Fouling mitigation on the Preheat, Furnace Convection Section and vaporizer

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Presentation Outline

• Potential problems affecting plant efficiency

• VCM and Coke Reaction Mechanisms

• Factors influencing the Fouling

• How to mitigate the fouling on the preheat, furnace convection section and vaporizer

• Case Histories
• Potential problems affecting plant efficiency

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• Case Histories
EDC/VCM Plant Process

EDC Manufacture

1. \( \text{CH}_2=\text{CH}_2 (g) + \text{Cl}_2(g) \xrightarrow{\text{FeCl}_3, \Delta H<0} \text{ClCH}_2\text{CH}_2\text{Cl} (l) \)

2. \( \text{CH}_2=\text{CH}_2 (g) + 2 \text{HCl} + 1/2 \text{O}_2 \xrightarrow{\text{CuCl}_2, \Delta H<0} \text{ClCH}_2\text{CH}_2\text{Cl} (g) + \text{H}_2\text{O} \)

VCM Manufacture

\( \text{ClCH}_2\text{CH}_2\text{Cl} (g) \xrightarrow{\text{heat, } 500^\circ\text{C}} \text{CH}_2=\text{CHCl} (g) + \text{HCl} \)
Mechanism 1: Radical Chain Reactions: 3 steps

Cl· catalyzed reaction mechanism

• Initiation: Cl· Radical generation

\[
\begin{align*}
& \text{CH}_2\text{ClCH}_2\text{Cl} \quad \text{CCl}_4 \\
\rightarrow \\
& \text{CH}_2\text{ClCH}_2\cdot + \text{Cl}\cdot \\
& \text{CCl}_3 \cdot + \text{Cl}^-. 
\end{align*}
\]

• Propagation: Abstraction of H by Cl·

\[
\begin{align*}
& \text{CH}_2\text{ClCH}_2\text{Cl} + \text{Cl}\cdot \\
\rightarrow \\
& \text{CH}_2\text{ClCHCl}\cdot + \text{HCl}. 
\end{align*}
\]

• Termination: Decomposition to VCM

\[
\begin{align*}
& \text{CH}_2\text{ClCHCl}\cdot \\
\rightarrow \\
& \text{C}_2\text{H}_3\text{Cl} + \text{Cl}-. 
\end{align*}
\]
VCM Reaction Mechanisms

Mechanism 2: Thermal Decomposition

\[ \text{CH}_2\text{ClCH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{HCl} \]

By-Products

1,1,2-trichloroethane \( \text{CHCl}_2\text{-CH}_2\text{Cl} \)
1,2-dichloroethylenes \( \text{CHCl}=\text{CHCl} \)
chloral (trichloroacetaldehyde) \( \text{CCl}_3\text{-CHO} \)
1,1,-dichloroethane \( \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \)
ethyl chloride \( \text{C}_2\text{H}_5\text{Cl} \)

Methyl chloride \( \text{CH}_3\text{Cl} \)
Dichloromethane \( \text{CH}_2\text{Cl}_2 \)
Chloroform \( \text{CHCl}_3 \)
Carbon tetrachloride \( \text{CCl}_4 \)
Chlorinated tars

Contaminants precursor of coke

- Acetylene (major) \( \text{C}_2\text{H}_2 \)
- 1,1,2-trichloroethane \( \text{CHCl}_2\text{-CH}_2\text{Cl} \)
- Butadienes \( \text{C}_4\text{H}_6 \)
- Chloroprene \( \text{C}_4\text{H}_5\text{Cl} \)
- Vinylacetylene \( \text{C}_4\text{H}_4 \)
- Methylchloride \( \text{CH}_3\text{Cl} \)

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VCM Reaction Mechanisms

- CCl₄ is a promotor

  \[
  \text{CCl}_4 \rightarrow \text{CCl}_3 + \text{Cl}^{-}
  \]

  Increase in Cl⁻ radical formation

  \[
  \rightarrow \text{C}_2\text{H}_3\text{Cl} \text{ conversion}
  \]

  \[
  \rightarrow \text{Coke formation}
  \]

  Coking

  - increase in the heat transfer resistance and
  - pressure drop

  - decrease in process efficiency and VCM selectivity

- EDC Conversion at the range 54 to 58+% 

- CCl₄ around 200 to 600ppm
Organic Fouling

- Cracking of EDC and other chlorinated organics due to heat and catalyzed by iron promoting polymerization
- Precipitation or loss of solubility of high molecular weight organics (Heavies $T_4/T_{4+}$)
- Coke from upstream

Typical deposit analysis:
- Loss on Ignition (550°C) 98%
- MeCl$_2$ Solubles 20%
- MeCl$_2$ Insolubles 80%
- % Carbon 40-80%
- % Hydrogen 1-2%
- % Chlorine 10-37%
- % Nitrogen <0.5%
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Factors influencing Fouling

- Heat Flux and high TMT (tube metal temperature)
- High amount of water and contaminants (acetylene, butadiene, chloroprene, vinylacetylene, methylchloride, chloral, Tri 1,1,2...)
- Iron Concentration ($FeCl_3/FeCl_2$)
  - Catalyst of Cracking Increases Fouling
- Purge Flow Rate
  - Low Flow → Increased Fouling
  - High Flow → Decreased Fouling
- Liquid level
  - Too Low → Fouling on Liquid/Vapor Interface
  - Too High → Longer Residence Time
Factors influencing Fouling
Impact of Iron

Test Method: Iron added to 1,2 EDC, heated to 120°C under nitrogen purge 2 hours, evaporated to dryness

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Fe form</th>
<th>ppm Fe</th>
<th>mg Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 ml EDC</td>
<td>None</td>
<td>None</td>
<td>15.4</td>
</tr>
<tr>
<td>2</td>
<td>10 ml EDC</td>
<td>FeCl$_3$</td>
<td>5000</td>
<td>700</td>
</tr>
</tbody>
</table>
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Methods to Reduce Fouling

• Use saturated steam in reboilers

• Maintain proper liquid level control

• Minimize water contamination of crude EDC

• Control corrosion on wash water and head column overheads and minimize steam leaks

• Maintain proper control of ferric chloride feed to the reactor

• Filtration

• High molecular weigh Dispersant
<table>
<thead>
<tr>
<th>Features</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly surface active chemistry</td>
<td>Prevents deposition of solids</td>
</tr>
<tr>
<td>Inorganic and Organic dispersant functionality</td>
<td>Effective fouling control of both salt deposition and entrapped HC</td>
</tr>
<tr>
<td>Prevents agglomeration of solids</td>
<td>Protection for downstream equipment</td>
</tr>
<tr>
<td>Cleanup capability at high dosages</td>
<td>Provides ability to respond to upsets</td>
</tr>
<tr>
<td>Process compatibility</td>
<td>Eliminates concerns for downstream contamination</td>
</tr>
<tr>
<td>Low water content</td>
<td>Eliminates corrosion concern</td>
</tr>
<tr>
<td>Used in all the designs</td>
<td>Proven technology</td>
</tr>
</tbody>
</table>
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Application Case
Preheat, Furnace Convection Section & Vaporizer

- High Pressure design
- Iron contamination in EDC going to the cracking furnaces

- Fouling on the preheat exchangers, furnace convection section & Vaporizer
- 1 cleaning of the convection section between 2 cleanings of the radiant section
- Outlet temperature of the convection section limited to 220°C

Economical impact
- Unplanned shutdown
- EDC feed reduction to furnace
- Loss in production
Preheat, Furnace Convection Section and Vaporizer

- EDC
- VCM Furnace
- Hot Quench Tower

Dispersant

EDC Vaporizer

Blowdown
Preheat, Furnace Convection Section and Vaporizer

EDC Vaporizer

Dispersant

VCM Furnace

Hot Quench Tower

to distillation

to Heavy ends

100°C

220°C

235°C

500°C

EDC

Blowdown

bottleneck

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EDC/VCM Cracking Furnace Convection Section

Delta T trend (°C)

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Results

- No shutdown for cleaning before furnace radiant decoking (preheat/convection)
- Increase in throughput due to rise in preheat outlet temperature (from 220 to 245 °C)----5% VCM production increase
- Runlength 5 year on the vaporizers
- Maintenance overcost reduction
- Reduced Personnel Exposure to toxic deposits
- Reduce hazardous waste disposal costs

TOTAL SAVINGS : 27000+ t/y VCM
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