Naphtha Valorization to its Highest Value

Presented at IOCL Petrochemical Conclave by
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Petrochemicals Have Higher Value

Technology

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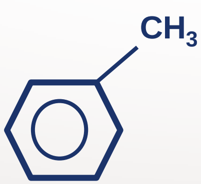
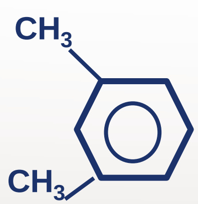
- Refiners have opportunity to upgrade naphtha into higher-value blendstock or petrochemicals
- By-product naphtha from cracking processes have great potential for upgradation
- Molecule management is the key to understanding the best method to process the naphtha

Component	Value Relative to Naphtha (Average Estimates)
Naphtha	**1.00**
Unleaded Gasoline	1.15
Toluene	1.20
Mixed Xylenes	1.25
Ethylene	1.50
Benzene	1.50
Paraxylene	1.55
Propylene	1.55
Styrene	1.70
Isoprene	2.10
C5/C9 HCR	2.5-3.00

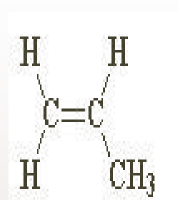
Benzene



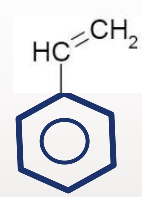
Toluene



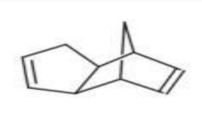
Mixed Xylene



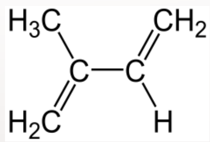
Propylene



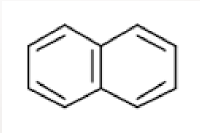
Styrene



DCPD



Isoprene



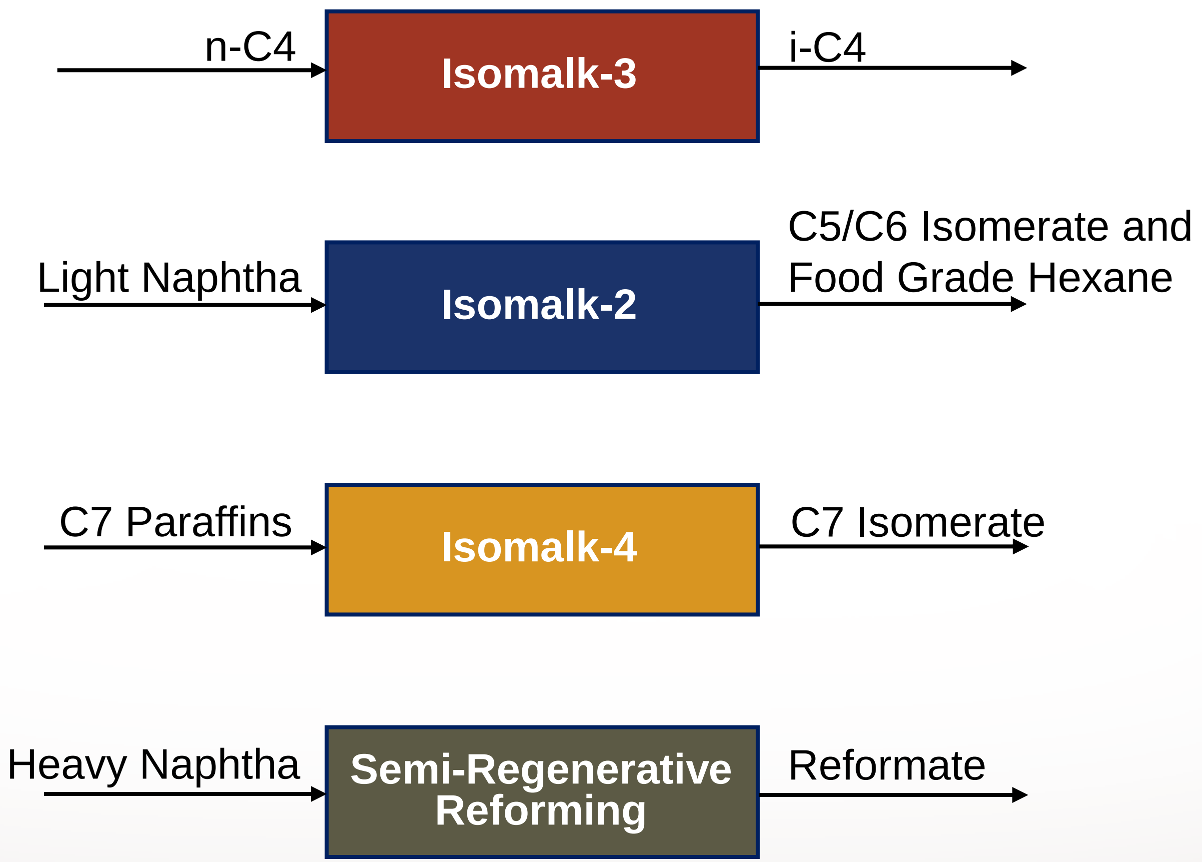
Naphthalene

Conventional Refinery Naphtha Utilization

Typical disposition

Straight Run (Paraffins) →	**Cracking, Isomerization, Reforming**
Thermal or Catalytic Cracked (Olefins) →	**Fuels or Gasoline**

Technology Options for Straight Run Gasoline



C5/C6 Isomerisation: Technology Choices

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Three light gasoline isomerization processes

- **Zeolite catalysts**
  - High operating temperature
  - Less favorable for formation of high-branched isomers

- **Chlorinated aluminum oxide catalysts**
  - Reasonable octane increase
  - Regular organochloride additions required
  - Spent caustic disposal also required
  - Extreme measures for H_20 and impurity removal

- **SI-2 Mixed metal oxide catalysts**
  - Advantages over chlorinated aluminum and zeolite, with none of the disadvantages

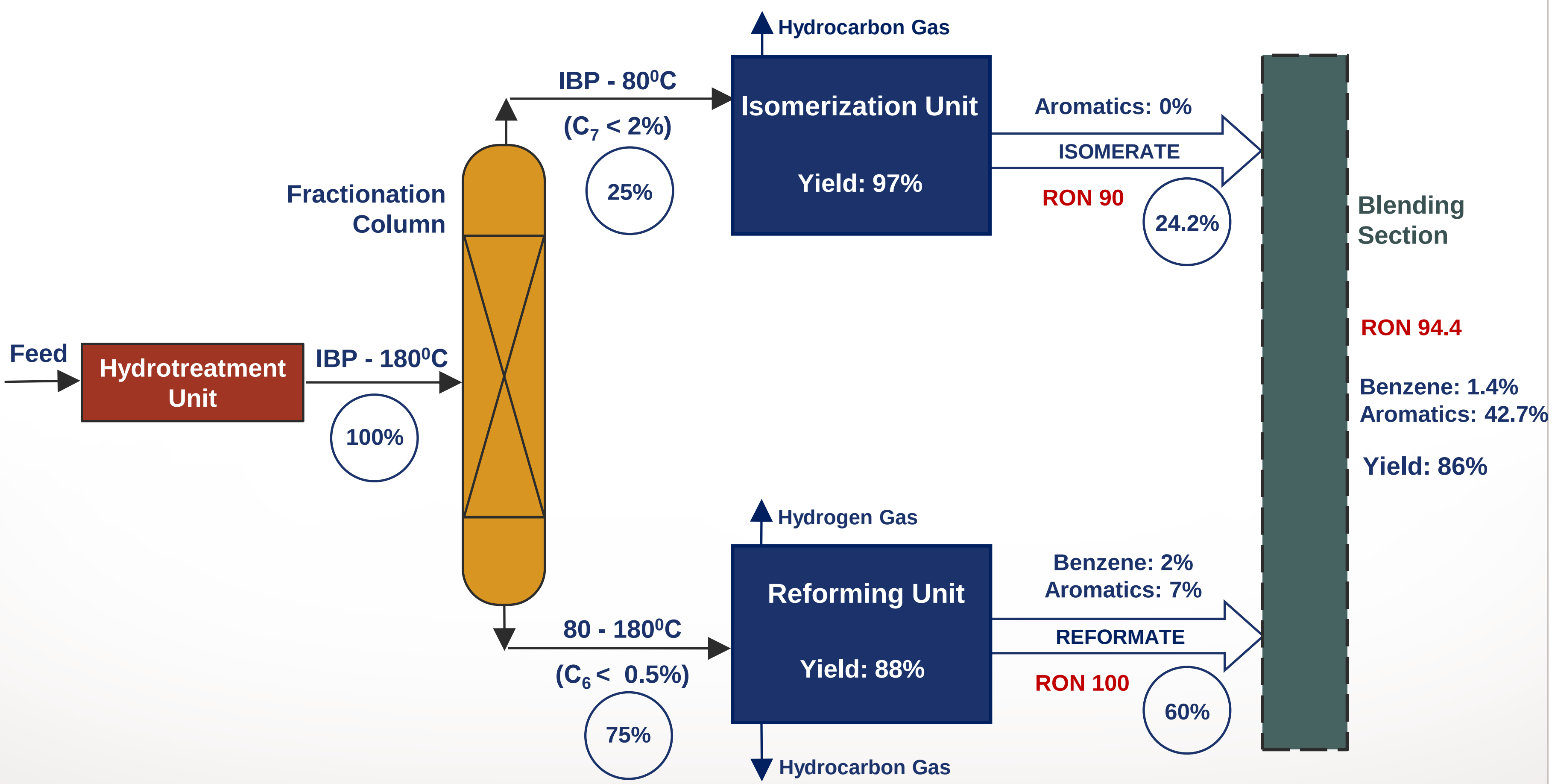
Technology	Performance	Robust Operation	Environment
Zeolite		✓	✓
Chlorinated Alumunim	✓		
Isomalk-2^{SM}	✓	✓	✓

Case study, World-Scale Grass-Root Isomalk-2^{SM} Unit.

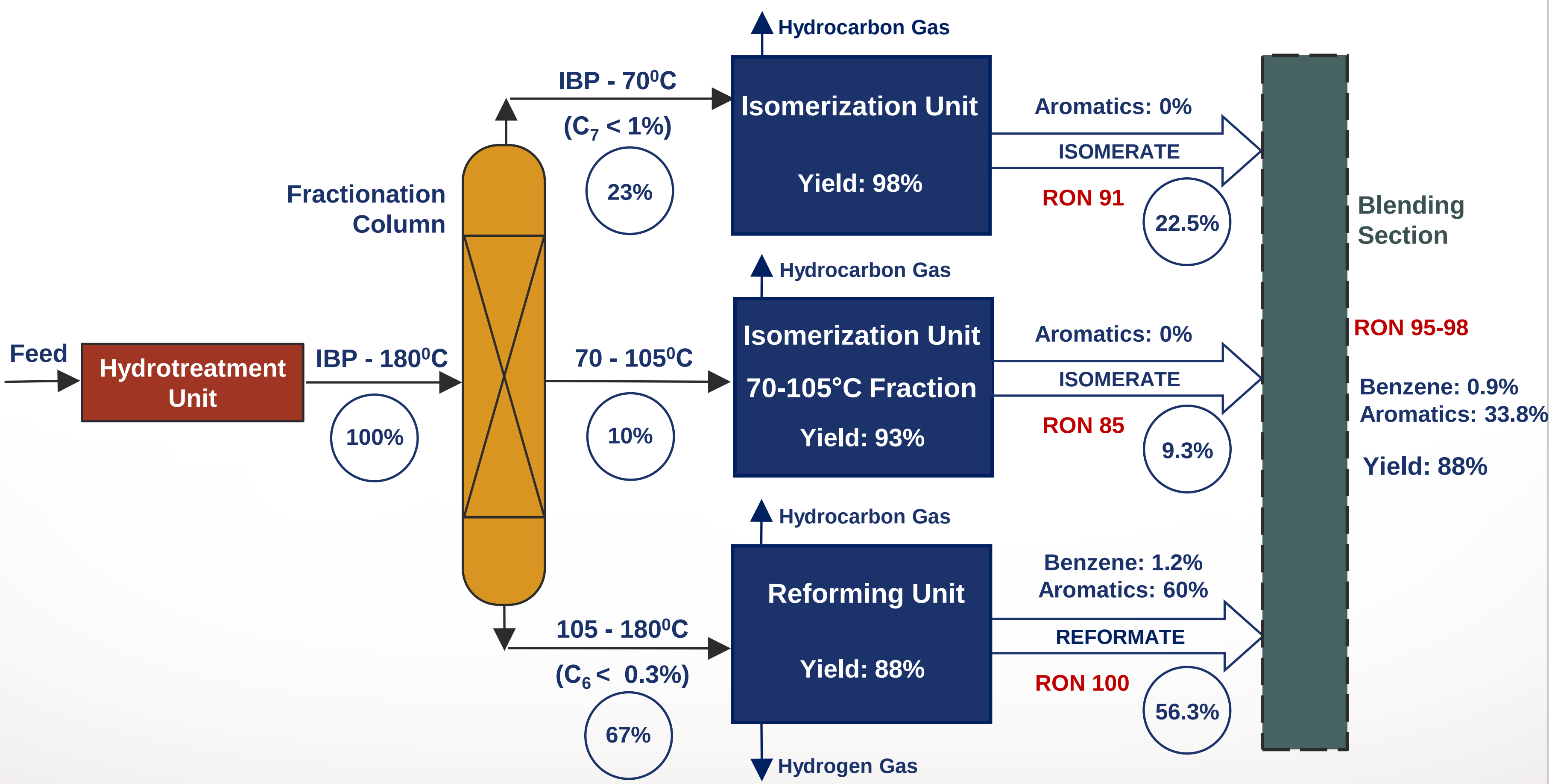
Process scheme	Full Recycle Scheme (DIP, DIH, DP)
Capacity, t/y	1.0 MMTA
Isomerate yield, %	99
i-Pentane cut, RON	92.0-93.0
Light Isomerate, RON	91.5-92.5
Space velocity in the reactor block, hour^{-1}	2.0 -2.5
Start-up year	November, 2010

First World-Scale isomerization unit to use non-chlorinated catalyst and achieve 92.5 RON for final isomerate

Typical BFD for Processing Light and Heavy Naphtha



BFD for naphtha processing with C_7 isomerization technology available



Comparison of the 2 process configurations

From a recent case study made for a plant with light naphtha Isomerization unit (DIP, Super DIH) and CCR Reforming unit for a 2 MMTA naphtha stream.

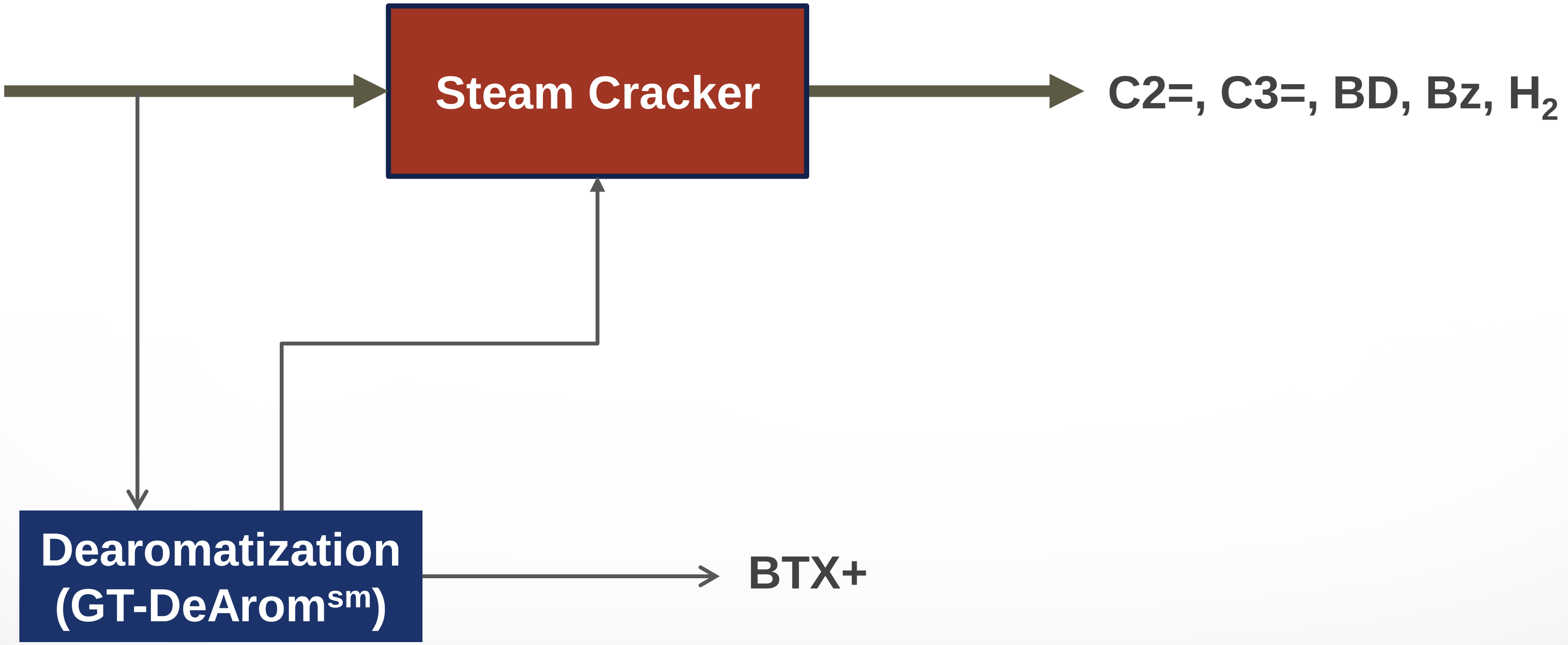
Configuration	Conventional	With Isomalk-4^{SM}	Benefit	Value to Refinery Per Annum
Overall gasoline yield, wt.%	88.7%	**90.8%**	**2.1%**	**16.8 MM USD ***
Octane Number, RON	94.0	**95.5**	**1.5**	**15.0 MM USD ***
Benzene in the gasoline pool, vol.%	1.5%	**0.6%**	**0.9% less**	**Varies**
Aromatics in the gasoline pool, vol.%	37.0%	**33.5%**	**3.5% less**	**Varies**

*** - based on $400/ton differential for liquid yield over gas; and $5/ton-octane number**

Total benefit is over 30 MM USD/yr with the C_7 paraffins routed to Isomalk-4^{SM}

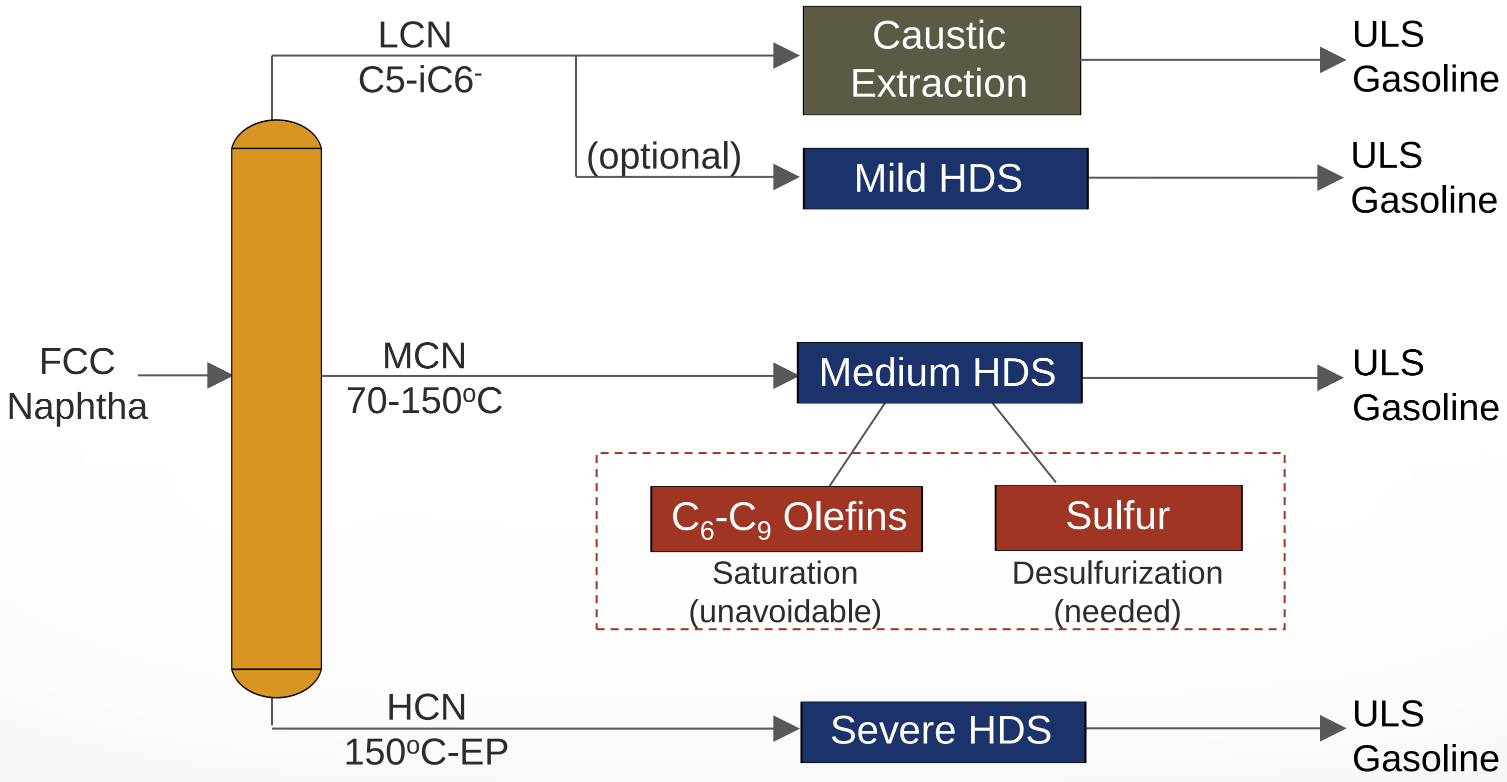
Aromatics Removal from Steam Cracker Feed

Tailoring the feed
may be useful



Cracked Gasoline Management – FCC Desulfurization

Conventional Three-Stage Process



FCC Gasoline Desulfurization

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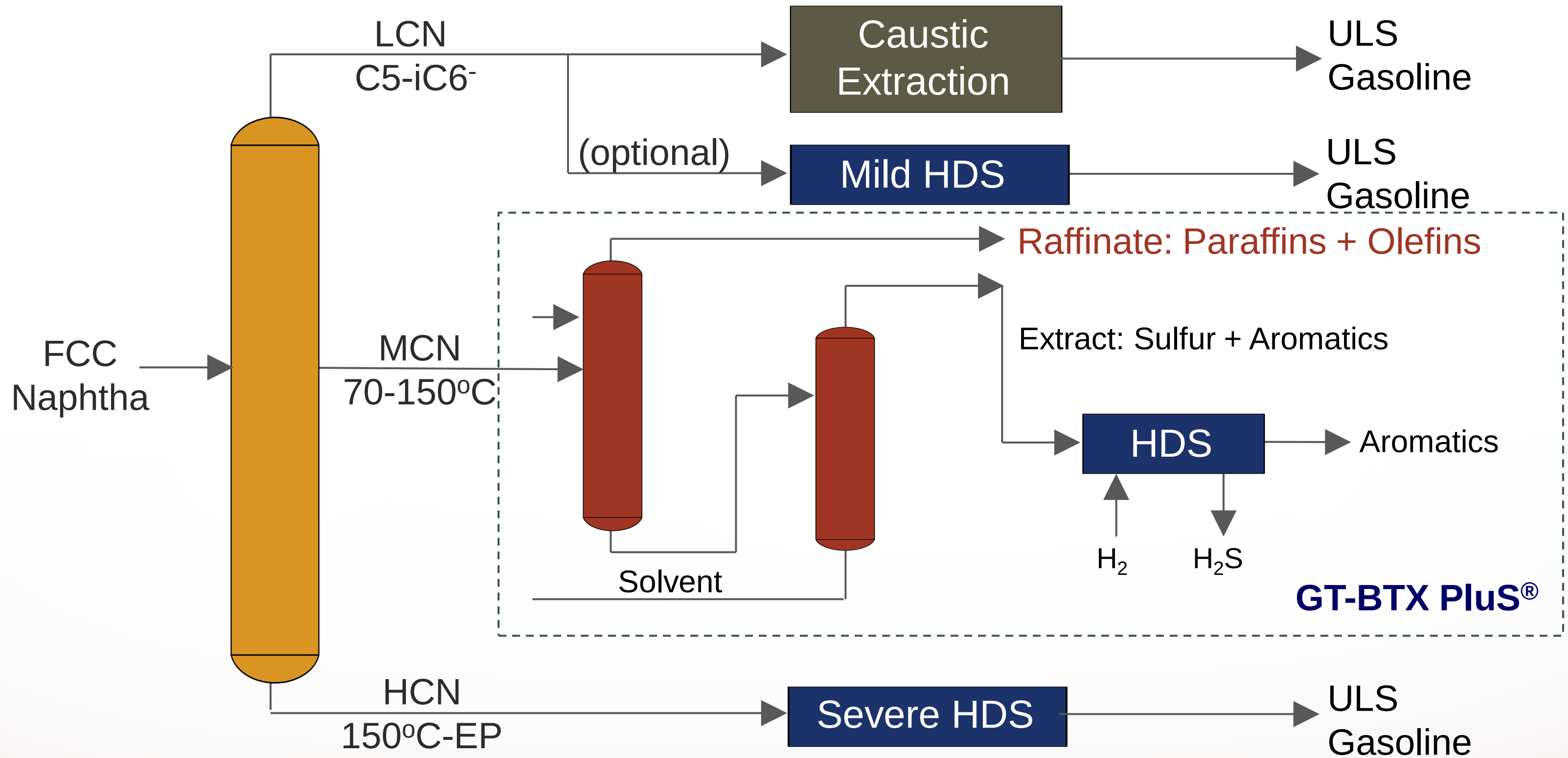
Alternate Option to Extract Sulfur from the Olefins

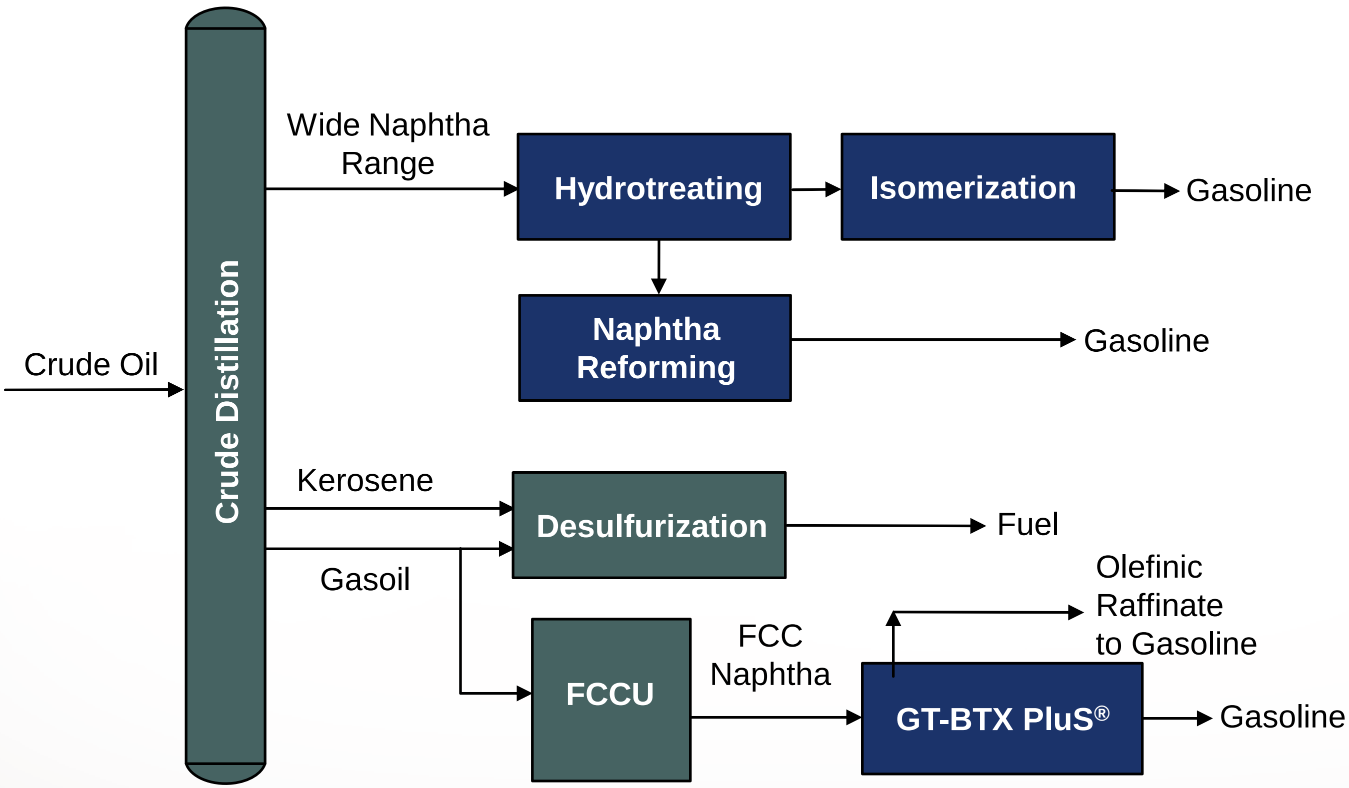


GT-BTX PluS® - Enabling Technology

- Technically advanced extraction process enables
  - Desulfurized gasoline to < 15 ppm sulfur with zero octane loss
  - Reduced benzene in cracked gasoline to < 0.5% benzene
  - FCC olefins preserved for conversion to aromatics or propylene

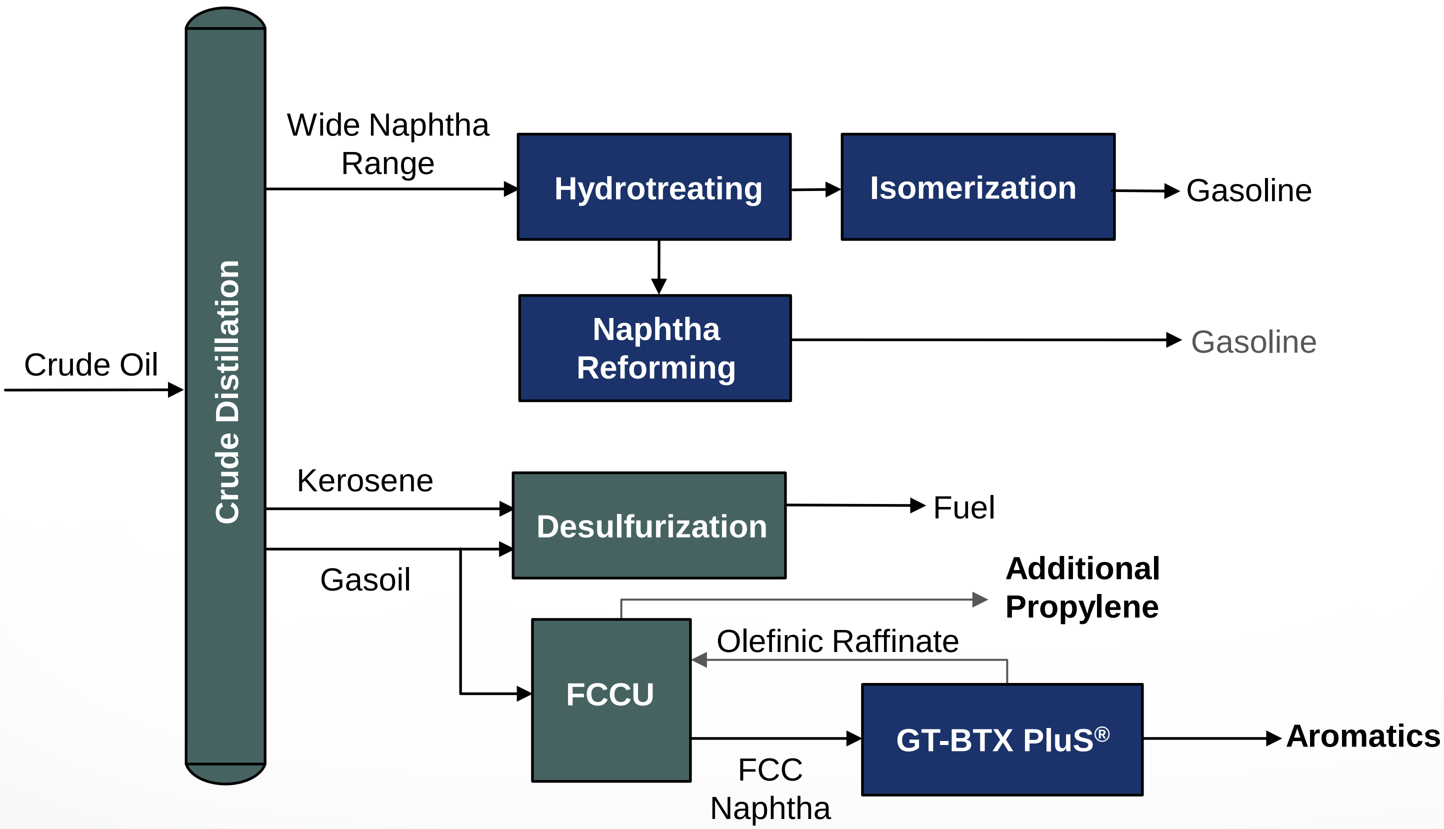
Patented process – available through GTC Technology

Typical Refinery Configuration with GT-BTX PluS® - Products to Gasoline



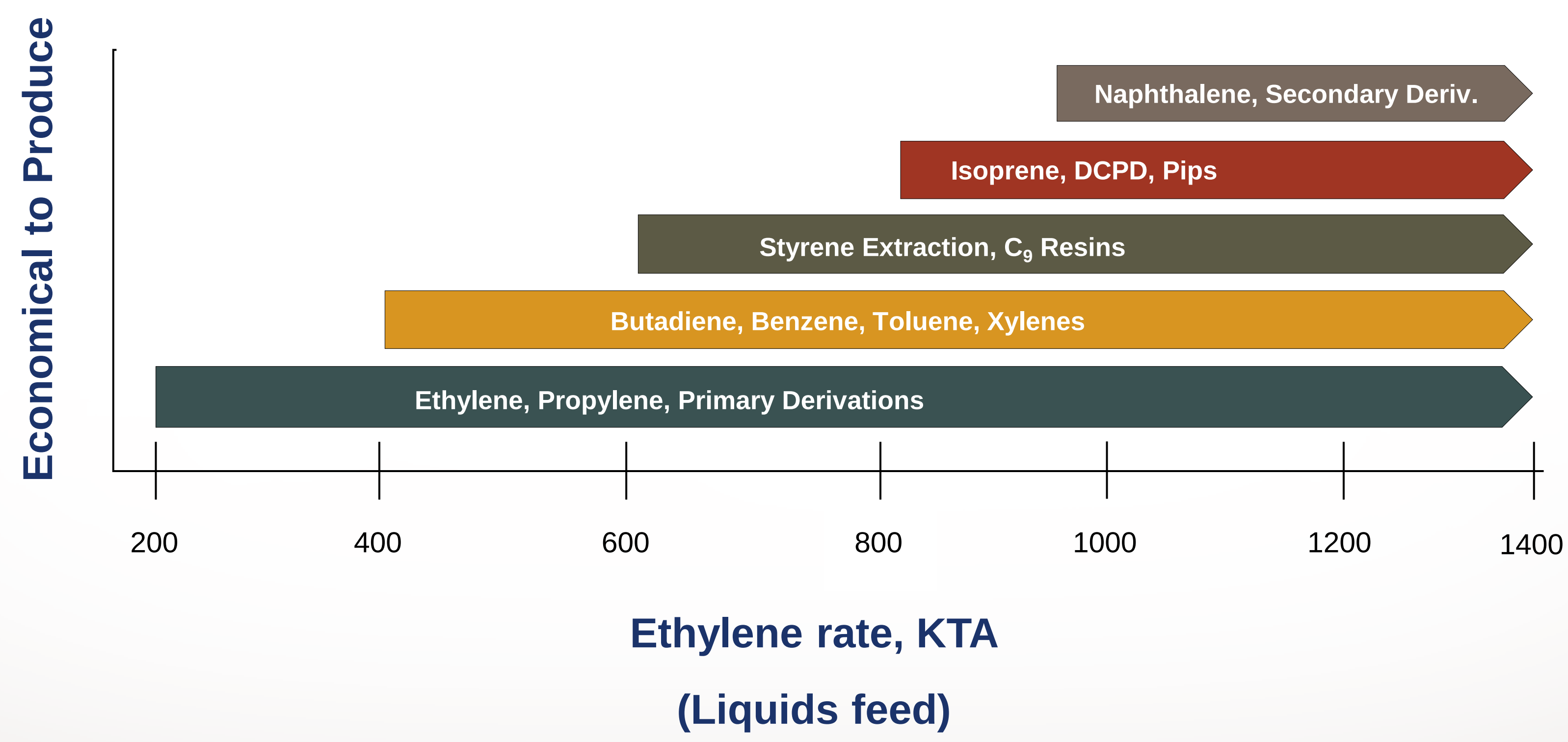
- Zero Δ in octane value
- Low benzene
- Low sulfur

Refinery Configuration with GT-BTX PluS®
to facilitate increased Propylene

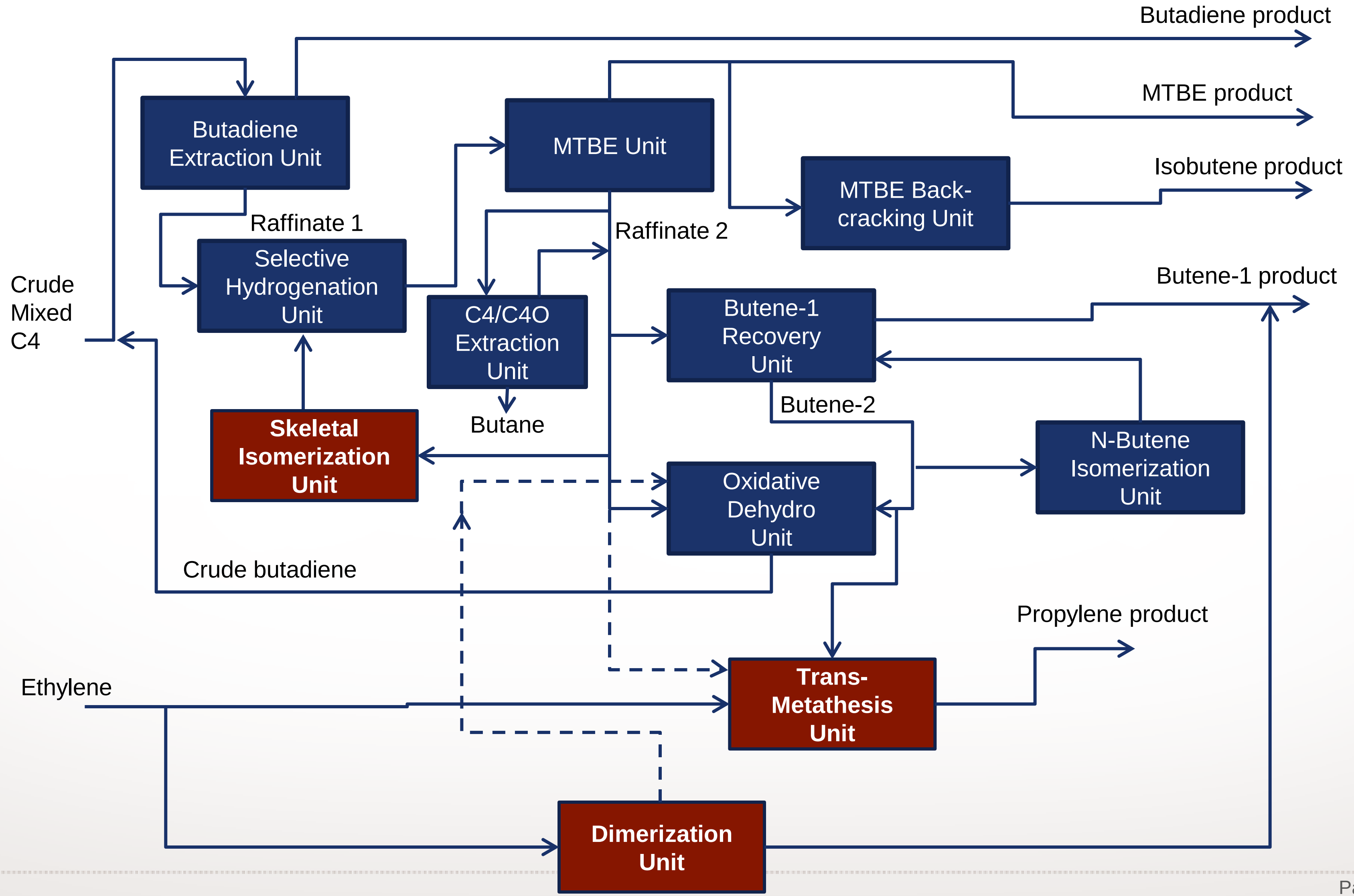


Extends Range of FCC Naphtha Recycle

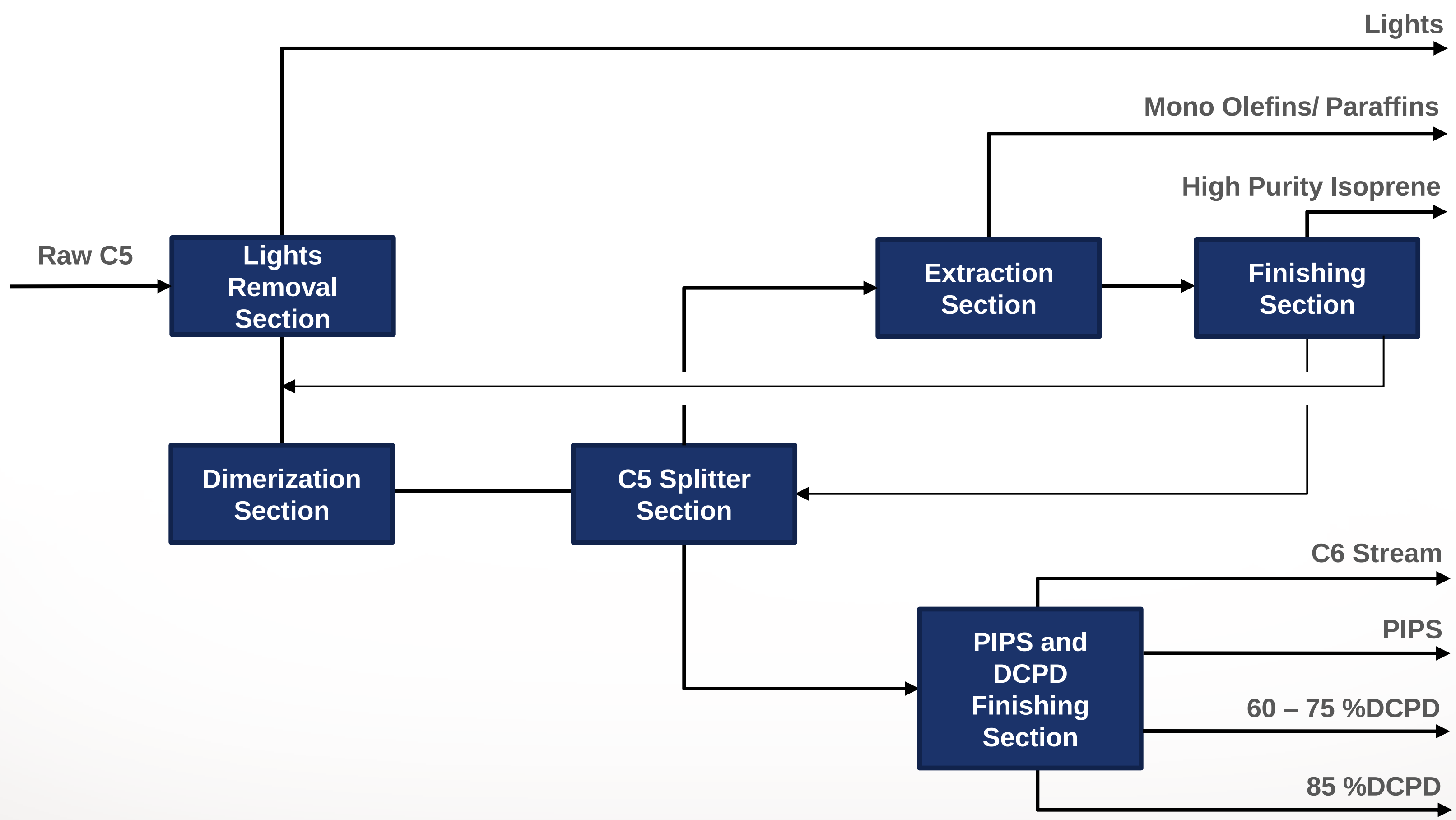
Economical Ethylene Capacity for Recovering By-products



C4 Utilization



Pygas C5 Utilization – GTC GT-C5/Isoprene



Pygas C6-C8 Utilization: GT-BTX®

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Extractive Distillation depends on a selective solvent to alter the boiling points of aromatics & non-aromatics to facilitate their separation by distillation.

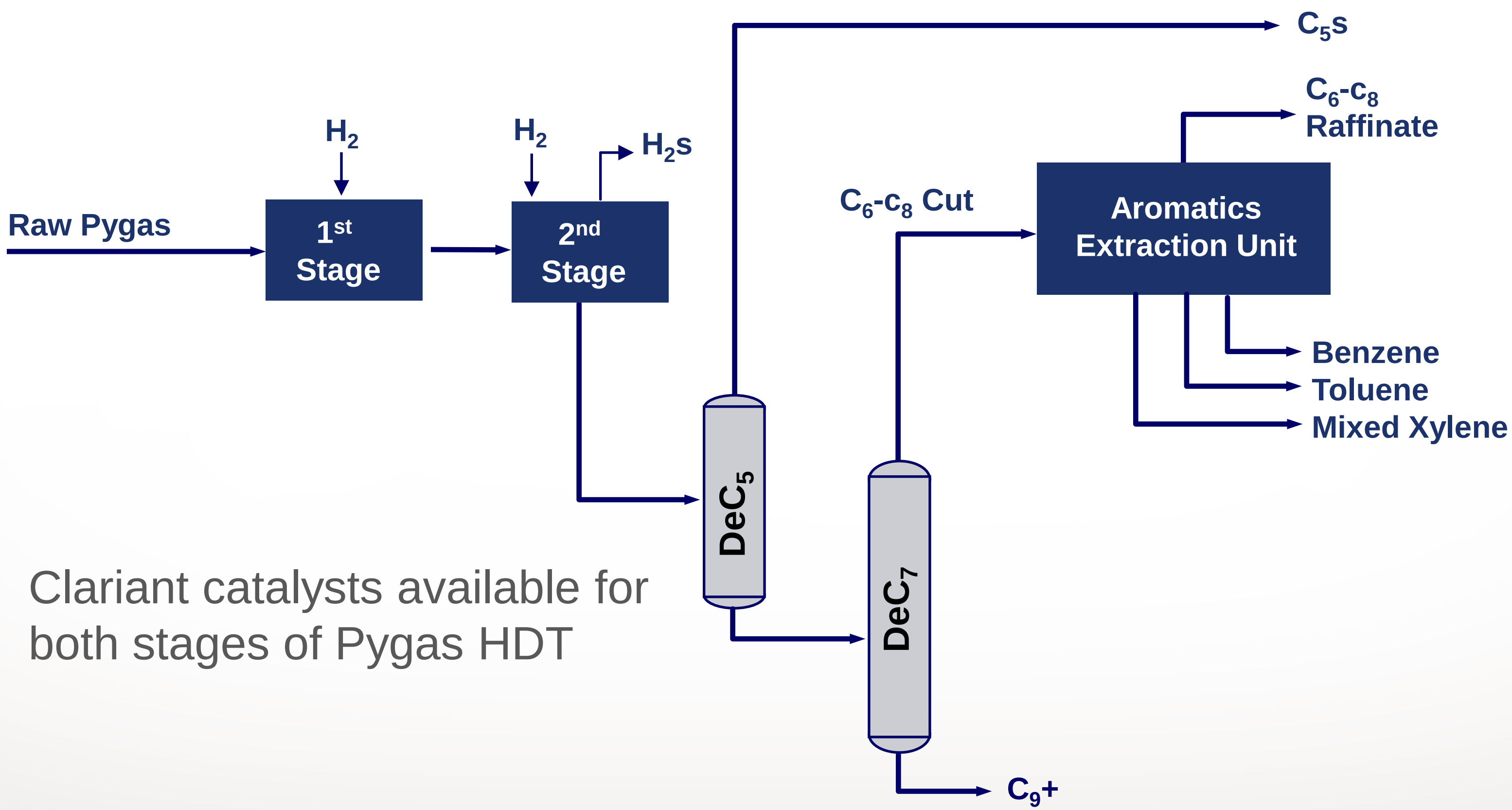
★ Solvent selectivity is critical

Solvent	α n-C_7/Benzene
Techtiv-100tm	2.44
Sulfolane	2.00
N-methyl Pyrolidone	1.95
N-formyl Morpholine	1.89
Glycol blends	1.35
None	0.57

Proprietary solvent of GT-BTX® Technology

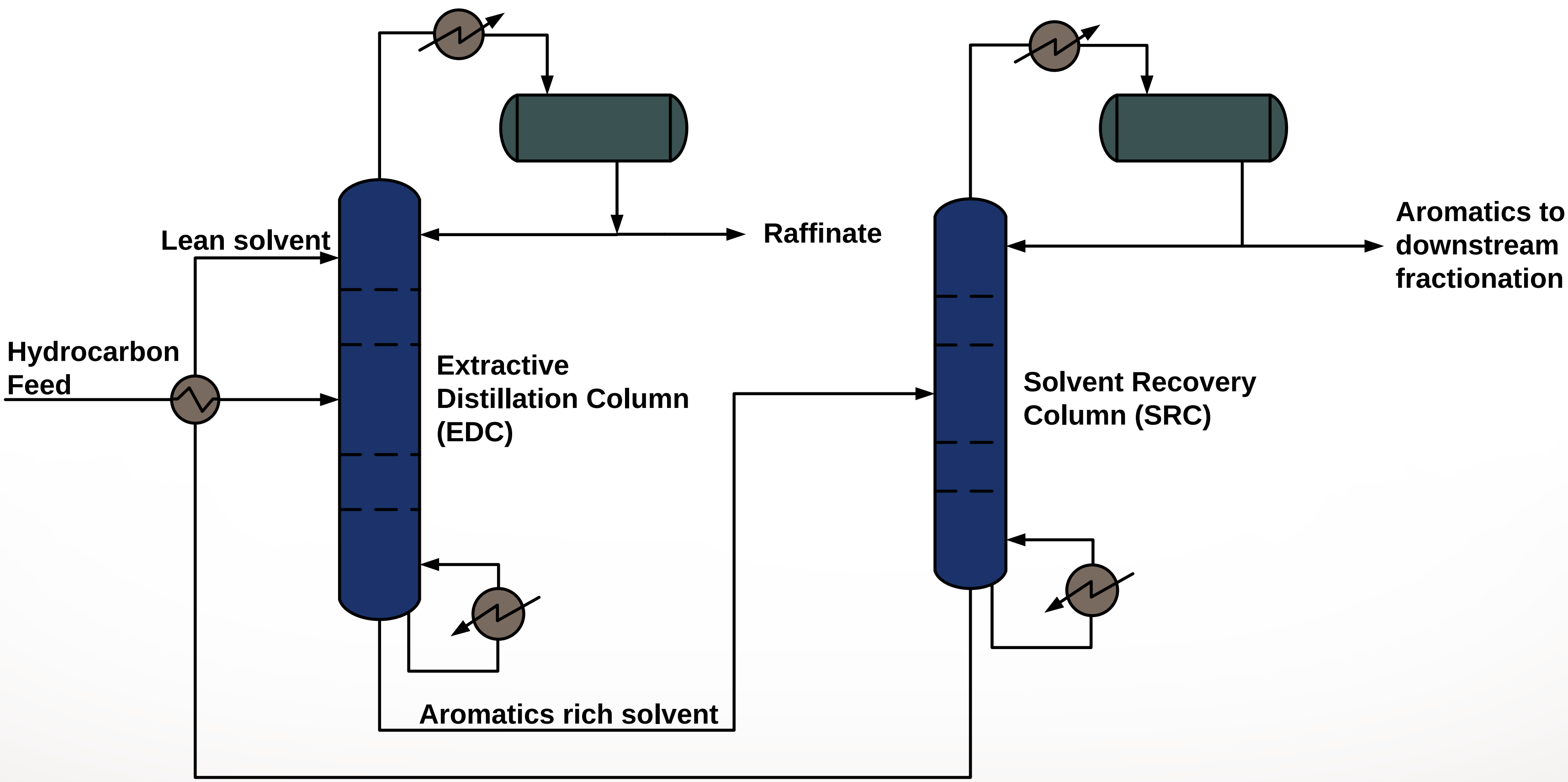
Pygas C6-C8 Utilization

Benzene, Toluene, Xylene need to be extracted from C6 – C8 cut of pygas in order to meet petrochemical quality



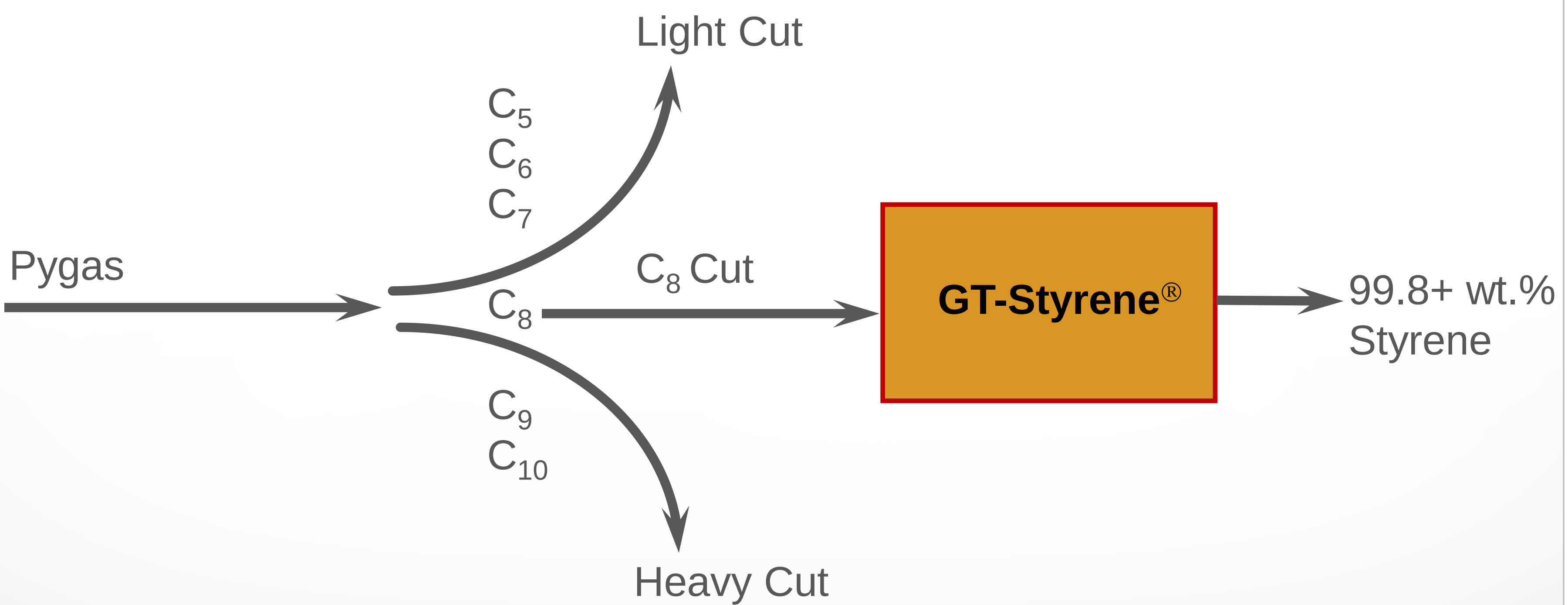
Clariant catalysts available for both stages of Pygas HDT

World-Class Extraction Technology for BTX Purification



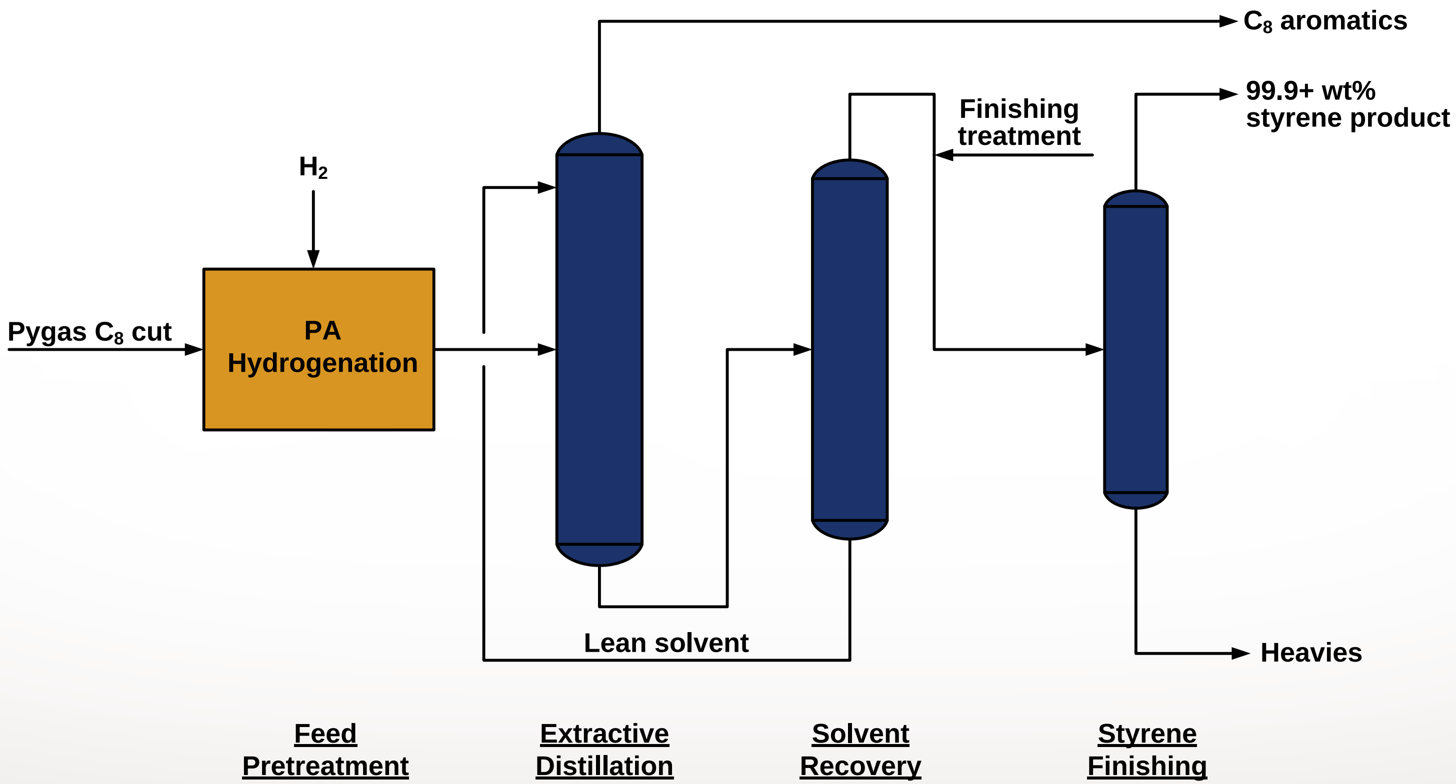
Pygas C8 Utilization – GT-Styrene

Heart cut distillation followed by ED



Pygas C8 Utilization – GT-Styrene

- Recovery of styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gas oils, and natural gas liquids (NGL)



Economics of Styrene Recovery
Basis - 25,000 mt/yr Styrene (2014 pricing)

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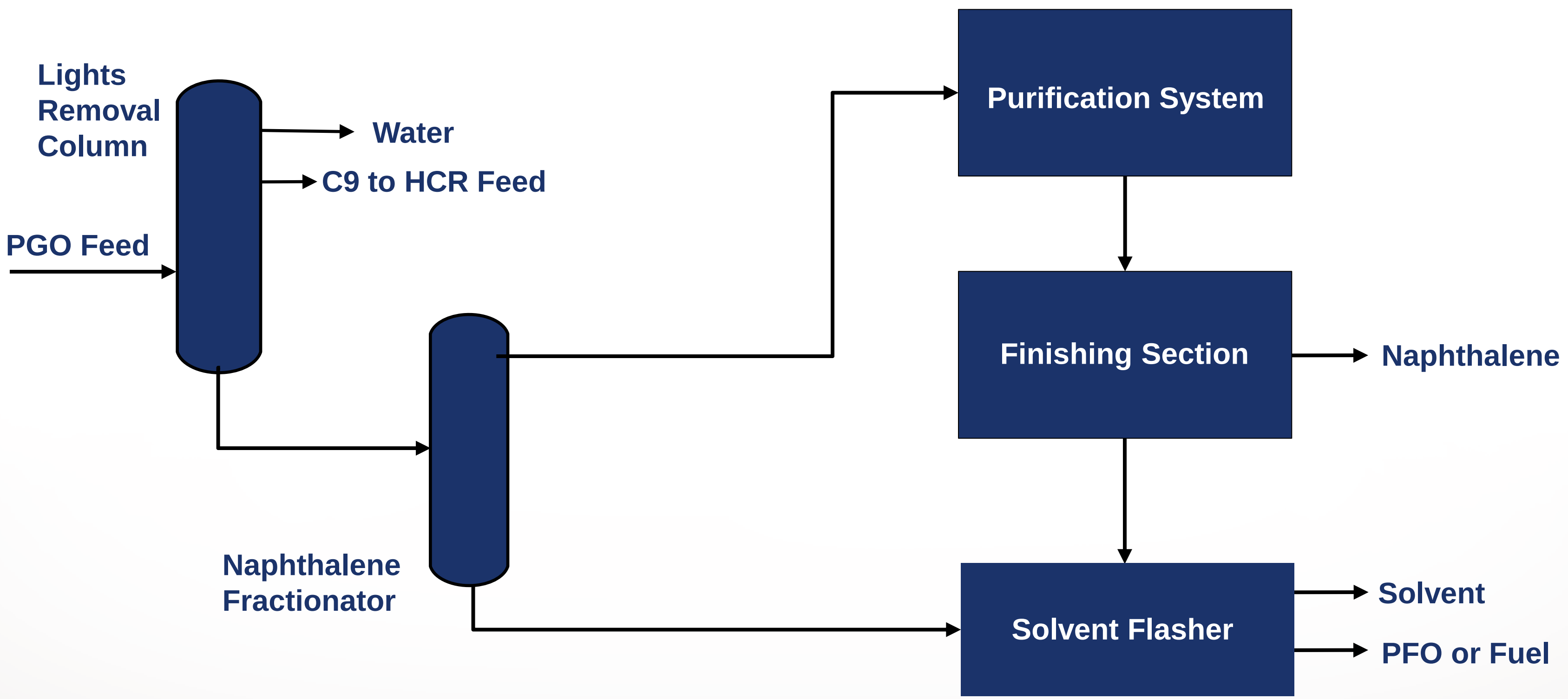
Parameters	GT-Styrene®
Capital cost	$28 MM
Feedstock cost, $/ton	$600
Processing cost, $/ton	$200
Total production cost, $/ton	$800
Sales price, $/ton	$1250
Net margin	$11.25 MM
Pre-tax ROI	40%

Pygas C9+ Utilization – Naphthalene, Solvent, & Resin



Conclusions

- The nature of raw materials leads to proper processing scheme
- Non-chlorinated isomerization catalysts are the optimum to boost gasoline octane for C4 – C7 fractions of straight run gasoline
- Refinery/petrochemical integration, in addition to propylene recovery, captures aromatics and preserves olefins from FCC gasoline
- Steam cracker by-products are important to recover from large plants using naphtha feedstock
- Technology is available to upgrade products from C4 – C12 boiling range

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