# Drive to Safety

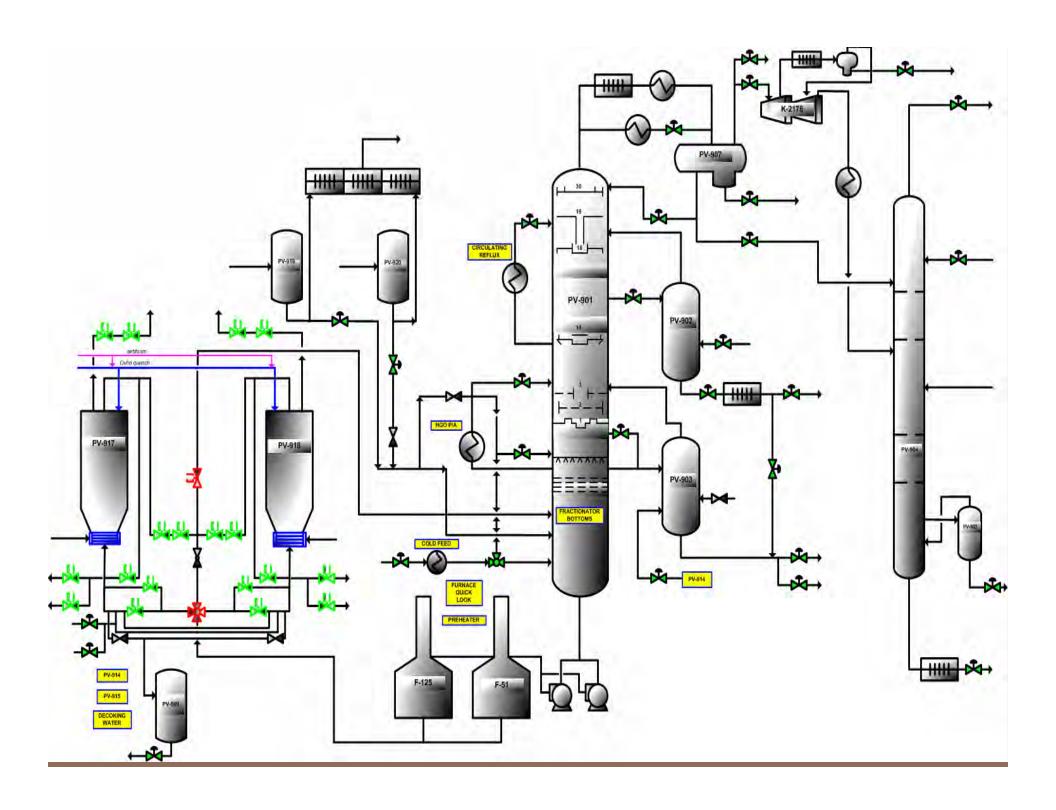


# Why Delayed Coking?

- 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**

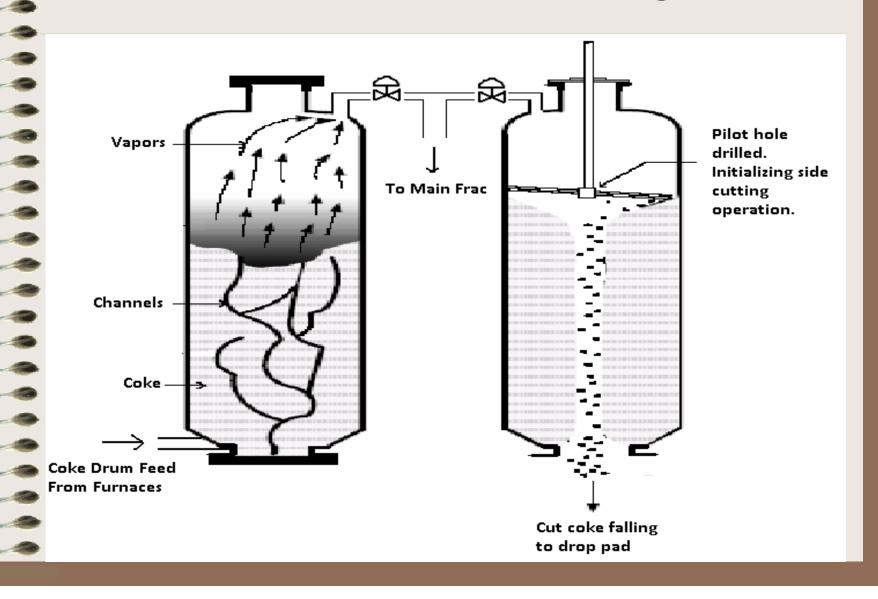
- Feed Source
  - Pitch from Distilling Vacuum Flasher
  - Clarified Slurry Oil from Catalytic Cracker
  - Cold Feed from Tankage
  - C16+ hydrocarbon with 90% pt of 1350 °F (SG=1)
- Products
  - Anode Grade Sponge Coke sold to Rain CII
    - Calcined at Rain CII for use in making carbon anodes for aluminum 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**

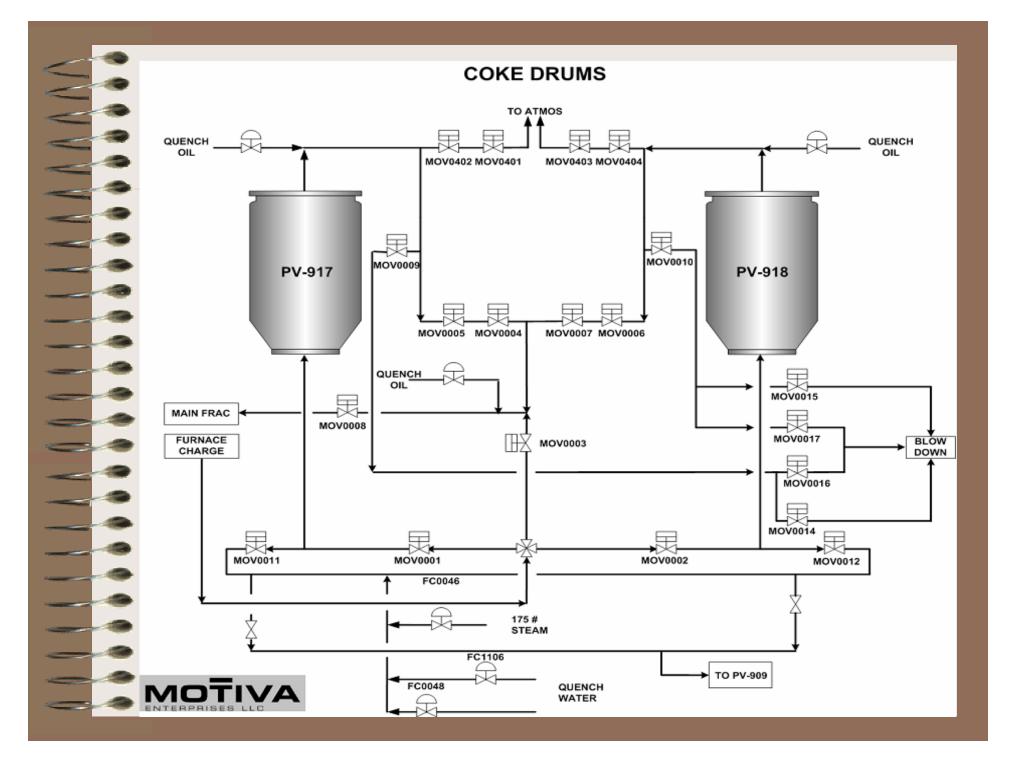
- Endothermic Reaction
- Thermal Cracking
- Hydrocracking Reactions
  - Partial Saturation
  - Hetero-atom removal
    - ✓ Desulfurization
    - ✓ Denitrogenation
    - ✓ Demetalization (metal present in heavy feeds)

# Coke Drum Filling



# **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....

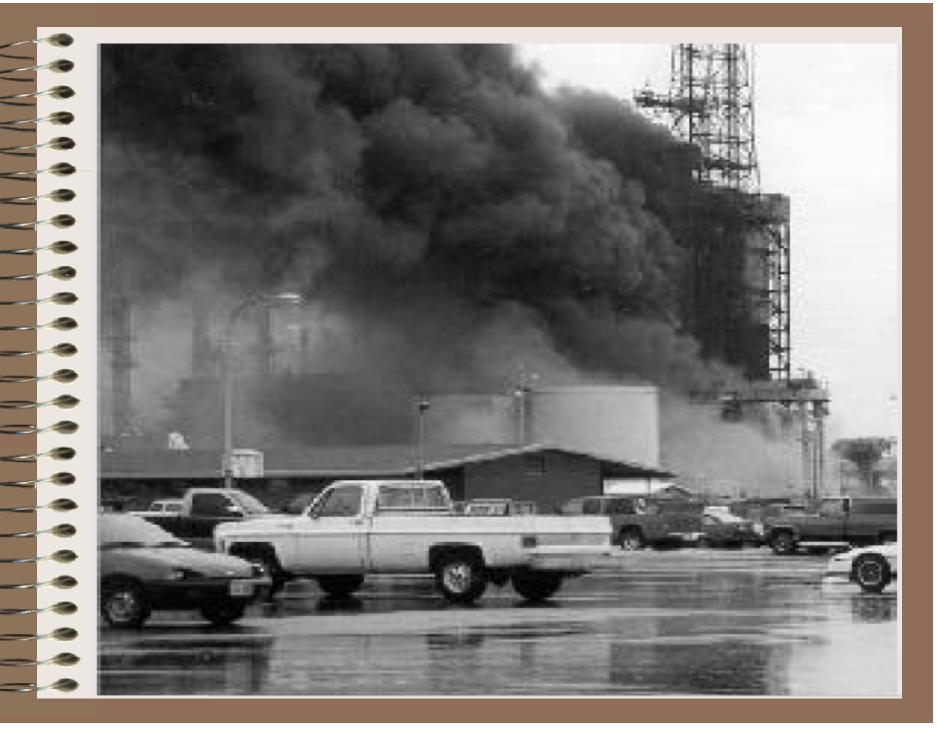
### Before Delta Valve



### Nov 24<sup>th</sup>, 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

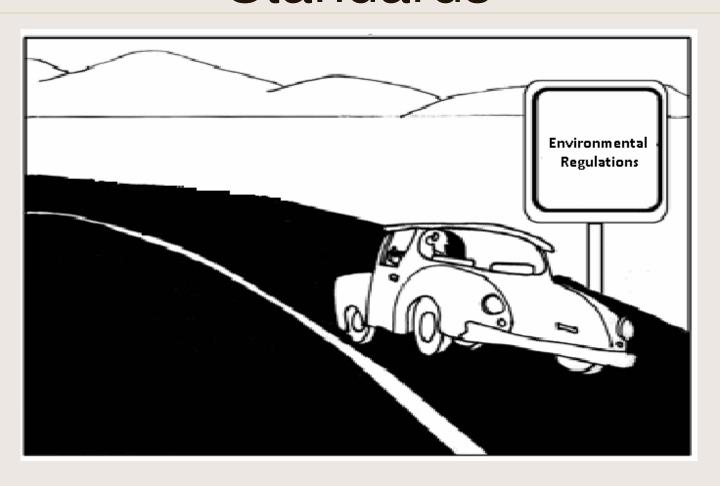




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# Drive to Environmental Standards



# 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

$$H \longrightarrow H$$





# 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

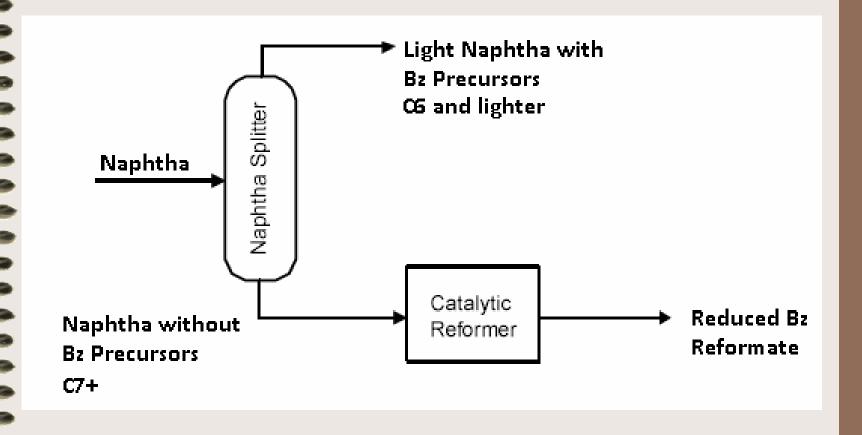
## Norco Responds

- 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.

