Impact of Feed Properties and Operating Parameters on Delayed Coker Petcoke Quality

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Categorizing Petroleum Coke

**Usage:**
- **Fuel Grade**
  - Power Generation
  - Cement manufacturing
- **Anode Grade**
  - Aluminum Grade
  - “Calcineable”
- **Electrode Grade**
  - Steel Electric Arc Furnace
  - “Calcineable”

**Appearance:**
- **Shot Coke**
  - Small spherical balls
  - “Beebees”
- **Sponge Coke**
  - Amorphous
  - May contain shot beebees
- **Needle Coke**
  - Crystalline
  - Clusters of aligned needles
Coke Formation

- Thermal cracking of paraffins & Paraffinic side chains.
- Polymerization & aromatic formation.
- Heavy aromatics condense to a mesophase.
- Mesophase converts to coke.
- Asphaltenes & very high MW aromatics rapidly convert to coke skipping mesophase.

- Thermal Cracking is endothermic
- Condensation & coke formation is exothermic
Petroleum Coke General Properties

- Volatile Combustible Matter (VCM)
- Hardgrove grindablity index (HGI)
- Contaminants
  - Sulfur
  - Nitrogen
  - Metals
- Ash
- Granulometry (fines)
Petroleum Coke General Properties: Volatile Combustible Matter (VCM)

- VCM is unconverted pitch
  - Target 12% Max, fuel coke 9% to 10%
  - 14% VCM is very high; Coke will be soft
- Increases green coke hydrogen content
- Rules of thumb for control in fuel coke
  - Increase heater outlet 5-7 °F for 1% decrease in VCM
  - Increase heater outlet 1-2 °F for each hour reduction in coking cycle time
- Best practice: Increase heater outlet 5-7 °F in final hours of coking cycle
Petroleum Coke General Properties: Hardgrove Grindability Index (HGI)

- Gauge of relative hardness and friability (tendency to form fines)
- Function of VCM, cycle time & coke type
- High Asphaltene feeds producing coke of 8-9% VCM may have HGI < 30 (18 hr coking cycle)
- Will increase with decrease in coking cycle
Petroleum Coke General Properties: Sulfur, Nitrogen, Metals & Ash

- Determined by feedstock & coke yield
- Intrinsic values & not readily controllable except by feed treatment
- Typical range:
  - Coke S = typically (1.25 to 1.4) x Feed S
  - Coke N = typically (2.25 to 3.0) x Feed N
- Feed metals & ash end up in coke
Petroleum Coke General Properties: Granulometry

- Granulometry: fines (<1mm) not desirable
- “soft” coke makes more fines: decrease VCM / HGI
- Fines generation:
  - Crusher comminution;
  - Jet pump specification & cutting nozzle wear, under-powered systems can lead to grinding
  - Coke cutting technique: do not use “washing”
  - Coke reclaim: Bridge crane vs FEL
  - Coke handling design: minimize no. of transfers
- Maintain wet coke at moisture levels of 7%+ to minimize coke drying and windborne fines
Feed Properties Affecting Coke Yield and Quality

- Gravity
- Distillation
- Concarbon residue (CCR)
- Asphaltenes (Heptane Insolubles / HIS)
- Sulfur
- Nitrogen
- Metals/ Ash
- Hydrogen content / Aromaticity
## Delayed Coking Control Variables

- Higher Temp → lower coke VCM content
- Low Pressure → higher liquid yields / lower coke yield
- Low Recycle → higher liquid yields / lower coke yield
- Shorter cycles require increase in temperature

<table>
<thead>
<tr>
<th>Variable</th>
<th>Fuel Coke</th>
<th>Anode Coke</th>
<th>Needle Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
<td>910 - 930</td>
<td>925 - 950</td>
<td>925 - 950</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>15 typical</td>
<td>18 – 60+</td>
<td>50 – 90+</td>
</tr>
<tr>
<td>Recycle Ratio</td>
<td>0 - 5% typical</td>
<td>0 – 50%+</td>
<td>60 – 120%+</td>
</tr>
<tr>
<td>Coking Time, hours</td>
<td>9 -18</td>
<td>24</td>
<td>36</td>
</tr>
</tbody>
</table>
Fuel Coke Units
Design & Operating Considerations

• Maximize liquids; minimize coke
  – Minimize pressure and recycle rate
  – Maximizes Heavy Coker Gas Oil (HCGO) and its end point

• Coke structure ranges from sponge to shot

• Shot Coke
  – Made with high Asphaltene (HIS) feed
  – Rule of Thumb: CCR / HIS < (2 – 2.2)
  – Need to mitigate coke drum hot spots/uncontrolled drum dumps
Best Practices for Shot Coke

1. **Coker Design**
   - Slide valve unheading
   - High steam sweep on inlet nozzle
   - Safety interlocks for drum isolation & operation

2. **Operational Techniques**
   - Complete water quench & fill; slow optimized quench; soak period or overflow operation
   - Track water flows to verify drum fill
   - Ramp COT esp. for short cycle operations
   - Maintain forward flow at all times
   - Optionally use decant oil/low temp for initial 1 – 2 hours
Best Practices for Shot Coke (cont’d)

1. **Operating Instructions & Safety Measures**
   - Audible & visual alarms
   - Non-essential personnel off structure during unheading & cutting
   - Operator awareness of hot spot tell-tales
   - Operators remain in shelters or operate remotely
   - Use PPE during head removal (non-slide valve)
   - Precaution when steam blowing transfer line
   - Verify that crane, FEL etc. operators are notified prior to unheading

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FOSTER WHEELER
# Fuel Coke: Typical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCM, Wt. %</td>
<td>12 Max.</td>
</tr>
<tr>
<td>Moisture, Wt%</td>
<td>8-12</td>
</tr>
<tr>
<td>HGI</td>
<td>35-70+</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>3.5-7.5</td>
</tr>
</tbody>
</table>

**Elemental Analysis** (DRY Basis: 10 VCM)

<table>
<thead>
<tr>
<th>Element</th>
<th>Content, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>88.0</td>
</tr>
<tr>
<td>H</td>
<td>3.8</td>
</tr>
<tr>
<td>S</td>
<td>5.0</td>
</tr>
<tr>
<td>N</td>
<td>1.65</td>
</tr>
<tr>
<td>O</td>
<td>1.2</td>
</tr>
<tr>
<td>Ash</td>
<td>0.35</td>
</tr>
<tr>
<td>HHV, Kcal</td>
<td>3926</td>
</tr>
<tr>
<td>LHV, Kcal</td>
<td>3896</td>
</tr>
</tbody>
</table>
Fuel Coke Marketing

• Typical markets:
  – Boiler fuel / Power
    • Circulating Fluid Bed with limestone S capture
    • Pulverized carbon (100% in arch PC boilers)
  – Fuel for Cement/Lime kilns
  – Co-firing with oil / coal / gas

• Total world production approx. 80 MM MTPA vs coal market 6500 to 7000
  – Higher caloric value (can be as high as 75%)
  – Lower ash content
  – But higher sulfur content compared to coal
  – Particularly attractive in cement/lime kilns which operate at higher temperatures and SO₂ from coke is absorbed by the process
Fuel Coke Marketing (cont’d)

• Market availability is not an issue
  – Sells at small discount to coal
  – displaces coal

• Netback value depends on
  – Contract / spot market sales
  – Refinery location
  – Discount at S > 5.5 wt%
  – Storage & transportation costs
Anode Coke

• Typical specification limits
  – S < 4 wt%; V < 400 ppmw; no shot / < 3% embedded
  – Premium grade: S < 1.5 wt%; V < 150 ppmw
  – Vibrated Bulk Density (VBD): > 0.85 g/cc on -28/+48 mesh

• VBD correlated to HGI & VCM
  – Increase heater outlet to increase VBD

• Feedstocks
  – Low sulfur / metals residues; unfiltered coal tar
  – Distillate tars demonstrated by Foster Wheeler
Anode Coke Units
Design & Operating Considerations

- Operating Conditions
  - Pressure: 18 to 60+ psig
  - Temperature: 15 to 40 °F higher than typical fuel operation
  - Recycle: 0% to 50%+

- Design considerations include:
  - High energy coke cutting
  - High design temperatures

- Operate in block operation with Fuel Coke
Feed Pretreatment for Anode Coke

Direct

Indirect

High S
High Metals
Residue

Residue
Hydrotreating

Anode
Delayed
Coker

Gas
LPG
Distillates

Anode
Coke

Residue

UOP/FW
Solvent
Deasphalting
Process

Optional
DAO
HDS

Delayed
Coker

Anode
Block
Operation

Fuel Coke
Block
Operation

Asphalt
## Anode Coke: Typical Properties

<table>
<thead>
<tr>
<th></th>
<th>Green</th>
<th>Calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCM, Wt. % Dry Basis</td>
<td>12 Max.</td>
<td>N/A</td>
</tr>
<tr>
<td>Sulfur, Wt. %</td>
<td>4.0 Max. (1)</td>
<td>3.5 Max</td>
</tr>
<tr>
<td>Ash, Wt. %</td>
<td>0.40 Max</td>
<td>0.40 Max</td>
</tr>
<tr>
<td>Nickel, ppmw</td>
<td>250 Max</td>
<td>200 Max</td>
</tr>
<tr>
<td>Vanadium, ppmw</td>
<td>400 Max (1)</td>
<td>350 Max</td>
</tr>
<tr>
<td>HGI</td>
<td>60 to 100 typical</td>
<td></td>
</tr>
<tr>
<td>Vibrated Bulk Density, g/cc (ASTM D4292)</td>
<td></td>
<td>0.87 Min</td>
</tr>
<tr>
<td>Real Density, g/cc</td>
<td></td>
<td>2.05 Min</td>
</tr>
<tr>
<td>Granulometry, + 4 mesh</td>
<td></td>
<td>30%</td>
</tr>
<tr>
<td>- 28 mesh</td>
<td></td>
<td>10%</td>
</tr>
</tbody>
</table>

(1) Variable depending on purchaser’s final coke blend.
(2) Additional metals specifications (Si, Fe, Ca, and Na) apply.
Anode Coke Marketing

- Current high demand
  - 0.4 lbs carbon anode consumed per lb aluminum produced

- World market approx. 17 to 20 MM MTPA

- Purchasers distinguish between anode grades
  - Premium
    (S < 1.5 wt%, V < 150 ppmw)
  - Regular
  - Blend coke
    (S ~ 4 wt% max, V ~ 400 ppmw max)
Needle Coke

- Feeds are aromatic tars with low sulfur & metals: best decant oil or thermal tar
  - Multi-ring aromatics with short aliphatic side chains
  - Nil asphaltenes
  - Feed desulfurization may be necessary
- Important specifications
  - Coefficient of thermal expansion (CTE): Varies with grade
  - Granulometry
  - S, N, ash & metals
- Operations
  - Pressure: typ. 50 to 90 psig
  - Recycle: 60 to 120%
  - Proprietary post-treatment
  - Drum Size: < 7.3 m
# Needle Coke: Typical Properties

<table>
<thead>
<tr>
<th></th>
<th>Green</th>
<th>Calcined</th>
<th>Graphite Artifact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, Wt%</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, Wt%</td>
<td>0.7</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Nickel, ppmw</td>
<td>5-7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ash, Wt. %</td>
<td>0.1 Max</td>
<td>0.1 Max</td>
<td>-</td>
</tr>
<tr>
<td>VCM, Wt. % Dry Basis</td>
<td>6 Max</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Real Density, g/cc</td>
<td></td>
<td>2.10-2.14</td>
<td></td>
</tr>
<tr>
<td>CTE, x 10^-7/ °C</td>
<td></td>
<td></td>
<td>2.5 (30-125°C)</td>
</tr>
<tr>
<td>Electrical Resistivity, Ohm-In x10^-6</td>
<td></td>
<td></td>
<td>320</td>
</tr>
<tr>
<td>Granulometry, wt%, + 6 Tyler (Maximum practical)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Needle Coke Marketing

- Small specialty market
- Approx. 1.2 MM MTPA
- Grades dependent on CTE
  - Regular
  - Premium
  - Super Premium
- Approx. half dozen manufacturers
  - Supply constrained – one with more than 50% share
  - Market demand – some manufacturers left market to increase refinery margin making fuel coke with low price heavy crude.
- Approx dozen purchasers
Foster Wheeler SYDEC\textsuperscript{sm} has Extensive Experiences in All Applications

- **Fuel Grade Coke**
  - 66 units [new + existing]
  - 42 in operation
  - 39 licenses in past 4 years

- **Anode Grade Coke**
  - 32 units
  - 5 licenses in past 4 years

- **Needle Coke**
  - 7 units
  - Major pilot plant evaluations

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