Benzene in Gasoline
Regulations & Remedies

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What is MSAT?

• Mobile Source Air Toxics are U.S. EPA classified hazardous air pollutants; i.e., benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, naphthalene resulting from non-point sources

• MSATs are known carcinogens and/or cause other serious health or environmental effects

• MSATs are a subset of Volatile Organic Compounds (VOCs) which contribute to ozone formation and possibly particulate matter (PM)

Source of Benzene Emissions

Source Category Contributions to Benzene Emissions, 1999 NEI
Total = 347,000 tons

- Nonroad: 19%
- Area and Other: 15%
- Major: 3%
- Fires: 14%
- Onroad: 49%

Source Category Contributions to Benzene Emissions, 2020
Total = 222,000 tons

- Nonroad: 18%
- Area and Other: 30%
- Major: 4%
- Onroad: 26%
- Fires: 22%

Source contribution before controls

Estimated source contribution after controls

Recent Benzene Monitoring Levels

- Point of reference: OSHA PEL = 3 mg/m³

Predicted Benzene Levels Sans Controls

Figure 3.2-2. Geographic Distribution of County Median Concentrations (µg/m³) of Benzene in 2020 Without Controls in this Rule.

2020 Cancer Risk for Benzene

Figure 3.2-10. 2020 County Median Cancer Risk for Benzene, Without Controls in this Rule.

MSAT Benzene Requirements

- Jan. 1, 2011 – EPA MSAT requires refiners to meet an annual average benzene content of 0.62% vol in gasoline (reformulated and conventional) nationwide
  - Current national content is ~1.0% vol
  - Refiners may average nationwide, trade, or bank benzene credits (ABT program)
  - California gasoline standards already meet MSAT requirements
- July 1, 2012 – requires refiners to meet a maximum average benzene standard of 1.3% vol
- EPA registered small refiners have a 4 year grace period
- New Vehicle cold (<75 °F) standards will be phased in from 2010 – 2015
- Portable container improvements starting in 2009

EPA Estimated Benefits

- Reduce MSAT emissions by 330,000 tons in 2030; benzene by 61,000 tons¹
- Gasoline will contain 38% less benzene overall
- New passenger vehicles will emit 45% less benzene
- Portable containers will emit 78% less benzene
- Reduction in PM emissions to avoid nearly 900 premature deaths annually; reduce costs by $6 billion in 2030

¹Source: “EPA Regulatory Announcement”, EPA420-F-07-017, February 2007
EPA Estimated Costs

- Additional gasoline processing costs of $0.0027 per gallon nationwide, $0.0040 per gallon for impacted refiners - $14 million investment per impacted refinery
- Industry wide refining capital investment will be $1,110 MM or $22,400 per ton benzene
- “Social costs” will be $400 MM in 2030; includes reduction in gasoline losses from portable containers
- Additional $1 per vehicle manufacturing/testing cost
- Additional $2 per portable container; offset by reduced gasoline losses

EPA Emerging Issues

- EPA is currently investigating other air toxics for possible controls:
  - Gasoline PMs (Particulate Emissions)
  - Metals, from gasoline, lubricants, catalyst wear, engine wear, brakes

Benzene Properties

- C₆H₆
- Molecular weight: 78.1
- CAS number: [71-43-2]
- Boiling point: 176 °F (similar to heptanes, C₇)
- Solubility in water: 1.79 g/L @ 76 °F
- Vapor pressure: 3.2 psia @ 100 °F (RVP)
- Flash point: 12.2 °F
- Autoignition temperature: 1042 °F
- Research octane number (RON): 106
Refinery Sources of Benzene

- Crude: typically < 0.1%vol benzene
- Crude Unit
  - Naphtha: typically 0.5 – 1.5%vol
- Catalytic Reforming Unit (Reformer)
  - Reformate: typically 4 – 9%vol
- Fluidic Catalytic Cracking Unit (FCC)
  - Naphtha: typically 0.5 – 1.5%vol
Generic Process Schematic

- **Crude Distillation**
  - Crude
  - LPG

- **Vacuum Distillation**
  - Petroleum Coke
  - Asphalt

- **Mid-Distillate Hydrotreating**
  - Jet, Diesel

- **FCC**
  - Gasoline

- **Naphtha Hydrotreating**
  - Gasoline
  - Isomerization, C5/C6

- **Hydrogen**
  - Gasoline, Aromatics

- **Catalytic Reforming, C7-400F**
  - Jet, Diesel

- **Hydrocracking**
  - Gasoline

- **Alkylation**
  - Gasoline
  - Cycle oil to hydrotreating or hydrocracking

- **Coking**
  - Gasoline
Major Gasoline Specifications

- Octane (RON + MON)/2
  - 87, 89, 91 (requires RON of 89+, 92+, 95+ respectively)
- RVP (Vapor Pressure at 100 degF)
  - 7.8 and 9.0 psi for conventional gas
- Sulfur
  - <30 ppm
- Benzene
  - <0.62% vol
## Gasoline Pool Dynamics

<table>
<thead>
<tr>
<th></th>
<th>RVP, psia</th>
<th>RON</th>
<th>%vol Bz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>52</td>
<td>93.5</td>
<td>0</td>
</tr>
<tr>
<td>Naphtha</td>
<td>5 - 9</td>
<td>53 - 73</td>
<td>0.5 – 1.5</td>
</tr>
<tr>
<td>FCC Naphtha</td>
<td>4 - 9</td>
<td>80 - 90</td>
<td>0.5 – 1.5</td>
</tr>
<tr>
<td>Reformate</td>
<td>3 - 8</td>
<td>91 - 104</td>
<td>4 - 9</td>
</tr>
<tr>
<td>Alkylate</td>
<td>2.5 - 4</td>
<td>91 - 96</td>
<td>0</td>
</tr>
</tbody>
</table>

RVP, octane, sulfur, and now Benzene regulations are making it increasingly difficult for refiners to blend gasoline. Butane can only be blended during winter months; hydrotreating FCC naphtha to remove sulfur reduces octane; reformate is used to boost octane but contains aromatics; alkylate utilizes Hydroflouric or Sulfuric acid.
### Benzene Pool Example

<table>
<thead>
<tr>
<th>%vol of Pool</th>
<th>%vol Bz</th>
<th>% Pool Bz</th>
<th>% Pool RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>11</td>
<td>0.6</td>
<td>3.1</td>
</tr>
<tr>
<td>FCC Gasoline</td>
<td>43</td>
<td>0.8</td>
<td>16.2</td>
</tr>
<tr>
<td>Reformate</td>
<td>38</td>
<td>4.5</td>
<td>80.7</td>
</tr>
<tr>
<td>Alkylate</td>
<td>8</td>
<td>0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Gasoline Pool** 2.12

This refinery pool example results in a Bz vol% of 2.12 which will require a reduction of 1.5 vol% or ~28,500 gallons per day based on a 100,000 bpd refinery.
Reformer Benzene Chemistry

- Benzene (Bz) rides through unchanged
- Cyclohexane (CH) is dehydrogenated to Bz; +3 H2, Rel. Rxn Rate = 100
- Methylcyclopentane (MCP) is ring isomerized to CH; +0 H2, Rel. Rxn Rate = 10
- n-Hexane undergoes dehydrocyclization to MCP; +1 H2, Rel. Rxn Rate = 1.0
- Heavy aromatics are hydrodealkylated to Bz; (-1) H2 (typically occurs at high pressure, high temperature)
Reformer Benzene Rxns

- **Naphthene dehydrogenation**
  \[
  \text{CH (83 RON)} \leftrightarrow \text{Bz (106)} \quad \Delta H_{\text{rxn}} \quad + \text{3H}_2 \quad 78.7 \text{ Kcal/mole}
  \]

- **Alkylcyclopentane isomerization**
  \[
  \text{MCP (89)} \quad \leftrightarrow \quad \text{CH (83)} \quad (-4.5) \text{ Kcal/mole}
  \]

- **Paraffin dehydrocyclization**
  \[
  \text{n-Hexane (25)} \quad \leftrightarrow \quad \text{MCP (89)} \quad + \text{H}_2 \quad 14.5 \text{ Kcal/mole}
  \]
Reformer Aromatic Yield Effects

- Aromatic yield is decreased by:
  - Lower temperature (decreases rxn rates)
  - Higher pressure (shifts equilibrium to left)
  - Higher space velocity (further approach to equilibrium)
  - Higher H2/HC mole ratios (shifts equilibrium to left)
  - Reduction of C6 paraffins in feed
Thermal Cracking (FCC) Benzene Chemistry

- Benzene (Bz) rides through unchanged
- Alkylaromatics are dealkylated to Bz
- Cyclization of paraffins followed by dehydrogenation
- Main impacts
  - Feedstock characteristics
    - Higher aromatic content tends to increase Bz
    - Hydrogen poor feeds tend to increase Bz
  - Operating factors
    - Higher conversion increases Bz
    - Shorter vapor contact time decreases Bz
  - Catalyst type
    - Rare earth zeolites have higher Bz
    - Octane catalysts have lower Bz
Benzene Removal Strategies

- Remove benzene precursors from Reformer feed
  - Cyclohexane, Methylcyclopentane, and n-Hexane
    - Impact: RON loss, less H2 from Reformer
      - With Isomerization (-1) to (-2) RON
    - Saturate benzene removed with precursors
      - Impact: RON loss; H2 consumption
- Saturate benzene in gasoline blending streams
  - Impact: RON loss; H2 consumption
- Solvent extract benzene from reformate
  - Can sell benzene as a product
    - Impact: volume loss; RON loss; Bz typ. has better margins
- Alkylate benzene to Ethylbenzene or Propylbenzene
  - Impact: volume gain; RON gain
Removing Benzene Precursors

- **Reformer prefractonation - Naphtha Splitter**
  - Removes CH, MCP, C6- paraffins
    - Suitable for most Isomerization units
  - Deeper cuts may remove Bz and some C7 paraffins
    - Typically not suitable for Isomerization units
  - Resulting Bz in reformate based on dealkylation rxns which are typically low in a low pressure reformer
- **Advantages**
  - Simple distillation
  - Improves reformer performance if C5/C6 are in feed
- **Disadvantages**
  - May not achieve <0.62%vol in pool
Removing Benzene Precursors Process

Full Range Naphtha → Naphtha Splitter → Light Naphtha
                      /    \                        /    \
                      |    |                        |    |
                      ▼    ▼                        ▼    ▼
                      Catalytic Reformer → Reduced benzene blendstock
UOP “Penex™” Isomerization Process
Saturating Benzene

• Bz saturation to CH

\[ \Delta H_{\text{rxn}} \]

Bz (106) \[ \rightleftharpoons \] CH (83 RON)

(- 3H₂) (-78.7) Kcal/mole

• May treat light naphtha from naphtha splitter
• May treat a Bz concentrated portion of a gasoline blend stream
  – Reformate draw
  – FCC naphtha – results in olefin losses

• Advantages
  – Saturation typically occurs with slightly greater than stoichiometric H2
  – Simple hydrotreating or distillation operations

• Disadvantages
  – Results in loss of RON and H2 consumption
  – Conversion may not be sufficient to achieve required Bz levels
UOP “BenSat™” Process
UOP “Penex-Plus™”

• Saturates Bz to CH
• Isomerizes C5/C6 paraffins to improve RON
• Combines UOP’s Penex™ and BenSat™ processes into one integrated unit
• Feed:
  – Light naphtha: C5/C6/Bz
• Reported investment: ISBL of $12MM based on 15,000 BPSD of light naphtha w/ 7%vol Bz
• # of units commissioned: Four (4)
• First unit started up in 1994
Axens “BENFREE™”

• Benzene reduction of reformate utilizing integrated reactive distillation
• Can retrofit existing reformate splitter to pull a benzene rich draw for saturation and provide overhead off-gas capability
• Feed:
  – Reformate splitter side draw
• Reported investment: ISBL of $3MM based on 10,000 BPSD for new unit
• # of units commissioned: Three (3)
Axens “Benfree™” Process
CDTECH “CDHYDRO™”

• Process hydrogenates benzene to cyclohexane in a catalytic distillation Bz-Toluene column

• Feed:
  – C5-C9 reformate

• Residual Bz: 0.5%vol
CDTECH “CDHYDROTM” Process
Solvent Liquid-Liquid-Extraction (LLE) & Extractive Distillation (ED)

- Utilize commodity glycols for extraction of aromatics
- Advantages
  - Recovers Bz as a valuable product
  - Non-licensed if free market glycol used
  - Proprietary solvents have proven efficiency gains
  - Well established technology
  - ED requires less equipment than LLE
- Disadvantages
  - Free market glycols less efficient
  - Proprietary solvents require higher level heat
  - Requires Bz storage/handling facilities
  - Requires isolated liquids collection system for unit
LLE Solvent Comparison

• More polar solvents have higher solvency & selectivity, but are more difficult to remove from the products
• More polar solvents reduce the solvent/HC ratio, equipment size, and energy consumption
• Less polar solvents are less corrosive, use lower stripping temperatures, less expensive, and are not licensed
LLE Process
UOP “CAROM™” LLE

- Utilizes Carom (80% tetra-ethylene glycol & 20% Carom concentrate)
- Feed:
  - C6-C7 Reformate Splitter overhead
- Residual Bz: <0.1%vol
- Reported investment: ISBL of $17.8MM based on 10,000 BPSD
- # of ED units commissioned: Six (6)
- Primarily developed as a capacity upgrade to older glycol based LLE units
UOP “CAROM™” Process
UOP “SULFOLANE\textsuperscript{SM}™” & “ED SULFOLANE\textsuperscript{TM}”

- Combines aromatic liquid-liquid extraction with extractive distillation
  - Utilizes Sulfolane (tetrahydrothiophene 1, 1-dioxide)
- ED unit utilizes extractive distillation only
- Feed:
  - C6-C7 Reformate Splitter overhead
- Residual Bz: <0.1\%vol
- Reported investment: ISBL of $14MM based on 11,200 BPSD of light reformate w/ 67\%vol C6/C7 aromatics
- # of ED units commissioned: Three (3)
GTC Technology “GT-BTX\textsuperscript{SM}” ED

- **Aromatic Extractive Distillation (ED)**
  - Utilizes lean solvent (Techtiv-100\textsuperscript{TM}) in a distillation column; overhead liquid (raffinate) is non-aromatics, bottoms is rich solvent to solvent recovery column
    - Solvent increases the relative volatility of n-C7/Bz
  - Solvent recovery column overhead liquid (extract) is aromatics

- **Feed:**
  - 10 – 95% Aromatics
- **Residual Bz:** $<0.1\%\text{vol}$
- **Reported investment:** ISBL of $6.5$MM based on 3,500 BPSD of light reformate
- **First unit startup in 2000**
GT-BTX\textsuperscript{SM} Process Diagram
Uhde GmbH “MORPHYLANE®” ED

- Utilizes Morphylane (N-Formylmorphylene) in an extractive distillation configuration
- Uhde offers a new single-tower configuration
- Feed:
  - C6-C7 Reformate Splitter overhead
- Residual Bz: <0.1%vol
- Reported investment: ISBL of $14MM based on 11,200 BPSD of light reformate w/ 67%vol C6/C7 aromatics
- First unit startup of single-tower design in 2004
Uhde “MORPHYLANE®” Process
Alkylate Benzene

- Benzene alkylation utilizes light olefins (C2= & C3=) to alkylate Bz to Ethylbenzene (EBz) & Propylbenzene (PBz)
- Potential source of light olefins is FCC offgas
- Advantages
  - Increases RON: EBz (124), PBz (127)
  - No H2 consumption
  - Potential volume swell
- Disadvantages
  - Pioneer technology
ExxonMobil “BenzOUT™” Bz Alkylation

- Fixed bed reactors
- Liquid phase reaction
- Requires pretreatment of FCC off-gas to remove Sulfur and Nitrogen contaminants
- Currently seeking pioneer refining application
- Based on extensive commercial petrochemical experience