Preparing for Bottom-of-the-Barrel Vessel Entry
Venezuelan Coker Unit Emergency Shutdown

Dr. Steve. Matza – Chief Scientist
Bottom-of-the-Barrel Vessels

1. Bottom of the Barrel Background
2. Venezuela Coker TAR Case Study
3. Bottom-of-the-Barrel Cleaning Options
4. Bottom of the Barrel TAR Best Practice
Where is the Bottom-of-the-Barrel?

- VDU
- Deasphalting
- Visbreaker
- Coker
- FCC
- Hydrocracker

Source: 2016 John Jechura, Colorado School of Mines
## What is Bottom of the Barrel?

<table>
<thead>
<tr>
<th>Crude Fraction</th>
<th>Number of Carbons</th>
<th>Boiling Point (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>1-4</td>
<td>&lt;32</td>
</tr>
<tr>
<td>Light Naphtha</td>
<td>5-7</td>
<td>80-200</td>
</tr>
<tr>
<td>Heavy Naphtha</td>
<td>6-10</td>
<td>200-350</td>
</tr>
<tr>
<td>Kerosene</td>
<td>10-15</td>
<td>350-550</td>
</tr>
<tr>
<td>Light Gas Oil</td>
<td>13-18</td>
<td>400-650</td>
</tr>
<tr>
<td>Heavy Gas Oil</td>
<td>16-40</td>
<td>600-1050</td>
</tr>
<tr>
<td>Residuum</td>
<td>&gt;40</td>
<td>&gt;1050</td>
</tr>
</tbody>
</table>

Case Study

Coker Unit Turnaround - Venezuela
Venezuela Coker Decontamination

Project

- Decontamination of the main fractionator coker column at a Venezuela refinery
- Main goal; eliminate delays in vessel entry by minimizing manual and mechanical cleaning activities of the tower

Challenge

- Large amounts of coke, \( \text{H}_2\text{S} \), and pyrophoric concerns
Past Procedure

- Traditional chemical cleaning every 4 years with 6 different hazardous chemicals requiring full body suits
- Chemicals circulated over an average of 36 hours
- Required 12 man crew per shift and 5 days of mechanical preparation

Past Procedure Results

- Left a tarry residue at the bottom of the tower up to 2 feet over the lower manway, completely burying bottom distributor
- Extensive mechanical cleaning was required under fresh air
- Leakage from chemical hoses required ground clean up
- Entry permits were delayed until all cleaning tasks were complete
Options

- Available refinery materials; BTX, heavy aromatic naphtha (HAN), gas oil, kerosene
- Chlorinated solvents
- Traditional/commodity chemicals; i.e. d-limonene
- Mechanical cleaning
- Mixed approach between methods

Results & Impacts

- Unpredictable results – often disappointing
- Removing value as feedstock (BTX)
- Long cleaning times
- High volume of waste
- Hazardous materials
- Multiple steps
Next Generation Best Practices

Rezyd-HPTM Cleaning Chemistry
ZymeFlow Decontamination Chemistry
- Custom blend including high Kb solvent and surfactant
- Applied as an additive to common refinery cutter stocks
- Low hazard (2, 1, 0)
- Biodegradable
- Dissolves and/or fluidizes deposits
- Significantly decreases final cleaning and total cleaning time
- Low volumes required and less waste than other methods

Results: loose coke for ease of removal.
(Pictured: coker strainer basket)
Preparing process units for safe entry in **8-12 hours**.

**Simultaneous Treatment**

- **Benzene**: 0 ppm
- **LEL**: 0%
- **H₂S**: 0 ppm
- **FeS**: Neutralized
- **Residual Oil**: Removed
- **Residual Solids**: Conditioned

- Distillation
- Oxidation
- Cleaning
- Quickest possible entry into process equipment
- Operations shuts down and de-inventories equipment using standard procedures
- Zyme-Flow UN657 chemistry is injected into the equipment with steam
- Same boiling point as water therefore chemistry contacts all surfaces with minimum injection points
- Proprietary blended chemistry added to oil wash for much faster and more complete tower bottoms fluidization
- Entire tower system decontaminated simultaneously using boil out and Vapour-Phase®
- Additional treatments available for pyrophoric treatment on tower trays/packing
**Oil Wash Enhancement Using Rezyd-HP™**

- Unit is de-inventoried under standard plant procedures
- A cutter stock circulation is performed on the bottom circuit including exchangers
- **Rezyd-HP** added to enhance penetrating effect of the cutter stock, breaking down deposits within the circuit
Boil Out with Vapour-Phase®

- Water is added to tower bottom (about 20% level)
- Steam injected into the bottom drain, or as close as possible
- *Zyme-Flow®* and *Rezyd-X®* added to water and temperature raised to above 100°C
Boil Out with Vapour-Phase®

- Solution continues to boil in the bottom of the tower during Vapour-Phase

- Injection of Zyme-Flow during the steaming phase will last 8-12 hours
- Hardened deposits will be eliminated or loosened for ease of removal
- Greatly reduces mechanical work
- Trays and packing should be significantly easier to remove or repair
- Additional equipment can be segmented throughout production such as filter baskets, piping, and heat exchangers

VDU beds post treatment requiring no mechanical cleaning upon opening. (Pictured – VDU in EU.)
**Bottoms Circulation**
Specialty Rezyd-HP chemistry added to the HVGO cutter stock and circulated at the refinery’s standard time and rate

**Vapour-Phase® Application**
Zyme-Flow UN657 injected into a strategically chosen steam line over a 10 hour period

**Continuous Monitoring**
Throughout the 10 hour Vapour-Phase, gas concentrations were monitored until H$_2$S, LEL, and benzene all consistently read zero

**Water Rinse with Zyme-Ox® Plus**
Flushed any remaining scale, oxidized any additional pyrophorics, and cooled unit faster for manned entry
Venezuela Coker Results

- Vessel was open and ready for inspection and hot work after 10 hours of Vapour-Phase
- Saved 7 days of mechanical preparation and cleaning
- All decontamination and maintenance work completed on schedule
- Tower free of oil with no traces of tarry hydrocarbon
- First time in vessel’s history, the bottom manway was not obstructed by solids
- Easily swept out a single foot of fluff coke (hydrocarbon free)
- 84% reduction in effluent

Bottom distributor was accessible and completely unplugged
Only 2 technicians per shift, 1 pneumatic pump, and 50 feet of half inch chemical hose

Injection points connected to existing steam and process lines completed in less than one shift

Eliminated several steps with simultaneous treatment of $\text{H}_2\text{S}$, LEL, and oxidation of pyrophorics

84% reduction in effluent; 6,875 gallons versus the 43,000 gallons with previous method
Venezuela Coker Benefits
Effects on Effluent and Waste Generation

Background
- No treatment facility on-site
- All effluent collected per site requirements

Oil Wash with Rezyd-HP
- Chemistry does not negatively effect cutter stock
- After circulation, cutter stock/chemistry combination sent to slop
- Only small dose required

ZymeFlow Vapour-Phase
- Large reduction in effluent (over 80% reduction) including post rinse
- Chemistry becomes part of steam – no water circulation required
- Reduced total steaming time (no pre or post steaming needed)
- Reduced cost; Non-hazardous
## TCO Comparison – Venezuela Coker

<table>
<thead>
<tr>
<th></th>
<th>ZymeFlow Decon</th>
<th>Previous Chemical Contractor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemicals Utilized</strong></td>
<td>3 chemistries</td>
<td>6 chemicals</td>
</tr>
<tr>
<td><strong>Application and Hours</strong></td>
<td>Vapour-Phase® 10 hrs</td>
<td>Circulation 36+ hrs</td>
</tr>
<tr>
<td><strong>Mechanical Prep Time</strong></td>
<td>&lt;12 hrs</td>
<td>120 hrs</td>
</tr>
<tr>
<td><strong>Personnel Required</strong></td>
<td>2 techs per shift</td>
<td>12 man crew per shift</td>
</tr>
<tr>
<td><strong>Equipment Setup</strong></td>
<td>1 pneumatic pump, 50 feet ½ in. hose</td>
<td>Several chemical hose circuits, stage heated frac tanks, major mechanical, fork lifts</td>
</tr>
<tr>
<td><strong>Special Requirements</strong></td>
<td>None</td>
<td>Haz suites, secondary containment, barricades</td>
</tr>
<tr>
<td><strong>Remaining Coke</strong></td>
<td>&lt;1’ fluff coke</td>
<td>Tarry coke 2’ above lower manway</td>
</tr>
<tr>
<td><strong>Mechanical Cleaning</strong></td>
<td>Fluff coke easily removed, no fresh air required</td>
<td>Extensive under fresh air</td>
</tr>
<tr>
<td><strong>Effluent</strong></td>
<td>6,875 gallons - no issues</td>
<td>43,000 gallons requiring disposal</td>
</tr>
</tbody>
</table>
Large differences between vessel entry methods – need to consider entire turnaround scope

Methods are available that are faster and more efficient than mechanical-only removal of hardened deposits such as coke

Decontamination affects not only on vessel entry but maintenance and entire turnaround schedule
Worldwide Leader in Decontamination

- Decontamination specialists for over 25 years
- 200+ TAR and emergency outage projects/year
- Experience in over 50 countries
- Wide range of specialty blended chemistries
- Various application options including Vapour-Phase®
- Zero recordable injuries in 25 year history
Conclusion & Questions

www.ZymeFlow.com

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