



# 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
  - “Calcinable”
- Electrode Grade
  - Steel Electric Arc Furnace
  - “Calcinable”

## Appearance:

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

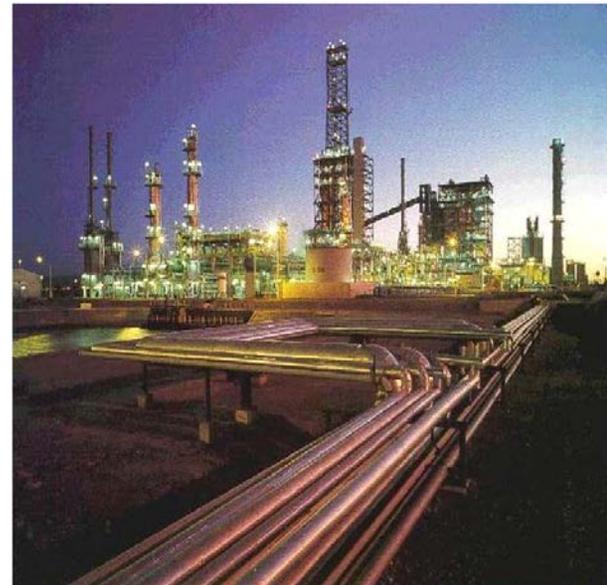


# Coke Formation

- 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.
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- Thermal Cracking is endothermic
  - Condensation & coke formation is exothermic

# Petroleum Coke General Properties

- Volatile Combustible Matter (VCM)
- Hardgrove grindability 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
  - Coke N = typically (2.25 to 3.0) x Feed
- 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

Variable	Fuel Coke	Anode Coke	Needle Coke
Temperature, °F	910 - 930	925 - 950	925 - 950
Pressure, psig	15 typical	18 – 60+	50 – 90+
Recycle Ratio	0 - 5% typical	0 – 50%+	60 – 120%+
Coking Time, hours	9 -18	24	36

# Fuel Coke Units

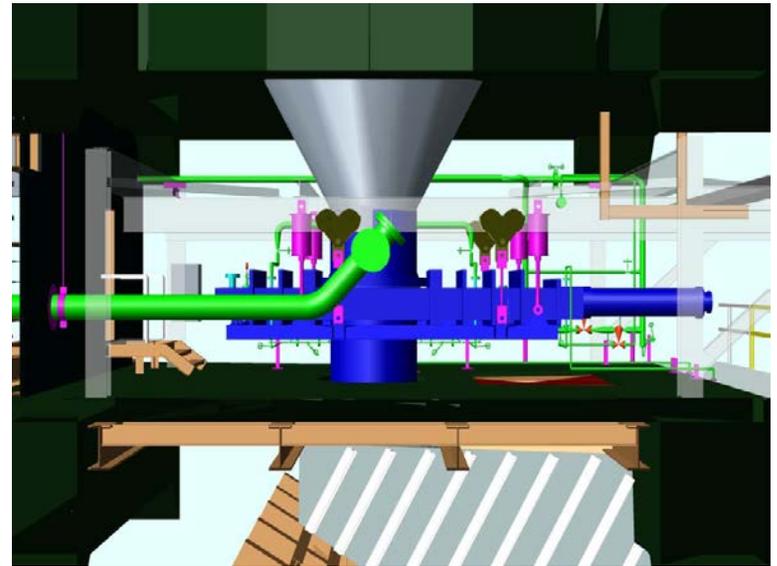
## Design & Operating Considerations

- 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)

## •(3) **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



# Fuel Coke: Typical Properties

VCM, Wt. %	12 Max.
Moisture, Wt%	8-12
HGI	35-70+
Sulfur, wt%	3.5-7.5
<u>Elemental Analysis</u>	<u>DRY</u>
Basis: 10 VCM	
C	88.0
H	3.8
S	5.0
N	1.65
O	1.2
Ash	0.35
HHV, Kcal	3926
LHV, Kcal	3896



# 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  $\text{SO}_2$  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  $S > 5.5 \text{ wt}\%$
  - 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

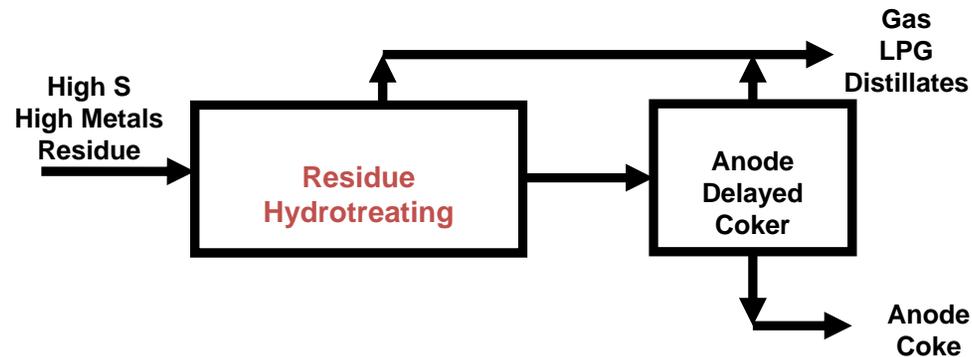
## Design & Operating Considerations

- 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

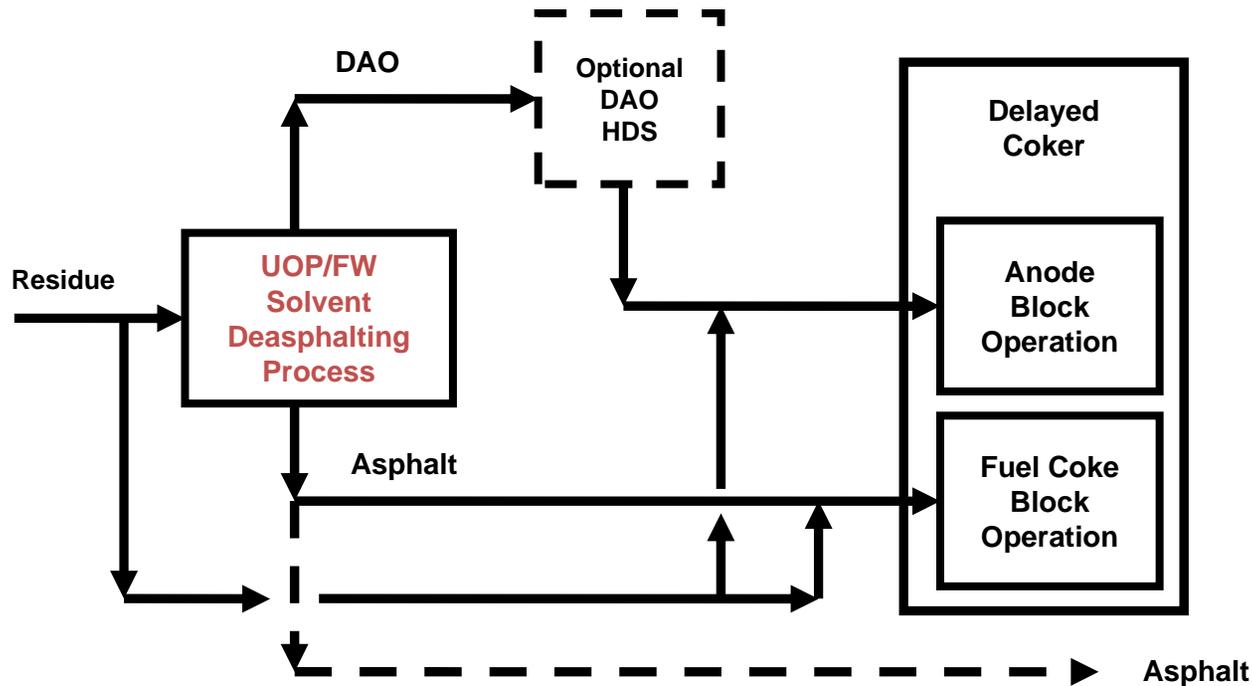


# Feed Pretreatment for Anode Coke

## Direct



## Indirect



# Anode Coke: Typical Properties

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

(1) Variable depending on purchaser's final coke blend.

(2) Additional metals specifications (Si, Fe, Ca, and Na) apply.



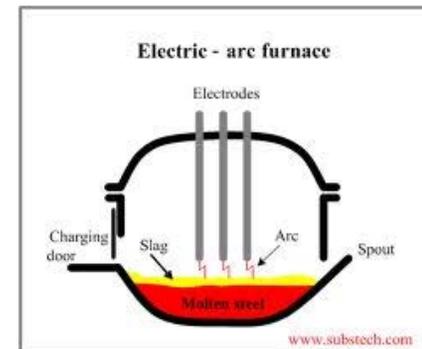
# Anode Coke Marketing

- 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

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



# 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<sup>sm</sup> 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

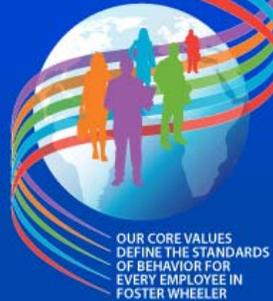


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