

***PROCESS***

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# Benzene in Gasoline Regulations & Remedies

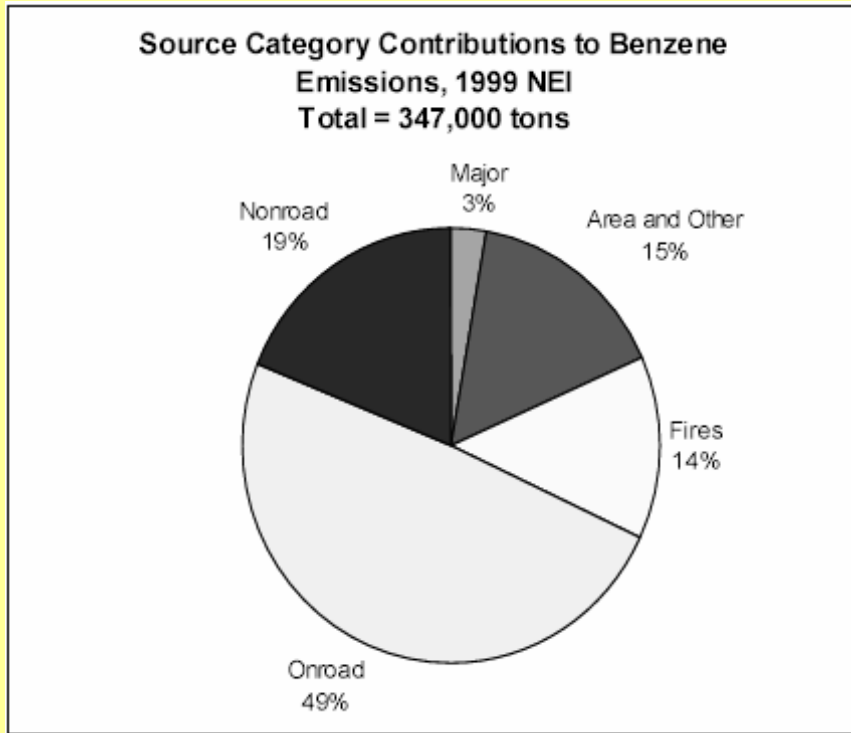
Ronald (Ron) F. Colwell, P.E.

# What is MSAT?

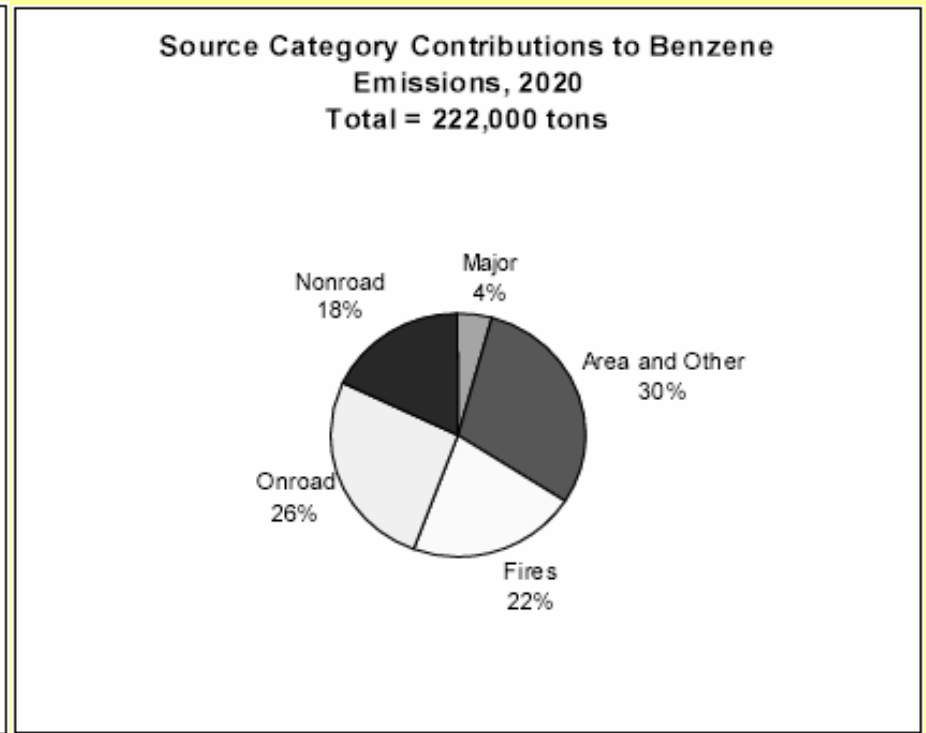
- Mobile Source Air Toxics are U.S. EPA classified hazardous air pollutants; i.e., benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, naphthalene resulting from non-point sources
- MSATs are known carcinogens and/or cause other serious health or environmental effects
- MSATs are a subset of Volatile Organic Compounds (VOCs) which contribute to ozone formation and possibly particulate matter (PM)

Source: “*EPA Regulatory Announcement*”, EPA420-F-07-017, February 2007

# Source of Benzene Emissions



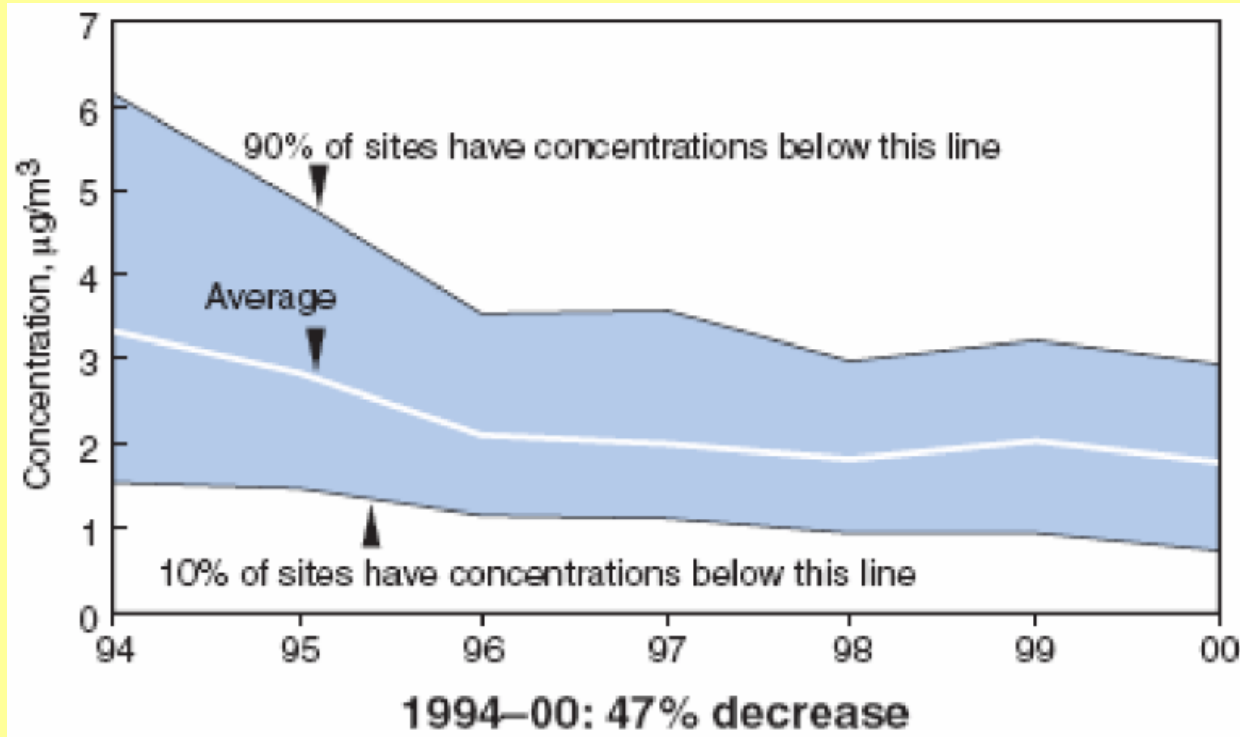
Source contribution before controls



Estimated source contribution after controls

Source: "SBAR Panel Report on Mobile Source Air Toxics", EPA420-R-05-901, November 2005

# Recent Benzene Monitoring Levels

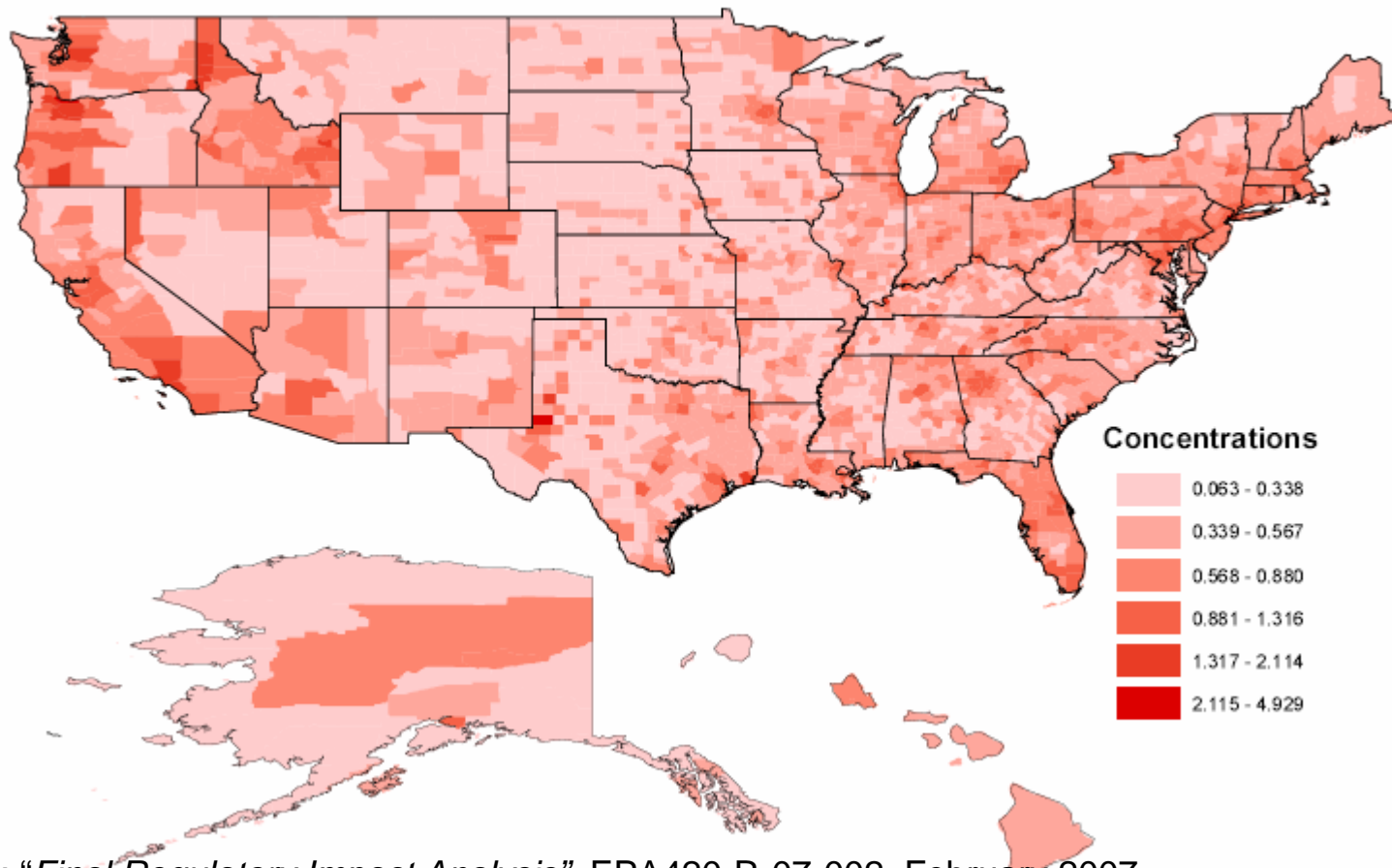


- Point of reference: OSHA PEL =  $3 \text{ mg}/\text{m}^3$

Source: "Final Regulatory Impact Analysis", EPA420-R-07-002, February 2007

# Predicted Benzene Levels Sans Controls

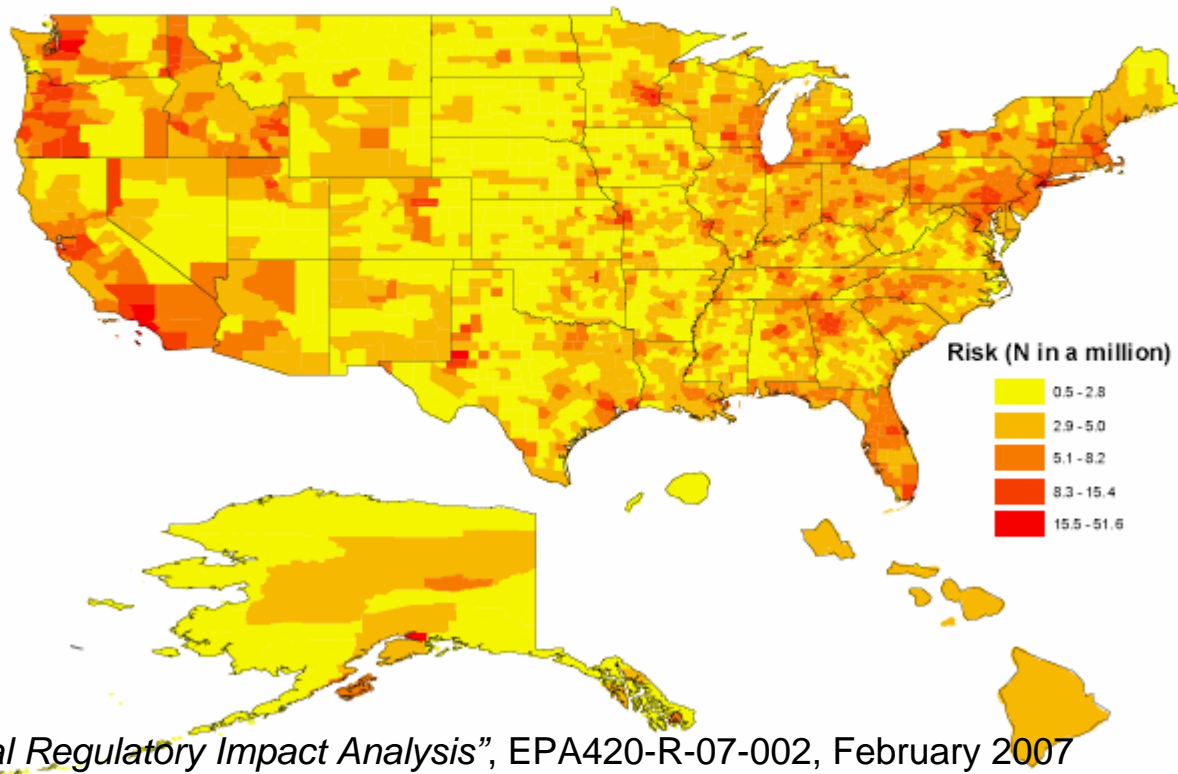
Figure 3.2-2. Geographic Distribution of County Median Concentrations ( $\mu\text{g}/\text{m}^3$ ) of Benzene in 2020 Without Controls in this Rule.



Source: "Final Regulatory Impact Analysis", EPA420-R-07-002, February 2007

# 2020 Cancer Risk for Benzene

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



Source: "Final Regulatory Impact Analysis", EPA420-R-07-002, February 2007

# 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

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

# EPA Estimated Benefits

- Reduce MSAT emissions by 330,000 tons in 2030; benzene by 61,000 tons<sup>1</sup>
- 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

<sup>1</sup>Source: “*EPA Regulatory Announcement*”, EPA420-F-07-017, February 2007

Source: “*Final Regulatory Impact Analysis*”, EPA420-R-07-002, 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

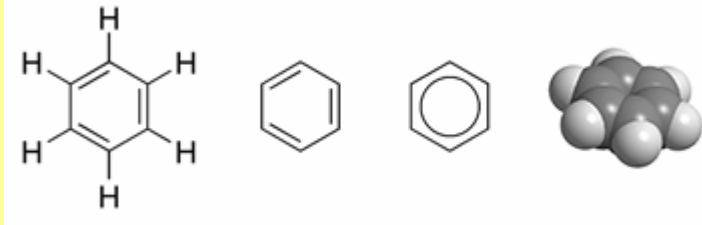
Source: “*Final Regulatory Impact Analysis*”, EPA420-R-07-002, February 2007

# 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

Source: “*Final Regulatory Impact Analysis*”, EPA420-R-07-002, February 2007

# Benzene Properties



- C<sub>6</sub>H<sub>6</sub>
- Molecular weight: 78.1
- CAS number: [71-43-2]
- Boiling point: 176 °F (similar to heptanes, C<sub>7</sub>)
- 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



# 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

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

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

	<u>%vol of Pool</u>	<u>%vol Bz</u>	<u>% Pool Bz</u>	<u>% Pool RON</u>
<b>Naphtha</b>	11	0.6	3.1	8.8
<b>FCC Gasoline</b>	43	0.8	16.2	42.6
<b>Reformate</b>	38	4.5	<b>80.7</b>	40.1
<b>Alkylate</b>	8	0	0.0	8.4
<b>Gasoline Pool</b>		<b>2.12</b>		

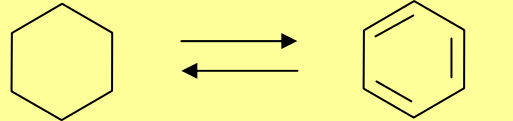
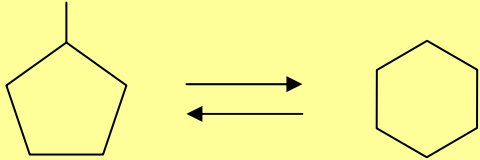
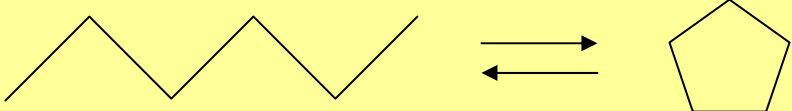
This refinery pool example results in a Bz vol% of 2.12 which will require a reduction of 1.5 vol% or ~28,500 gallons per day based on a 100,000 bpd refinery.



# Reformer Benzene Chemistry

- Benzene (Bz) rides through unchanged
- Cyclohexane (CH) is dehydrogenated to Bz; +3 H<sub>2</sub>, Rel. Rxn Rate = 100
- Methylcyclopentane (MCP) is ring isomerized to CH; +0 H<sub>2</sub>, Rel. Rxn Rate = 10
- n-Hexane undergoes dehydrocyclization to MCP; +1 H<sub>2</sub>, Rel. Rxn Rate = 1.0
- Heavy aromatics are hydrodealkylated to Bz; (-1) H<sub>2</sub> (typically occurs at high pressure, high temperature)

# Reformer Benzene Rxns

- Naphthene dehydrogenation  $\Delta H_{\text{rxn}}$   
CH (83 RON)      Bz (106)  
 + 3H<sub>2</sub>      78.7 Kcal/mole
- Alkylcyclopentane isomerization  
MCP (89)      CH (83)  
 (-4.5) Kcal/mole
- Paraffin dehydrocyclization  
n-Hexane (25)      MCP (89)  
 + H<sub>2</sub>      14.5 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 H<sub>2</sub>/HC mole ratios (shifts equilibrium to left)
  - Reduction of C<sub>6</sub> 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

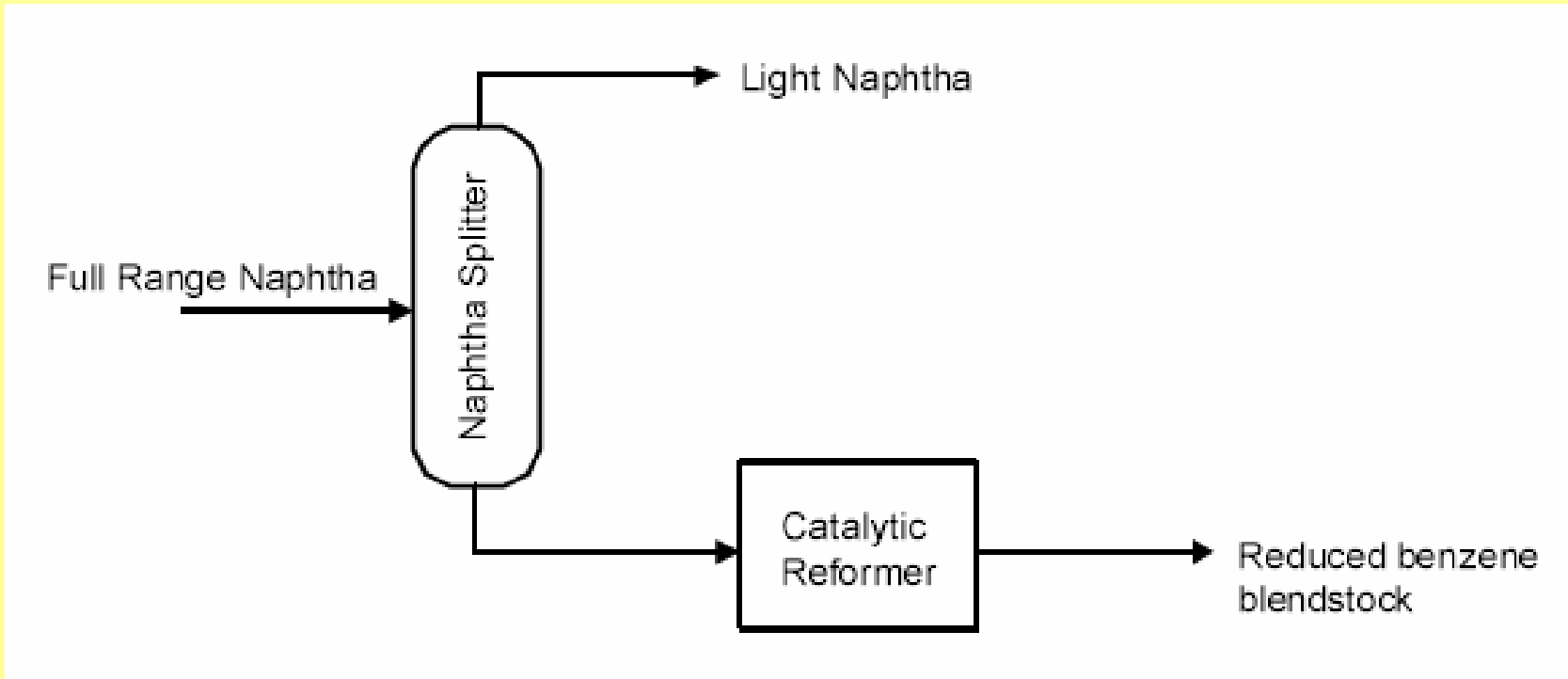
# Benzene Removal Strategies

- Remove benzene precursors from Reformer feed
  - Cyclohexane, Methylcyclopentane, and n-Hexane
    - Impact: RON loss, less H<sub>2</sub> from Reformer
      - With Isomerization (-1) to (-2) RON
  - Saturate benzene removed with precursors
    - Impact: RON loss; H<sub>2</sub> consumption
- Saturate benzene in gasoline blending streams
  - Impact: RON loss; H<sub>2</sub> 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

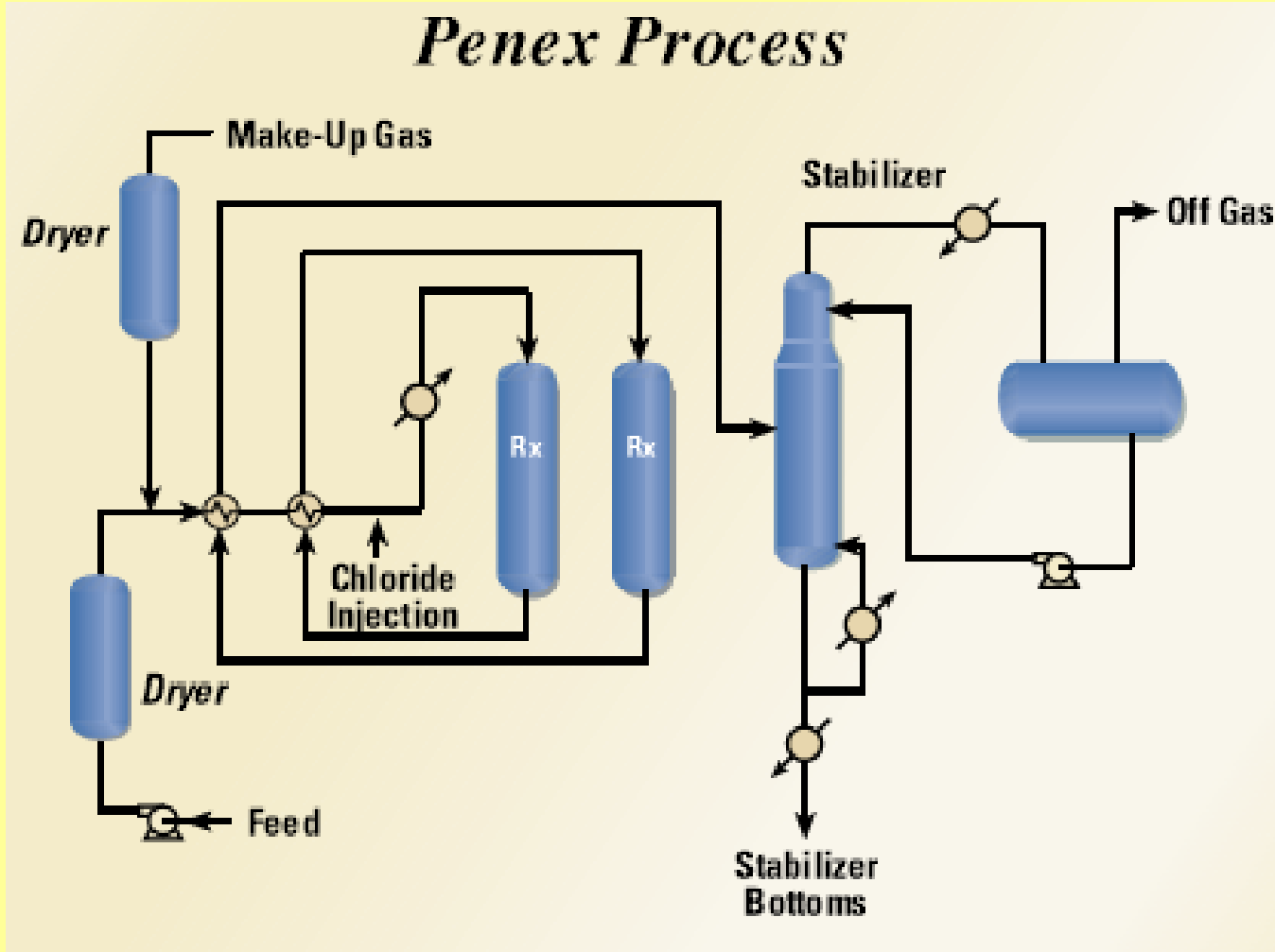
# Removing Benzene Precursors

- Reformer prefractionation - 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



# UOP "Penex™" Isomerization Process

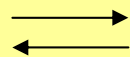
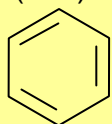




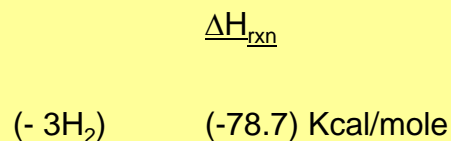
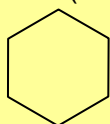
# Saturating Benzene

- Bz saturation to CH

Bz (106)

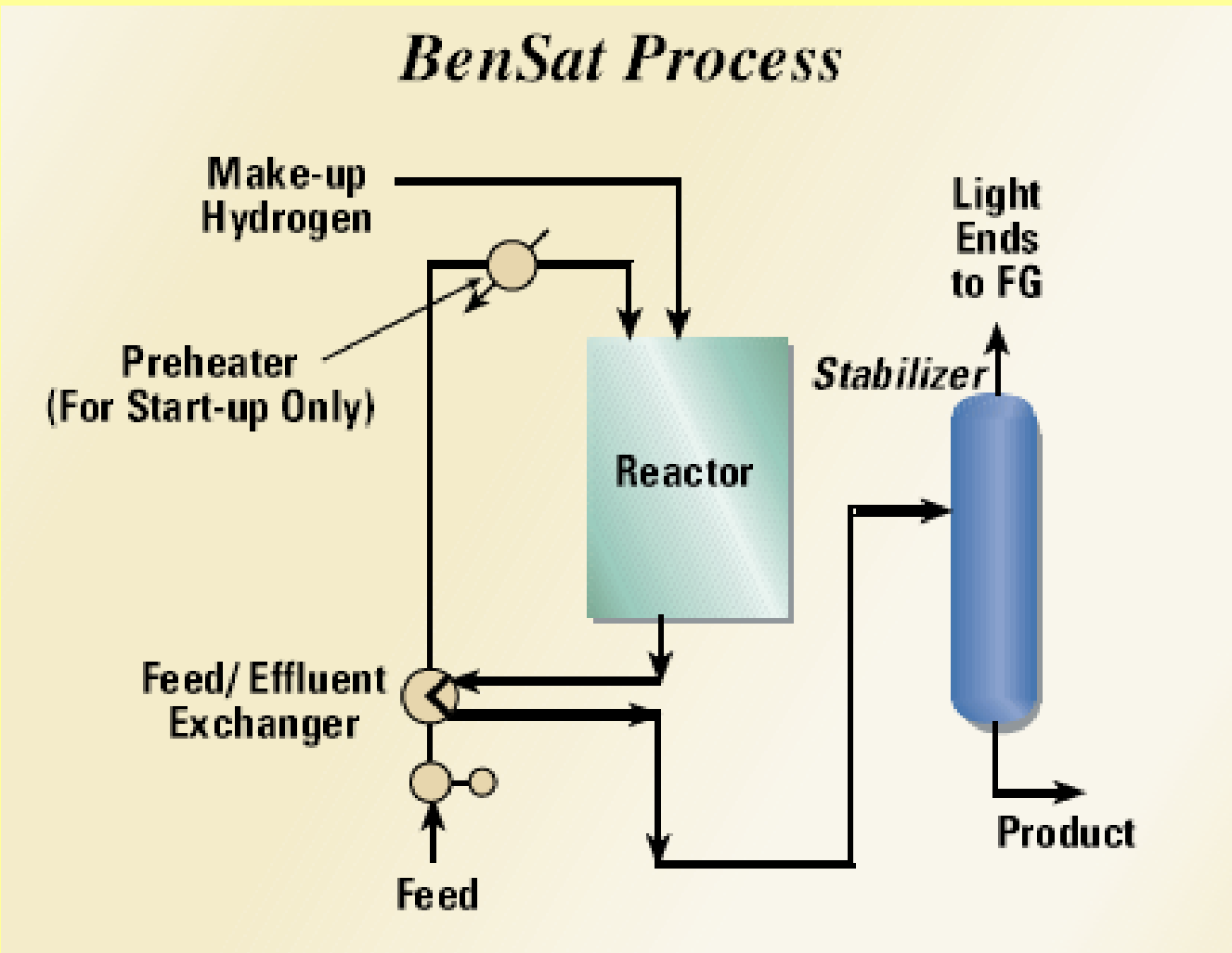


CH (83 RON)



- 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 H<sub>2</sub>
  - Simple hydrotreating or distillation operations
- Disadvantages
  - Results in loss of RON and H<sub>2</sub> consumption
  - Conversion may not be sufficient to achieve required Bz levels

# UOP "BenSat<sup>TM</sup>" Process



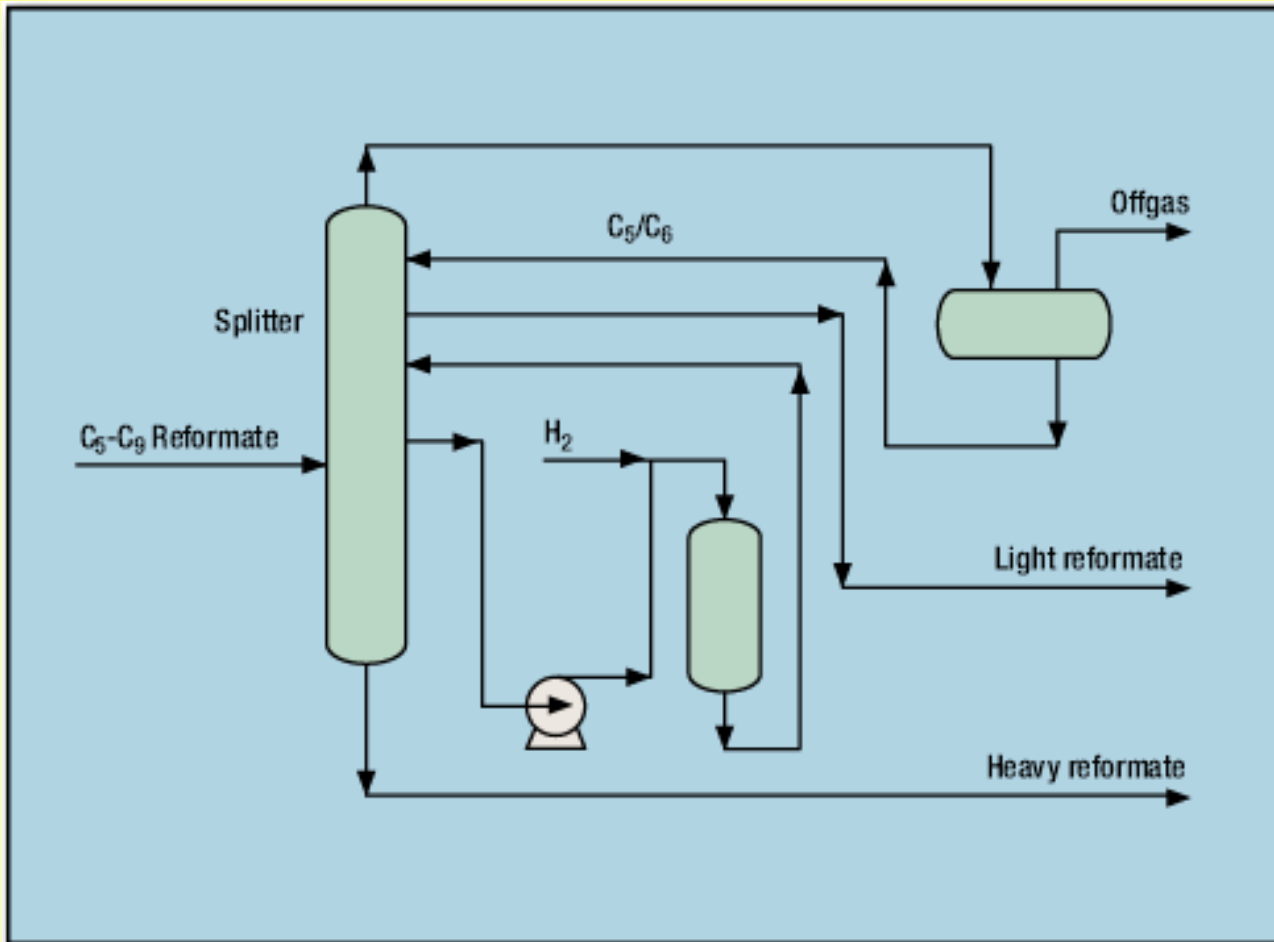
# UOP “Penex-Plus™”

- 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)

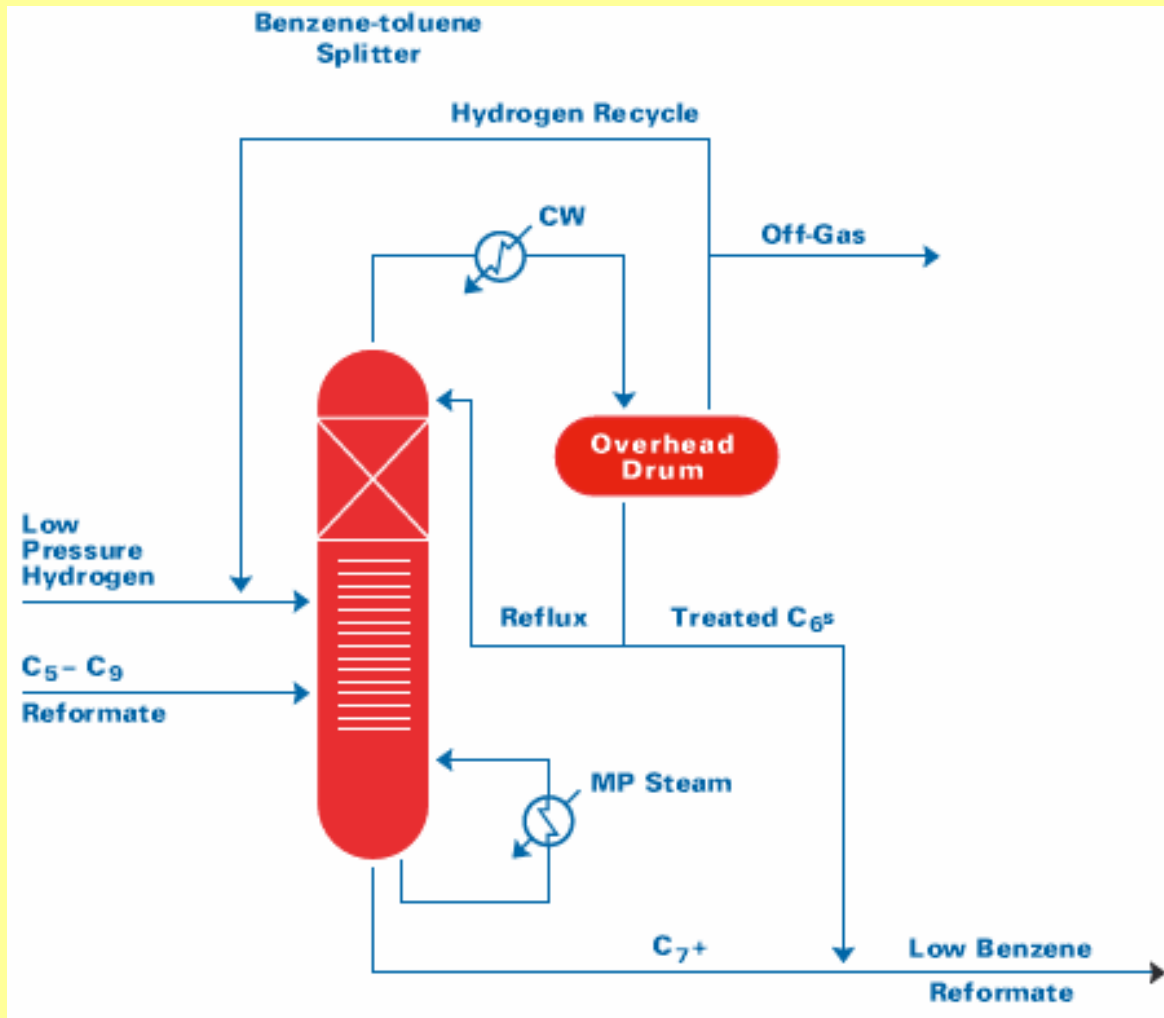
# Axens "Benfree<sup>TM</sup>" Process



# CDTECH “CDHYDRO™”

- Process hydrogenates benzene to cyclohexane in a catalytic distillation Bz-Toluene column
- Feed:
  - C5-C9 reformate
- Residual Bz: 0.5%vol

# CDTECH “CDHYDRO™” Process

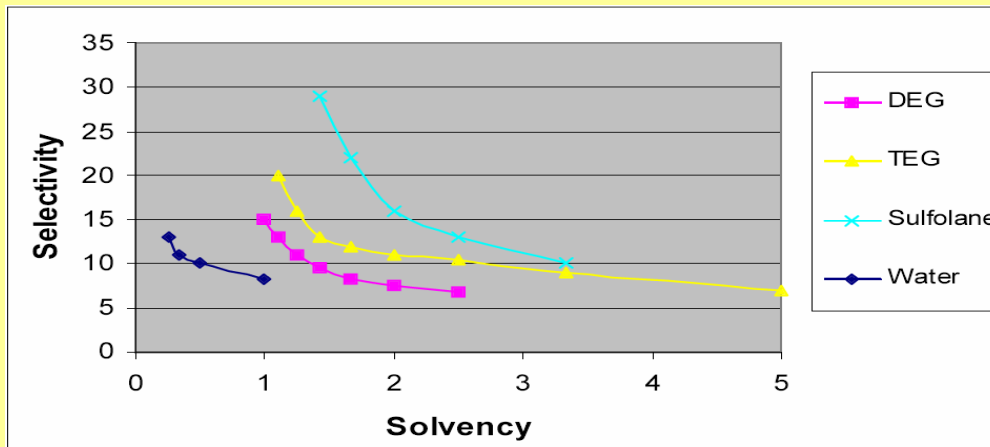


# Solvent Liquid-Liquid-Extraction (LLE) & Extractive Distillation (ED)

- 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

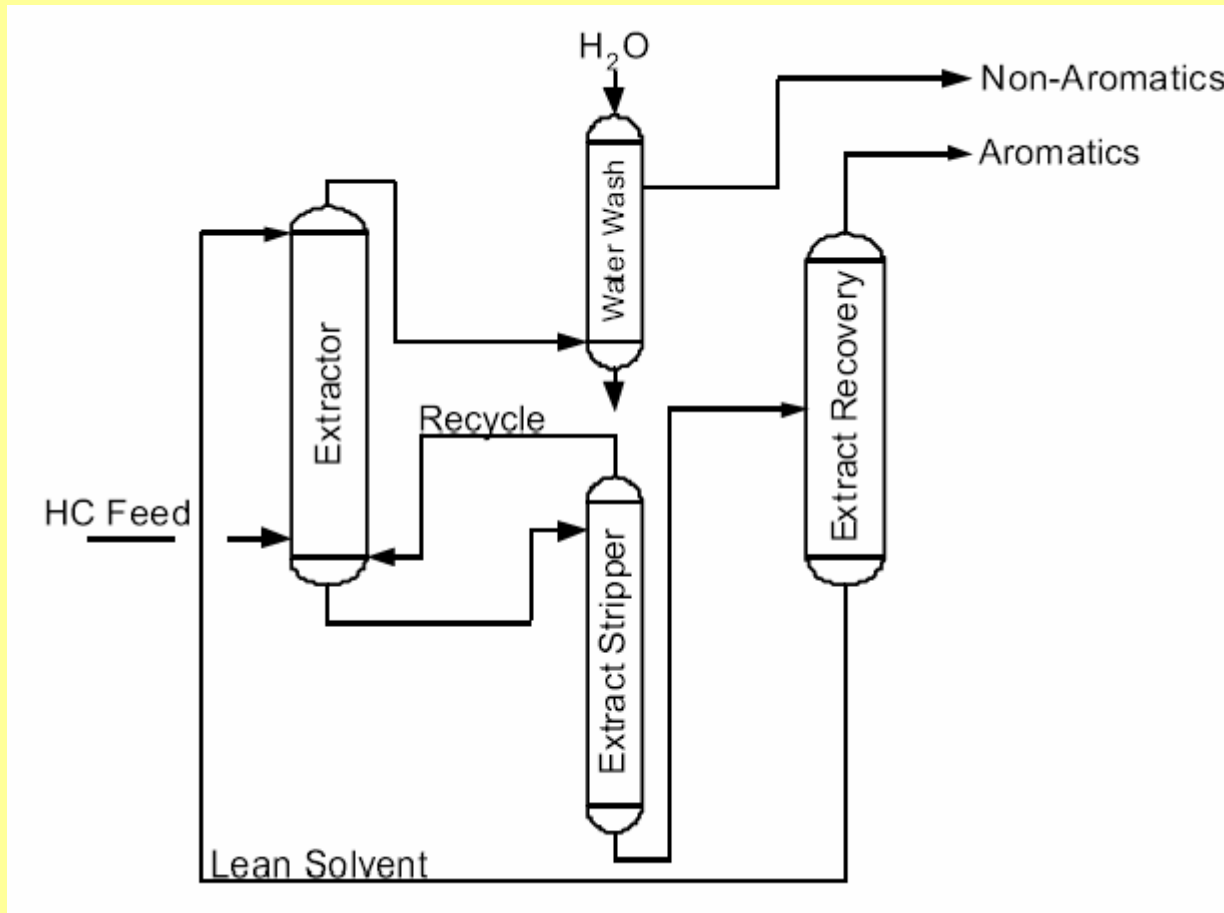


# LLE Solvent Comparison



- 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

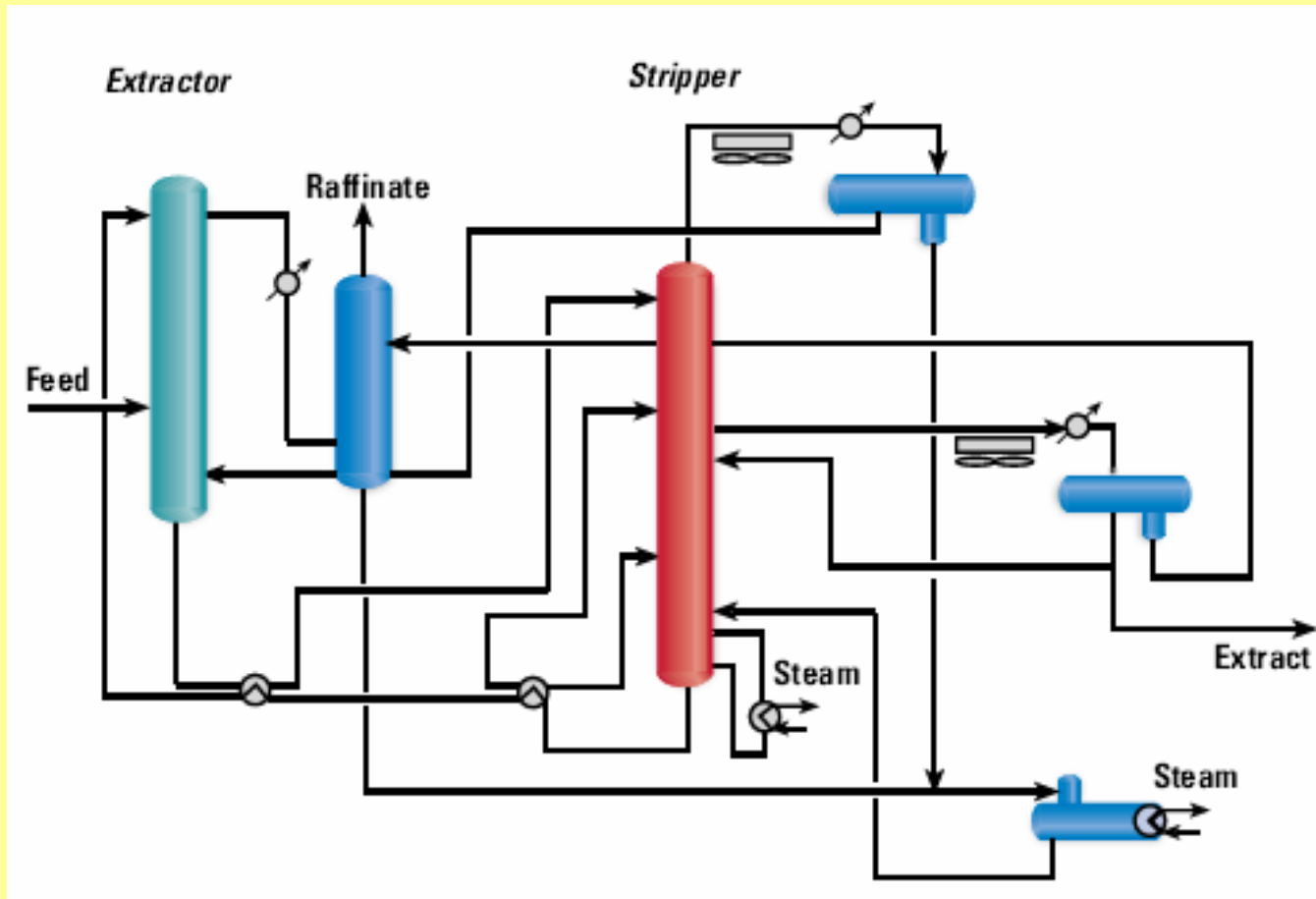
# LLE Process



# 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



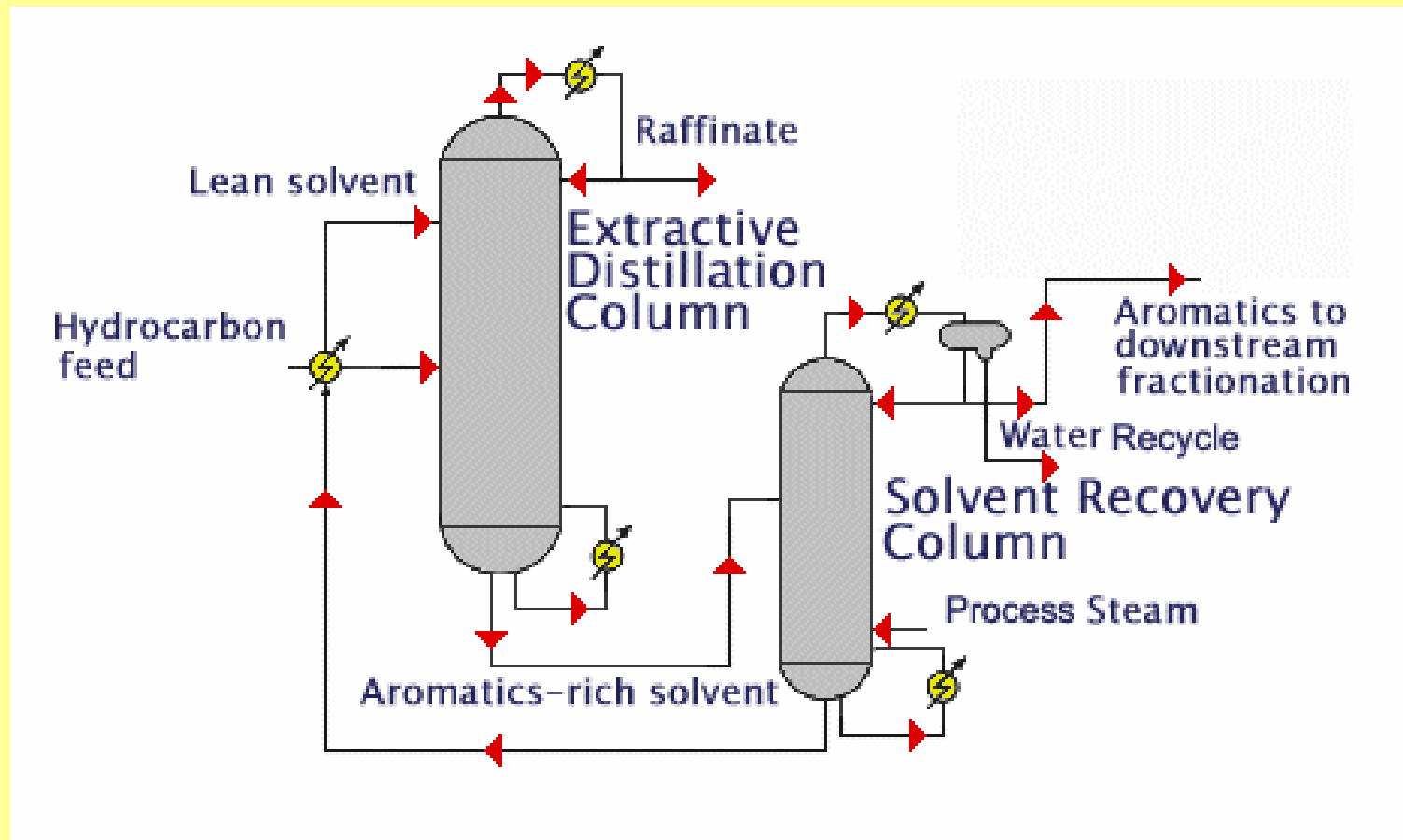
# UOP “SULFOLANE<sup>SM</sup>” & “ED SULFOLANE<sup>TM</sup>”

- 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<sup>SM</sup>” ED

- Aromatic Extractive Distillation (ED)
  - Utilizes lean solvent (Tectiv-100<sup>TM</sup>) 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%vol
- Reported investment: ISBL of \$6.5MM based on 3,500 BPSD of light reformate
- First unit startup in 2000

# GT-BTX<sup>SM</sup> Process Diagram

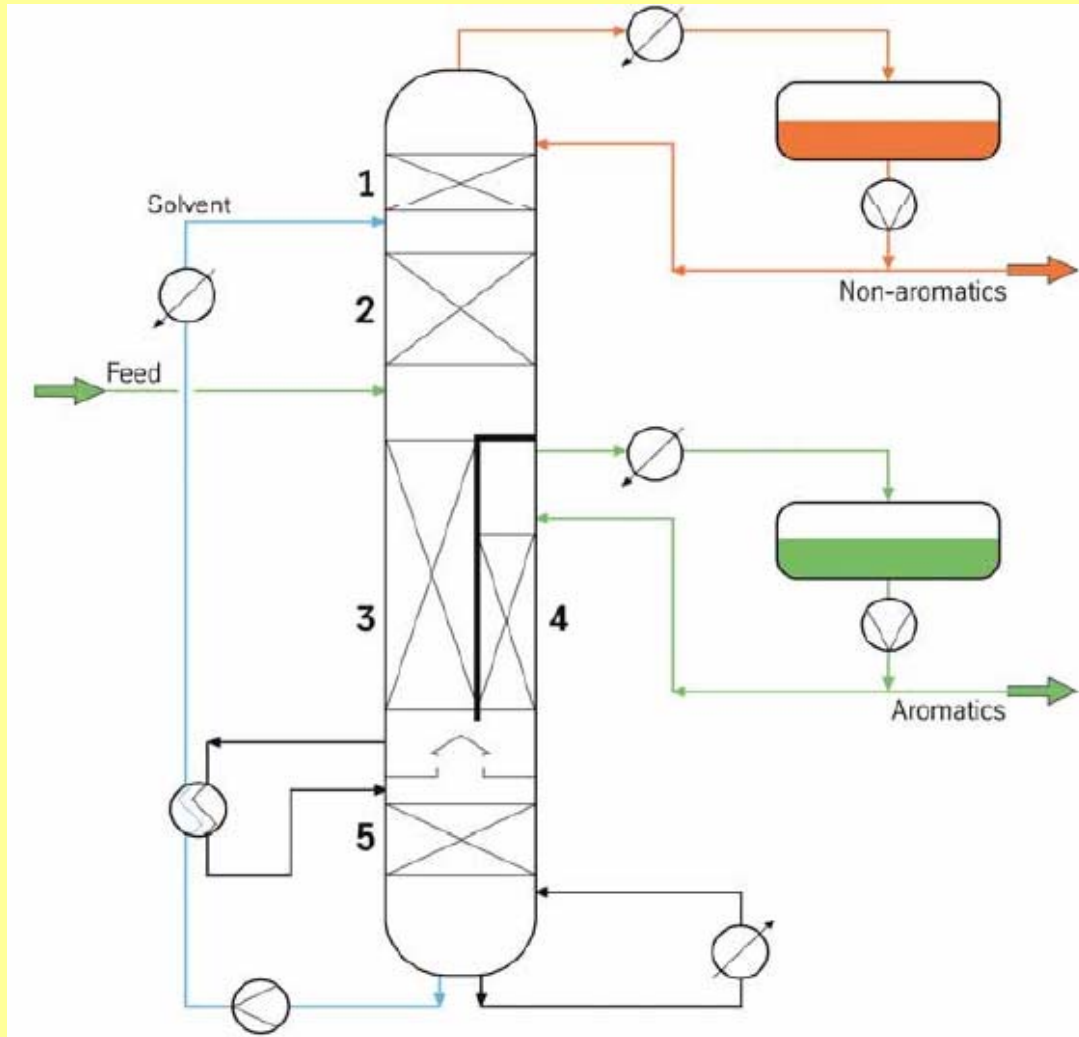


# Uhde GmbH “MORPHYLANE<sup>®</sup>” ED

- Utilizes Morphylane (N-Formylmorpholine) 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<sup>®</sup>” 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 H<sub>2</sub> 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