Drive to Safety
Why Delayed Coking?

- Semi-batch process
- Convert bottom-of-the-barrel material into usable products
  - Converts low-value vacuum residuum to higher value liquid hydrocarbon products, gas, and solid coke.
Coker Feeds & Products

• Feed Source
  – Pitch from Distilling Vacuum Flasher
  – Clarified Slurry Oil from Catalytic Cracker
  – Cold Feed from Tankage
  – C16+ hydrocarbon with 90% pt of 1350 °F (SG=1)

• Products
  • Anode Grade Sponge Coke sold to Rain CII
    • Calcined at Rain CII for use in making carbon anodes for aluminum industry
  • Heavy Gas Oil to Catalytic Cracking Unit
  • Light Gas Oil to Diesel Hydrotreater
  • Gasoline to Naphtha Hydrotreater
  • Dry Gas to Fuel Gas Treater
Coking Chemistry

- Endothermic Reaction
- Thermal Cracking
- Hydrocracking Reactions
  - Partial Saturation
  - Hetero-atom removal
    - Desulfurization
    - Denitrogenation
    - Demetalization (metal present in heavy feeds)
Coke Drum Filling

Vapors

Channels

Coke

Coke Drum Feed From Furnaces

To Main Frac

Pilot hole drilled. Initializing side cutting operation.

Cut coke falling to drop pad
Coke Drum Operations

- The coking operation alternates between a pair of drums, so that residuum charging and fractionation can be continuous.

- **Active Drum**
  - Vacuum residuum transformed to lower gravity hydrocarbon vapors and solid coke.
  - Injected with antifoam to help prevent foam overs

- **Inactive Drum**
  - Coke is steam stripped and subsequently quenched with water.
  - After the drum is cooled, the drum is opened to atmosphere and the solid coke is hydraulically cut from the drum.
  - Drum is then closed and warmed up and ready to be switched into.
Bottom Unheading Dangers

• Geysers/Eruptions
  – Typically caused by feed interruptions or loss of steam/water quench
  – Hot spots can be caused by steam/water not permeating through coke bed. If residual water contacts the pockets of hot coke, a geyser of steam, hot water, coke particles, and hydrocarbon from bottom head emerges

• Hot Tar Ball Ejection/Tarry Drum
  – Typically caused by feed interruptions or loss of steam/water quench
  – Mass of hot (~800°F) tar-like material that can be rapidly ejected from the bottom head opening.

• Undrained Water Release
  – Scalding hazard if hot undrained water remains when bottom head removed

• Shot Coke Avalanche
  – Individual spherical shaped coke chunks are flowable and may dump from the drum when the bottom head is removed
Manual Unheading

- Hot coke drum bed and tarry drum are dangerous scenarios, especially when the coke drums were manually unheaded.
- Manual unheading involves....
Before Delta Valve
Nov 24th, 1998—Equilon Refinery

- Severe storm caused an electric power outage
- The coker was shutdown with the active drum an hour online—tarry drum scenario
- Lost steam production—hot coke drum bed scenario
- Once steam was restored, unable to inject it into the hot tarry drum through the normal route because plugged piping due to tarry oil solidifying and plugged channels
- Allowed the drum bed to cool for two days with no water or steam. Temperature indicators on drum were low and drum vessel cool to the touch
- When the bottom head was lowered with the dolly, the petroleum vapors burst into flames.
- 6 PEOPLE WERE CAUGHT IN THE FLAMES AND DID NOT SURVIVE
NORCO Responds

• In 2006, Norco site installed bottom head delta valves that could be remotely operated from the board.
Drive to Environmental Standards
Historical Gasoline Regulations for Benzene

- Reformulated Gasoline limited to 1% vol benzene
- Conventional Gasoline regulated based on historical base-line levels
Historical Gasoline Blending at Motiva Norco

- Norco’s annual average Benzene concentration in gasoline was 1.3 % vol.
- Norco produces the most gasoline than any of our sister refineries in Motiva/Royal Dutch family of companies.
- Various streams are used for gasoline blending, including:
  - Naphtha from Catalytic Cracker—0.7% Bz
  - Straight Run Motorbase—1.7% Bz
  - Alkylate—0% Bz
  - Reformate—3% Bz
  - Butanes—0% Bz
  - Hydromate and Naphtha from Hydrocracker—1% and 0.3% Bz, respectively
  - Naphtha from Naphtha Hydrotreater—1.2% Bz
Benzene in Reformate

- Typically, reformate contributes over 50% of the benzene in the blend pool.
- Benzene in reformate chemistry:
  - Benzene enters with the feed and passes through the unit unchanged
  - Cyclohexane dehydrogenation to benzene
  - Methylcyclopentane (MCP) isomerization to cyclohexane then dehydrogenated to Bz
  - C6 paraffin ring formation to MCP then isomerized to cyclohexane and finally dehydrogenated to Bz
Mobile Source Air Toxics Rule

- Published in February 2007
- Beginning January 1, 2011
  - All refiners must meet an annual benzene concentration in gasoline of 0.62 %vol
  - Ability to use benzene credits (either generated or bought) to meet above regulation
- Beginning July 1, 2012
  - Maximum annual benzene concentration in gasoline of 1.3 %vol when credits are used to meet the 0.62 %vol standard

Source: http://www.epa.gov/fedrgstr/EPA-AIR/2008/October/Day-16/a24591.htm
Norco Responds

• Norco’s Benzene Removal Unit (BRU) successfully started up in December 2009 utilizing the modified existing Gasoline Hydrotreater Unit
  – The BRU is rated to run 33 MBPD Reformate from the reformer
  – The Reformate is fractionated into 24 MBPD combined C7+ Gasoline bottoms plus C4/C5 light ends overhead product along with an 8 MBPD C5/C6/C7 upper side-draw stream.
  – The side-draw stream is sold to Shell Chemical to be used as Olefin Plant furnace feed.
  – The C4/C5/C7+ combined overhead and bottoms stream is returned to Motiva and blended into gasoline.
• The unit was designed to have less than 0.1% Benzene in the bottoms stream
• Since startup, the bottoms stream has averaged between 0.0 and 0.02 %vol benzene
**Additional Options**

- Treating the naphtha entering the reformer using light naphtha splitting and/or isomerization by removing benzene precursors.
- Treating the reformate stream exiting the reformer using benzene extraction or benzene saturation or benzene alkylation
  - Benzene alkylation - converts benzene into other aromatic compounds by the addition of alkyl groups to the benzene ring. Xylene, toluene and cumene are typical products.
Removing Bz Precursors in Reformer Feed
Benzene Saturation

- Benzene saturation-selectively hydrogenates benzene into cyclohexane.