Strategies for Mitigating Fouling in Refineries Processing LTO

May, 2015
Galveston, TX
LTO Effect On Crude Preheat Fouling

Throughput reduced due to required exchanger cleaning

Furnace Inlet Temperature Loss (°F) vs. Run Day

- ∆T
- ∆T Regression Without LTO
- ∆T Regression With LTO

Exchanger Cleaning

Not Processing LTO

Processing LTO

Run Day

0 200 400 600 800 1,000 1,200

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Impact On Crude Furnace Fouling When Processing > 90% LTO

Crude furnace run length from 2 – 4 years to < 180 days
Crude Unit Fouling

- **P: Waxes & Solids**
- **S: W/W, C&D, AF**

- **CRUDE STORAGE**

- **COLD PREHEAT**

- **DESALTER**
  - **P: Solids, Desalter Carry-over**
  - **S: Desalter Optimization & Chemical, C&D, AF**

- **ATMOSPHERIC FURNACE**
  - **P: Asphaltenes, Solids, PAH**
  - **S: AF, Velocity, Exit Temp, Pass Balance**

- **TOWER**

- **VACUUM TOWER**
  - **P: Asphaltenes, Solids, PAH**
  - **S: C&D, AF, Velocity**

- **VACUUM FURNACE**

- **P: Amine Salts, Phosphorous**
  - **S: AF, Salt Dispersant, Acidification, Caustic**

- **Customer Profits**
Mechanical & Operational Possible Causes

- Poor desalter operation
- Chemical additive treatment (caustic, etc.)
- Low excess $O_2$ rates
- Flow imbalance between passes
- Poor heat distribution

- Inadequate mass velocity
- High heat flux
- Excessive vaporization in the crude preheat and heater
- High furnace $\Delta T$
Operational Considerations > 90% LTO

- Increased vaporization can result in deposition of solids
- Increase in furnace outlet temperature of 10 – 40°F corresponded with 50 – 600% higher fouling rates
- Higher levels of excess O2 can improve the heat distribution, and low excess O2 can result in soot formation which can impact tube outside diameter fouling.
  - Excess O2 > 2% recommended
Root Cause Analysis: Fouling Mechanism

- Deposit analysis
  - Identify and quantify elemental components
  - Interpret organic and inorganic nature
- Stream characterization
  - Identify and quantify fouling precursors
- Fouling simulation and Chemical selection
  - Simulate process fouling (mechanisms)
  - Screen chemicals
- Together help describe probable fouling mechanisms
## Typical Deposit Analysis LTO Fouling

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Downstream of desalter (100% LTO)</th>
<th>Upstream of crude furnace (LTO, WTI, Canadian Blend)</th>
<th>Atmospheric Tower Bottoms (100% LTO)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organic Materials</strong></td>
<td>11.00%</td>
<td>88.23%</td>
<td>73%</td>
</tr>
<tr>
<td>Soluble Organics</td>
<td>5.00%</td>
<td>52.00%</td>
<td>24%</td>
</tr>
<tr>
<td>Coke, polymers</td>
<td>6.00%</td>
<td>36.23%</td>
<td>49%</td>
</tr>
<tr>
<td><strong>Inorganic Materials</strong></td>
<td>89.70%</td>
<td>7.71%</td>
<td>18%</td>
</tr>
<tr>
<td>Iron Salts:</td>
<td>40.60%</td>
<td>5.67%</td>
<td>9.30%</td>
</tr>
<tr>
<td>Other Salts including Volatile Salts:</td>
<td>49.10%</td>
<td>2.05%</td>
<td>8.70%</td>
</tr>
</tbody>
</table>

| Probable Mechanism        | Solids carry-over from desalter   | Asphaltene destablization                          | PAH formation                       |

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# Crude Characterization Eagle Ford Blend

## Cation Concentration (ppm)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>1.2</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.0</td>
</tr>
<tr>
<td>Iron</td>
<td>13.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>3.1</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>6.8</td>
</tr>
</tbody>
</table>

## Characteristic Measurement

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>32%</td>
</tr>
<tr>
<td>Polar</td>
<td>2.1%</td>
</tr>
<tr>
<td>Aromatic</td>
<td>8.4%</td>
</tr>
<tr>
<td>Asphaltene</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Acid No.</td>
<td>0.11 mg KOH / g</td>
</tr>
<tr>
<td>Solids</td>
<td>63 ptb</td>
</tr>
<tr>
<td>Water</td>
<td>0.1%</td>
</tr>
<tr>
<td>BS&amp;W</td>
<td>0.2%</td>
</tr>
<tr>
<td>NMR Aromatic Carbons</td>
<td>13.3 mole%</td>
</tr>
</tbody>
</table>

Solids, Iron, & Ni + V a concern

Porphyrin Metals V, Ni, Fe
ATB Contaminants in LTO

Highly variable V level

Correlated to increased heater fouling

Effect Of ATB V On Fouling Rate

Normalized TMT Slope (°F/Day)

ppm

Run Day

Eagle Ford V ATB
Bakken Blend V ATB

V In ATB
Crude Oil Compositional Analysis

- Crude Oil
  - Pentane or heptane
  - De-asphalted Oil
    - Alumina
      - Oils
        - Alumina
          - Saturates
            - SARA: hydrocarbon structure differences by solubility & chromatography
          - Aromatics
    - Resins
      - Asphaltenes

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Crude Oil Components
Insoluble In $N$-Alkane “Non-solvent”

Plausible Asphaltene Structure

Plausible Polycyclic Aromatic Hydrocarbon (PAH) Structure

“Aromatic sheets”
Molecular Interactions In Crude Oil

A simplified view...

“Sea” of saturates & aromatics

Resin-Stabilized Asphaltene Colloid

Polar Functional Group

Aromatic Sheet

Aliphatic Side-Chain

Resin

Asphaltene
Colloidal Instability Index
SARA Analysis Column Chromatography

<table>
<thead>
<tr>
<th>Measurement</th>
<th>EF Blends</th>
<th>Bakken Blends</th>
<th>Permian Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>32 - 43%</td>
<td>29 - 37%</td>
<td>28 - 42%</td>
</tr>
<tr>
<td>Polar (resins)</td>
<td>&lt; 1 - 2%</td>
<td>1.4 - 3%</td>
<td>1.9 - 2.6%</td>
</tr>
<tr>
<td>Aromatic</td>
<td>2.1 - 8%</td>
<td>8 - 8.8%</td>
<td>8.2 - 9.5%</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Colloidal Instability Index</td>
<td>&gt; 3.0</td>
<td>2.6 - 3.6</td>
<td>2.6 - 3.7</td>
</tr>
</tbody>
</table>

The SARA analysis results in the loss of volatile species, which can include both saturates and aromatics. Because of the material loss, the CII is never used in isolation, but instead used in conjunction with other test methods to better understand relative stability risks. Generally, a CII greater than 1.2 is considered a potential stability risk.

Colloidal Instability Index = \( \frac{(\text{saturates} + \text{asphaltenes})}{(\text{aromatics} + \text{resins})} \)
Crude Stability Analyzer

- Intrinsic stability “S” concept as per ASTM D 7157
- Simple to operate, repeatable results
- Results obtained in about 20 minutes
  
  \[ S = \text{Stability} \]
  
  \[ S_o = \text{Solvency Power of Oil} \]
  
  \[ S_a = \text{Asphaltene Solubility} \]
Unconventional Crude Blending

Blending heavier asphaltenic crudes with LTO can result in reduced stability.
Blending Order: Heavy and Light

Blending order matters. Adding heavy asphaltenic oil to LTO will result in lower stability. Tankage sludge buildup, desalter emulsion growth, and increased fouling can result.
Analysis of a LTO Blended Crude Sample

Precipitant is polar aromatic

Thermal Stressing results in reduced stability

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>84</td>
</tr>
<tr>
<td>H</td>
<td>7.8</td>
</tr>
<tr>
<td>N</td>
<td>0.9</td>
</tr>
<tr>
<td>S</td>
<td>6.3</td>
</tr>
</tbody>
</table>
100% LTO Furnace Simulation

Foulants are typically 0.2 – 40 pounds / 1000 barrels in the crude based on HLPS deposit weight.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>HLPS Deposit</th>
<th>Field Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2 - 18%</td>
<td>4 - 15%</td>
</tr>
<tr>
<td>S</td>
<td>6 - 17%</td>
<td>4 - 11%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5 - 0.6%</td>
<td>0.5 - 1.5%</td>
</tr>
<tr>
<td>C</td>
<td>51 - 78%</td>
<td>54 - 73%</td>
</tr>
<tr>
<td>H</td>
<td>5 - 7%</td>
<td>2.3 - 7.8%</td>
</tr>
<tr>
<td>N</td>
<td>0.8 - 2.7%</td>
<td>0.3 - 1.6%</td>
</tr>
<tr>
<td>C:H</td>
<td>10 - 13</td>
<td>8.7 – 13</td>
</tr>
</tbody>
</table>

HLPS Test Equipment
PNA Formation (Coking) Mechanisms

Paraffin Cracking

Paraffin molecules crack, form olefins, reform into cyclic molecules and aromatize when forming PAH.

\[ RCH_2CH_2CH_2CH_2CH_3 \rightarrow RCH_2CH_3 + CH_2=CHCH_3 \]

Aromatization

Existing resins, cyclic molecules and aromatic molecules fuse and dehydrogenate when forming PAH.

Fusion and Dehydrogenation

Existing resins, cyclic molecules and aromatic molecules fuse and dehydrogenate when forming PAH.
Mechanism Summary

- Foulants are typically 0.2 – 40 pounds / 1000 barrels in the crude based on HLPS deposit weight.
- The strength of the asphaltene-resin interaction can be reduced through blending operations and thermal stressing.
- LTO reduces stability of crude blends which can lead to asphaltene deposition.
- LTO can form PAH molecules which deposit due to poor oil solvency power.
- Improving the crude’s oil solvency power or the use of stabilizing additives can reduce the fouling rate associated with processing light tight oils.
Mitigation Strategies

Mechanical Options
- Preflash columns
- Add heat transfer surface area
- Change exchangers from parallel to series to increase velocities
- Helical baffles
- Twisted tube exchangers

Operational Options
- Clean exchangers
- Lower furnace exit temperature
- Balance passes on tube metal temperature
- Optimize desalter
- Change crude diet
- Increase pumparound rates
Chemical Options

- Chemical Cleaning
- Desalter solids removal aids
- Caustic reduction
- Dispersants
- Coke suppressants
100% Eagle Ford Crude Furnace Case Study

Crude Furnace HLPS Study
> 90% LTO

- 45% improvement in deposit weight
- 94% reduction in $\Delta T$

![Graph showing the comparison between untreated and treated crude furnace HLPS study. The treated curve shows a 94% reduction in deposit weight compared to the untreated curve. The graph plots $\Delta T$ against time (min) with a significant improvement observed.]
> 90% Eagle Ford Crude Furnace

Improving stability reduced the fouling rate 70%

Crude Heater - Normalized TMT Change

- Normalized TMT Change Untreated
- Normalized TMT Change Treated

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Recommended Monitoring

- Heat transfer modelling
- Furnace monitoring
- Filterable solids testing (ASTM D-4807)
- Crude intrinsic stability testing (ASTM D-7157)
- Deposit analysis
- Economic evaluation
Fouling Control Program Evaluation Tips

- Evaluate changes on a $ / BBL or $ / year basis for comparison purposes
- Remember that garbage in = garbage out for simulation software
- Normalized Furnace Inlet Temperature (NFIT) is industry standard method for evaluating network fouling
  - Fouling factors are more independent than U values
    - \( R_f = \frac{1}{U_{\text{actual}}} - \frac{1}{U_{\text{clean}}} \)
  - Shell Duty \( \neq \) Tube Duty in practice so reconciliation is important
  - LMTD applies only to single pass exchangers, Ft correction factor is required for all others
- Don’t forget about network effects when evaluating exchanger cleaning priorities
Network Fouling Monitoring

- Furnace Inlet Temperature (FIT) – good measure of network fouling
- Great deal of “noise” in FIT data
- Therefore, normalize the FIT to evaluate fouling
Cleaning Economics

- Total Cost of Operation (TCO)
  - optimum cleaning cycles for each exchanger
  - minimum annualised cost of fouling
    - savings from cleaning – cost of cleaning
  - compare with scheduled cleaning
  - costs if cleaned now
  - include antifoulant cost