

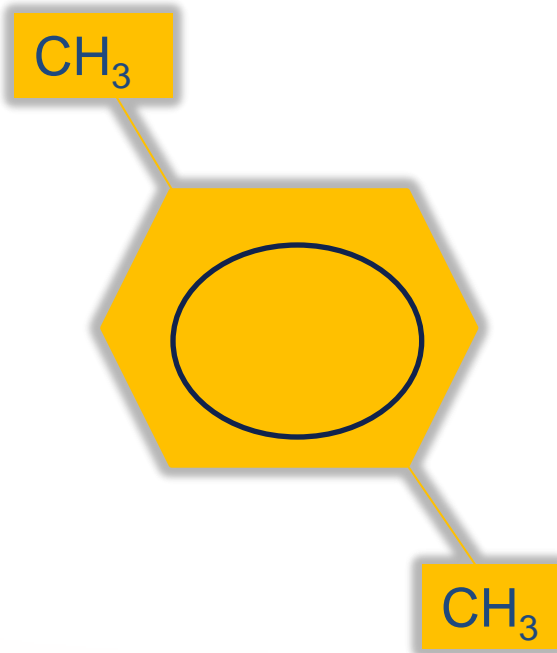


**GTC Technology**

## **Rethinking Xylenes Production via Toluene Methylation**

Joseph C. Gentry – Director, Global Licensing  
IOCL Petrochemical Conclave – New Delhi – February 7, 2014





Para-dimethylbenzene (PX)

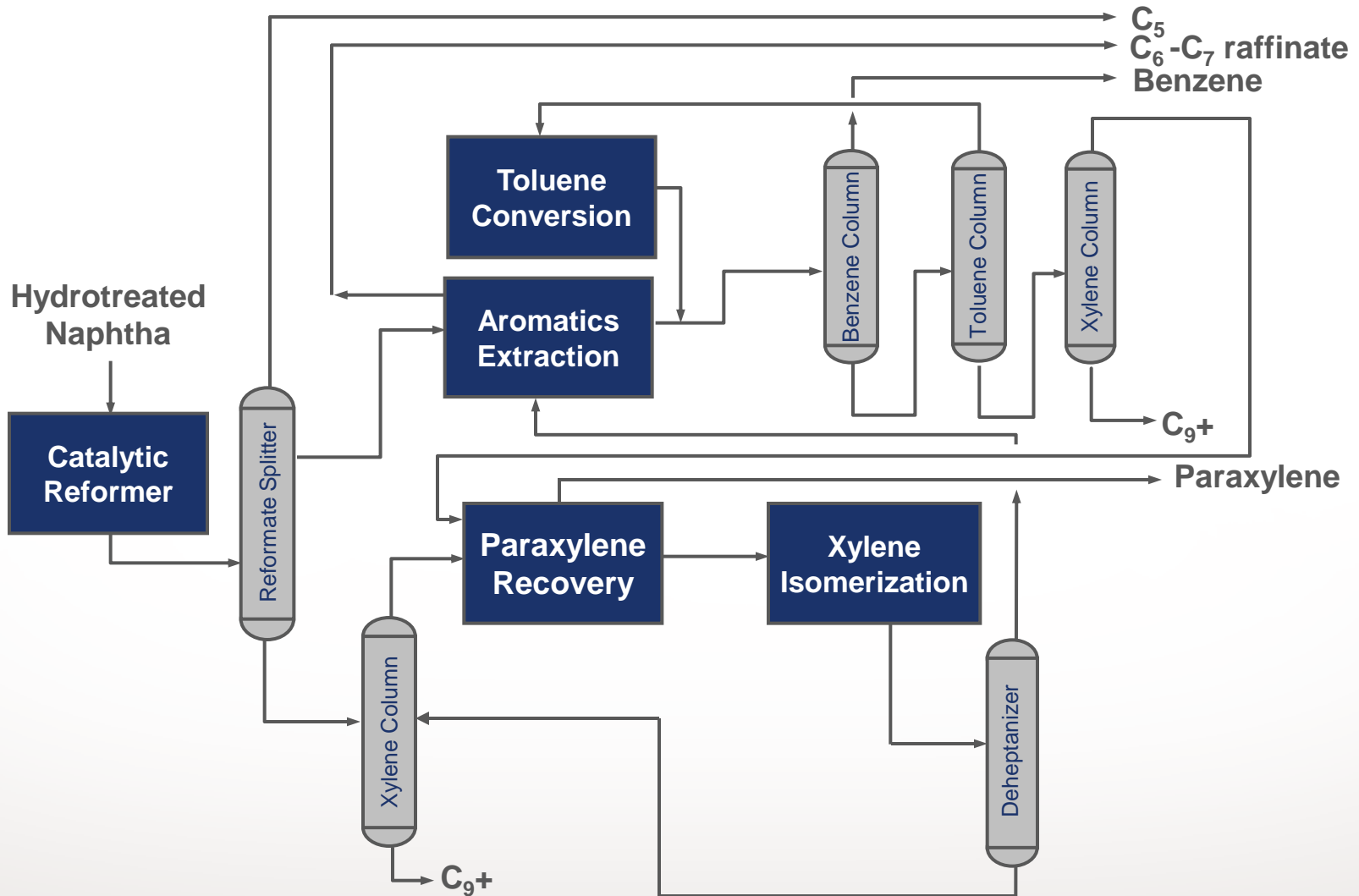
- Intermediate for polyester manufacture
- Among fastest-growing petrochemicals

- Overview of paraxylene production, with benzene by-product

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

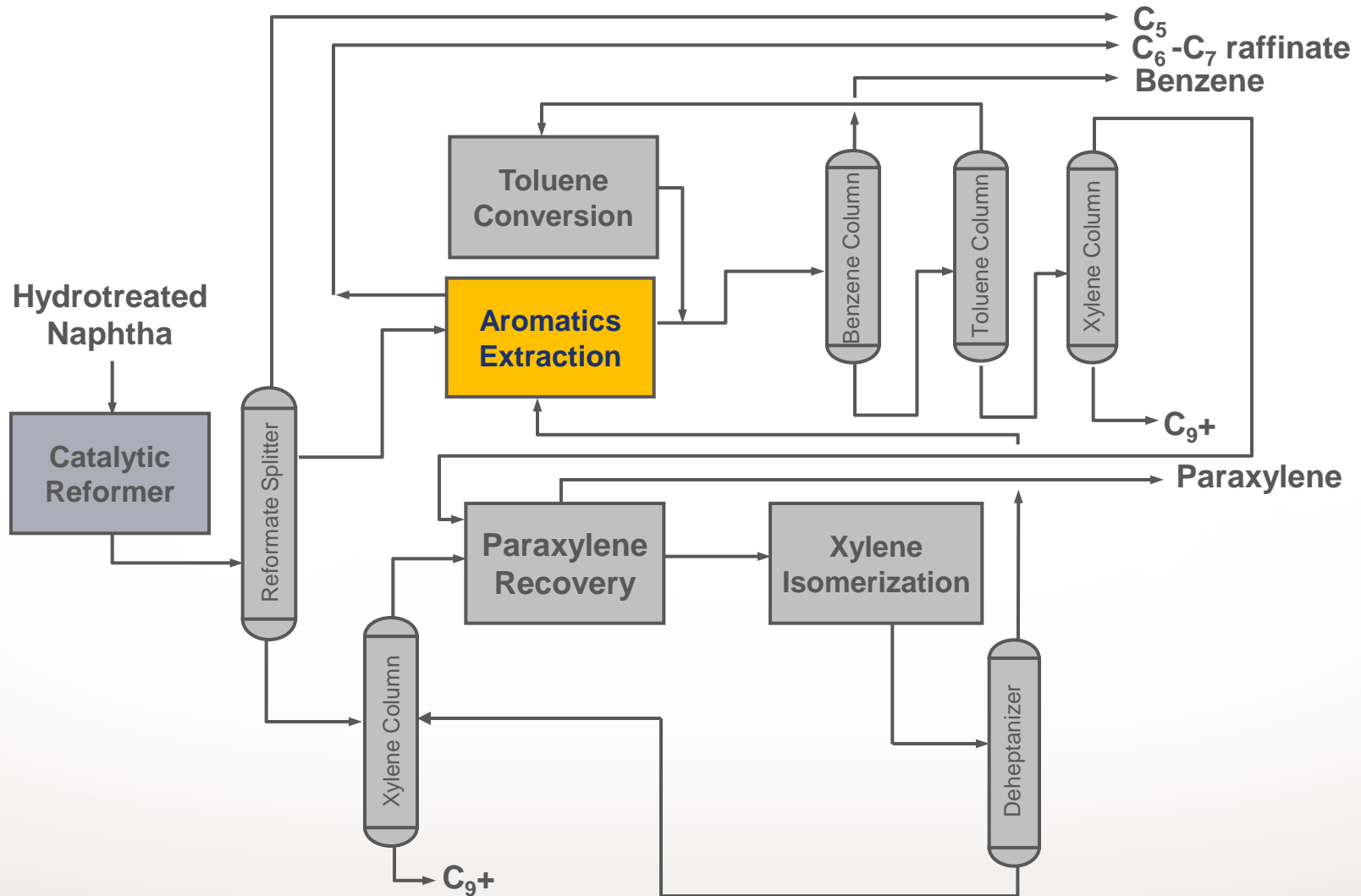
- Overview of paraxylene production, with benzene by-product
- Conventional processes do not address the fundamental problem of methyl group shortage
- **GT-ToAlk<sup>sm</sup>** is the unique technical solution to maximize PX production from mixed aromatics

# Typical Aromatics Complex for PX

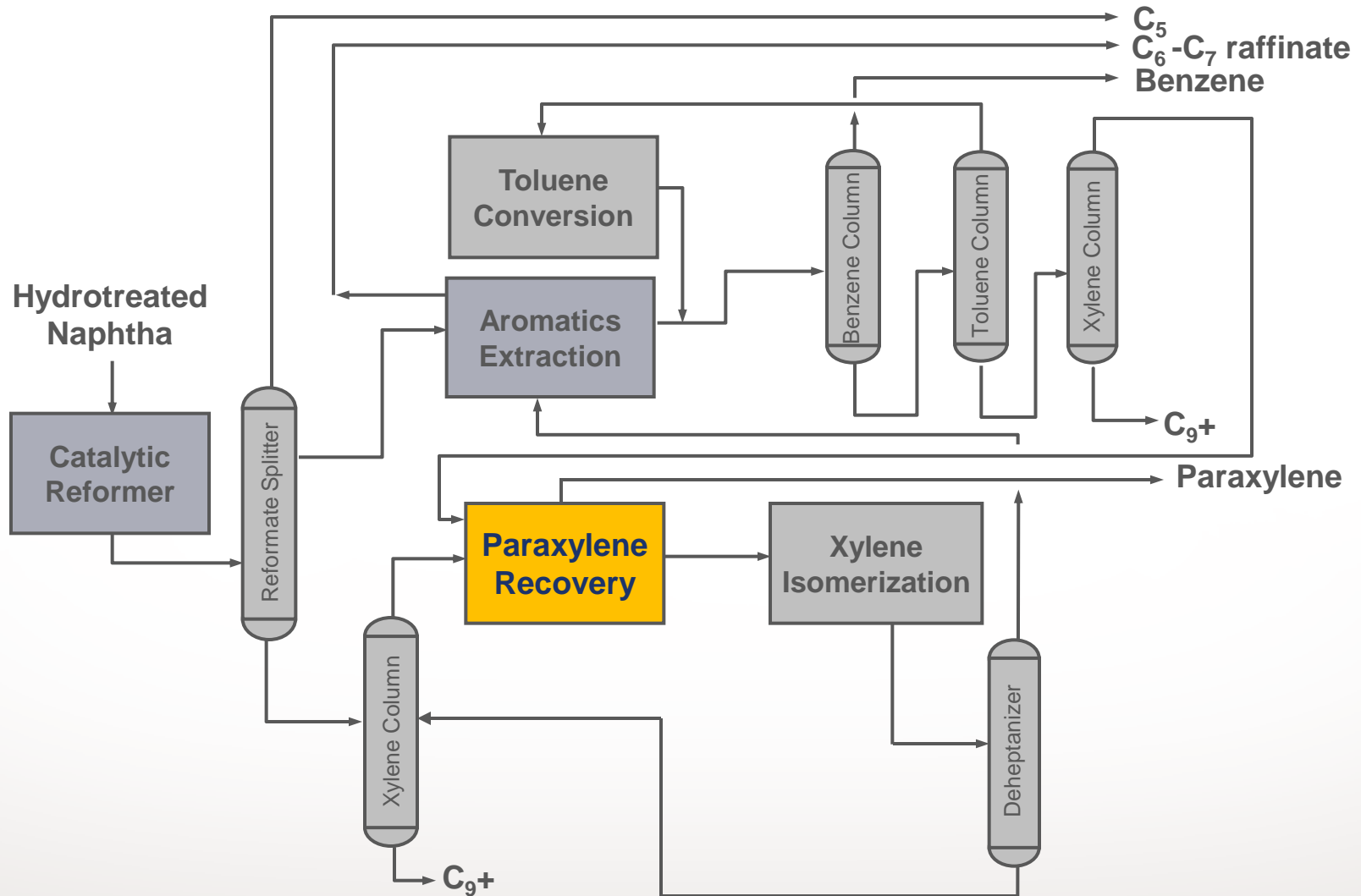




# Benzene/Toluene Purification

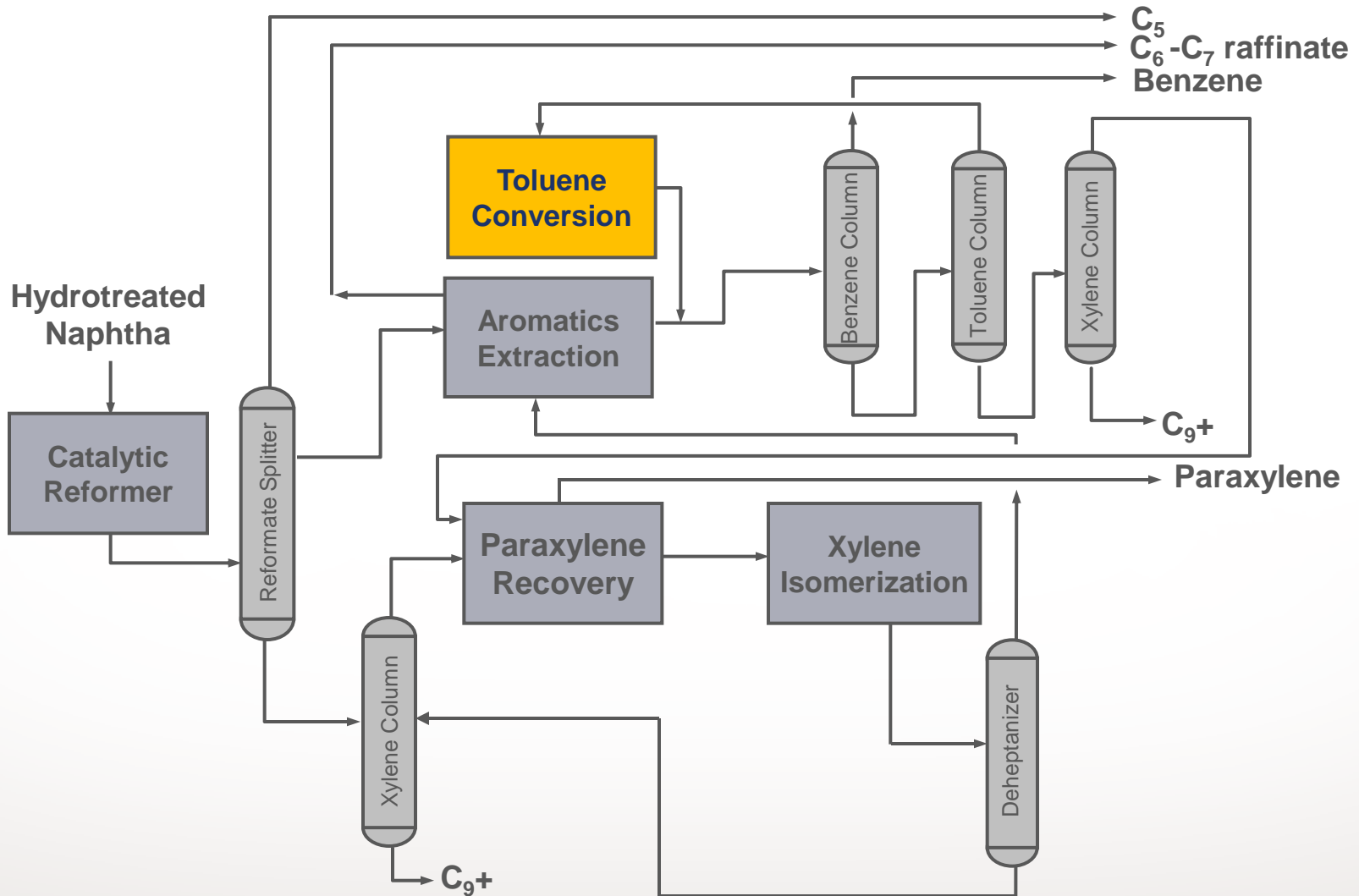


# Paraxylene Recovery





# Transalkylation / Disproportionation



# Limitation for PX from Reformate – Methyl Group Shortage

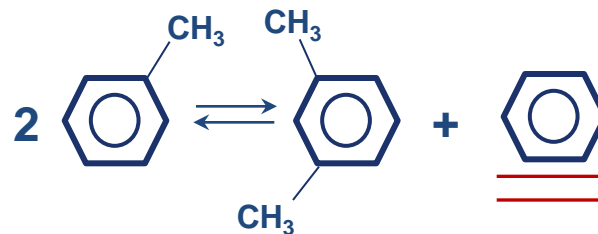
Aromatics derived from reformate has a **shortage of methyl groups** to maximize PX

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

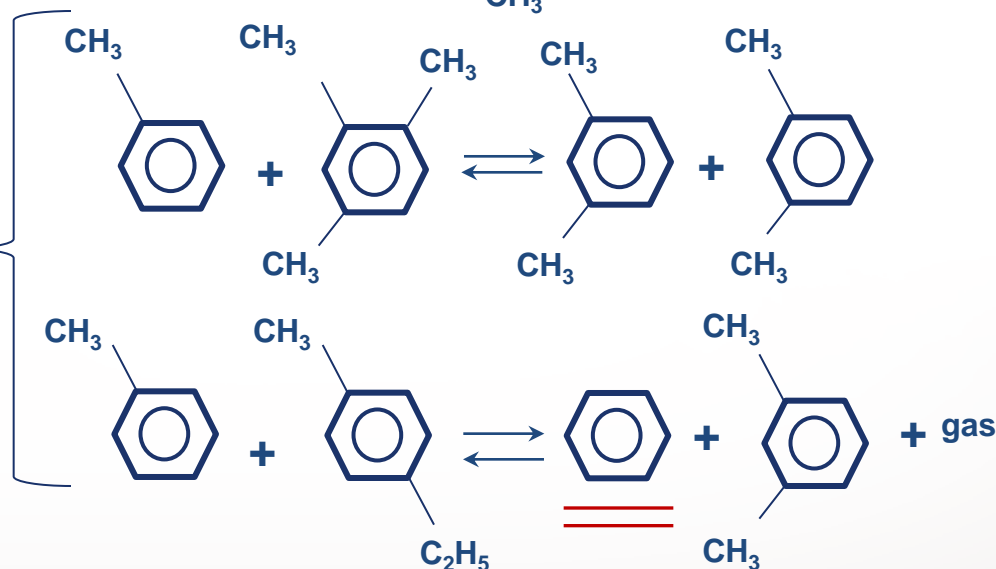
# Transalkylation Technology

**Transalkylation simply shifts methyl groups from one aromatic to another**

- Toluene disproportionation (TDP)



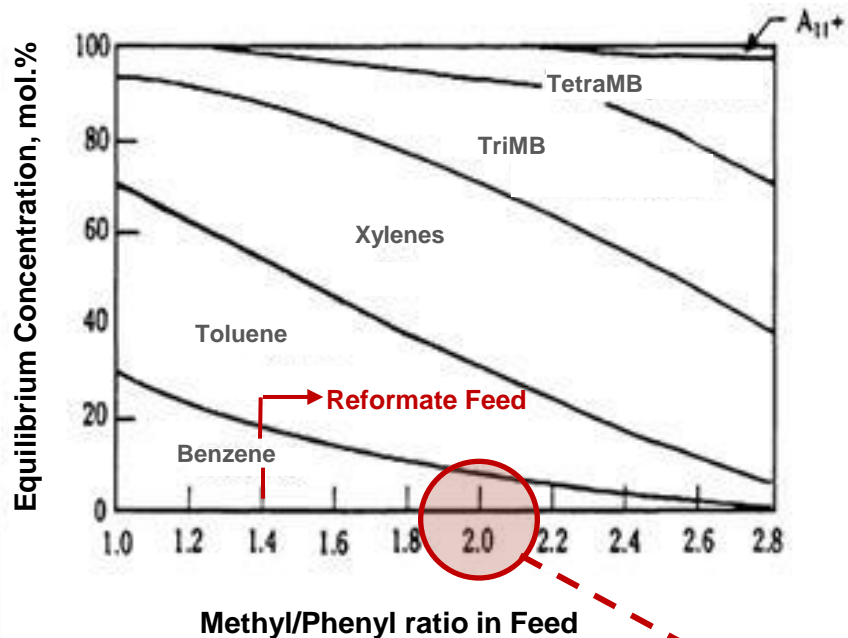
- Toluene transalkylation (TA) with C9+



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

# Yield Pattern of Toluene/A<sub>9</sub>/A<sub>10</sub> Transalkylation

Equilibrium Distribution of methyl substituted aromatics



Transalkylation rearranges the methyl groups.

To maximize PX, methyl groups must be added.

Goal for Xylenes = 2.0

# 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

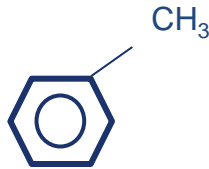
# Need to Lower Feedstock Cost, and Optimize the Product Mix

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



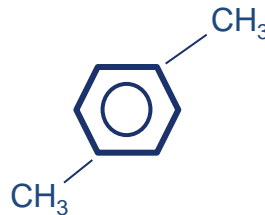
Benzene

1000-1500 USD/MT



Toluene/A<sub>9</sub>/A<sub>10</sub>

1000-1150 USD/MT



Paraxylene

1250-1400 USD/MT



Supporting price for  
BTX is crude oil

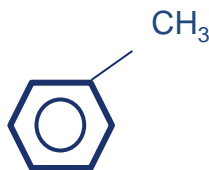
# Molecule Management with New Feedstock

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



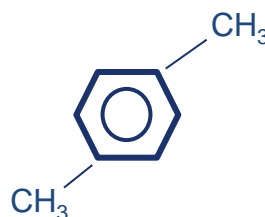
Benzene

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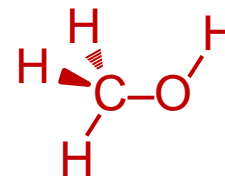
Toluene/A<sub>9</sub>/A<sub>10</sub>

1000-1150 USD/MT



Paraxylene

1250-1400 USD/MT



Methanol

200-400 USD/MT



Supporting price for  
methanol is natural gas

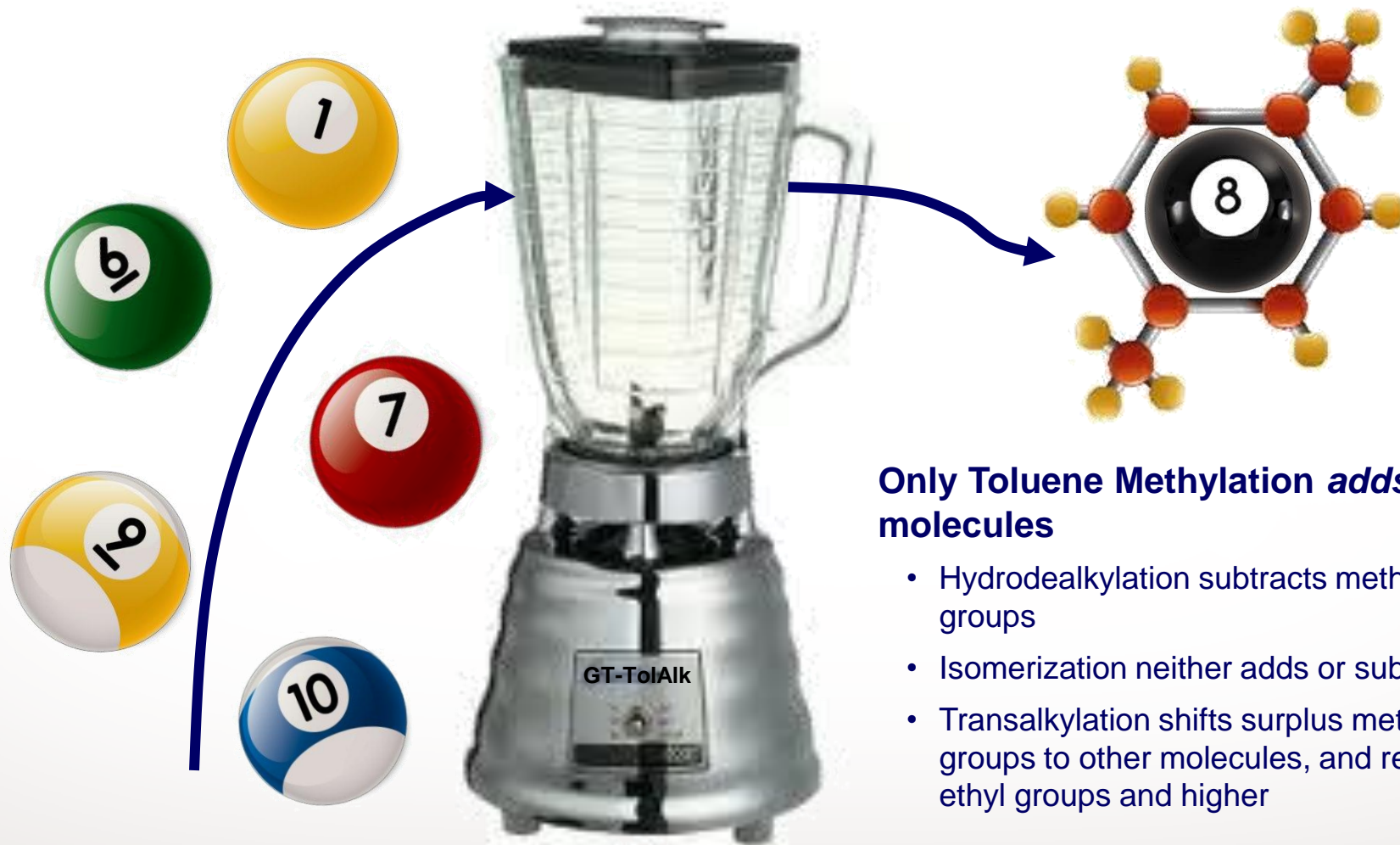
# “If I were a chemist . . . . .”



- 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.

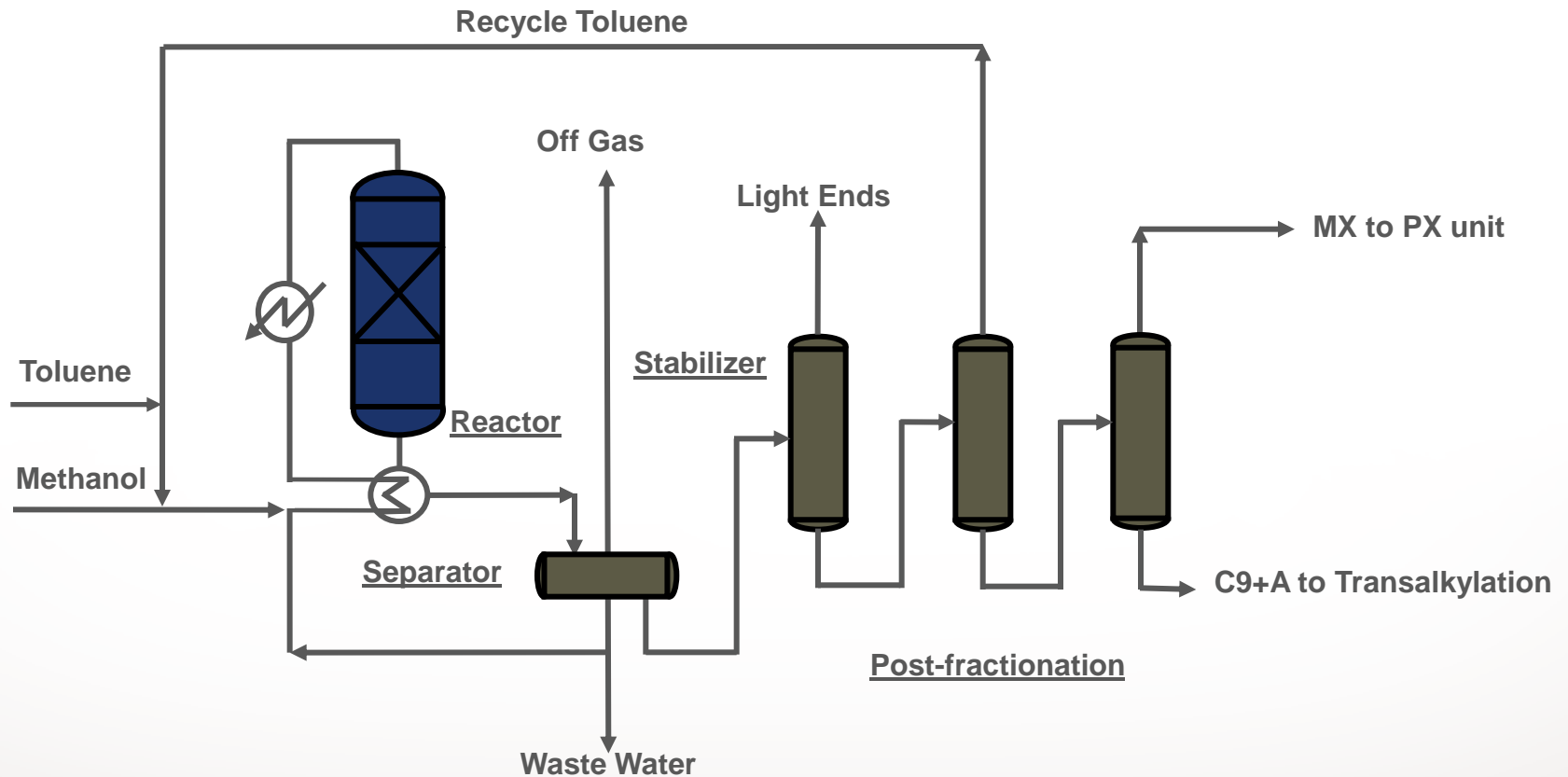
**Transalkylation** and **Isomerization** re-arrange methyl groups and remove higher alkyl groups.

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



# GT-ToIAIk<sup>SM</sup> Process Scheme

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



# Typical Condition and Yields for TM

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

# Economics for GT-TolAlk<sup>SM</sup>



Engineered to Innovate

**Basis: 400 KTA Toluene / 2013 Raw Material and Product Prices (IHS)**

<b>Feedstock</b>	<b>KTA</b>	<b>Unit price, \$/ton</b>	<b>Annual \$MM</b>
Toluene	400	1140	456
Methanol	189	389	74
<b>Feed Costs</b>			<b>\$530</b>
<b>Products</b>			
Fuel Gas	14	725	10
Mixed Xylenes	389	1320	513
A <sub>9</sub>	80	1130	91
Process Water	107	-10	-1
<b>Products Value</b>			<b>\$ 613</b>
Utilities			38
<b>Net Margin</b>			<b>\$ 45</b>
TIC (USGC, 2013, reaction plus fractionation)			<b>\$ 42</b>

**Simple ROI = 12 Months**

# GT-TolAlk<sup>SM</sup>, 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<sup>SM</sup> 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



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



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+ Engineered to Innovate

