New Technology Controls
High Temperature Coker
Heater Fouling

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Discussion Topics

1. Impact of fouling on DCU and refinery operations
2. Coker heater fouling mechanisms
3. Stages of fouling
4. Design of custom MILESTONE™ additive programs
5. Coking Stability Index (CSI)
6. Case histories
7. Summary

MILESTONE
MILESTONE is a trademark of Baker Hughes Incorporated
Economic Impacts of Coker Heater Fouling

Throughput Losses
2-5% ~ $5 MM

Conversion Losses
1% ~ $3 MM

De-coking Costs
$25K - $50K/coil

Increased Fuel Usage
2% > $200,000

Reduced Flexibility
Can be > $5 MM

E, H & S Concerns

(All Values Based on Typical 40,000 B/D Unit)

Coker Heater Design & Operation

- Operating Parameters Affecting Coking Rates
  - Fluid velocity
  - Continuous throughput

Continuous Flow and Adequate Velocities are Critical to Good Operations!
Coker Heater Design & Operation

- Operating Parameters Affecting Coking Rate
  - Heater Outlet Temperatures
  - Uneven Heat Distribution - “Hot Spots”
  - Poor Flow Distribution

Feed Factors Impacting Fouling

- Asphaltene content and stability
  - Higher asphaltene content leads to more coke generation in the coils
  - Low stability feeds result in increased fouling

- Content of solids/inorganics
  - Corrosion by-products
  - Filterable solids and salts
  - Sodium concentration
Sources of Inorganic Materials

- Iron sulfide, rust (corrosion by-products)
  - Crude oil storage and transmission
  - Upstream process units
- Salts: sodium, calcium, and magnesium chlorides
  - From crude oil producing formation
  - Brine contamination from transportation
- Caustic
  - NaOH injections into desalted crude
- Clay, dirt, catalyst fines
  - From producing formation
  - From upstream process units

Asphaltene Micelle In Solution

- Resins
- Asphaltene Core
Asphaltene Destabilization

- Readily destabilize when subjected to stress
  - Changes in pressure, temperature, pH and solution environment can cause destabilization
  - Can occur when oils are blended and processed
- Disruption of asphaltene – resin interaction
- Thermal cracking conditions (>400°C) cause progressive loss of asphaltene solubility in the bulk oil phase
- Asphaltenes loose paraffinic side-chains and naphthenic portions are de-hydrogenated to aromatic rings

Thermal Decomposition of Oil

- Concentration of paraffin compounds increases
- Resins are partly lost due to conversion to asphaltenes
- Naphthenes become aromatic
- Aromatics condense to form asphaltenes – lose solubility in bulk oil

[Chemical diagrams showing the process of asphaltene destabilization and thermal decomposition of oil]
Asphaltene Precipitation

Stress

Asphaltene Destabilization & Disruption of Resins

Aggregation

Deposition

Degradation

Hot Tube Surface

Stages of Fouling

• Initial layer formed on tube surface
  - Metal catalyzed coking
  - Fast - at the startup of the unit when coils are clean and metal is exposed

• Secondary layer of deposition
  - Decreased asphaltene solubility in bulk oil
  - Thermal breakdown of asphaltenes
  - Precipitation of thermally converted asphaltenes or coke
  - Slower
MILESTONE™
Fouling Control Additive Technology

Stabilize Asphaltenes

Withstand High Temperatures

Program Success Requirements

Polar functionality to adsorb on active metal sites

Disperse Inorganic & Organic Particles

Additive Program Design

- Feedstock characterization test protocols
- Deposit characterizations
- Property ratios, correlations with fouling tendency
- Development of the Coking Stability Index
- Benchmark fluid characteristics with others in data base
CSI Coking Stability Index

- Predictive tool for determining fouling potential and rate of fouling
- Uses an NIR laser to detect the onset of asphaltene precipitation
- Titration technique with non-solvent
- Used in conjunction with oil characterizations to determine stability of coker feed
- Chemical additive screening

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<table>
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<tr>
<th>Coker Feed</th>
<th>Furnace Run Length</th>
<th>CSI</th>
<th>Asphaltenes/Resin Ratio</th>
<th>Saturate/Aromatic Ratio</th>
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<tr>
<td>Canadian</td>
<td>2.4 Months</td>
<td>99.5</td>
<td>0.348</td>
<td>2.63</td>
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<td>Midwest</td>
<td>5.0 months</td>
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<td>West Coast</td>
<td>9.0 Months</td>
<td>192.0</td>
<td>0.458</td>
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</tbody>
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CSI Coker Stability Index
Furnace Feed Stability

![Graph Showing CSI Coker Stability Index](image)
Fouling Control Technology:
MILESTONE Additives

MILESTONE Additive Technology:
- Interacts with metal surfaces to reduce catalytic effects on surface coking reactions
- Stabilizes compounds in the feedstock to inhibit their precipitation
- Disperses organic & inorganic particles

MILESTONE Technology:
Pilot Scale Demonstrations

- JIP – Joint Industry Project, Using Department of Energy (DOE) Pilot Delayed Coking Unit (University of Tulsa)
  - Investment by major refiners to study coker operating variables, including coker heater fouling
  - Pilot unit studies confirmed suspected heater fouling mechanisms
  - Pilot unit tests also confirmed efficacy of Baker Petrolite fouling control technology
Case Histories – Refinery A

Improvements obtained with MILESTONE Program

- Throughput increase from 15,000 BPD to 19,000 BPD
- Tube skin temperature increase to 0.7°C/day, still less than target 0.8°C/day

Case Histories – Refinery A

MILESTONE Technology Case History

Tube Skin Temperature Increases

- With MILESTONE Program & Heater Outlet Temperature Reduced by 3°C
- With MILESTONE Program & Normal Heater Outlet Temperature
Summary

- Delayed coker furnace fouling is a complex phenomenon involving heavy hydrocarbon compounds and inorganic materials.
- Two stages of fouling: initial catalytic stage and thermal or steady-state stage.
- Costs of delayed coker furnace fouling can be significant especially when throughput is restricted either during operation or during de-coking cycles.

Summary

- The Baker Petrolite research group has developed a successful mitigation program for delayed coker furnace fouling.
- A multi-component program is utilized to combat the various mechanisms of heater fouling.
- Treatment programs have been used in several applications with outstanding results.
Thank You for Your Attention!

Any Questions?

MILESTONE
Heater Fouling Control