

18-19th , July , 2016, Parsian Azadi Hotel, Tehran, Iran



Methanol+Toluene
to Xylenes

SINOPEC MTP and MTX technologies



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July 18th, 2016



◆ MTP

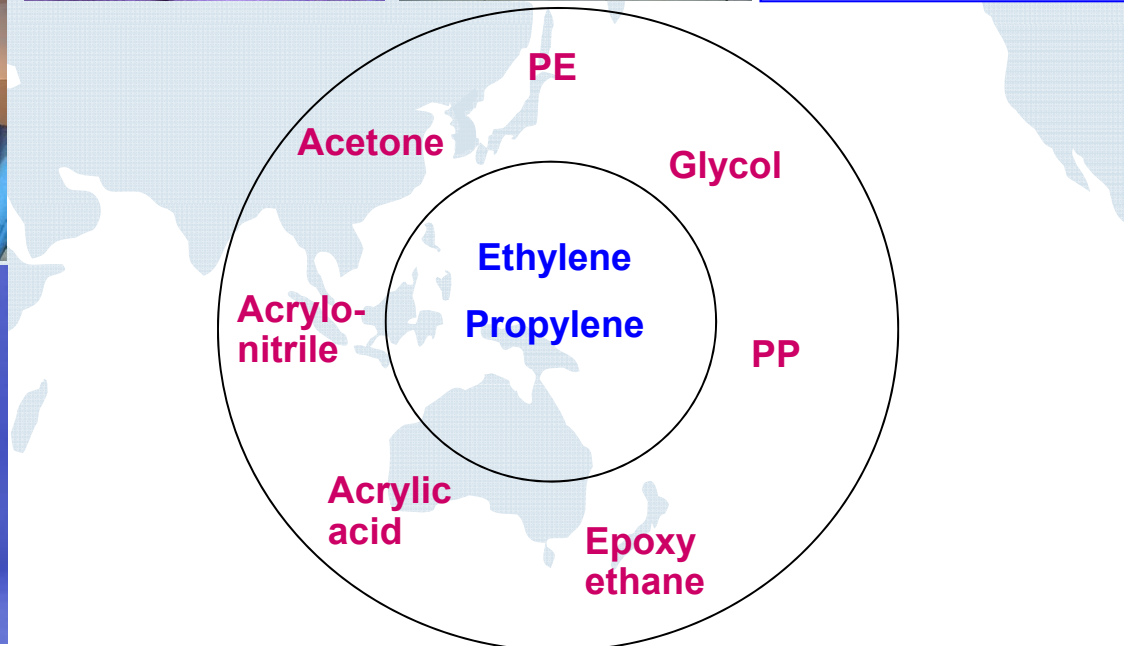
- Introduction
- S-MTP process
- S-MTP catalyst
- Latest advance of S-MTP

◆ MTX

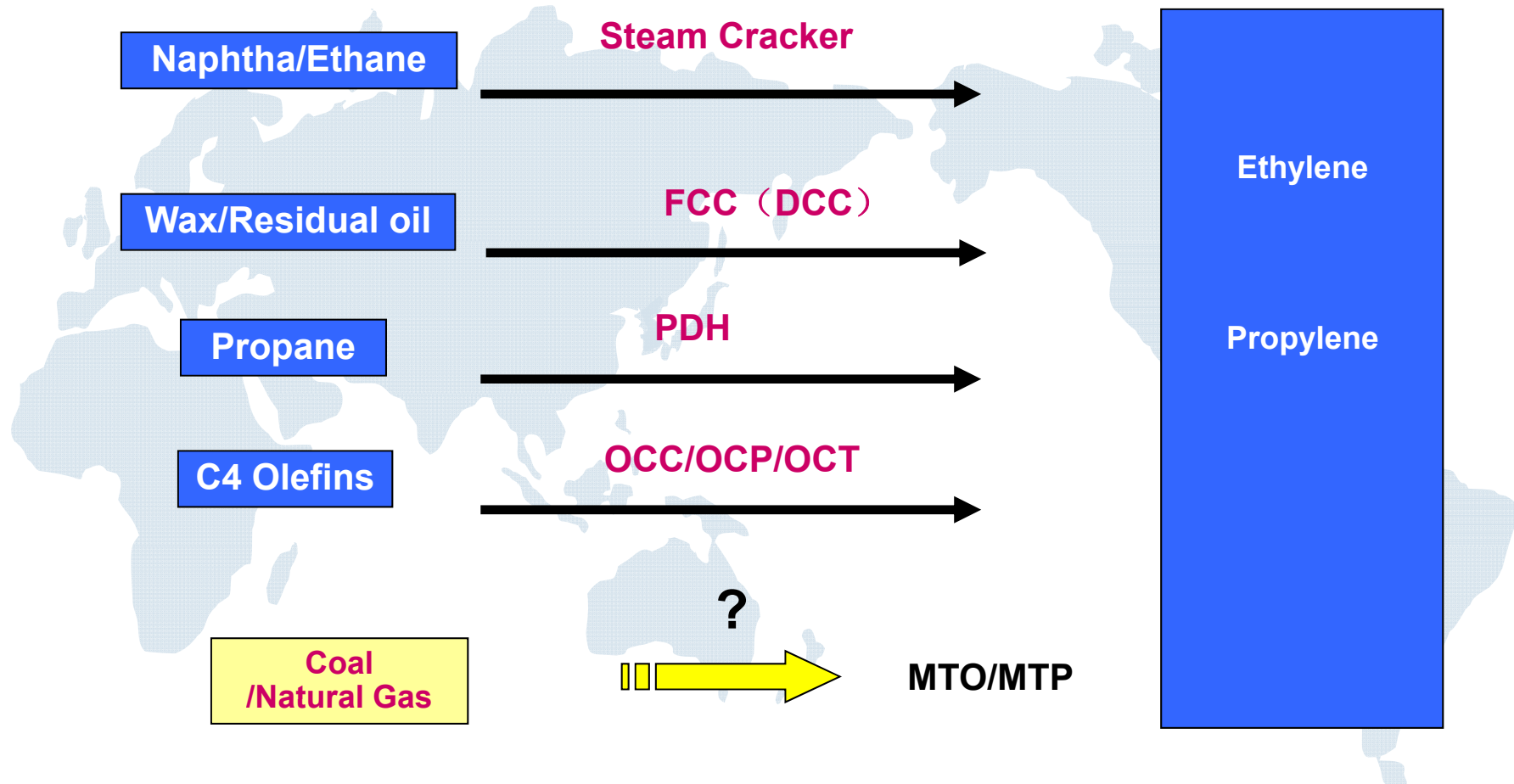
- Technical background
- MTX Technology
- 200 KTA industrial demonstration



Olefins are closely related to our daily life

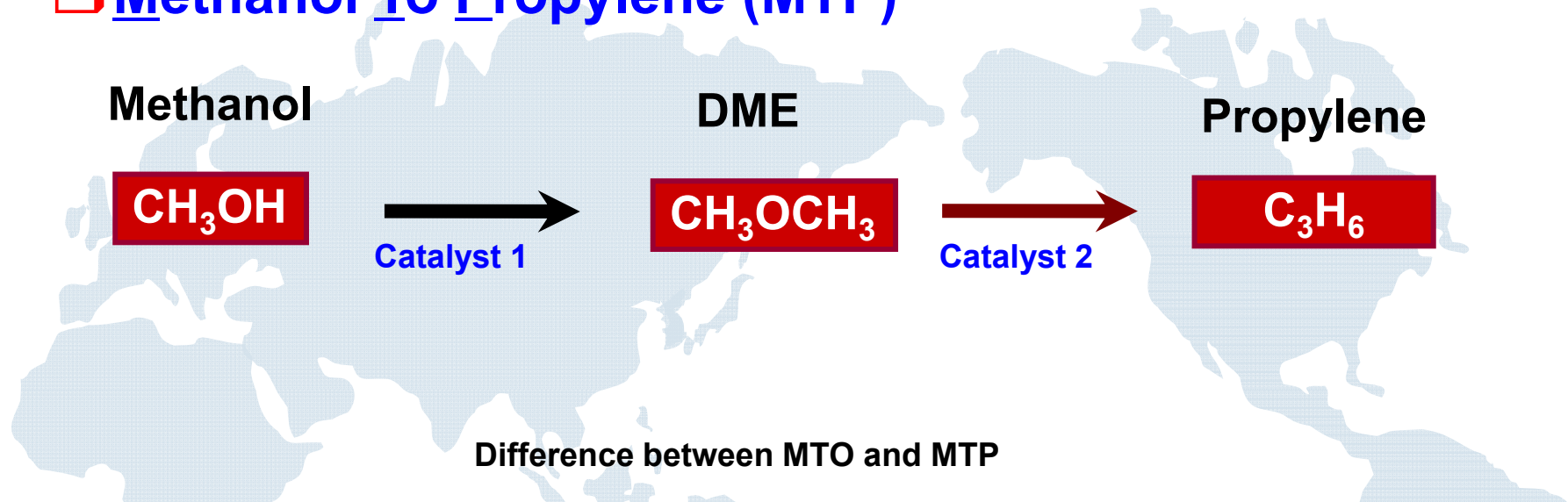


Technical Routes for Producing olefins



- Feedstock for traditional routes to olefin mainly depends on oil
- Is there any other source of ethylene and propylene?
- Natural Gas/Coal to Chemicals is becoming a promising technical route

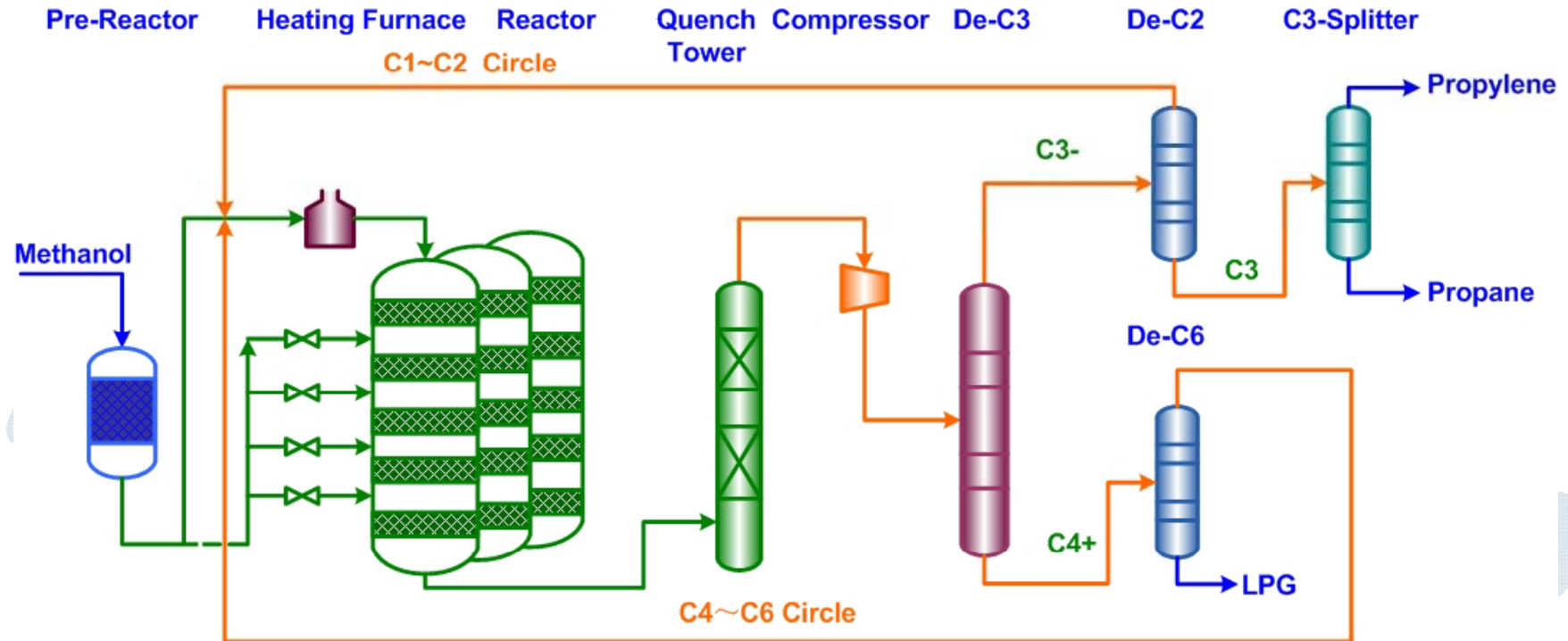
□ Methanol To Propylene (MTP)



Difference between MTO and MTP

Process	MTO	MTP
Product	Ethylene + Propylene	Propylene
Catalyst	Small pore zeolite: such as SAPO-34(CHA)	Medium pore zeolite: such as ZSM-5(MFI)
Preferred Reactor	Fluidized-bed reactor	Fixed bed reactor

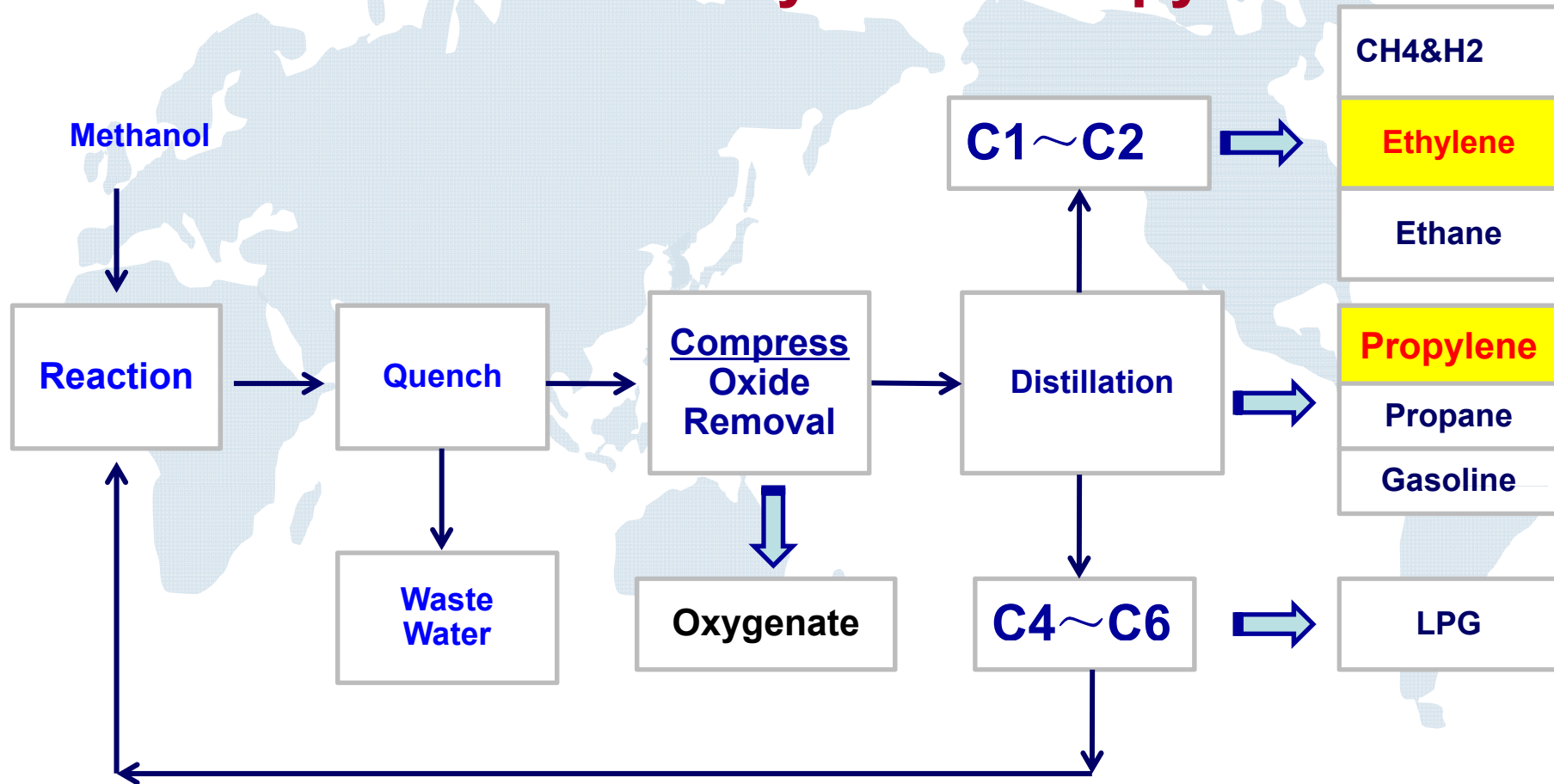
Typical S-MTP Process



Simplified PFD of S-MTP Process

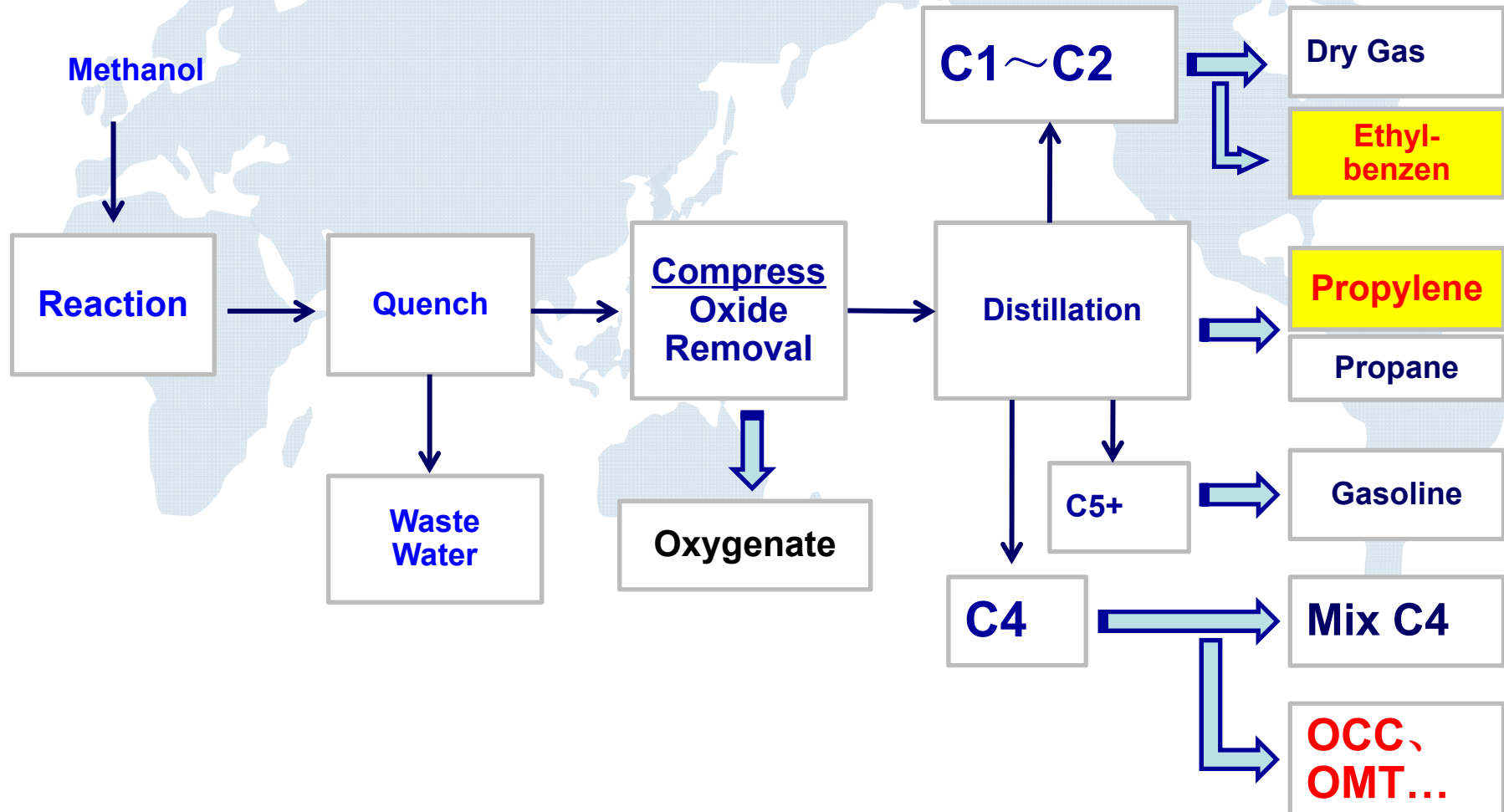
Optional S-MTP Process

Maximum of Ethylene & Propylene



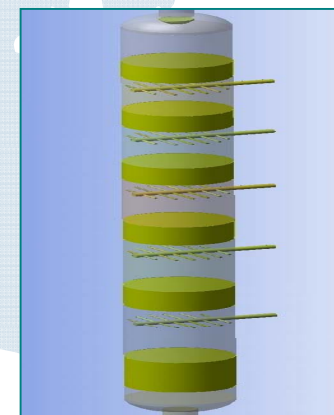
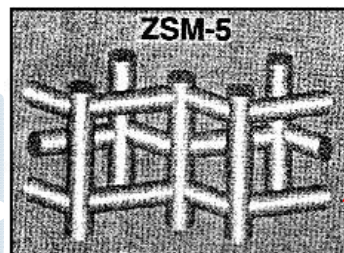
Optional S-MTP Process

Minimum of Investment



MTP know how

- **Adiabatic multistage-layered fixed-bed Reactor**
- **Low energy consumption separation system**
- **Catalyst with long cycle length**

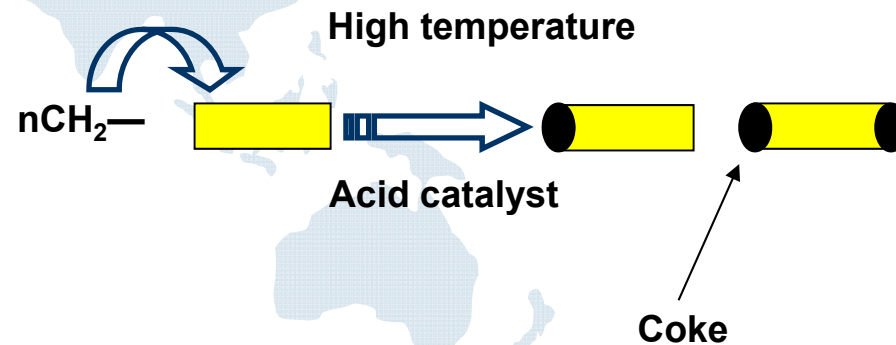


Reaction	n	$\Delta G/(\text{kJ/mol})$	$\Delta H(\text{kJ/mol})$
$n\text{CH}_3\text{OH} \rightarrow (\text{CH}_2)_n + n\text{H}_2\text{O}, n=2,3,4\dots$	2	-115.1	-23.1
	3	-186.9	-92.9
	4	-241.8	-150.0

MTP: Strong exothermic reaction

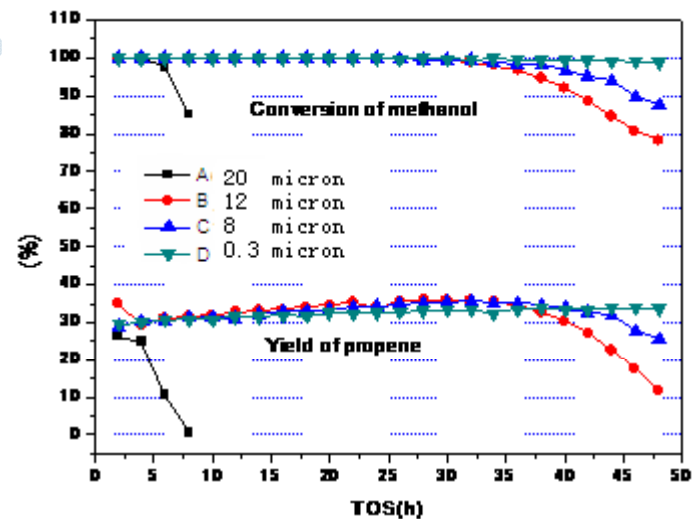
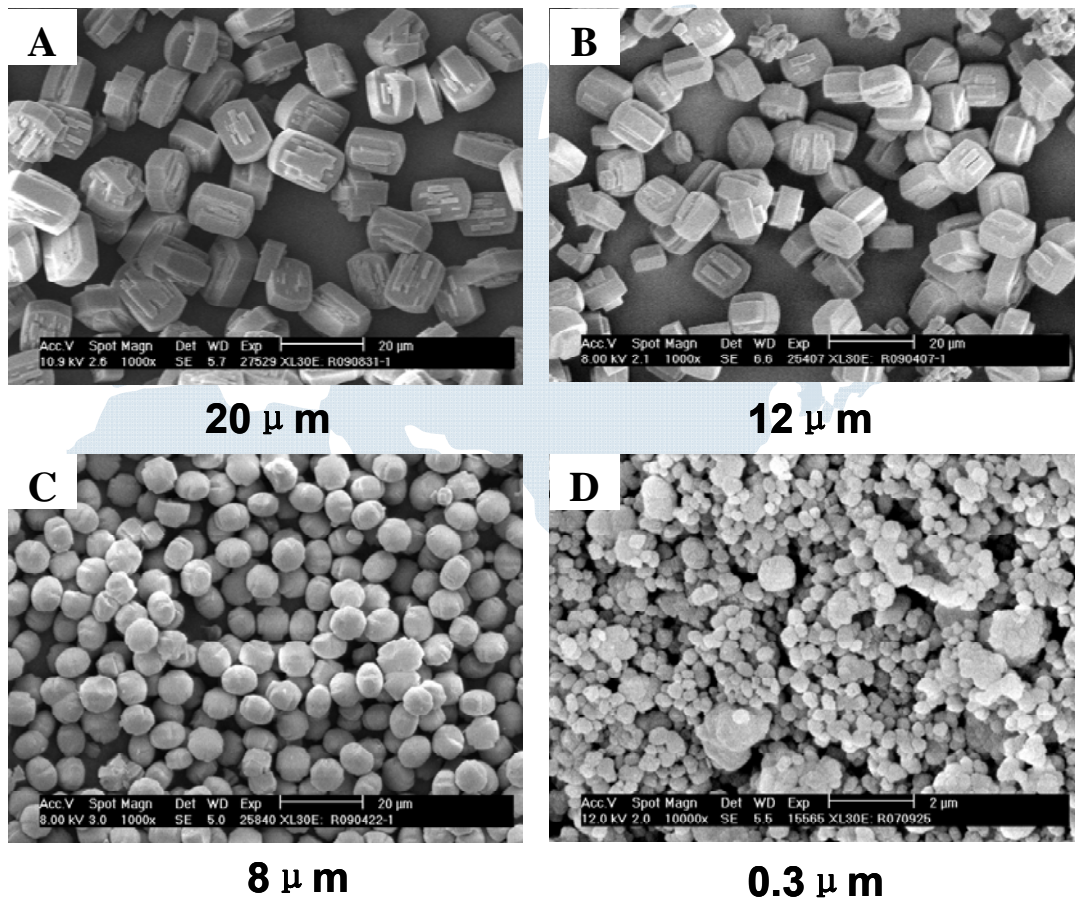
MTP Catalyst Deactivation

- MTP catalyst: ZSM-5 zeolite
- After 500-800 hours operation, MTP catalyst regeneration is needed.



□ Coke covered the active sites and led to deactivation of the catalyst

Synthesis of ZSM-5 with small particle size



Effect of crystal particle size on stability of MTP catalyst

Catalyst with smaller crystals size shows better stability



MTP Catalyst Deactivation

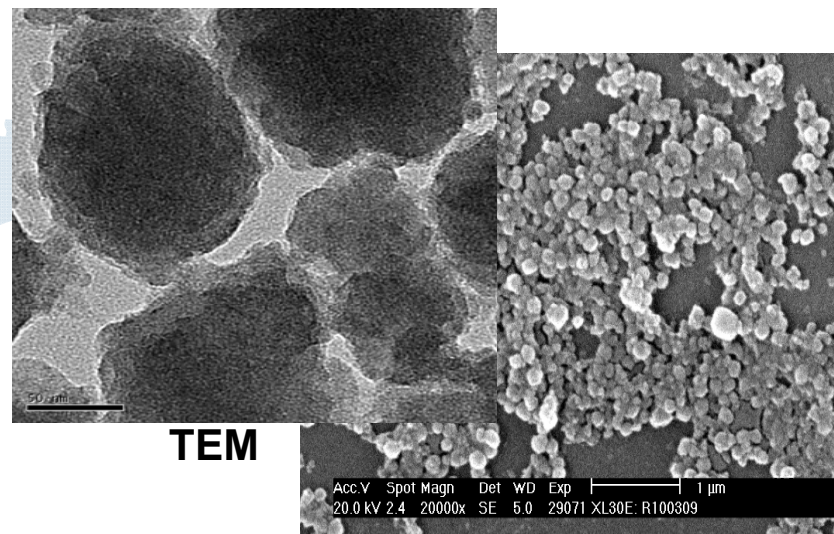
□ Sinopec Know-How

□ ZSM-5 with small crystal size —improve the resistance to coking

□ Full crystalline ZSM-5 catalyst

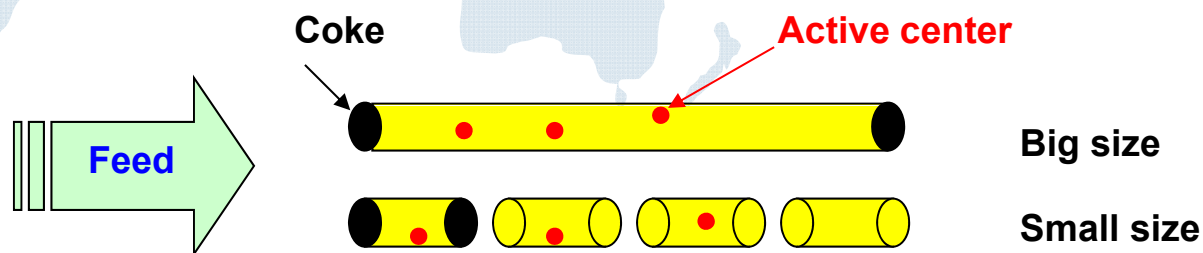
Synthesis of ZSM-5 with small particle size

- ZSM-5 with small particle size
 - Strong resistance to coking
 - 50-80 nm



TEM

SEM

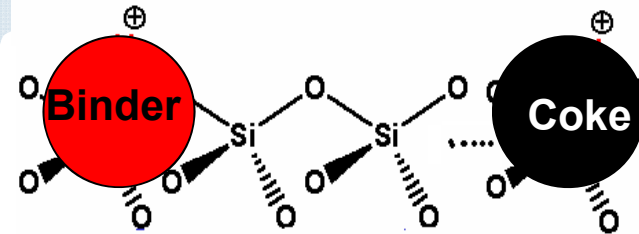


A model for Coke on zeolite with different particle size

Full crystalline ZSM-5 catalyst

- **Shaping of commercial catalyst**
 - Extrusion
 - Pilling
 - Spray drying

- **30-70 wt.% of binder is added**



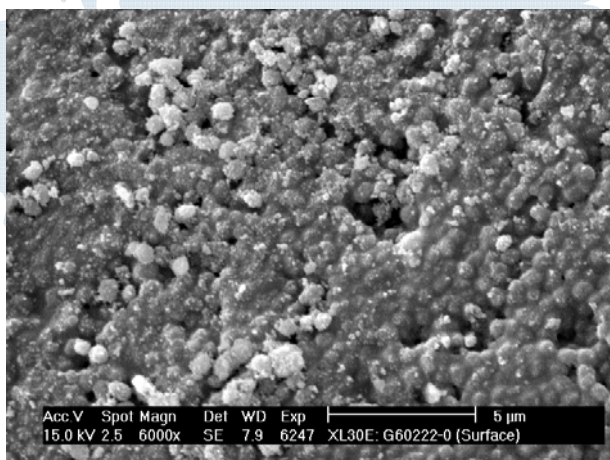
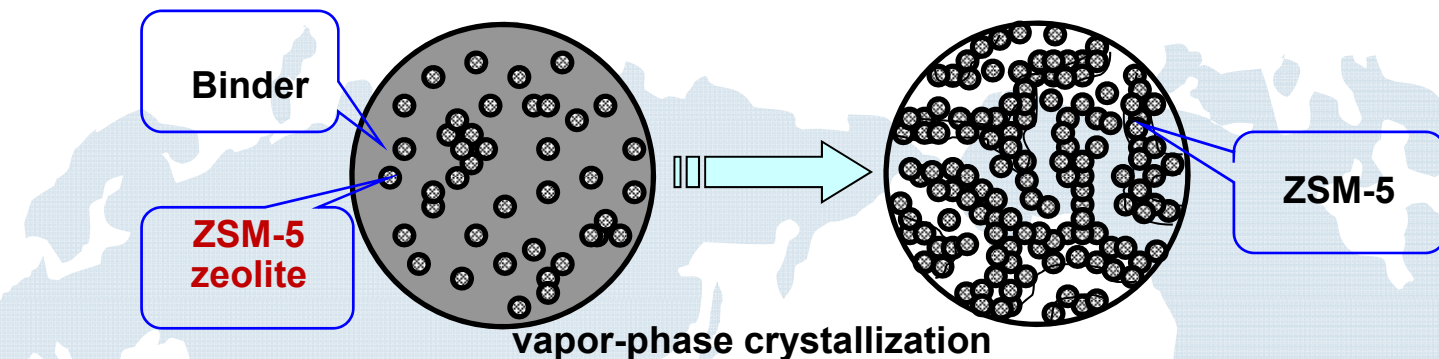
Advantages

- Good mechanical strength
- Easy to shape

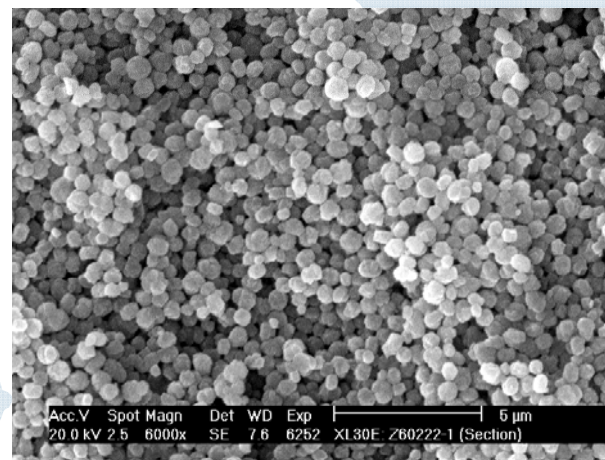
Disadvantages of binder addition

- Binder is inert, no active center
- Binder covers catalytic active centers
- Hinder diffusion of reactant

Full crystalline ZSM-5 catalyst



Conventional ZSM-5 catalyst
(Amorphous binder+ZSM-5)



Sinopec MTP catalyst (ZSM-5)

SINOPEC MTP Catalyst

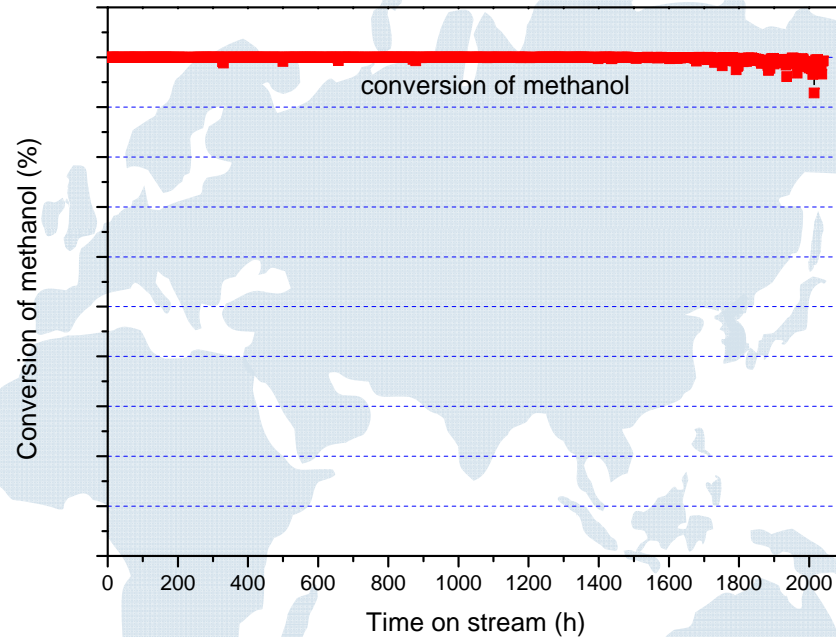
- Binders is transferred into ZSM-5
- Qualified mechanical strength

SINOPEC MTP Catalyst

	Full crystalline catalyst	Conventional catalyst	Improvement
Crystallization (XRD)	130	100	30%
BET (m ² /g)	350	277	26.4%

- Crystallization degree increased by 30%
- Surface area (BET) > 350 m²/g, increased by 26.4%
- The volume of micropore and mesopore increased by 48% and 79% respectively

Catalytic performance of MTP



SINOPEC catalyst stability in MTP



S-MTP catalyst

- The catalyst cycle time is over 2000h (83days)
- Catalyst can be manufactured in large scale.

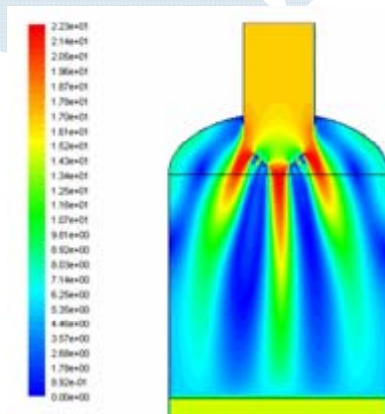
S-MTP Demo unit



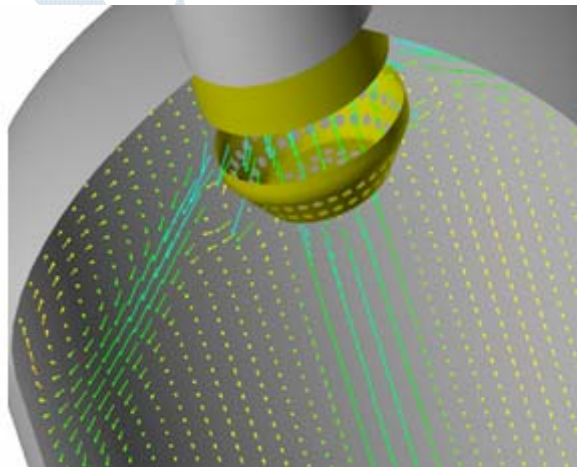
- S-MTP Demo unit was started up in December 2012.
- Selectivity of propylene is over 66%.
- Reactor and reaction process have been commercially proven.

S-MTP PDP technology

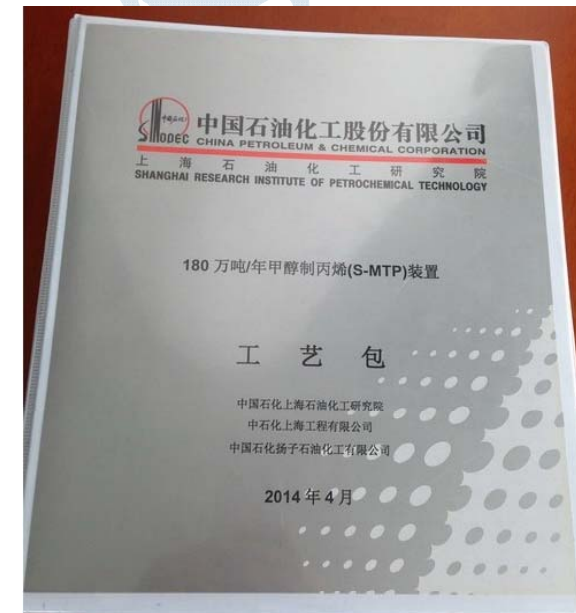
- SINOPEC is devoting to develop S-MTP packaged technology, the MTP process design package (propylene capacity is 500 KTA) has been finished **in Sep 2013**.
- Over **70** patents on S-MTP have been applied.



Velocity Distribution Reactor Inlet



Gas Distribution Reactor Inlet



◆ MTP

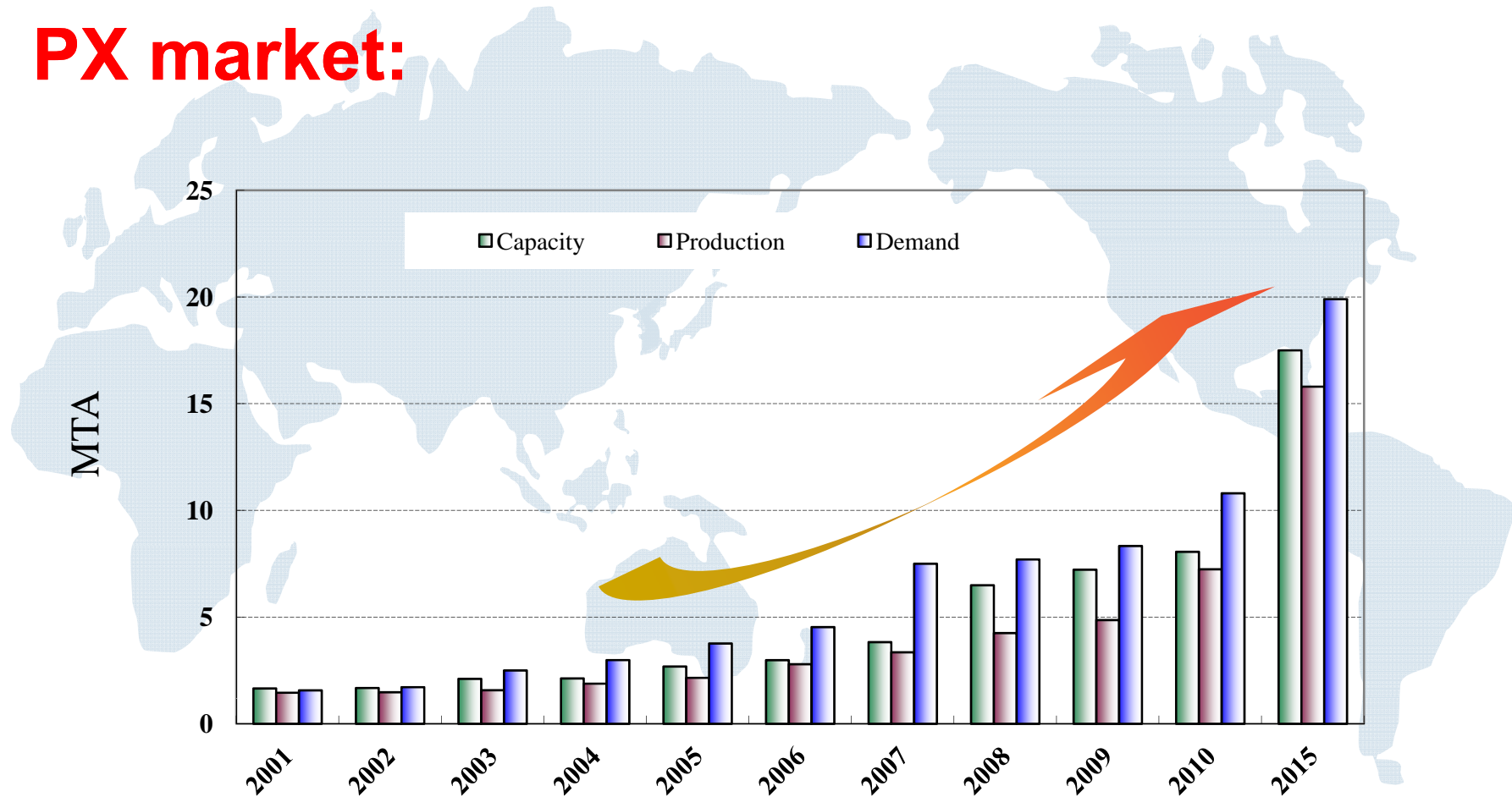
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- Technical background
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Technical background

PX market:



PX demand increases by 20% annually, approaching 20MTA in 2015

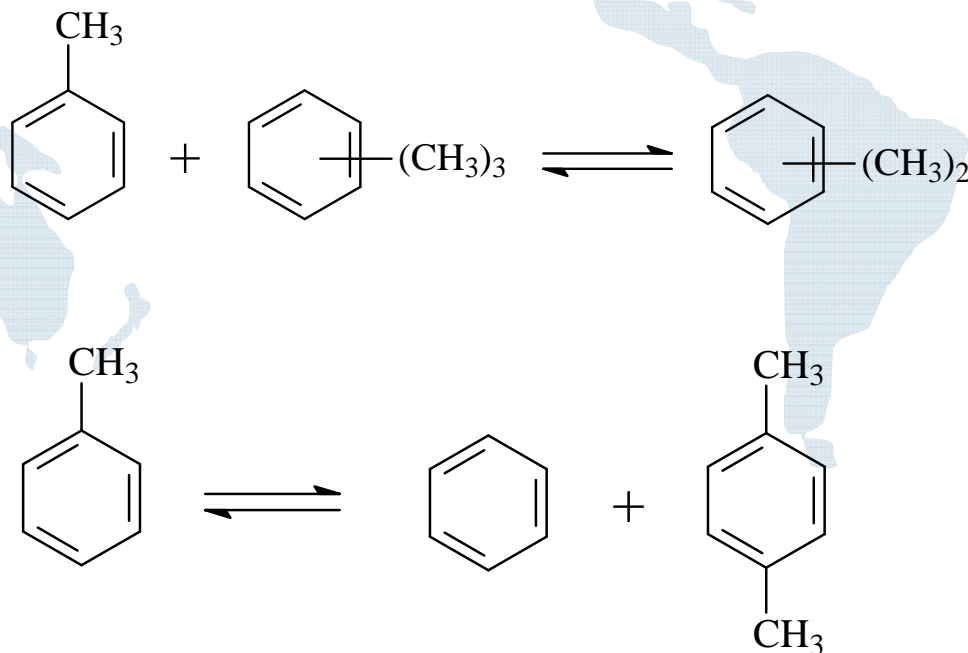
Production routes of xylenes

1. Catalytic Reforming

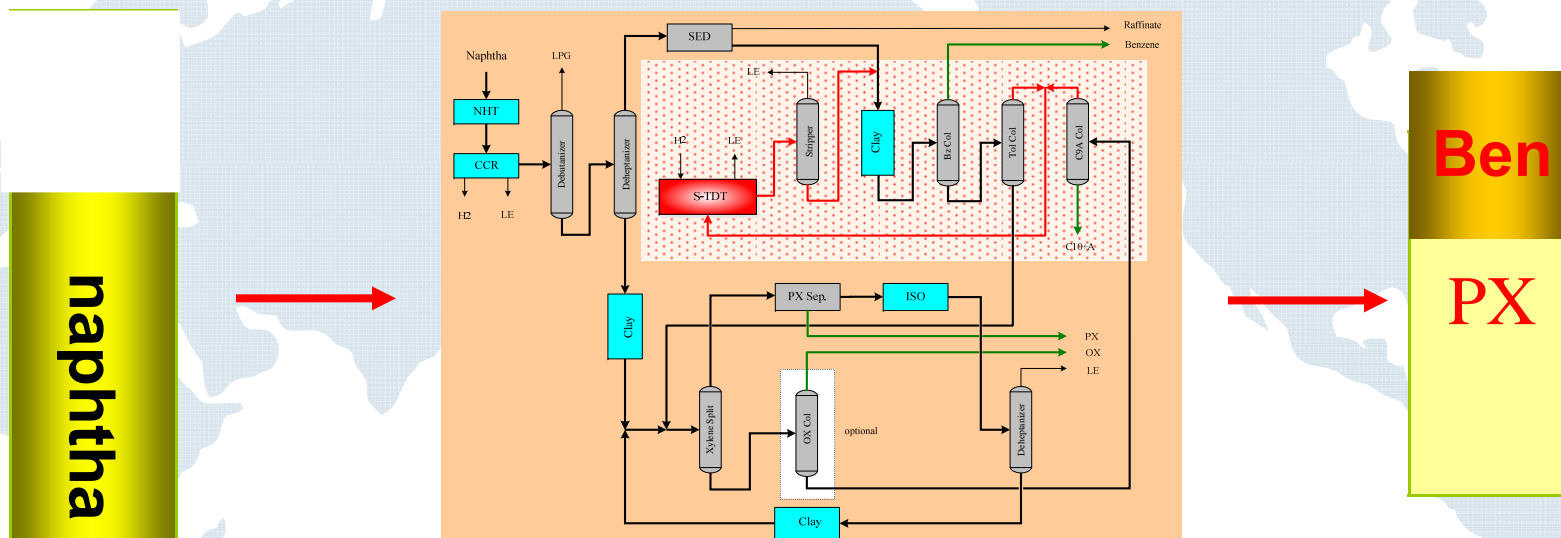
2. Steam creaker

3. Toluene
disproportionation and
transalkylation

4. Shape-selective toluene
disproportionation

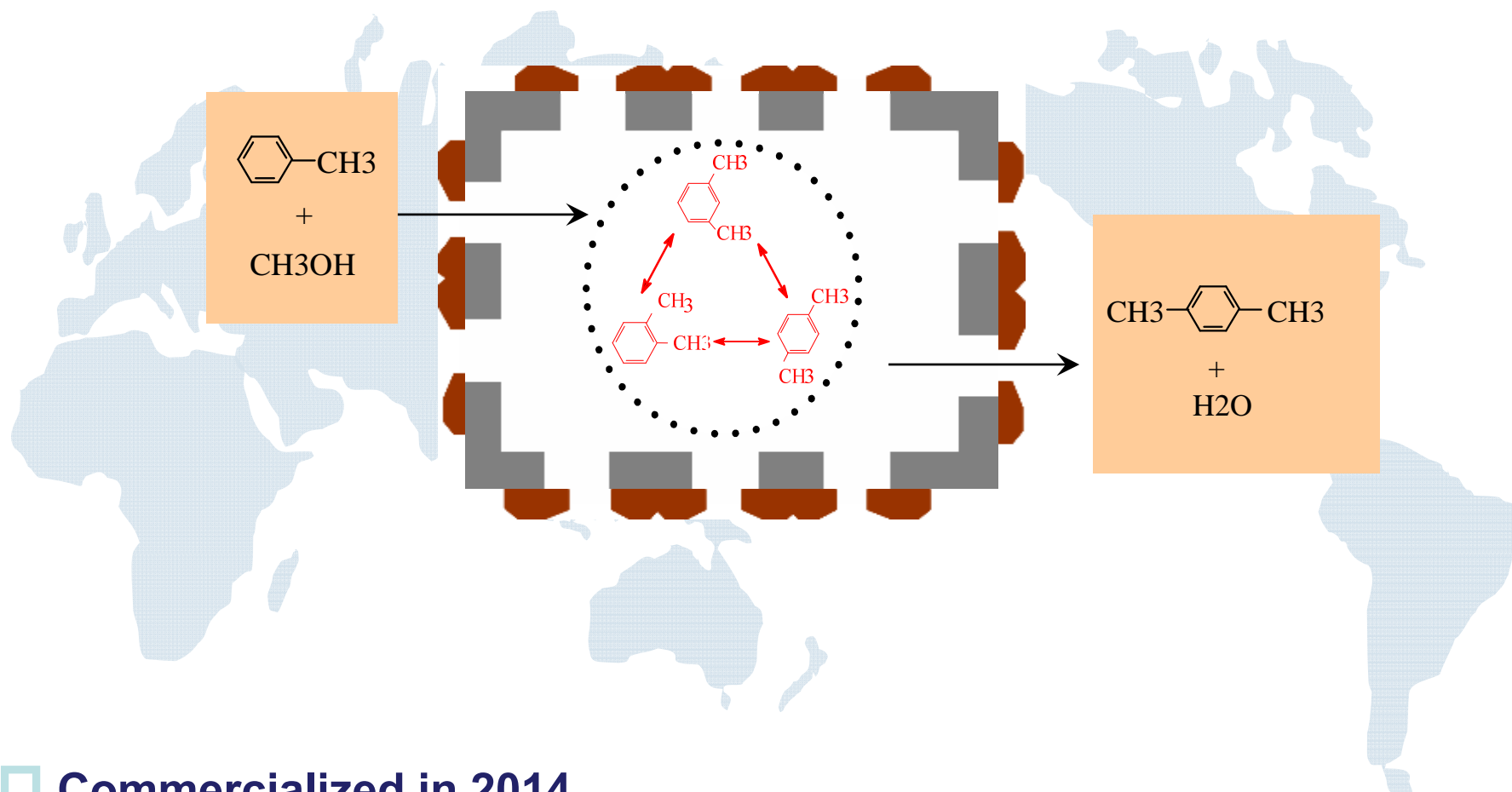


Technical Background



Xylenes output can be increased by 30-50% by introducing methanol into PX complex

Technical Background



- Commercialized in 2014.
- SINOPEC is the first company to introduce to PX production.

MTX Technology

Operation conditions

- Temperature: **350-480°C**
- Pressure: **0.1-1.5 MPa**
- Toluene WHSV: **2-5 h⁻¹**
- Tol./methanol: **1-4mol/mol**

Process performance

- Toluene conversion: **≥30 wt%**
- Methanol conversion: **≥99 wt%**
- Xylene selectivity: **≥80 wt%**
- Service life: **≥24 months**

200 KTA industrial demonstration

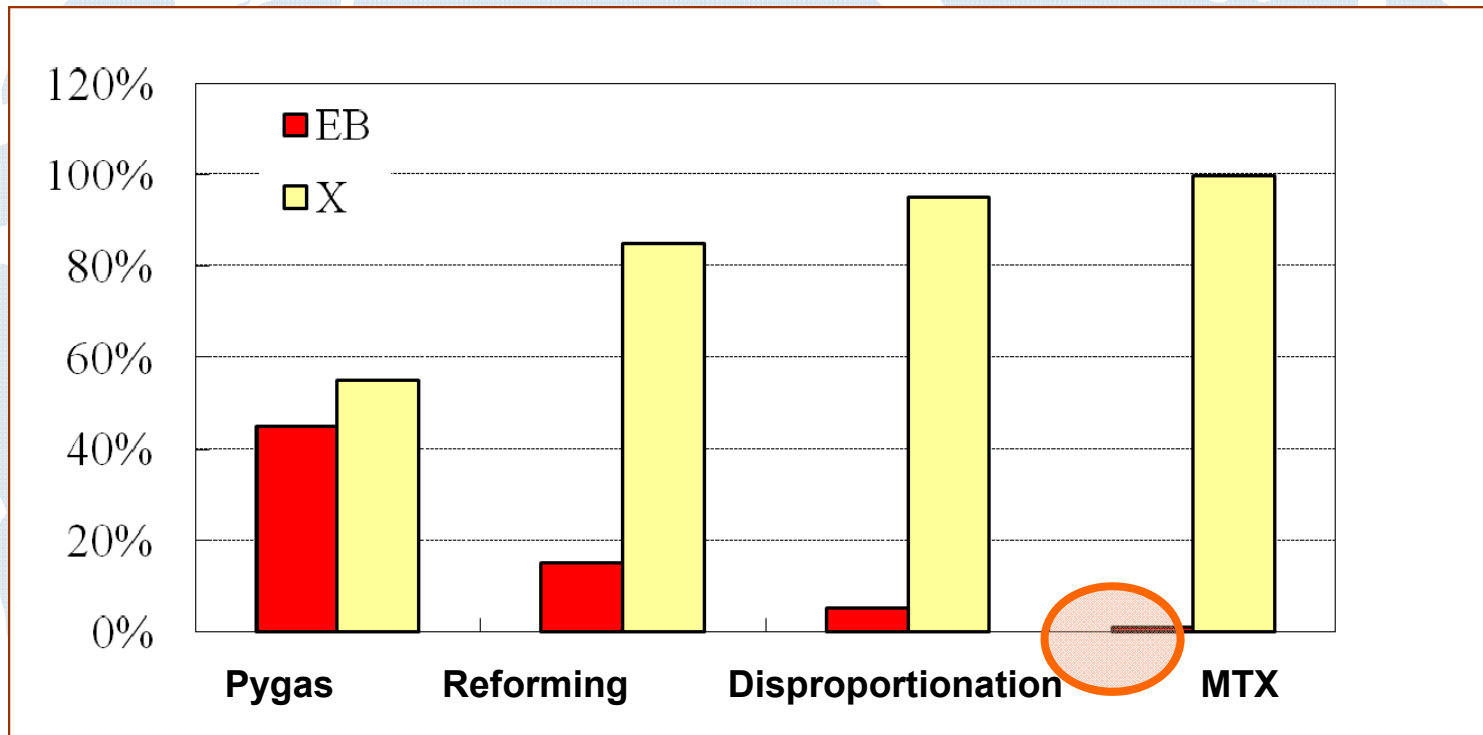
It's the first time that methanol was converted into aromatics complex in industrial scale in the world.



Performance

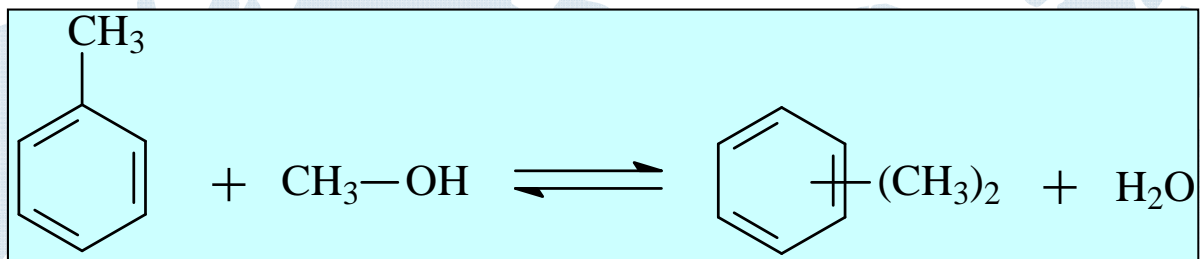
- Toluene conversion \geq 30wt%
- Xylene selectivity \geq 80wt%
- EB/C₈A=0.5%

High performance catalyst



Low EB in C₈A stream

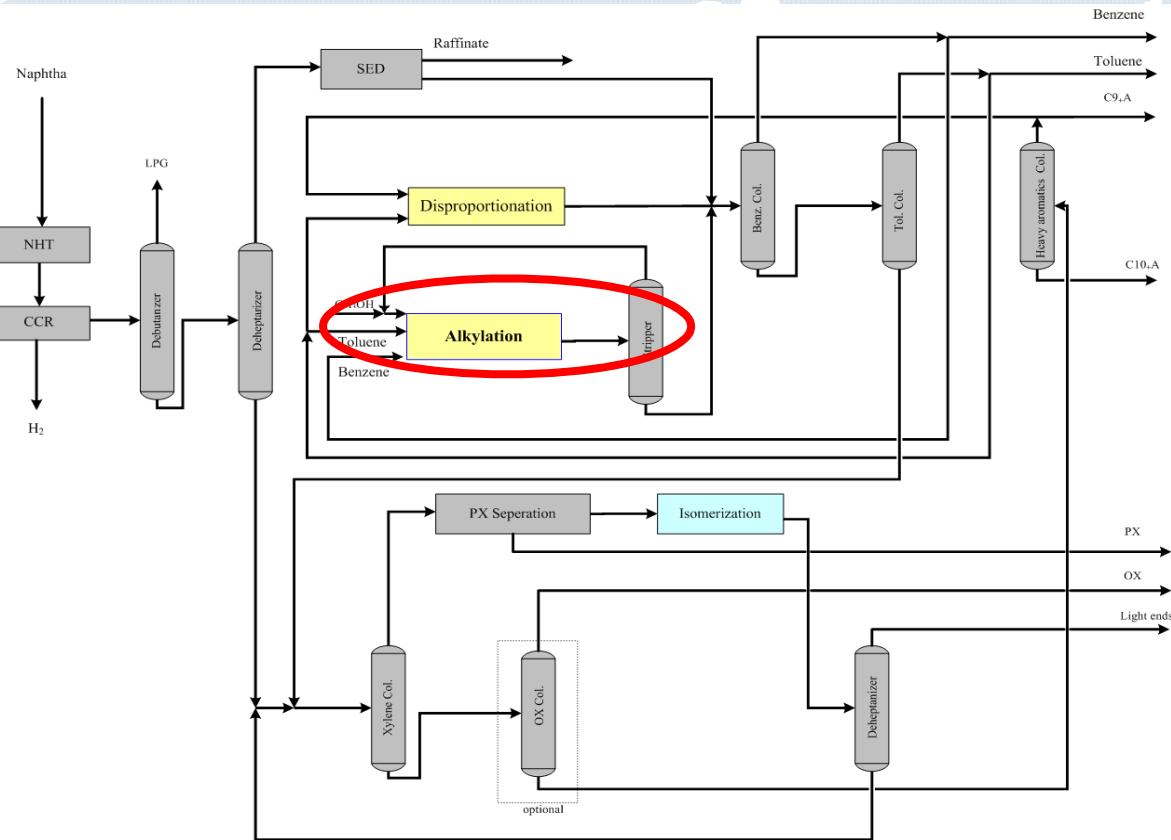
Application



Advantages of toluene methylation process:

- ✓ Diversification of raw materials using methanol
- ✓ No need of separation of xylenes and benzene
- ✓ Combination of methanol with petrochemical industry

Introduction of methanol in aromatics complex



Methanol as raw material to produce xylenes for capacity expanding

Thanks for your attention!

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