr>
<td>Solids (PTB)</td>
<td>390</td>
<td>1600</td>
</tr>
<tr>
<td>Ash, wt.%</td>
<td>0.143</td>
<td>0.19</td>
</tr>
<tr>
<td>Hexane Insolubles, wt.%</td>
<td>15.9</td>
<td>45.9</td>
</tr>
<tr>
<td>Ramsbottom Carbon, wt.%</td>
<td>12.2</td>
<td>14</td>
</tr>
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</table>
Deposit Analysis

Inorganic constituents are mostly associated with catalyst fines. To determine the true catalyst fines content of the deposit, the silicon and aluminum should be converted to the oxides.

<table>
<thead>
<tr>
<th>Elemental Analysis of 105°C Dried Sample</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>6.8</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6.2</td>
</tr>
<tr>
<td>Iron</td>
<td>6.2</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>2.3</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.8</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.6</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.7</td>
</tr>
<tr>
<td>Carbon</td>
<td>48</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Loss at 800 C</td>
<td>50</td>
</tr>
<tr>
<td>CH2Cl2 Extractables</td>
<td>12</td>
</tr>
</tbody>
</table>

Organic component is indicated by the C, H, and N, and by the loss at 800 C. The high carbon to hydrogen ratio indicates a high degree of fusion to form a coke-like deposit.
Slurry Fouling Control

- Root Cause determination
  - Slurry Characterization
  - Deposit Analysis
  - Lab scale evaluations

- Antifoulant Selection
  - Dispersants (organic, inorganic)
  - Coke inhibitors
  - Size limiters

- Monitoring
  - Fouling Resistance (Monitor)
  - Heat Transfer Coefficient
  - Pressure Drop
  - Fractionators Bottoms Temperature
  - Pump-around Rate
  - Steam Production
  - Cleanings per month/year
Dispersant Interaction

A simplified view of a stabilized slurry by synthetic resin additive

Polar Functional Group

Synthetic resin

Aromatic Sheet

Aliphatic Side-Chain

Polynucleo Aromatic (PNA)

= =

Synthetic resin-stabilized

PNA Colloid
Dispersant Testing
Case Study FCCU Slurry Fouling Control

- 380 t/h FCCU unit processing VGO and 15% Atres.

- DCO rundown exchangers started to foul rapidly and had to be cleaned weekly. The heat exchange capacity dropped 50% in 3 days.

- Normal DCO outlet temperature were 90-100°C, fouled the temperature increased to the maximum 120°C.

- The increased temperature gave slurry settling issues and the cleanings throughput limitations.
Case Study FCCU Slurry Fouling Control

Base Case Untreated
Case Study FCCU Slurry Fouling Control

- Samples of the slurry were investigated and indicated a high fouling potential with high fused aromatic content.
- Analysis of the fouling material indicated organic fouling.
- Lab evaluations determined EC3019A, a dispersant type antifoulant was most suited to treat the problem.
- Product was injected in the suction of the slurry P/A pumps and fouling immediately stopped.
- The return for the refinery is estimated at 3-8 million Euro.
Case Study FCCU Slurry Fouling Control

Treated with Antifoulant
Nickel Effects On FCCU Operation

 Deposited nickel acts as a dehydrogenation catalyst:
- increases hydrogen yield
- increases delta coke (and regenerator temperature)

Nickel deposits on outer edge of the catalyst particle and is relatively immobile

Nickel Activity
- Function of nickel concentration on equilibrium catalyst
- Function of catalyst type
  - pore volume and distribution
  - matrix composition
  - use of nickel encapsulation/agglomeration technology
- Function of nickel age
  - catalyst replacement rate
  - oxidation to less active species
  - interaction with catalyst matrix
# Ni and Sb Impact on FCC Yields

<table>
<thead>
<tr>
<th>Ni, ppm</th>
<th>100</th>
<th>2500</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb Used?</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Rx Temp, °F</td>
<td>980</td>
<td>980</td>
<td>980</td>
</tr>
<tr>
<td>Regen Temp, °F</td>
<td>1265</td>
<td>1285</td>
<td>1273</td>
</tr>
<tr>
<td>Cat/Oil</td>
<td>6.0</td>
<td>5.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Equil. MAT</td>
<td>70</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>Conv, vol%</td>
<td>81.5</td>
<td>79.9</td>
<td>80.8</td>
</tr>
<tr>
<td>C2 &amp; lighter, wt%</td>
<td>3.1</td>
<td>3.9</td>
<td>3.3</td>
</tr>
<tr>
<td>H2, wt%</td>
<td>0.05</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>5.6</td>
<td>5.7</td>
<td>5.6</td>
</tr>
</tbody>
</table>

**YIELDS, vol%**

<table>
<thead>
<tr>
<th>Product</th>
<th>100</th>
<th>2500</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>2.9</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Propylene</td>
<td>9.8</td>
<td>9.6</td>
<td>9.7</td>
</tr>
<tr>
<td>IC4</td>
<td>5.8</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>NC4</td>
<td>1.8</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>C4 Olefins</td>
<td>10.8</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Gasoline</td>
<td>62.2</td>
<td>60.5</td>
<td>61.9</td>
</tr>
<tr>
<td>LCO</td>
<td>14.0</td>
<td>15.0</td>
<td>14.4</td>
</tr>
<tr>
<td>Slurry Oil</td>
<td>4.5</td>
<td>5.1</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Sb Passivator Product

- Liquid product injected in hot feed to the riser
- Binds with Ni
  - e-cat Sb:Ni range 0.08 - 0.75
- 50 to 70% reduction of Ni effects
- Program benefits >> cost. 10 to 100:1 payout.
- Watch CO promoter usage (may increase 30%)
- Watch product fractions for antimony; Sb in LCO can poison Ni-Mo hydrotreater catalyst

- No residual sodium
  - some products on the market contain residual sodium
  - sodium is a catalyst poison

- Antimony toxicity?
  - used since 1976 with no environmental- or health-related issues
  - Sb$_2$O$_5$ not singled out; Sb$_2$O$_3$ suspected carcinogen
  - SbH$_3$ (stibine) not formed at unit temperatures
  - Ni and V much more toxic
  - Sb low leachability from catalyst
Case Study RFCC Nickel Passivation

- An RFCC processing 75 kbpd Atres was suffering from high dry gas make.
- Feed Metals content was very high with avg 13 ppm feed Ni and up to 6000 ppm Ni on E-cat.
- Unit was Wet Gas Compressor limited.
- Several Catalysts were tried but constraints remained.

- Nalco Nickel Passivation Plus® Program was selected.
- The passivator was injected in the feed to the riser with an initial high baseload dosage.
- The dry gas make and delta coke responded immediately with a sharp decrease.
- The refinery immediately used the spare capacity to increase throughput and severity.
Case Study RFCC Nickel Passivation

- WGC limitation reduced
- Throughput increased > 10%
- Severity and Conversion increased with several %
- Net result for the refinery >>10 M$/y
Other FCCU Treatments

- MF Tower top NH4Cl salt control/removal
- MF OVHD corrosion control
- Carbonate cracking control
- Feed Fe, Ca removal
- DCO catalyst fines removal
- Vanadium passivation
Thank You!

Questions?