New Technology Controls High Temperature Coker Heater Fouling

Coking.com Safety Seminar
Calgary, Alberta
September 18,2007

Bruce Wright

BAKER HUGHES
Baker Petrolite

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
Heater Fouling Control

BAKER HUGHES
Baker Petrolite

MILESTONE is a trademark of Baker Hughes Incorporated

Economic Impacts of Coker Heater Fouling

Throughput Losses
2-5% ~ $5 MM

De-coking Costs
$25K – $50K/coil

Reduced Flexibility
Can be > $5 MM

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

Conversion Losses
1% ~ $3 MM

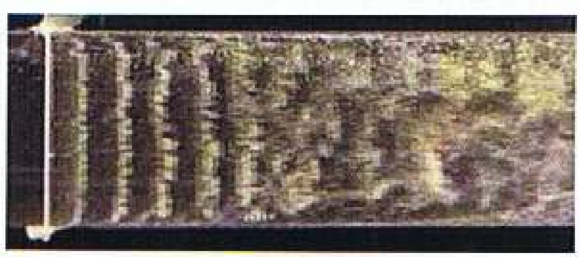
Increased Fuel Usage
2% > $200,000

E, H & S Concerns

Coker Heater Design & Operation

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

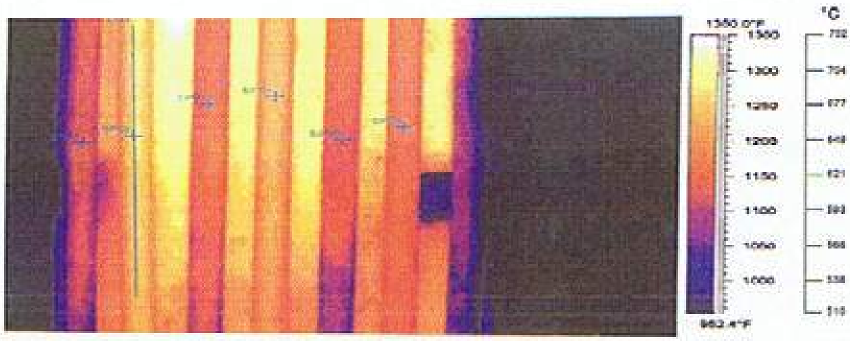
Continuous Flow and Adequate Velocities are Critical to Good Operations!



Baker Hughes
Baker Petrolite

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

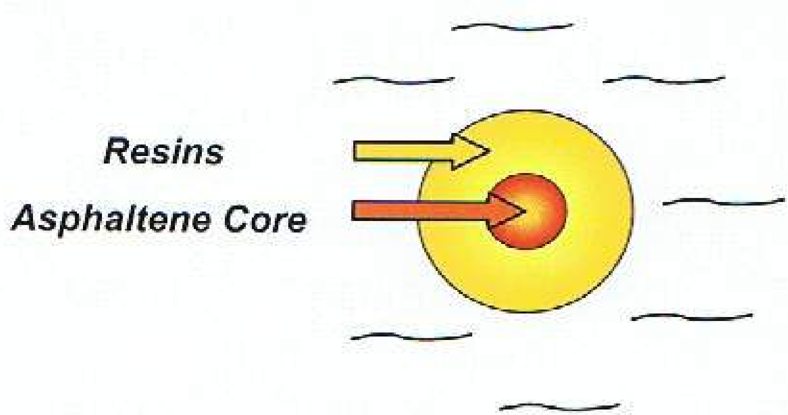
BAKER HUGHES

Baker Petrolite

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



Baker Petrolite

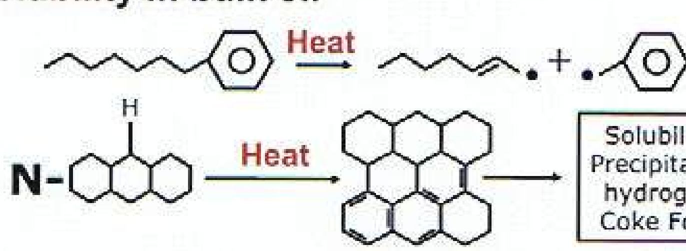
Asphaltene Destabilization

- 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

Baker Petrolite

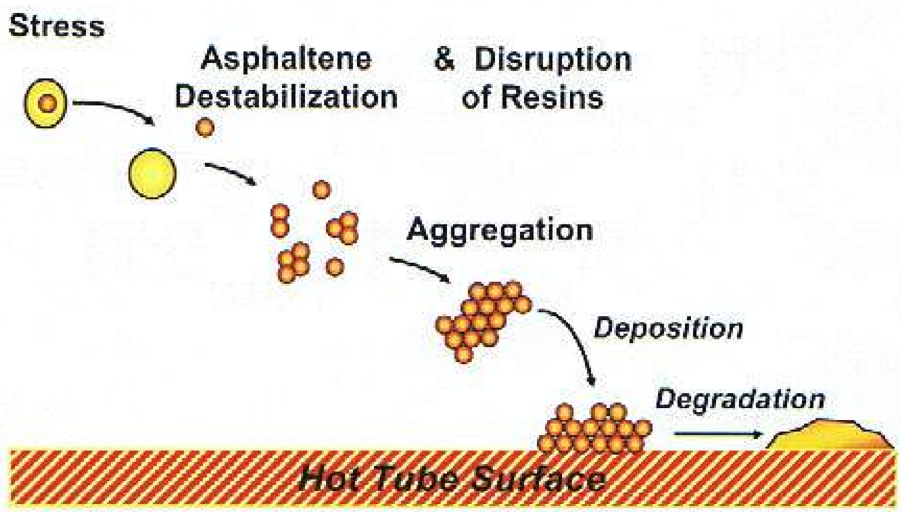
Thermal Decomposition of Oil

- 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



Solubility Loss, Precipitation, De-hydrogenation, Coke Formation

Asphaltene Precipitation

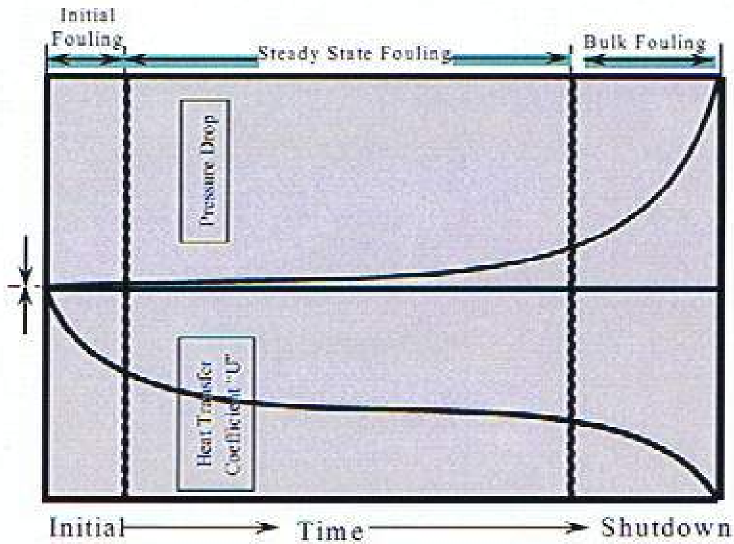


Stages of Fouling

- **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

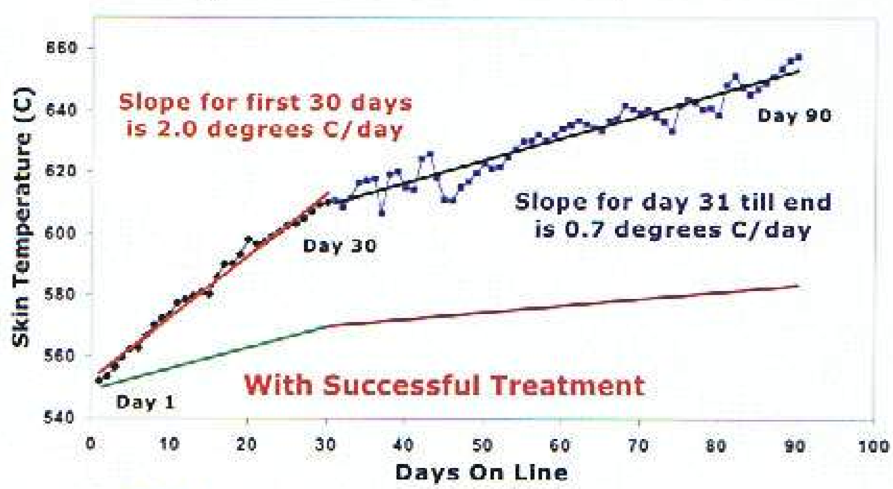
Baker Petrolite

Stages of Fouling



Target Treatment Results

Delayed Coker Heater Skin Temperatures



BAKER HUGHES

Baker Petrolite

MILESTONE™
Fouling Control Additive Technology

Baker Petrolite

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

Baker Petrolite

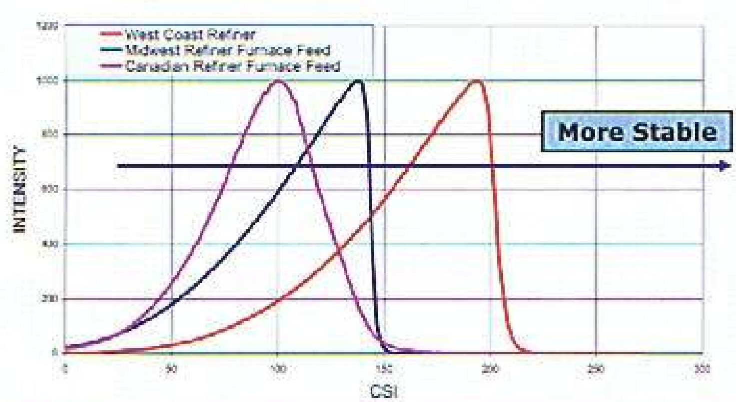
CSI Coking Stability Index

- 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

BAKER HUGHES
Baker Petrolite

Coker Feed	Furnace Run Length	CSI	Asphaltene/Resin Ratio	Saturate/Aromatic Ratio
Canadian	2.4 Months	99.5	0.348	2.63
Midwest	5.0 months	137.1	0.325	3.85
West Coast	9.0 Months	192.0	0.458	2.94

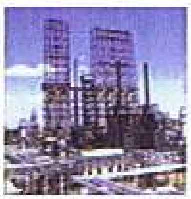
CSI Coker Stability Index
Furnace Feed Stability

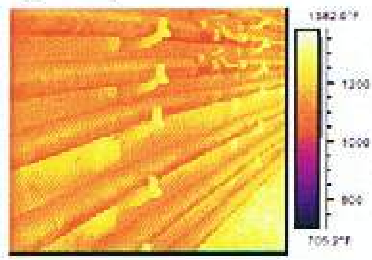


Fouling Control Technology: MILESTONE Additives

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

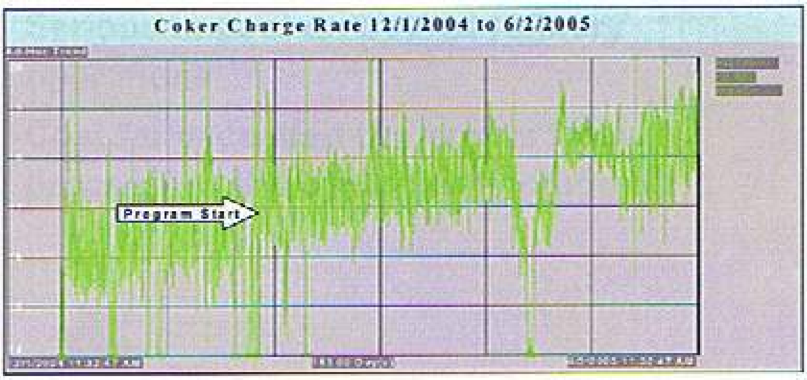
BAKER HUGHES

Baker Petrolite

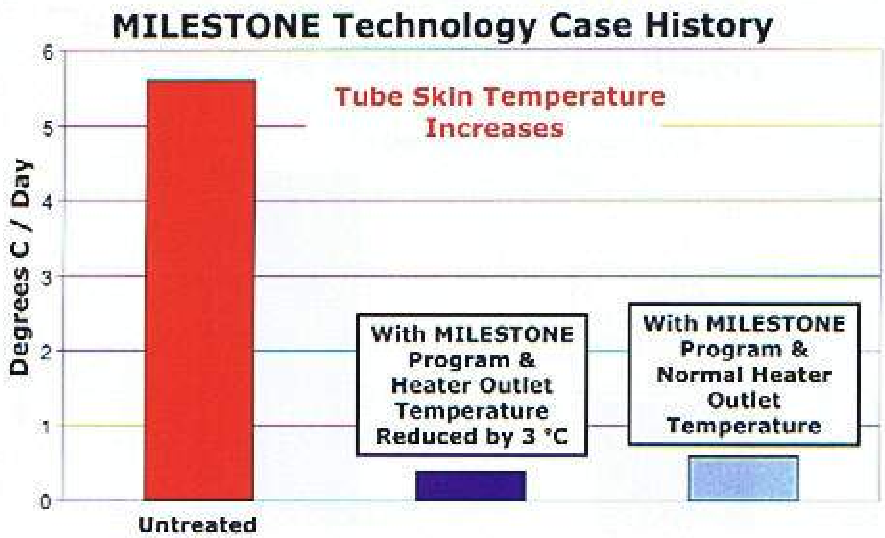
Case Histories – Refinery A

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



BAKER HUGHES

Baker Petrolite

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

BAKER HUGHES
Baker Petrolite

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

BAKER HUGHES
Baker Petrolite

Thank You for Your Attention!

Any Questions?

MILESTONE

Heater Fouling Control

BAKER HUGHES

Baker Petrolite