Rethinking Xylenes Production via Toluene Methylation

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IOCL Petrochemical Conclave – New Delhi – February 7, 2014

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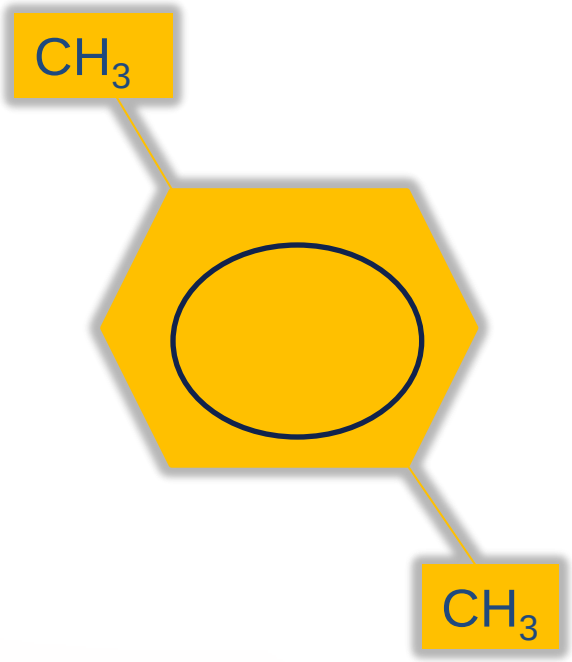
Re-thinking Xylenes



Para-dimethylbenzene (PX)

- Intermediate for polyester manufacture
- Among fastest-growing petrochemicals

PX Manufacturing

- Overview of paraxylene production, with benzene by-product

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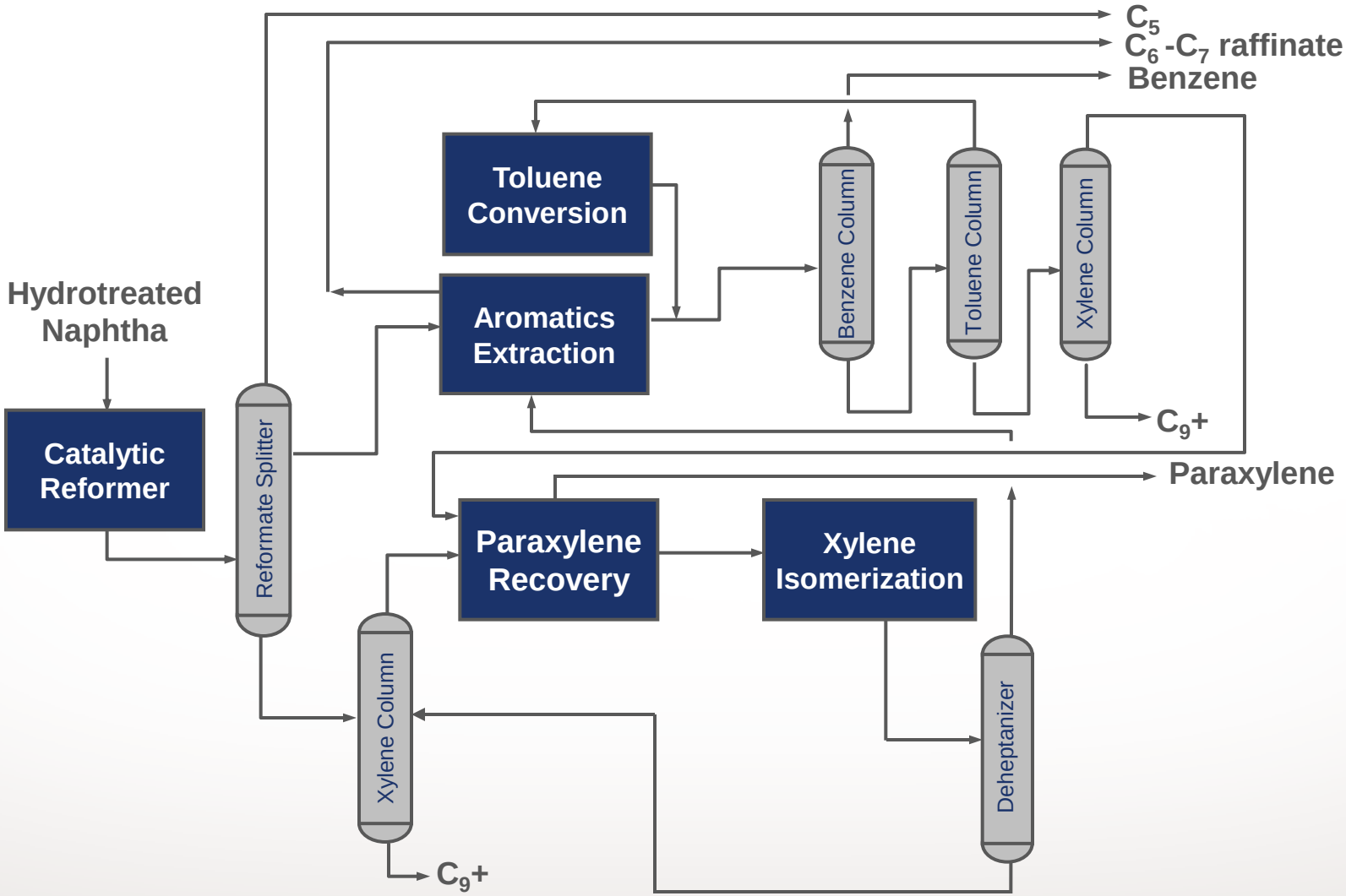
- Conventional processes do not address the fundamental problem of methyl group shortage

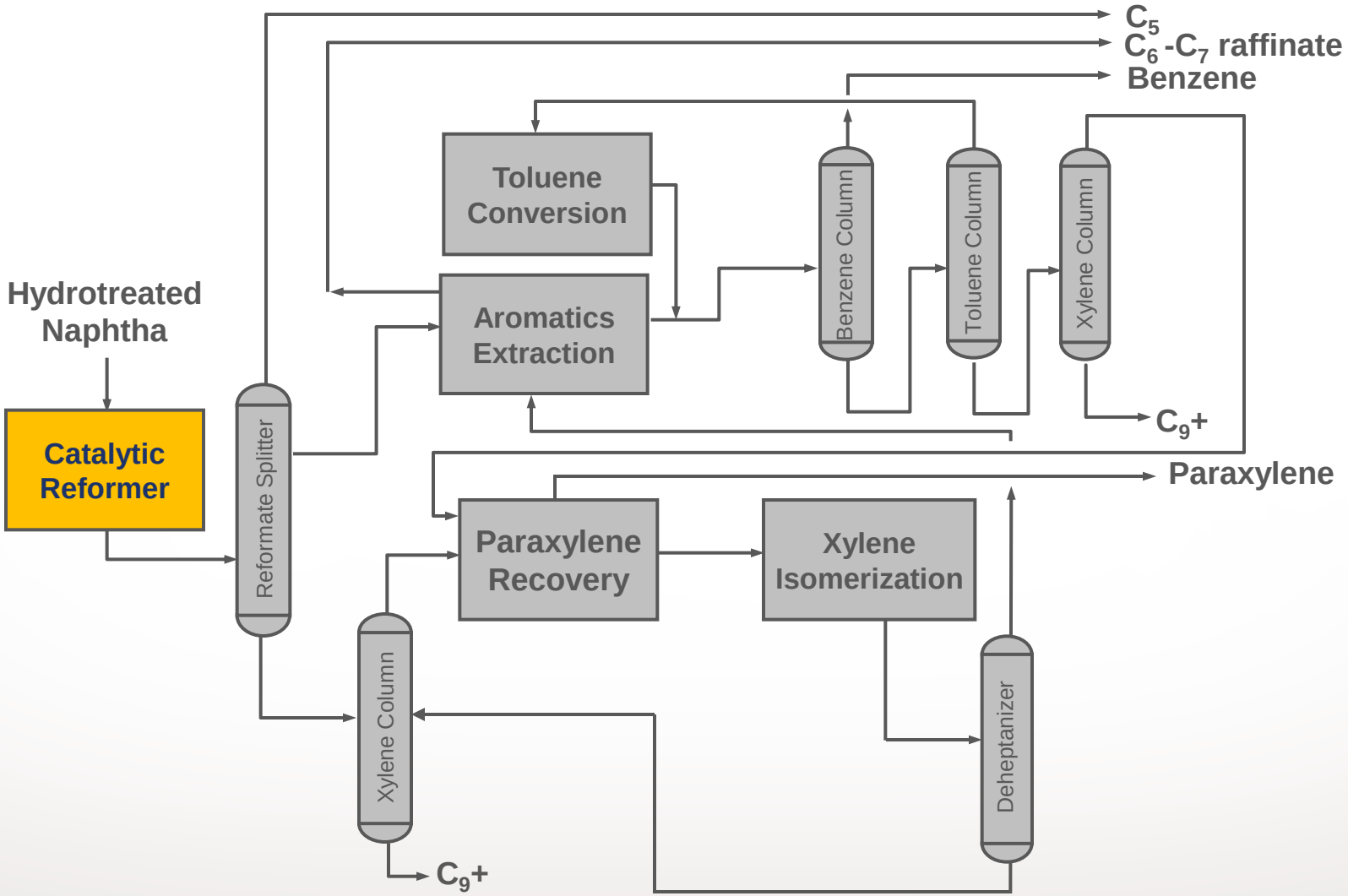
PX Manufacturing

- Overview of paraxylene production, with benzene by-product
- Conventional processes do not address the fundamental problem of methyl group shortage
- ***GT-TolAlk^{sm}*** is the unique technical solution to maximize PX production from mixed aromatics

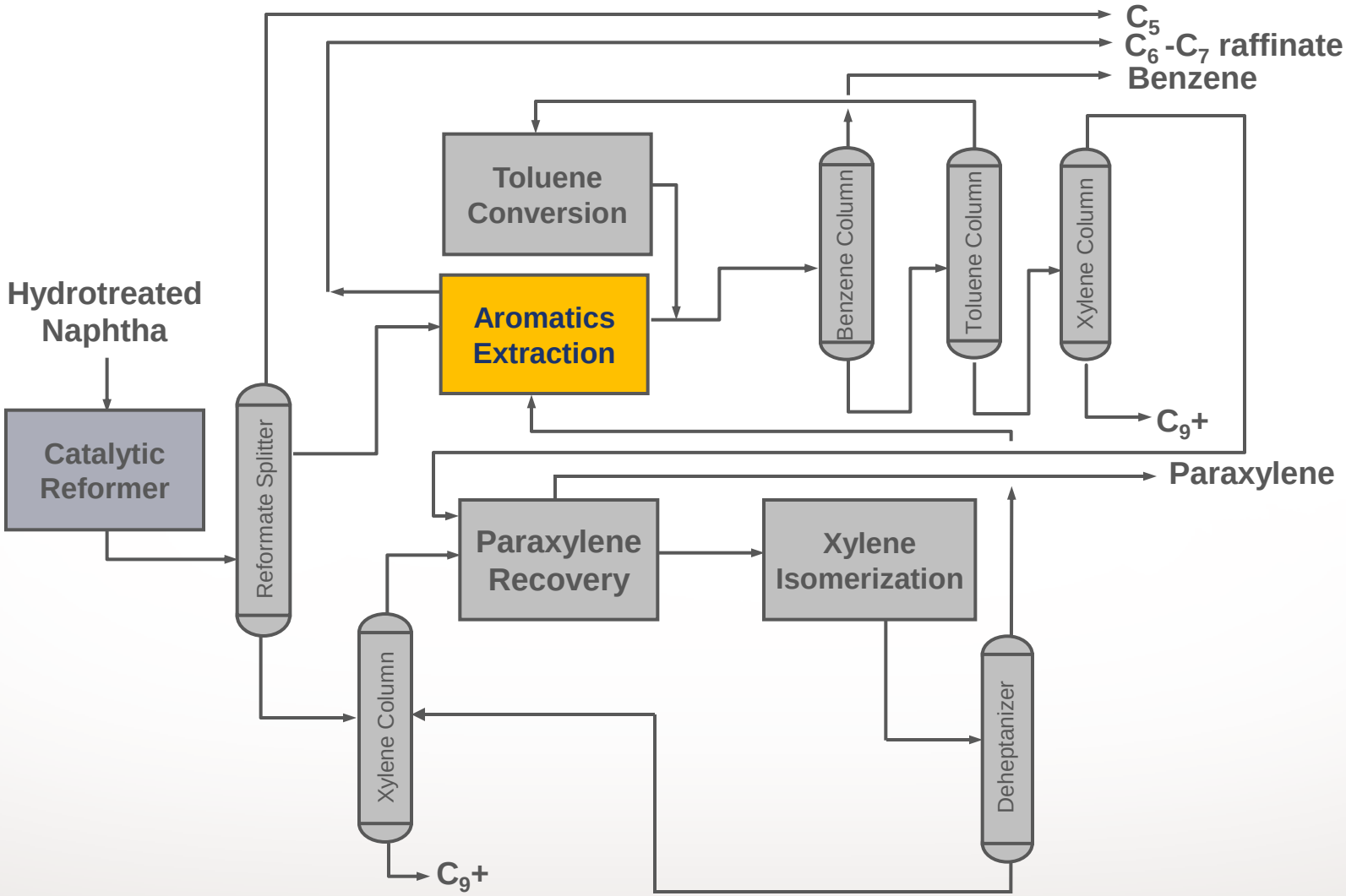
Typical Aromatics Complex for PX



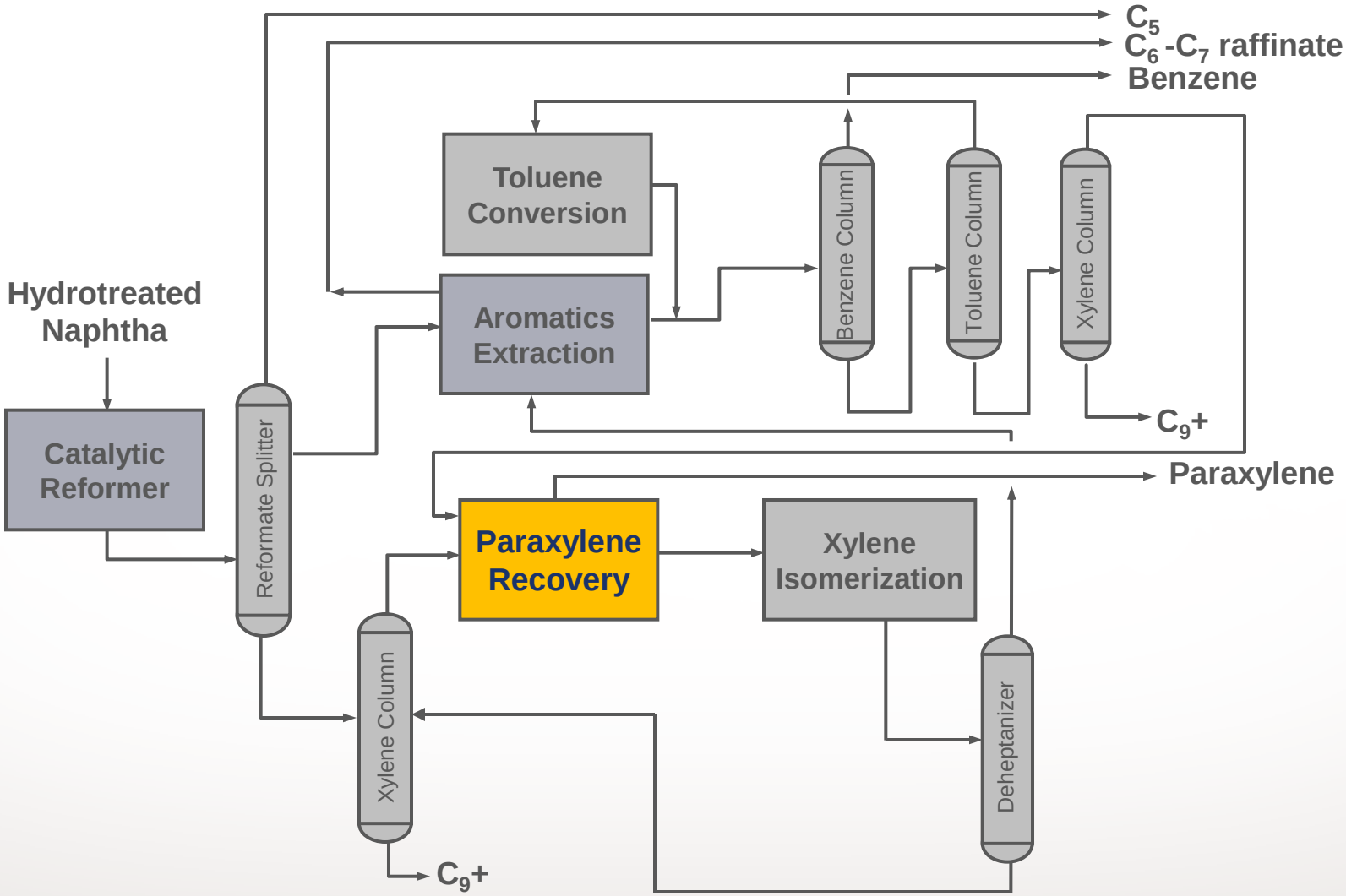
Aromatics Generation



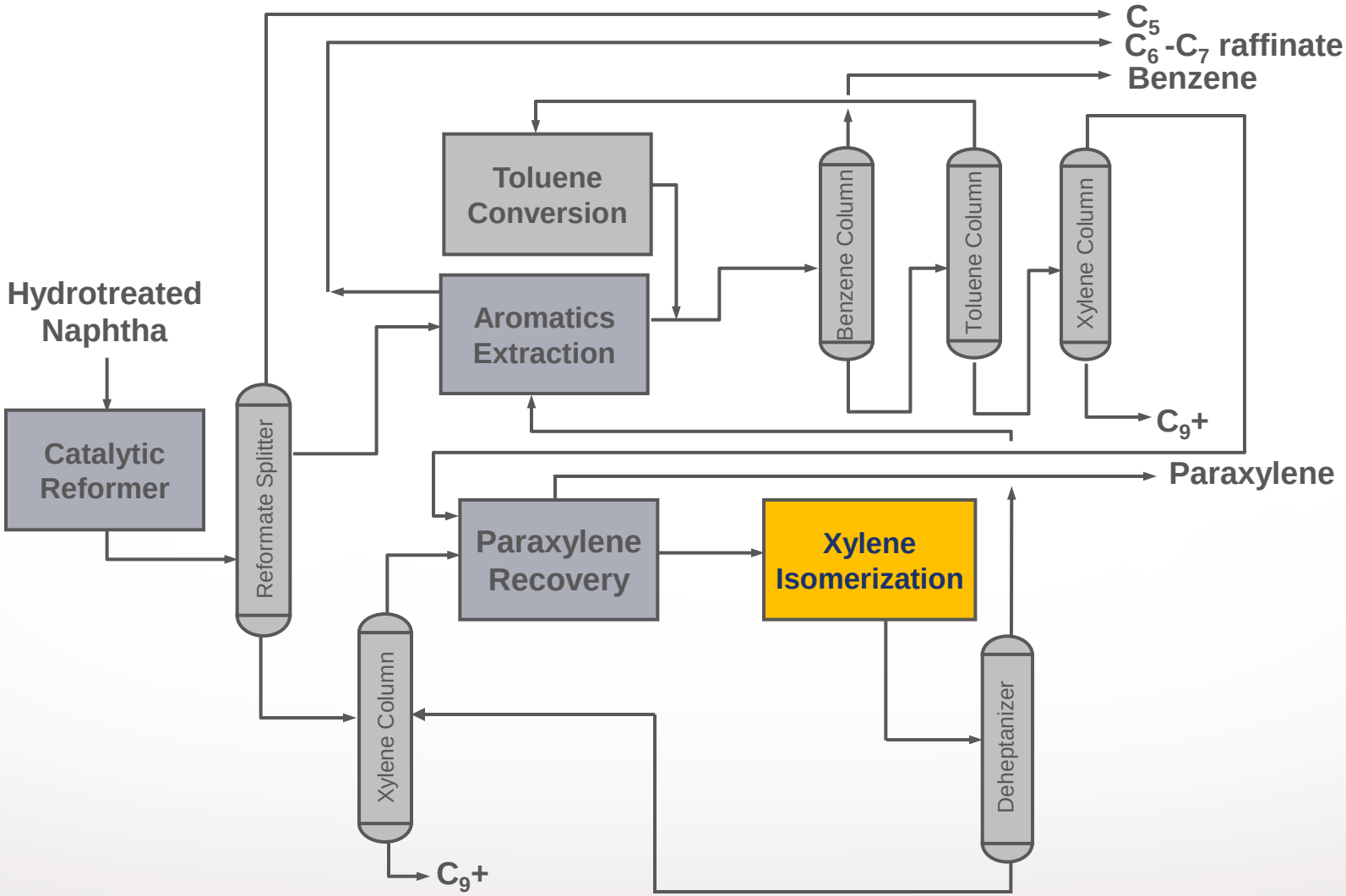
Benzene/Toluene Purification



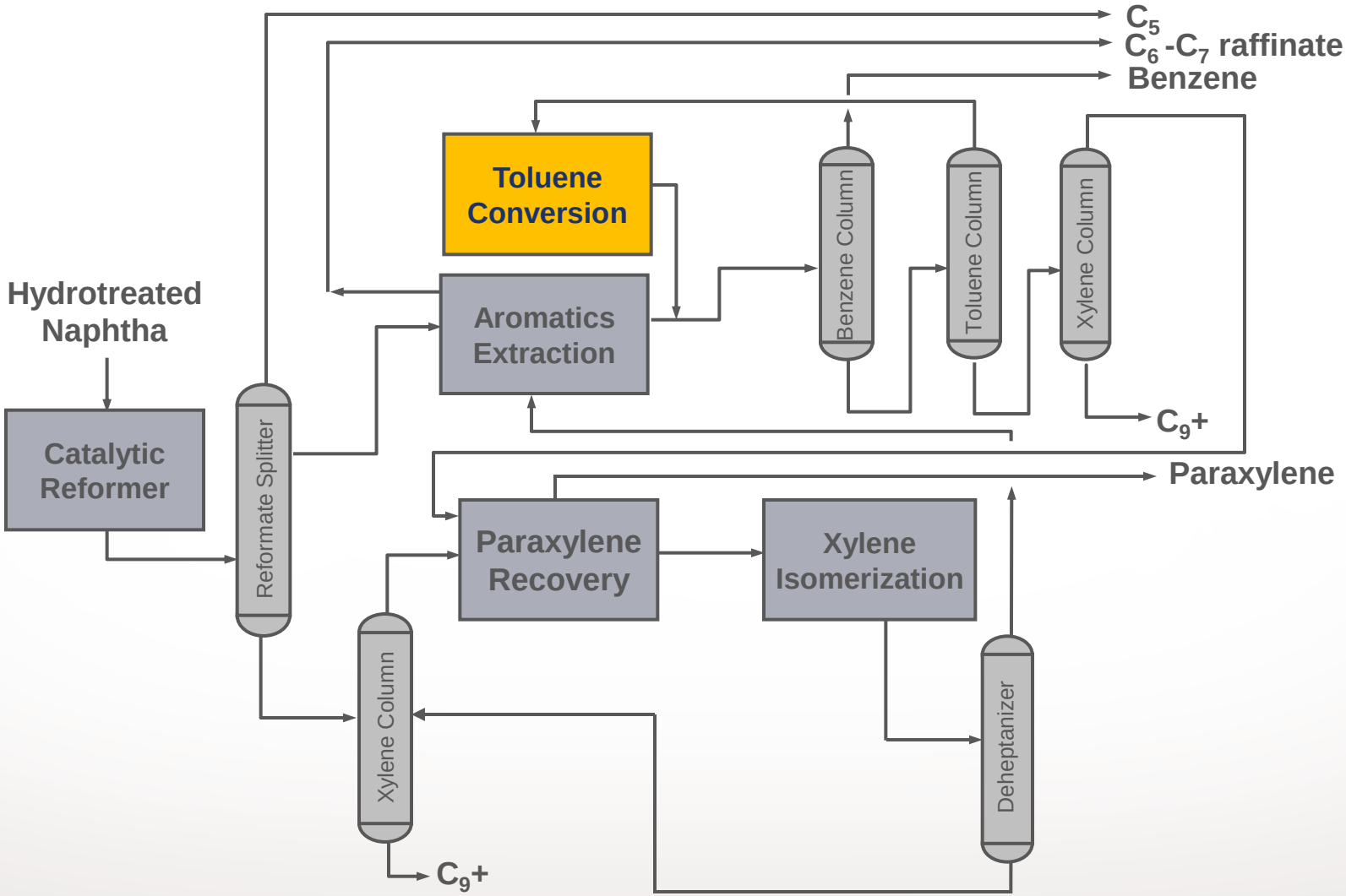
Paraxylene Recovery



Isomerize M-Xylene and O-Xylene into PX



Transalkylation / Disproportionation



Limitation for PX from Reformate – Methyl Group Shortage

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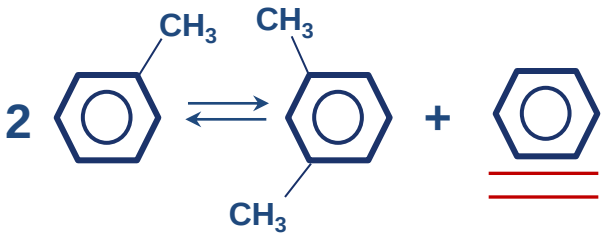
Aromatics derived from reformate has a shortage of methyl groups to maximize PX

	Typical in Reformate (wt%)	Required to make PX	Methyl Group Shortage
Benzene	10	Two methyl group addition	2
Toluene	29	One methyl group addition	1
Ethylbenzene	6	Ethyl group converting into two methyl group	0 or 2
Mixed Xylenes	28	Purification and isomerization	0
C9+ Aromatics	12	C2+ alkyl group removal and methyl group transalkylation	-0.5

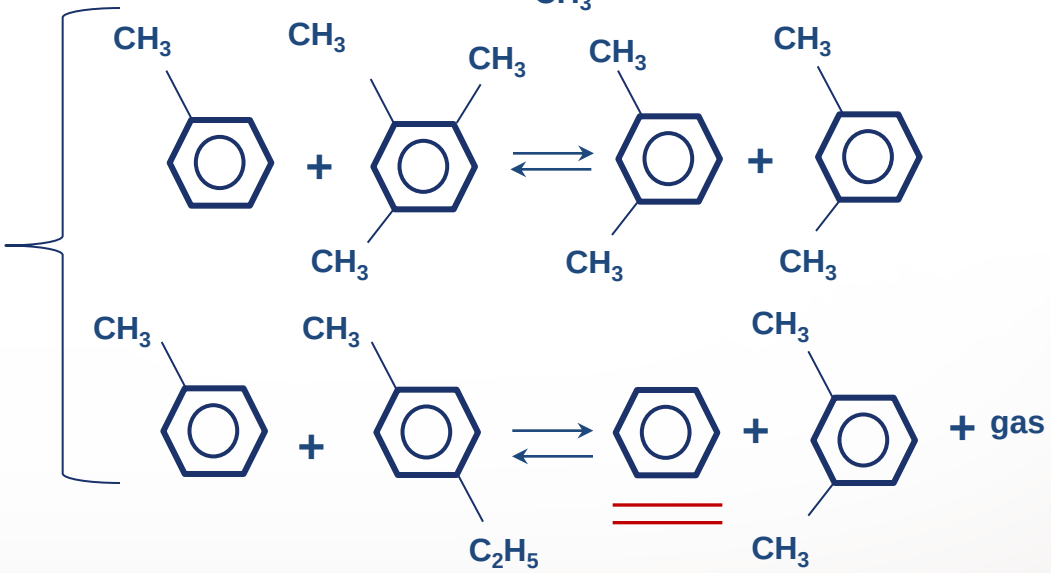
Transalkylation Technology

Transalkylation simply shifts methyl groups from one aromatic to another

- Toluene disproportionation (TDP)



- Toluene transalkylation (TA) with C9+



By-product benzene is inevitable due to imbalance of methyl groups in the feed

Yield Pattern of Toluene/A_9/A_{10} Transalkylation

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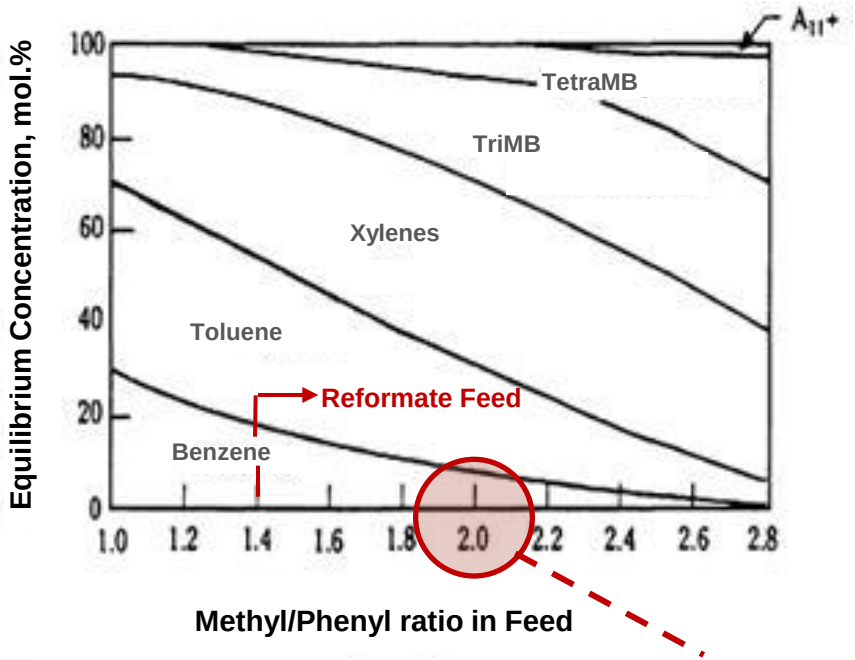
Equilibrium Distribution of methyl substituted aromatics



Transalkylation rearranges the methyl groups.

To maximize PX, methyl groups must be added.

Benzene – Not an On-Purpose Product

Benzene pricing is volatile, and sometimes low

- A significant portion of world benzene supply is from co-product of PX manufacture.
- Benzene periodically goes into oversupply due to market reasons; and is in chronic oversupply on a regional basis.
- TDP, STDP, and transalkylation yield by-product benzene due to deficiency of methyl groups.

Benzene

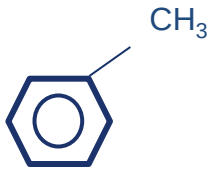
1000-1500 USD/MT

Need to Lower Feedstock Cost, and Optimize the Product Mix

- Maximize the value among benzene, toluene, mixed xylenes, PX
- Make petrochemicals, not fuels
- PX for polyester is the goal

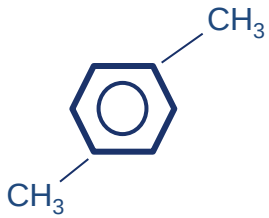
Benzene

1000-1500 USD/MT



Toluene/A_9/A_{10}

1000-1150 USD/MT



Paraxylene

1250-1400 USD/MT

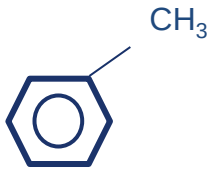
Supporting price for BTX is crude oil

Molecule Management with New Feedstock

- Methyl group addition is the only way to counter the lower yield of xylenes. This is done by alkylating low-cost methanol.

Benzene

1000-1500 USD/MT



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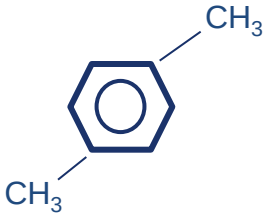

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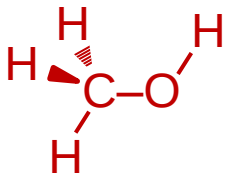


Methanol

200-400 USD/MT

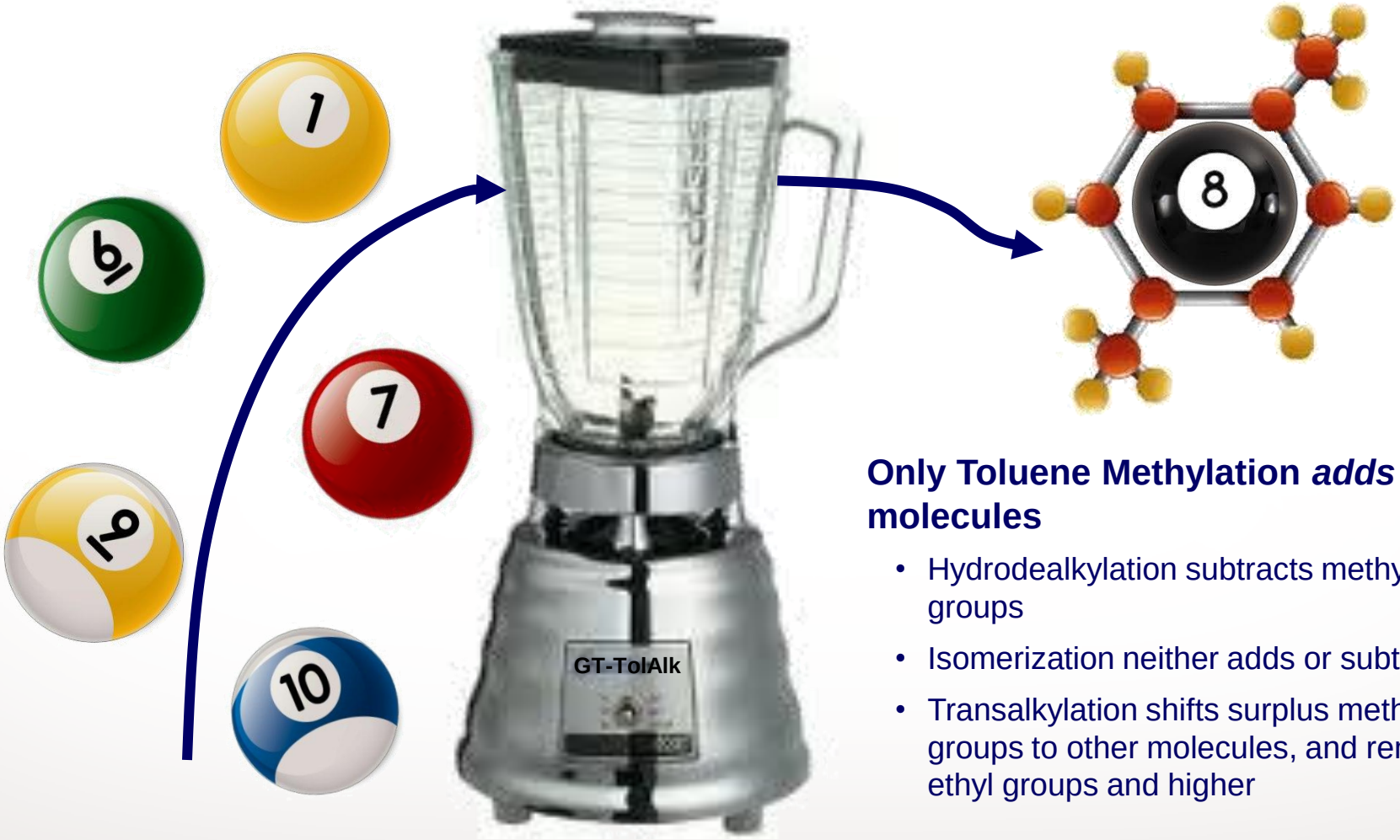
Supporting price for methanol is natural gas

“If I were a chemist . . . . .”

- Conventional PX technologies utilize existing molecules.
- Chemists synthesize new molecules by adding individual parts.

How do you integrate new methods, with traditional production techniques?

The Magic Number is “8” (Carbons)



Only Toluene Methylation *adds* molecules

- Hydrodealkylation subtracts methyl groups
- Isomerization neither adds or subtracts
- Transalkylation shifts surplus methyl groups to other molecules, and removes ethyl groups and higher

Methyl Group Management

Hydrodealkylation removes methyl groups to produce on-purpose benzene. By-product is fuel gas.

Transalkylation and Isomerization re-arrange methyl groups and remove higher alkyl groups.

Toluene Methylation adds methyl groups to produce xylenes. By-product is water.

GT-TolAlk℠ Process Scheme

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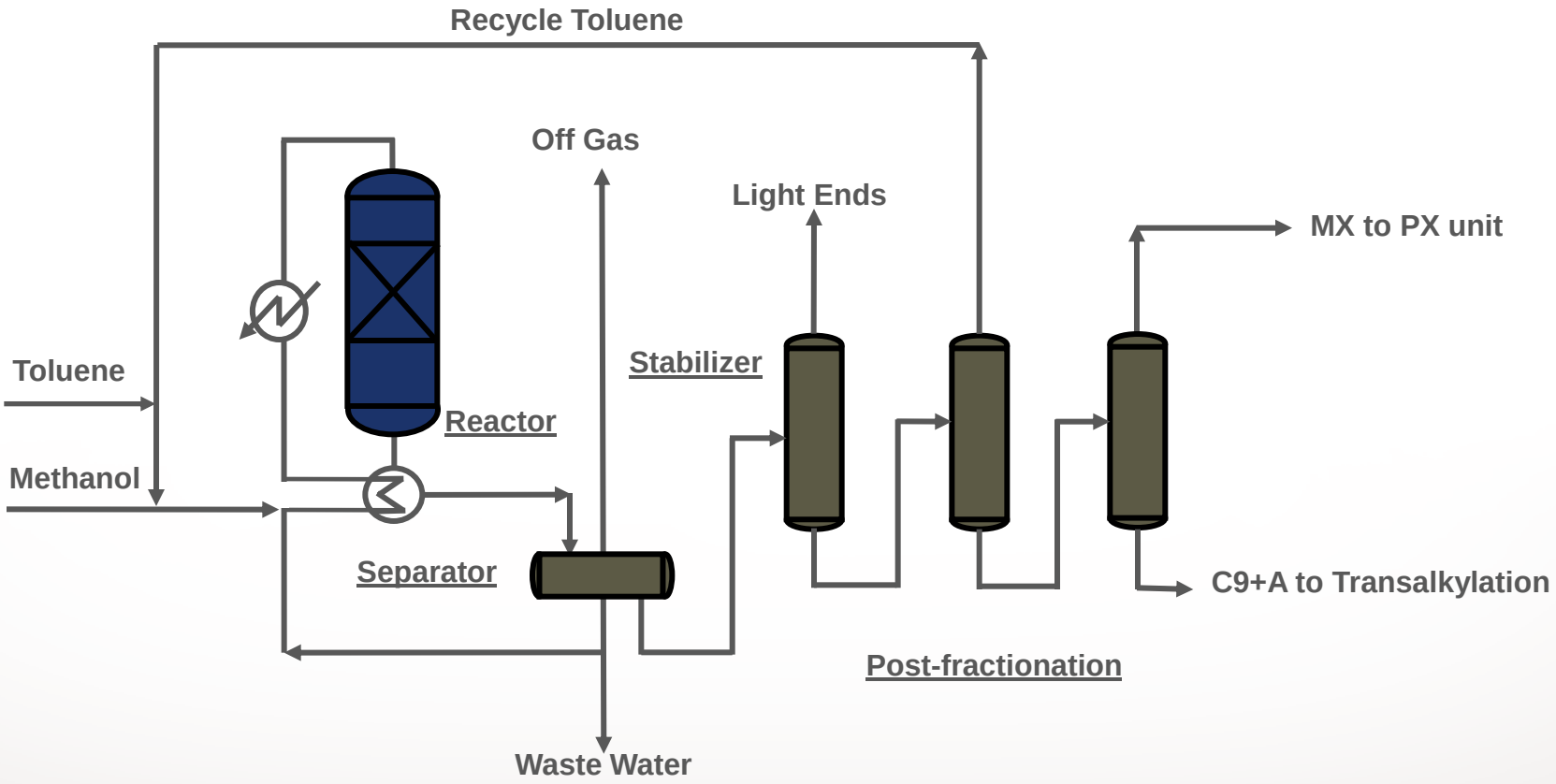
Simple, fixed-bed design with no hydrogen compressor or circulation



Typical Condition and Yields for TM

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	Condition
Catalyst	ZSM-5 based
Temperature	450-550°C
Pressure	3 kg/cm^2
H_2O/HC	2/1
WHSV	4 hr-1
Toluene conversion (per pass)	0.20-0.35
Methanol utilization (methyl group to aromatic ring)	86 wt%

Economics for GT-TolAlk℠

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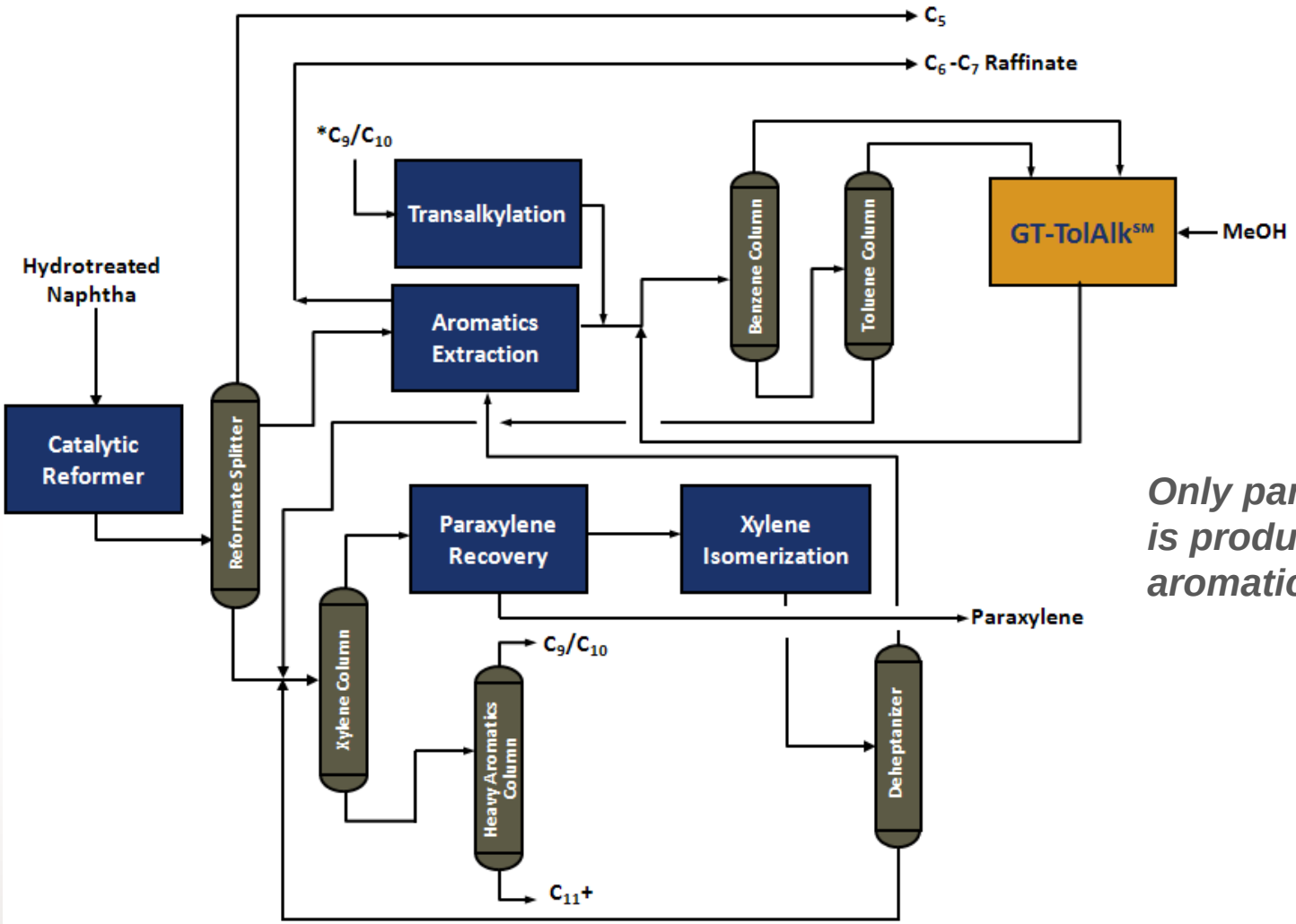
Basis: 400 KTA Toluene / 2013 Raw Material and Product Prices (IHS)			
Feedstock	**KTA**	**Unit price, $/ton**	**Annual $MM**
Toluene	400	1140	456
Methanol	189	389	74
Feed Costs			$530
Products			
Fuel Gas	14	725	10
Mixed Xylenes	389	1320	513
A_9	80	1130	91
Process Water	107	-10	-1
Products Value			$ 613
Utilities			38
Net Margin			$ 45
TIC (USGC, 2013, reaction plus fractionation)			**$ 42**

Simple ROI = 12 Months

GT-TolAlk℠, Drop-in to Existing Aromatics Complex



Only paraxylene is produced from aromatic feed.

Summary

- Relative shortage of xylenes from traditional refinery sources; regional surplus of benzene
- GT-TolAlk℠ replenishes the methyl group shortage to yield more xylenes
- Simple fixed-bed, low pressure process
- No hydrogen is needed
- Very low EB yield in the xylenes; debottlenecks adsorption separation systems
- Unique process system can convert 100% of aromatic molecules to PX with zero benzene by-product; *or* maximize benzene production if market justifies

Cutting Edge Cutting Edge Processes for PX Production

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- ✓ ***CrystPX***℠ - low-cost efficient crystallization process for paraxylene production
- ✓ ***AdsorbPX***℠ - PX recovery by selective adsorption
- ✓ ***GT-Hybrid PX***℠ - Combination of adsorption plus crystallization for reliable, low-cost PX manufacture in revamps and grassroots applications
- ✓ ***GT-TolAlk***℠ - PX manufacture from lower-cost raw materials, with no benzene production
- ✓ ***GT-BTX PluS***℠ - Patented process to recover aromatics from FCC gasoline by direct extraction
- ✓ ***GT-Aromatization***℠ - Aromatics created from C4-C8 olefins, LPG, and light naphtha
- ✓ ***GT- IsomPX***℠ and ***GT-TransAlk***℠ - Aromatics transformation using catalysts from Clariant

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