Valuable Chemicals From Cracker Pygas

Maintain Competitiveness for Naphtha Crackers

SULZER GTC Technology US, INC

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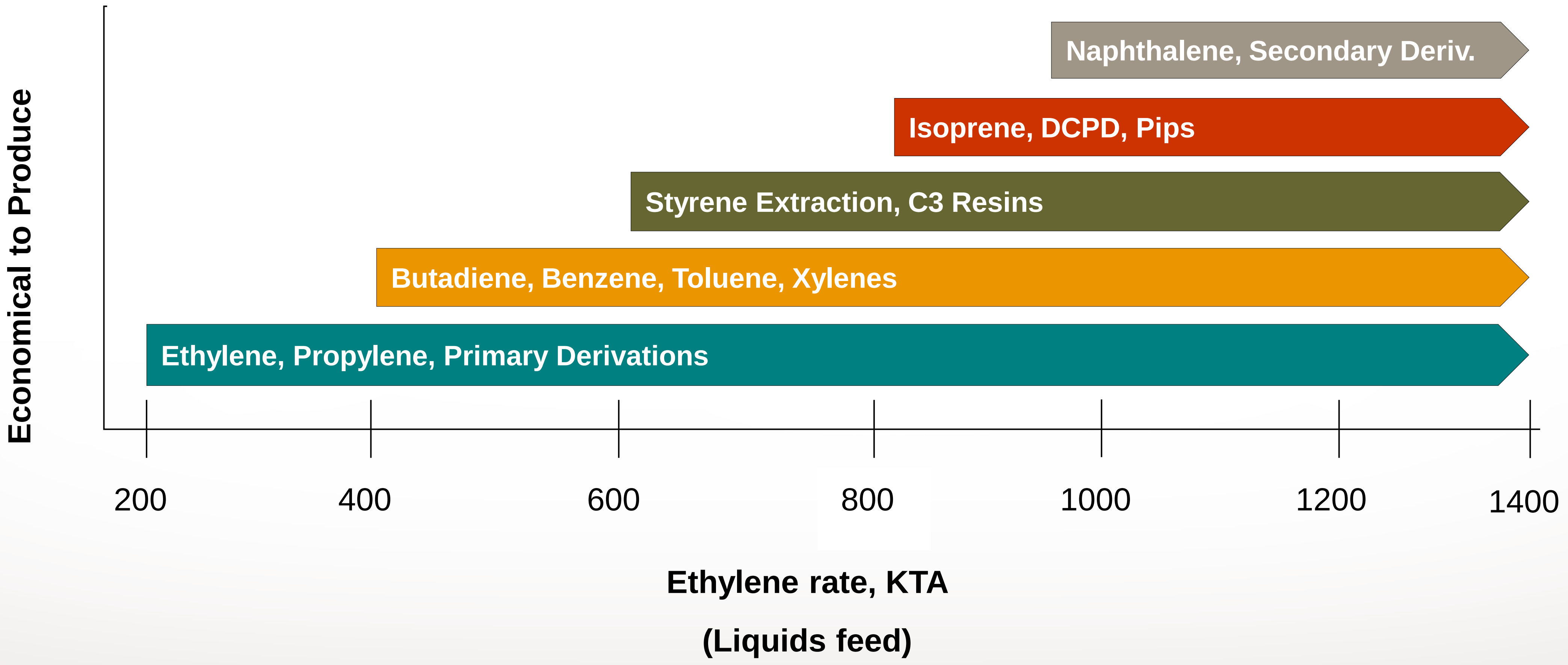
Economical Ethylene Capacity for Recovering By-products



Naphtha Cracker Byproducts – Pygas
GTC- Offered Overall Processing Scheme

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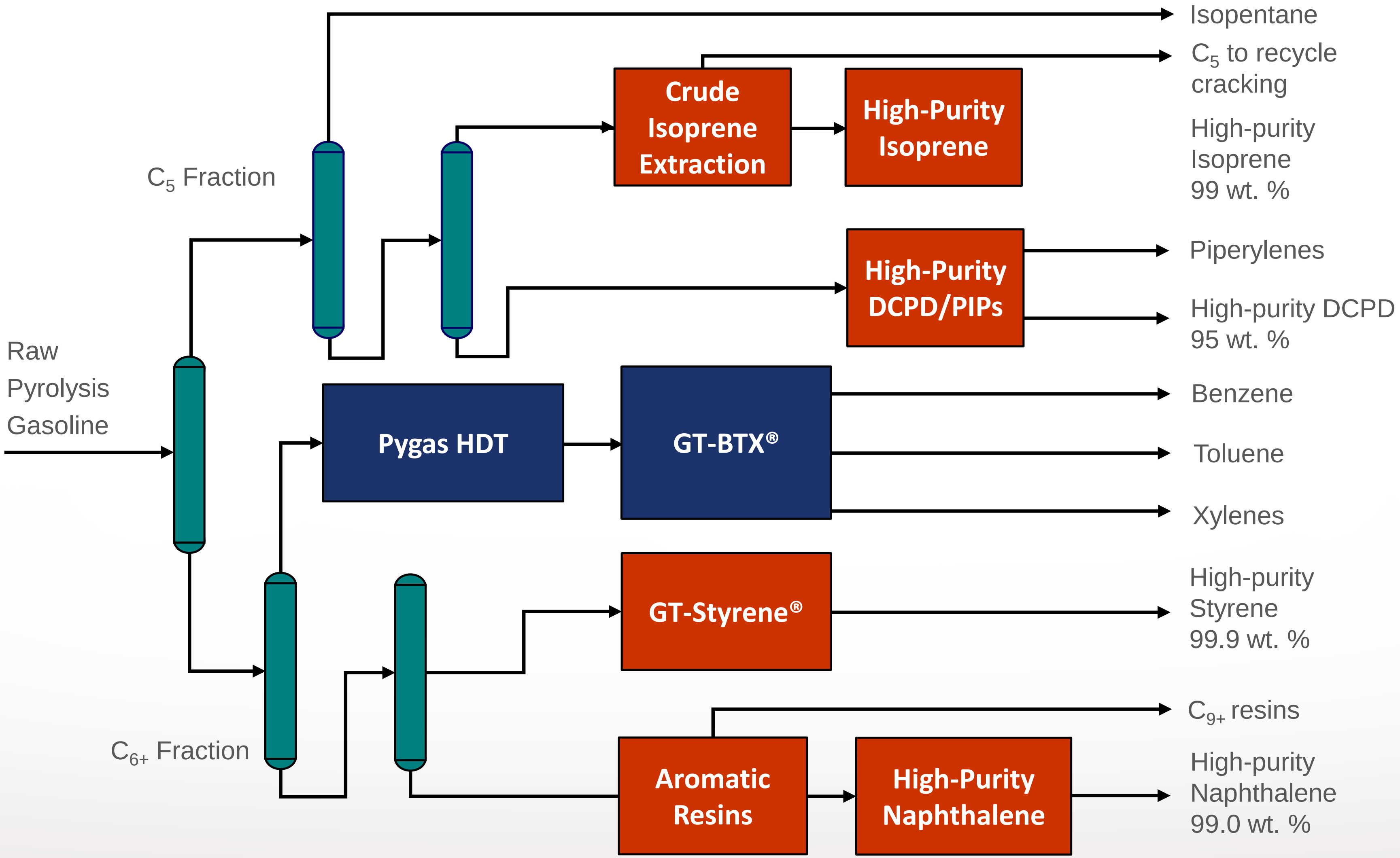

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C5 UTILIZATION

Pygas C5 Utilization

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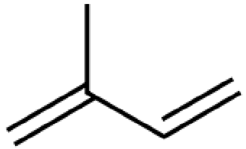
Primary Components of Interest

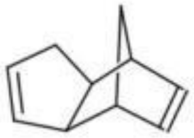
- Isoprene (2 methyl 1, 3 butadiene)



- Piperylenes (*cis* & *trans* 1, 3 pentadiene)

- CPD (cyclopentadiene)

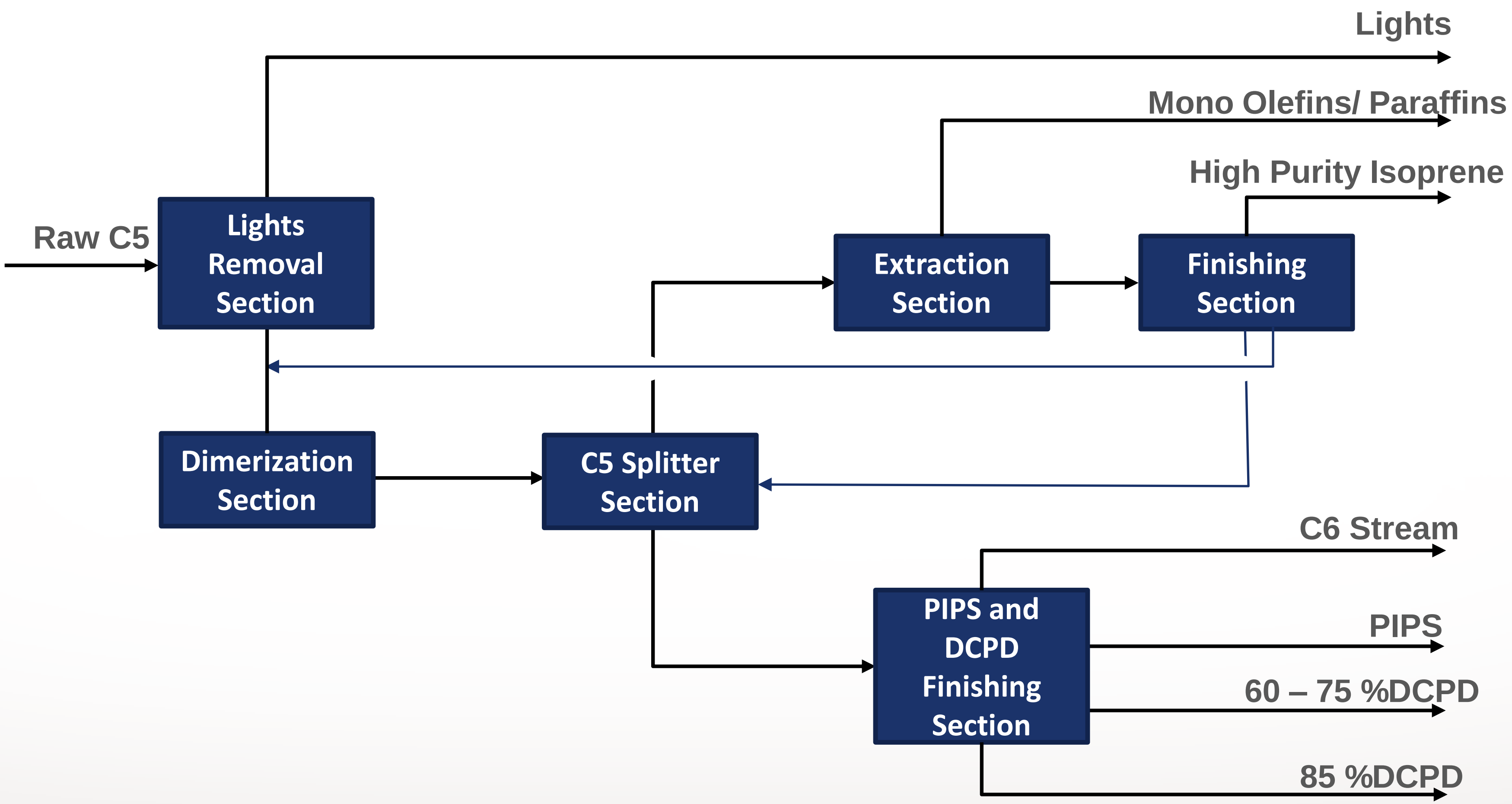
- DCPD (dicyclopentadiene)



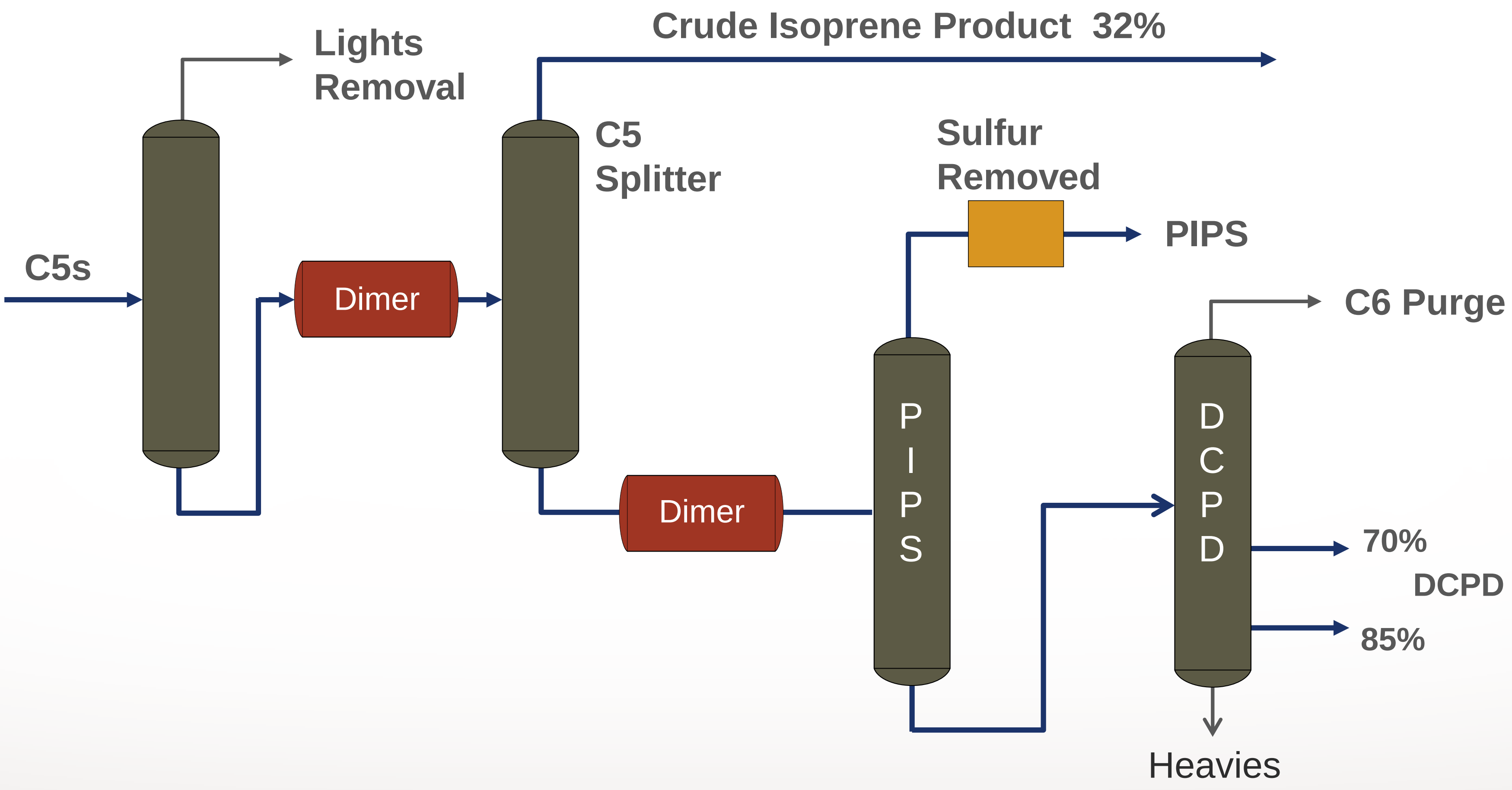
Other Components

Isopentane	Gasoline blendstock
C5 Mono-olefins	TAME, cracking, aromatization, resins
Paraffins	Cracker feed

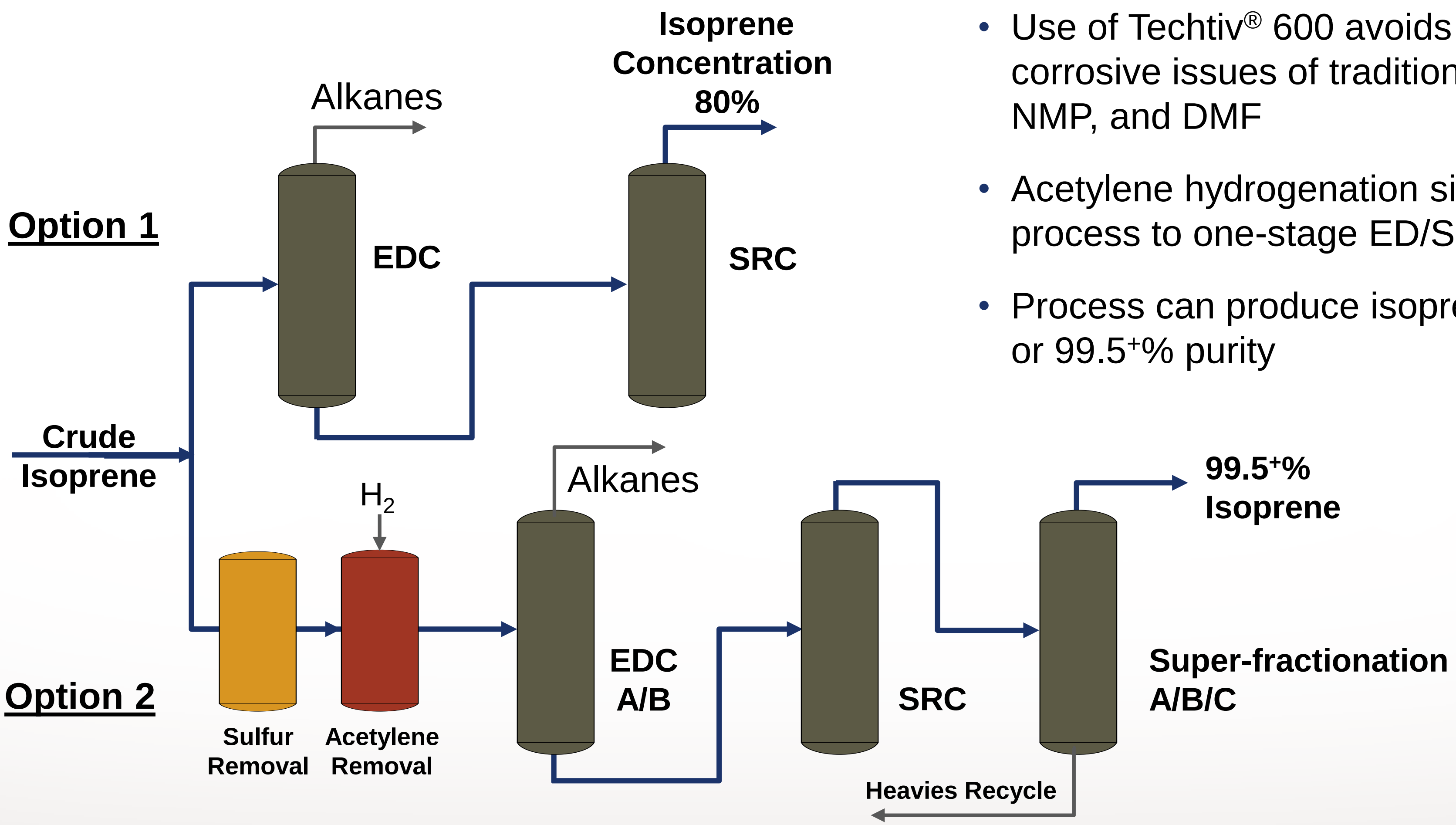
Pygas C5 Utilization – GTC GT-C5/Isoprene



Pygas C5 Utilization – GTC GT-C5



Pygas C5 Utilization – GTC GT-Isoprene



- Use of Techtiv® 600 avoids toxicity and corrosive issues of traditional ACN, NMP, and DMF
- Acetylene hydrogenation simplifies process to one-stage ED/SRC
- Process can produce isoprene at 80% or 99.5^{+}% purity

Pygas C5 Utilization – GTC GT-C5

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- Lower energy and capital cost for C_5 separation
  - Improved CPD/DCPD dimerization
  - State of the art separation
  - High value intermediates created for HCR
- High Selectivity catalyst used for selective acetylene hydrogenation
- Integrated C_5 recovery/HCR Product synergies
  - Improved feedstocks enhance performance of the HCRs
  - Improved system economics return of non-reactives
  - Guaranteed product off take for Pips and DCPD, with optional production of isoprene if desired
  - Reduced energy and capital by matching Pips & DCPD specs to HCR plant needs

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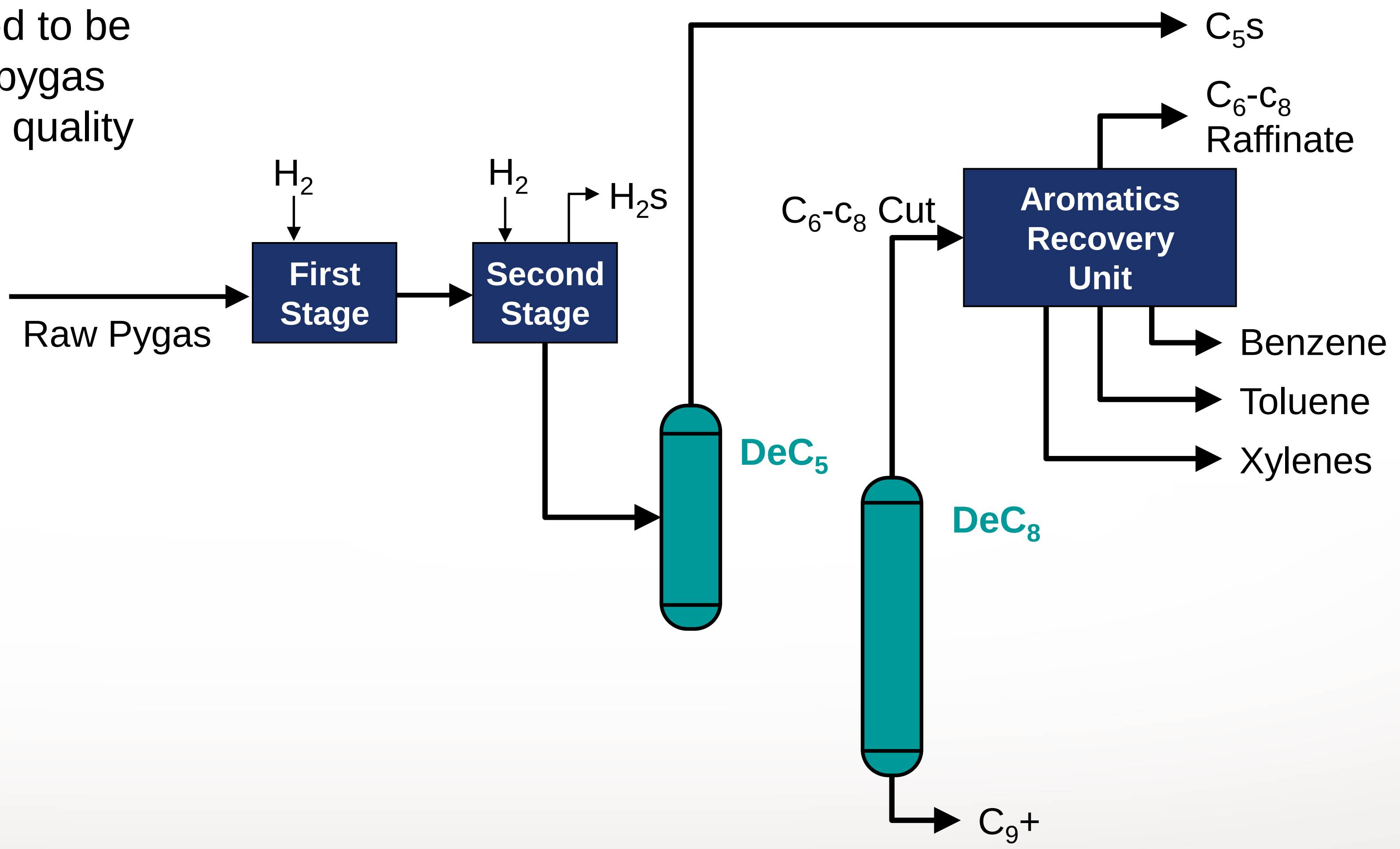
C6-C8 UTILIZATION

Pygas C6-C8 Utilization

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



Pygas C6-C8 Utilization

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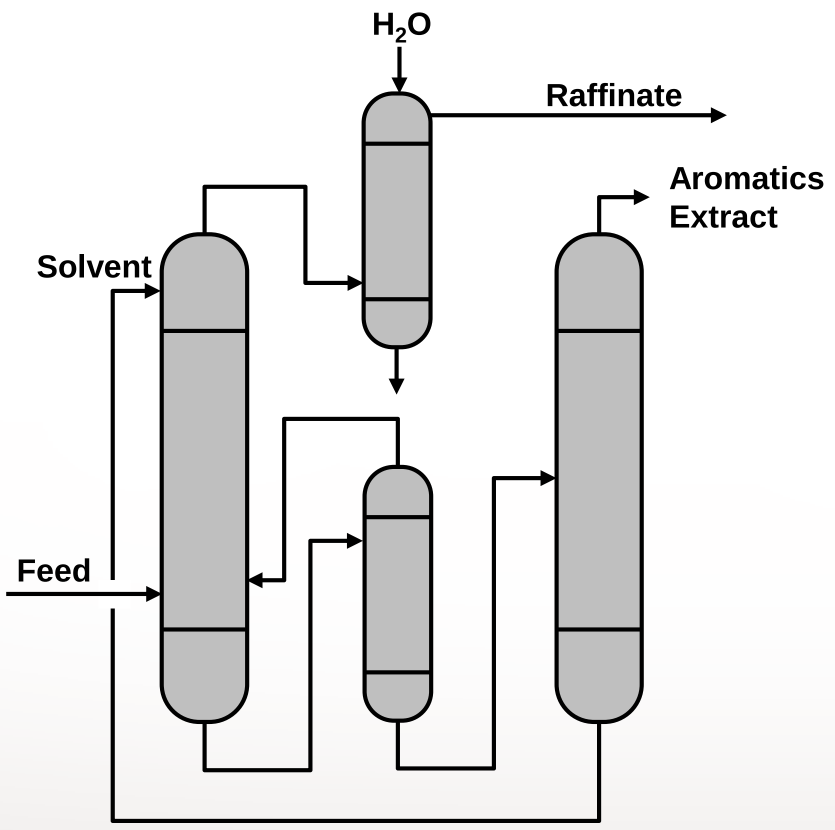
Technologies for BTX Extraction

Liquid-Liquid Extraction (LLE)	Extractive Distillation (ED)
Conventional and out-dated	Most recent technology
More & larger equipment	Less & smaller equipment
Higher capital and larger plot size	Lower capital and smaller plot size
Higher utility consumption	Lower utility consumption
Complicated control	Simple control, easier to operate
Corrosion	None

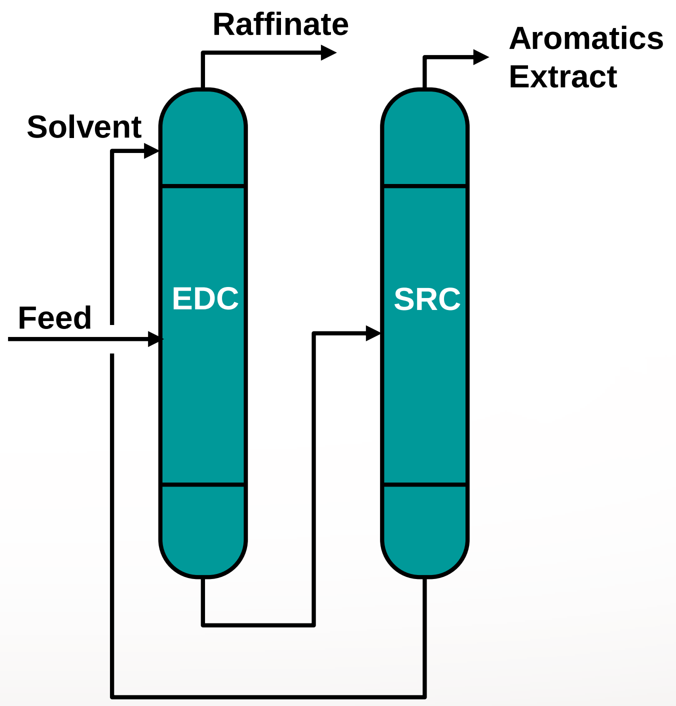
Pygas C6-C8 Utilization

LLE vs ED

Liquid-Liquid Extraction



Extractive Distillation



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

Proprietary solvent of GT-BTX® Technology

Solvent	α n-C_7/Benzene
Techtiv®-500	2.44
Sulfolane	2.00
N-methyl Pyrolidone	1.95
N-formyl morpholine	1.89
Glycol blends	1.35
None	0.57

Pygas Upgrade

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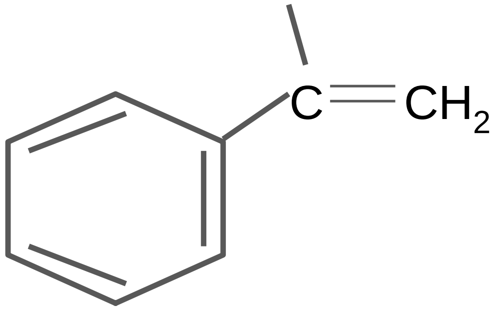
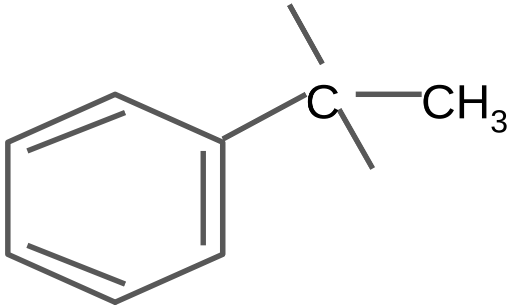
C8 UTILIZATION

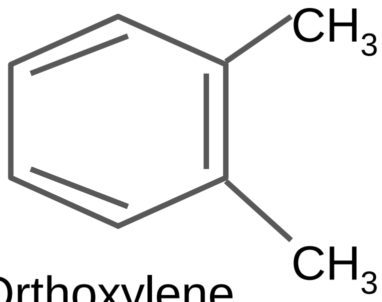
Styrene And Close-boiling Pygas Components



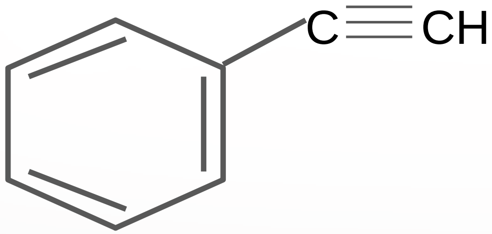
Styrene
NBP 145ºC



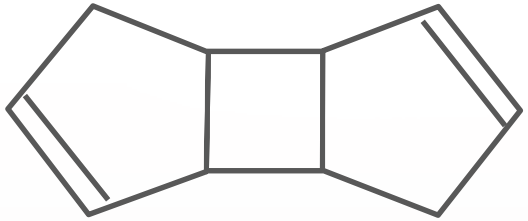
Ethylbenzene
NBP 136ºC



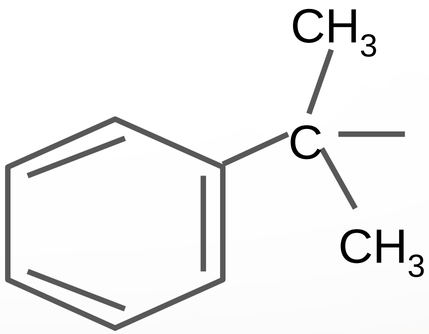
Orthoxylene
NBP 144ºC



Phenyl Acetylene
NBP 142ºC



Dicyclopentadiene
NBP 152ºC



Cumene
NBP 152ºC

Separation Between Styrene and Close-boiling Components

- Solvent-based system to extract and purify styrene
- Extractive distillation alters boiling points of components

Component	NBP (º C)	Relative volatility to Styrene	Relative volatility to Styrene (Enhanced)
Styrene	145	-	-
Ethylbenzene	136	1.3	2.6
Ortho-xylene	144	1.0	1.8
DCPD	152	0.6	1.4

Pygas C8 Utilization – GT-Styrene®

Technology
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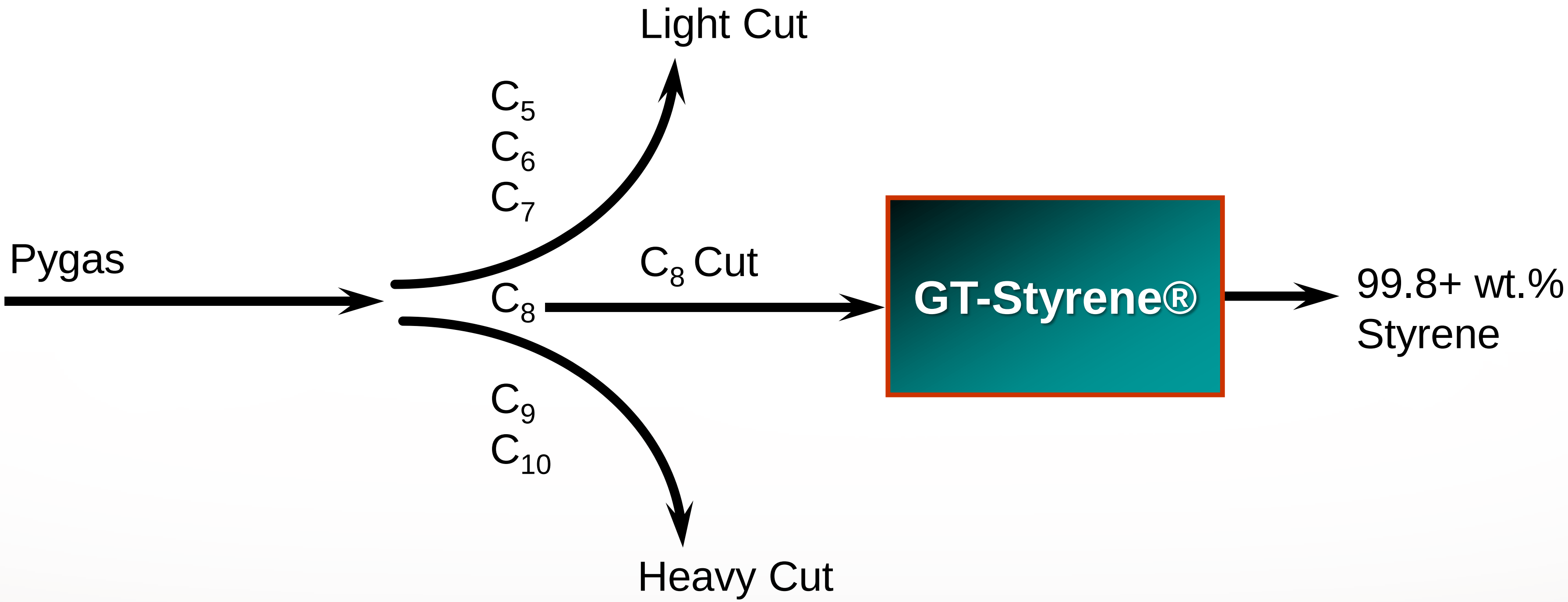
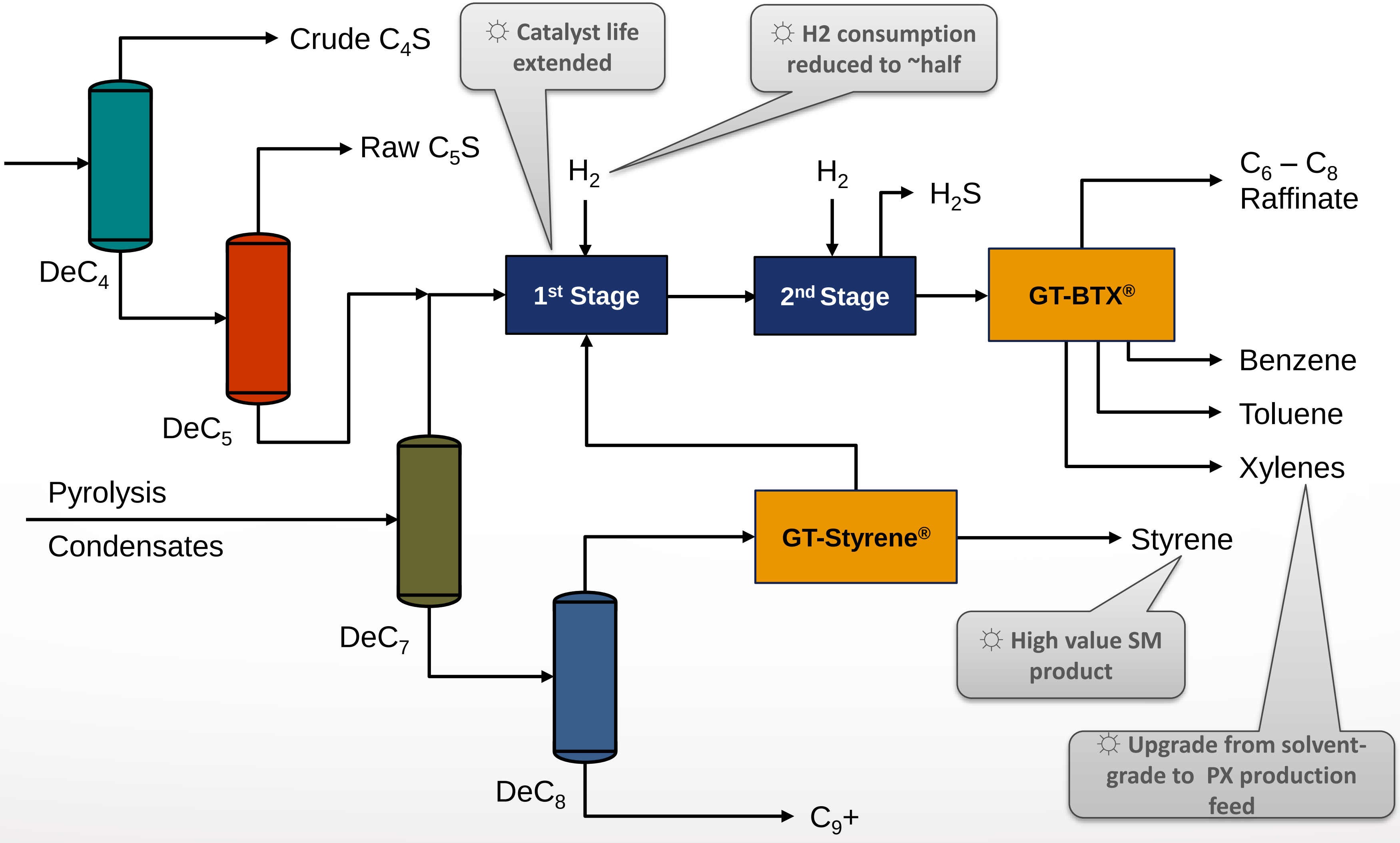
Heart cut distillation followed by ED



Pygas C8 Utilization – GT-Styrene®



Pygas C8 Utilization – GT-Styrene®

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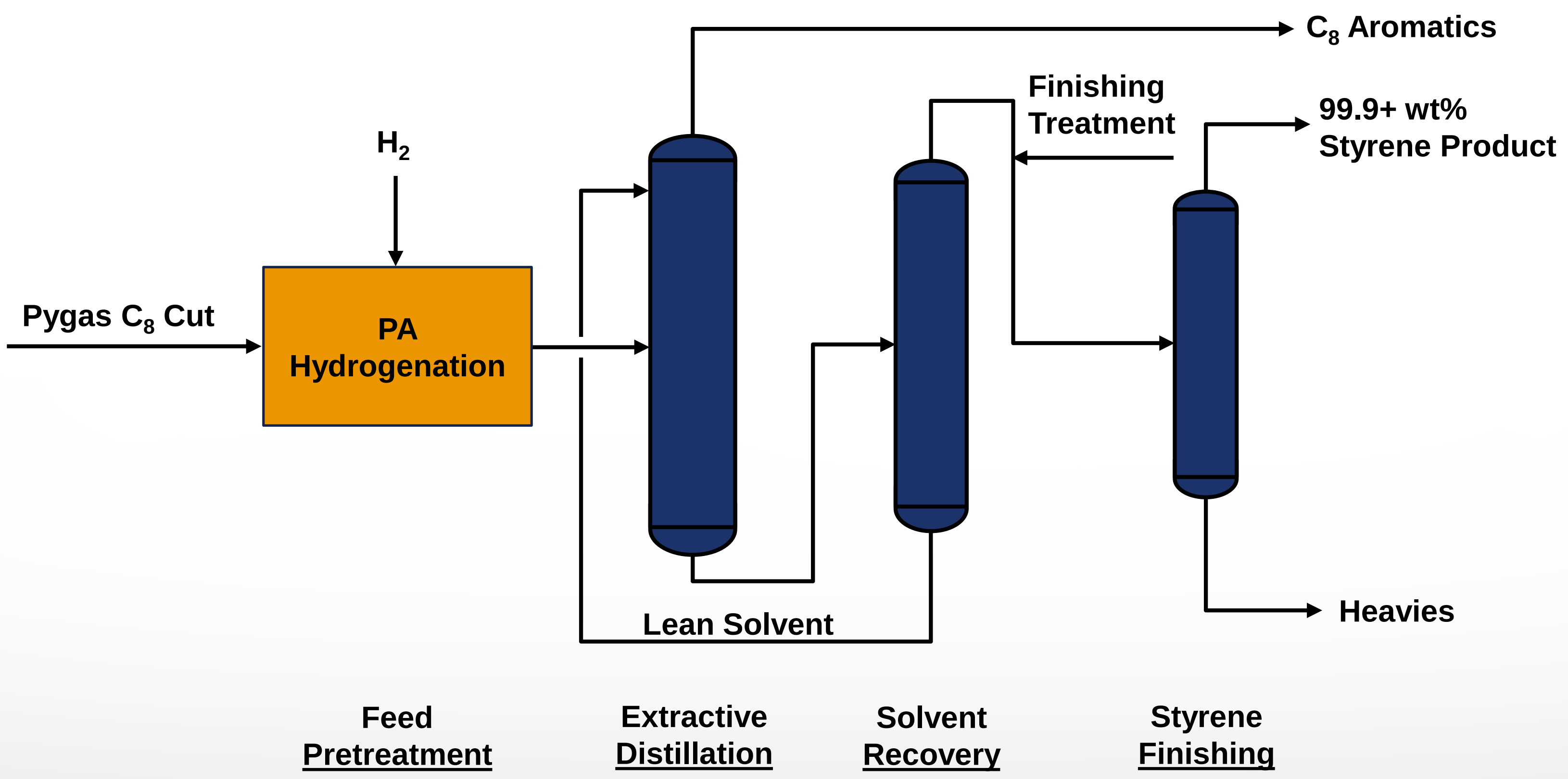
Recovery of styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gas oils, and natural gas liquids (NGL)



ASTM Specifications

Styrene Monomer product shall meet the general standard specification for Styrene ASTM D2827-13 as follows:

Property	Unit	Specification	ASTM Test Method
Color	Pt/Co scale	15 max	D5386
Styrene purity	wt%	99.8 min	D5135 or D7504
Aldehydes (as benzaldehyde)	wt%	0.01 max	D2119 or D7704
Peroxides (as H_2O_2)	mg/kg	50 max	D2340
Polymer	mg/kg	10 max	D2121, Test Method A
Inhibitor	mg/kg	10-15	D4590
Ethylbenzene	mg/kg	500 max	D5135 or D7504
Benzene	mg/kg	1 max	D6229
Appearance		Clear liquid free of sediment and haze at 65 (18 ^{0}C) to 78^{o}F (25 ^{0}C)	

Pygas C8 Utilization – GT-Styrene®

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- Produces polymer-grade styrene at 99.8+% purity
- Allows the recovery of low EB-content mixed xylenes for paraxylene production
- Debottlenecks pygas hydrotreater and extends cycle length
- Reduces hydrogen consumed in hydrotreating
- Optimized solvent system and design provide economical operating costs

Pygas C8 Utilization – GT-Styrene®

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Basis: 30,000 tpa styrene

Typical USGC grassroots capital cost (ISBL)	$40 million
Styrene value in pygas	$600/ton
Styrene product sales value	$1300/ton
Net processing cost	$200/ton
Net profit	$14 million/yr
Simple annual ROI	35%

- Existing HDT greatly debottlenecked for lower H_2 consumption and longer catalyst life
- Additional value for xylenes upgrade

GT-Styrene®

→ Engineered to Innovate®

- GT-Styrene® technology - effective complement to world-scale naphtha crackers
- GT-Styrene® provides excellent value for steam crackers which produce more than 600,000 tpa ethylene, based on liquid feedstock or 1,200,000 tpa ethylene from a typical mixed feedstock
- Reduced-EB xylenes available as co-product of GT-Styrene®
- H_2 consumption is reduced using GT-Styrene®
- **6 licensed units, 3 in operation for more than 5 years**

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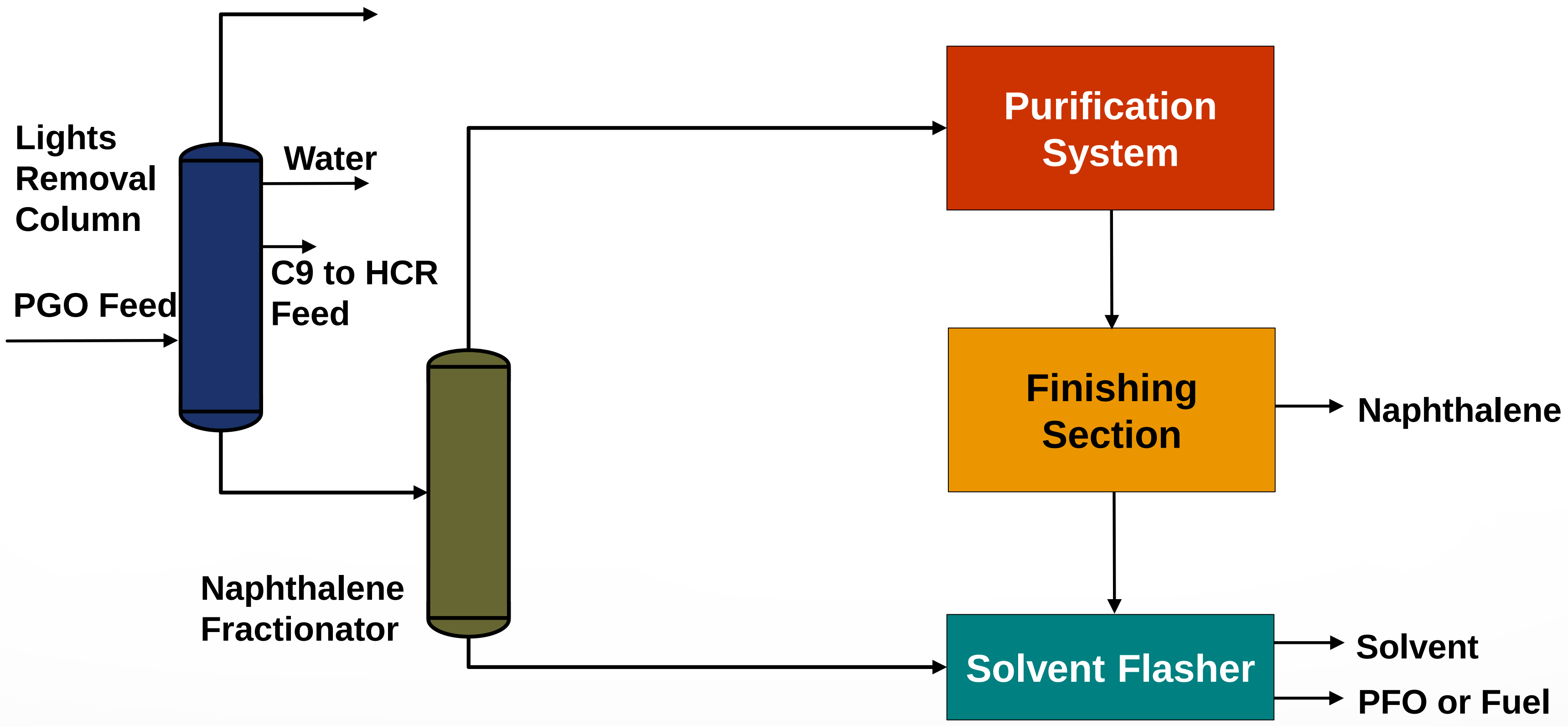
C9+ UTILIZATION

Pygas C9+ Utilization – Naphthalene, Solvent, & Resin



Pygas Upgrade Summary

Summary of Upgrade Options			
C5 - C12	GT-Product Area	Capital MM$	~ Payback (years)
C5	Piperylenes/DCPD : GT-C5 for HCR GT-Isoprene™	25 35	3
C6-C8	Benzene, Toluene, Xylenes (GT-BTX®)	25	2
C8	Styrene (GT-Styrene®)	40	2.5
C9	Resin Oil, HCRs	10	1
C10	Naphthalene	15	2
C11 - C12	Aromatic Solvents	5	1

GTC's cutting-edge technologies and innovative process design help the liquid crackers greatly improve the economics and competitiveness.