Introduction to SINOPEC SRIPT ’s Benzene Derivatives Production Technologies

SINOPEC Shanghai Research Institute of Petrochemical Technology

SINOPEC GROUP

Contents

1. Transakylation Technologies

2. Ethylbenzene Technologies

Introduction to SINOPEC SRIPT ’s Transalkylation Technologies

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1. Background
2. Aromatic Transalkylation Technology of SRIPT
3. Catalyst Optimization Cases
4. Summary

What is PX?

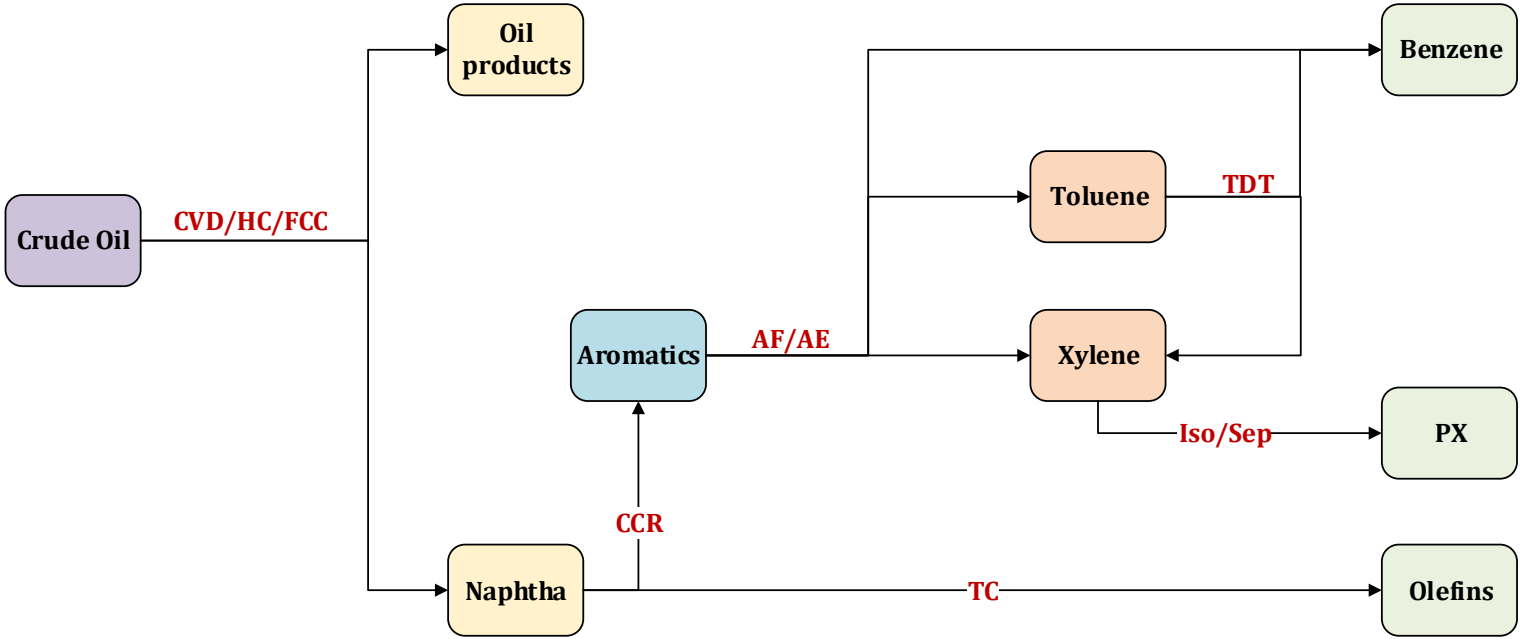
Wide Use of Paraxylene

Para-xylene
（PX）

⇩

Purified Terephthalic Acid
（PTA）

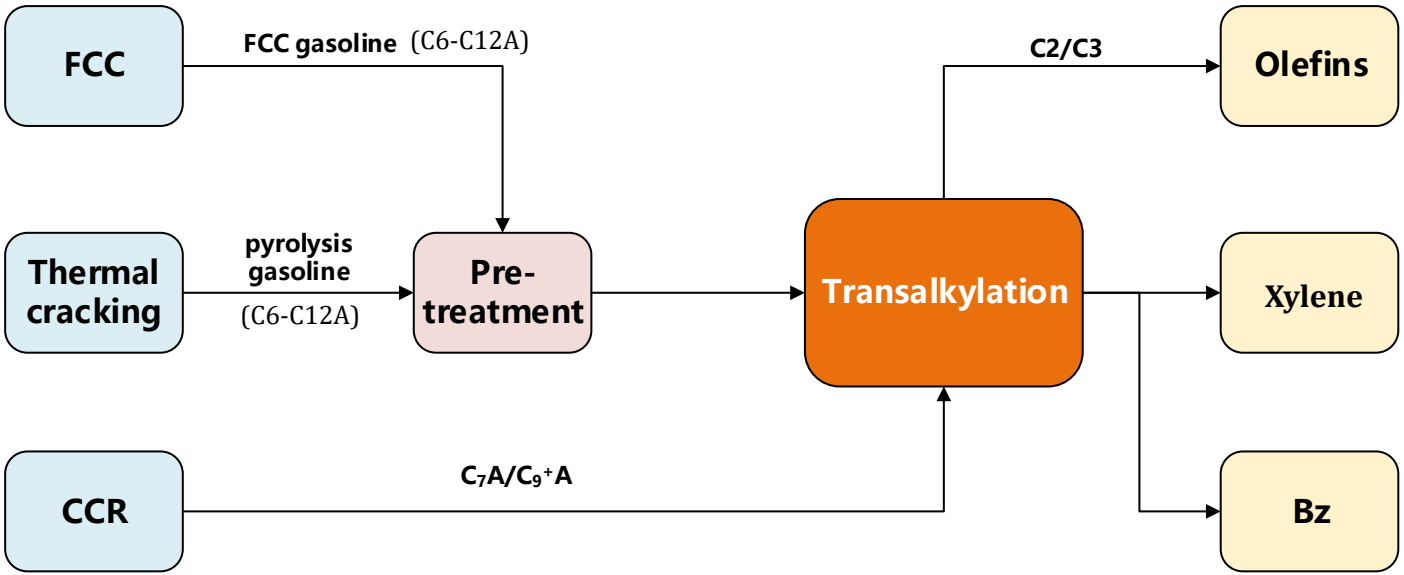
From Refinery to Chemicals



Transformation of refining and chemical industry

Aromatic Transalkylation Technology of SRIPT

What are we doing?



integration of refining & chemical industry

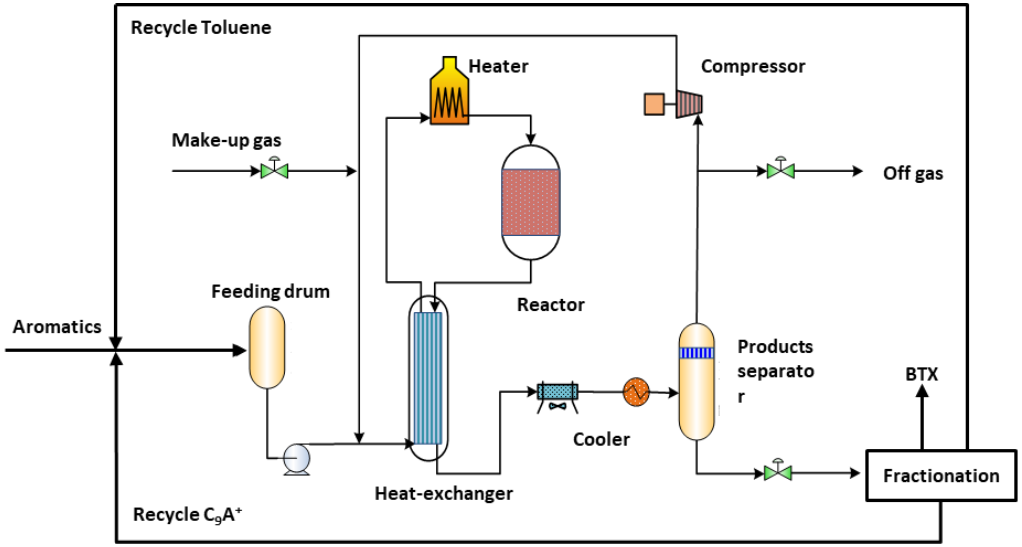
What process technologies do we have?

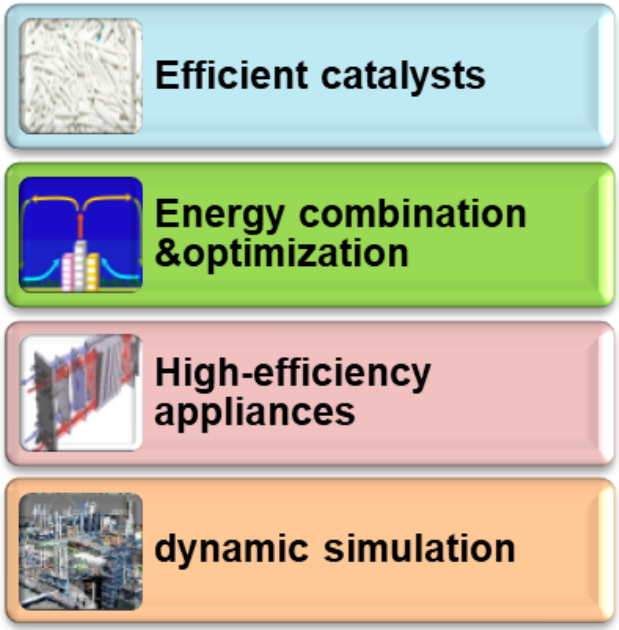
Process Portfolio

PX process	Process description	Similar process	Remarks	start-up Year	Catalysts
S-TDT™	Toluene + C_9^+A→ C_8A+benzene Toluene→ C_8A+benzene	• TATORY • Trans-Plus • Trans-Plus • MTDP	Largest capacity 3500 KMTA. 15 UNITS	1997	HAT™/HLD™ series
S-HAP™	heavy aromatics C_9^+A→ C_8A+light gas(C_2/C_3)	• /	Largest capacity 1000 KMTA	2016	HAP™ series
MTX™	Benzene+CH_3OH→ C_8A(rich PX) Toluene +CH_3OH→ C_8A(rich PX)	• EMTAM • EMTA	Largest capacity 200 KMTA	2012	MTX™ series
SSTDP™	Toluene→ C_8A(rich PX)+benzene	• PX-Plus • STDP • PX-Max	Largest capacity 200 KMTA	2007	SD™ series

Aromatic Transalkylation Process of SRIPT (S-TDT)

S-TDT process

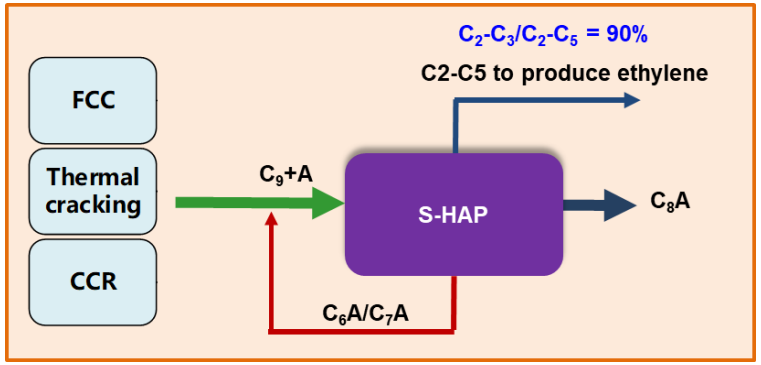




- The largest design capacity is 3500KMTA

Aromatic Transalkylation Process of SRIPT(S-HAP)

S-HAP process



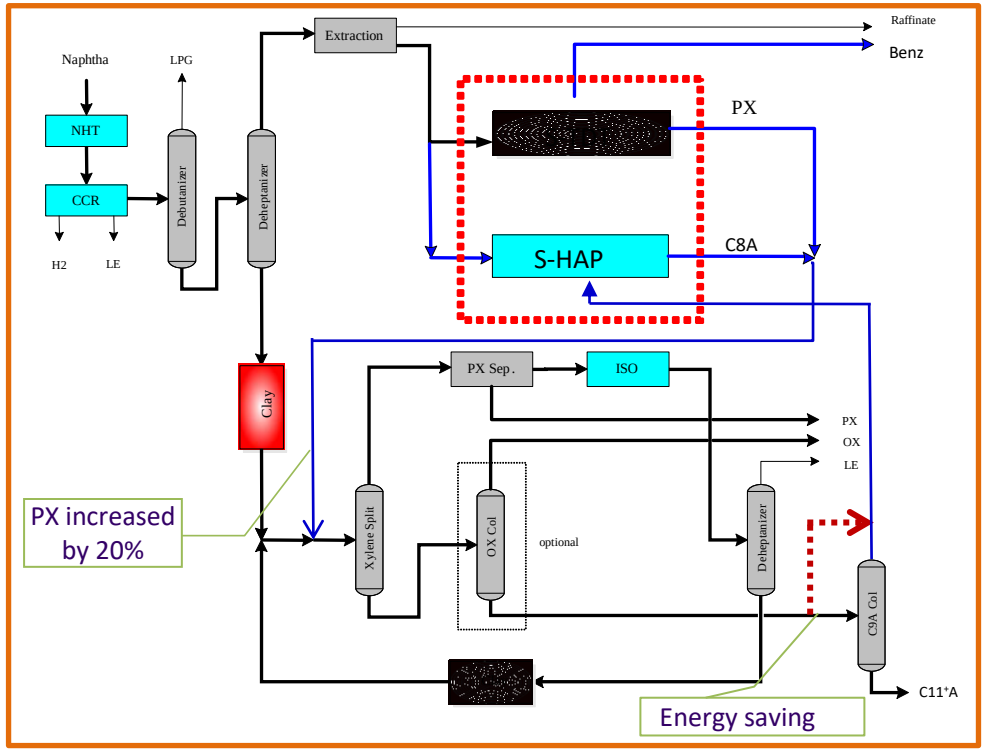
Feed	Product	Content (wt%)
C_9^+A	C_1	0.1
	C_2-C_4	16
	C_8A	83
	C_{10}^+A	0.9

- ◆*C_9^+A Heavy Aromatics → Xylene + ethylene*
- ◆*Maximize the xylene production*
- ◆*Convert inferior gasoline to more valued C8A*

Process advantages

- ➢ **C_9^+A as the only feedstock**
- ➢ **Produce C_8A and light ends**
- ➢ **Flexible products structure**
- ➢ **Low H_2 consumption**
- ➢ **Flexible for existing unit**

Sinopec’s Technology of Processes Integration



Integration of S-TDT™ & S-HAP™ process

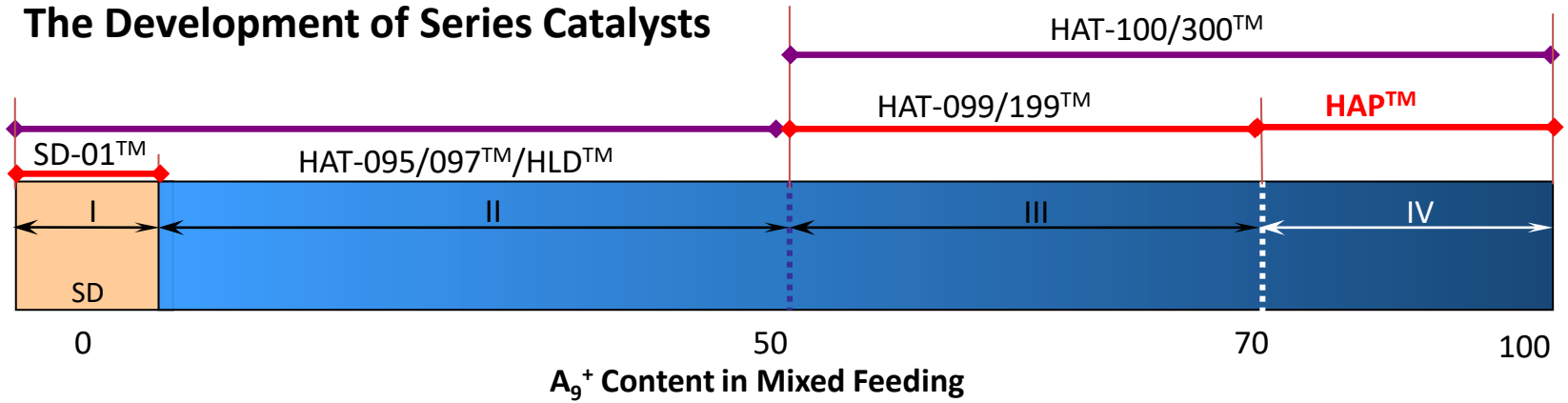
- ✓ Increased Heavy Aromatics utilization
- ✓ Enhanced PX concentration in product and the productivity of the units
- ✓ Energy saving, Decrease the energy consumption of PX recovery unit
- ✓ Flexibility of product distribution adjustment

What catalysts do we have?

Catalyst Portfolio

Catalyst Type	Specialty	Applicable Process	Features	Remarks
HAT™/ HLD™	$C_7A + C_9^+A \rightarrow C_8A+Bz$ $C_7A \rightarrow C_8A+Bz$	1. Tatoray 2. Transplus 2. Xylene-Plus 3. TDP-3 4. Sinopec Technology	·High conversion ·Low ring loss ·Long cycle	· Feed flexibility · High xyl yield & Bz purity (>99.93%) · Commercialized ~90 times · Large scale Unit (2*3500KTA)
HAP™	$C_9^+A \rightarrow C_8A$+light ends(C_2/C_3)	1. Tatoray/Transplus 2. Xylene-Plus 3. TDP-3 4. Sinopec Technology	·High conversion ·High xylene yield ·Deal with C_9^+A containing naphthalene or NA or olefins	· Feed flexibility · C9+A conversion >55% · Commercial scale 1000 KTA
BAT™	$Bz + C_9^+A \rightarrow C_8A+C_7A$	1.Tatoray/Transplus 2. Xylene-Plus 3. TDP-3 4. Sinopec Technology	· High Conv. and Sele. · Low ethylbenzene/C_8A	·Total conversion >55% · EB/C_8A≤3%
SD™	$C_7A \rightarrow C_8A$(rich PX)+Bz	1. MTPX 2. TDP-3 3. PX-Plus 4. Sinopec Technology	·High toluene conversion ·High PX selectivity ·High enzene purity	· PX/X >90% · Toluene conversion >30%

Aromatic Transalkylation Catalysts of SRIPT



- High feed flexibility and can handle 100% toluene and 100% C_9^+
- Atom economics: Most $C_{10}A$ and part of $C_{11}A$ can be used for C_8A production
- high conversion efficiency and high selectivity
- lower Aromatic loss and H_2 consumption, High benzene purity
- Higher capacity for Inferior heavy aromatics： aromatics containing naphthene, naphthalenes and olefins
- Whole fraction heavy aromatics: simplify the separation process

Catalyst Comparison

Licensor	Ref 1	Ref 2	Ref 3	SINOPEC
Catalyst series	A	B	C	HAT™/HLD ™
Metal loading	Noble metal	Noble metal	Noble metal	Non-noble metal
Pre-sulfurization	Yes	Yes	Yes	No
Feedstock	Tol, C_9A, $C_{10}A$	Tol, C_9A, $C_{10}A$	Tol, C_9A, $C_{10}A$	Tol, C_9A, $C_{10}A$
Inlet Pressure, MPa	2.5～3	2.5～3	2～2.5	2.5～3
RIT, ℃	360～480	350～480	380～480	350～460
H_2/HC, mol/mol	3	3	2～3	2～3
WHSV, h^{-1}	2-3.5	2-3.5	2-3.5	2-4

Commercial Application of HAT™ /HLD™ Catalyst

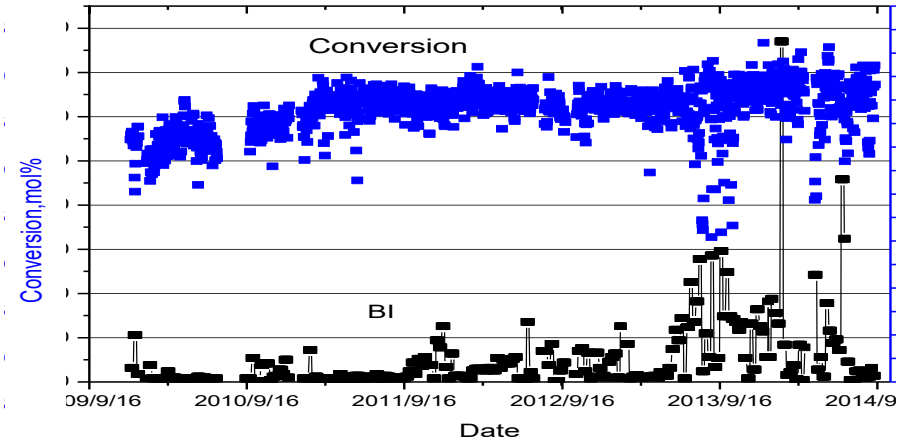
large-scale Units application（capacity>1000KTA）

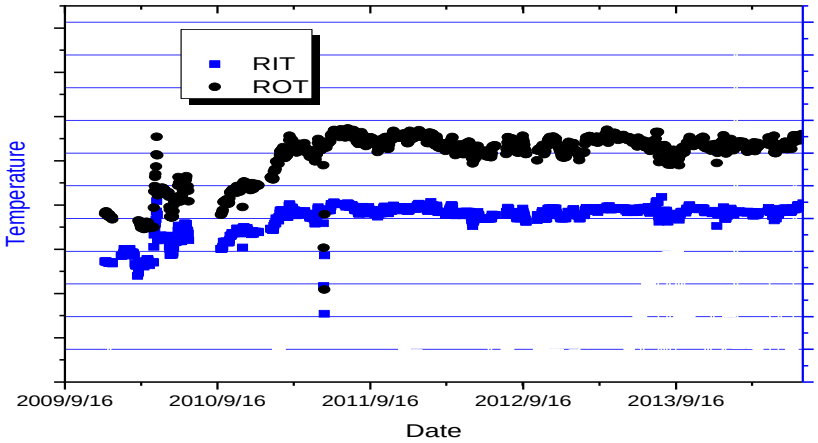
Client	PX Capacity (KTA)	Process Licensor	Catalyst Supplier	Start up year
1	1000	other	SINOPEC	2009
2	1000	SINOPEC	SINOPEC	2010
3	1600	other	SINOPEC	2015
4	2250x2	SINOPEC	SINOPEC	2019
5	1000	SINOPEC	SINOPEC	2021
6	2000x2	SINOPEC	SINOPEC	2021
7	2200	SINOPEC	SINOPEC	2022
8	2000	SINOPEC	SINOPEC	2022
9	1600	SINOPEC	SINOPEC	2022
10	1000	SINOPEC	SINOPEC	2023

Commercial Application

Sinopec Catalyst application Case 1

- The third batch of Sinopec catalyst is under stable operation





Performance of Sinopec catalyst in company A

Commercial Application

Sinopec Catalyst application Case 2

- Sinopec catalyst obtained improved performance
- Preparing for the supply of the third batch of Sinopec catalyst

Catalyst	Reference Catalyst	Sinopec Catalyst
$C_{10}A$ Conv., wt%	ST	ST+20%
Xyl yield, wt%	ST	ST+2%
EB/C_8A	ST	**50%ST**
benzene purity, wt%	99.90	99.95

Commercial Application

Sinopec Catalyst application Case 3

- H_2/HC=~2.0 mol/mol, far lower than normal
- It has kept the stable running with high conversion till now

Catalyst	Reference Catalyst	HAT-099P
Conversion, wt% Selectivity, wt%	Rapid drop 3-4%	Stable
Temp rise rate, ℃	Frequent rise by 60℃ in 2 months	~1℃/month

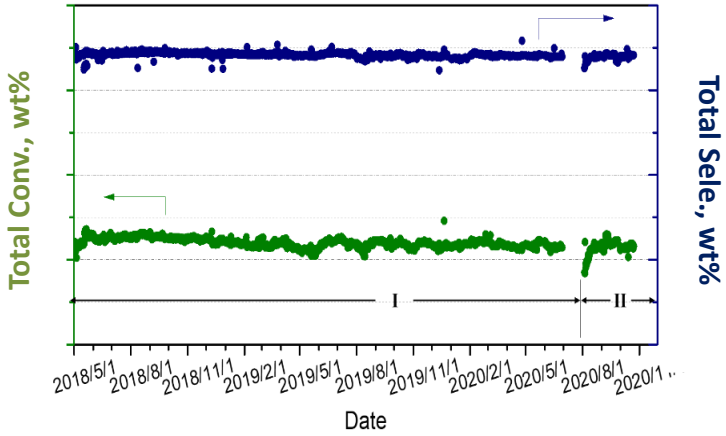
Catalyst Optimization

A. Direct Capacity Expansion (Without Equipment Revamp)

Performance upgrading

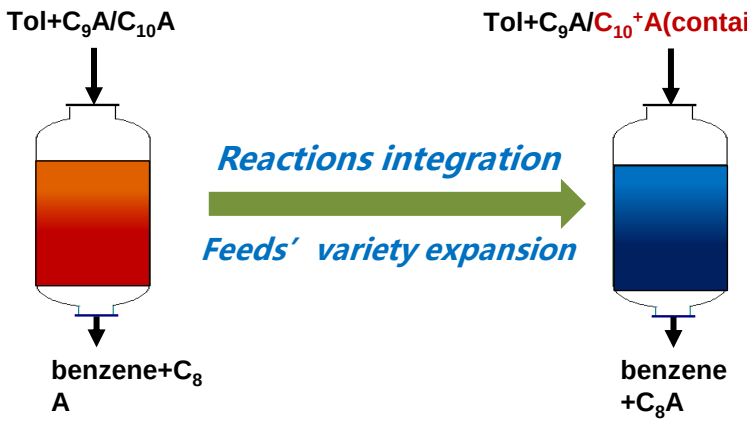
	Typical Cat	Upgrading Cat
Licensor	Sinopec	Sinopec
WHSV, h^{-1}	ST	Up to 160%*ST
Make-up F, KNM^3/h	ST	45%*ST
H_2/HC, mol/mol	ST	73%*ST
Conv., wt%	ST	ST
Sele., wt%	ST	ST+1%
C_8A Sele., wt%	ST	ST+3%

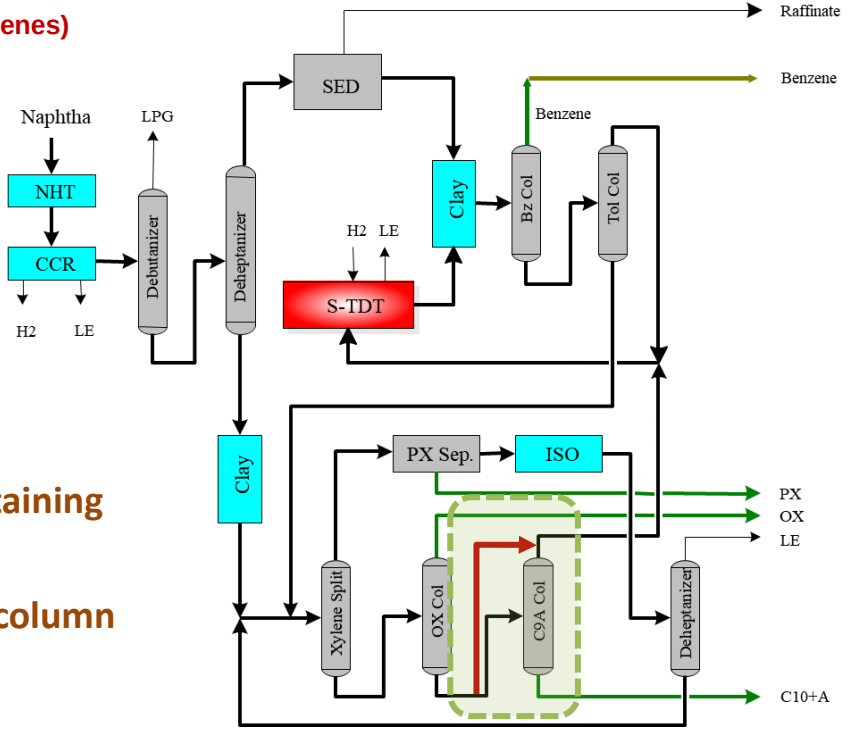
Long period operation



- Capacity Expansion to 130% directly
- Less investment and fast return
- Higher selectivity, lower H_2 consumption

B. Energy Saving of Heavy Aromatics Column





- ✓ Direct utilization of xylene column bottom stream containing naphthalenes
- ✓ Decrease the energy consumption of heavy aromatics column
- ✓ Better economic efficiency

Summary

Summary

- Series catalysts meet the different operation conditions and various requirement of product structure.
- Strong adaptability to feedstocks from pure Tol to 100%C_9^+A containing Non-aromatic, olefin, naphthalenes.
- A catalyst supplier integrating research, production and process design, able to provide professional, tailor-made solutions to customers.
- All the technical service for free.
- Rapid catalyst supply and response.

THANK YOU

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SRIPT's Catalysts for Ethyl-Benzene Production

Development and Industrial Application

Shanghai Research Institute of Petrochemical Technology

(SRIPT)

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1 Introduction

2 Vapor-Phase EB Catalyst
(Pure Ethylene)

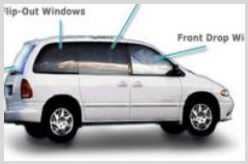
3 Vapor-Phase EB Catalyst
(Dilute Ethylene)

4 Liquid-Phase EB Catalyst

1. Introduction

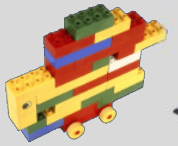
- Ethylbenzene (EB) is one of the most important chemical intermediates and mainly used in the production of styrene.
- Styrene monomer (SM), EB's dehydrogenation product, is used in polymer production of polystyrene, ABS, SAN resins, etc.
- Global overall capacity is about 40 MTA and has an increase rate at 3% annually.
- The growth of EB is rapid in Asia, particularly in China.


Construction/Infrastructure





Automobile/Aviation

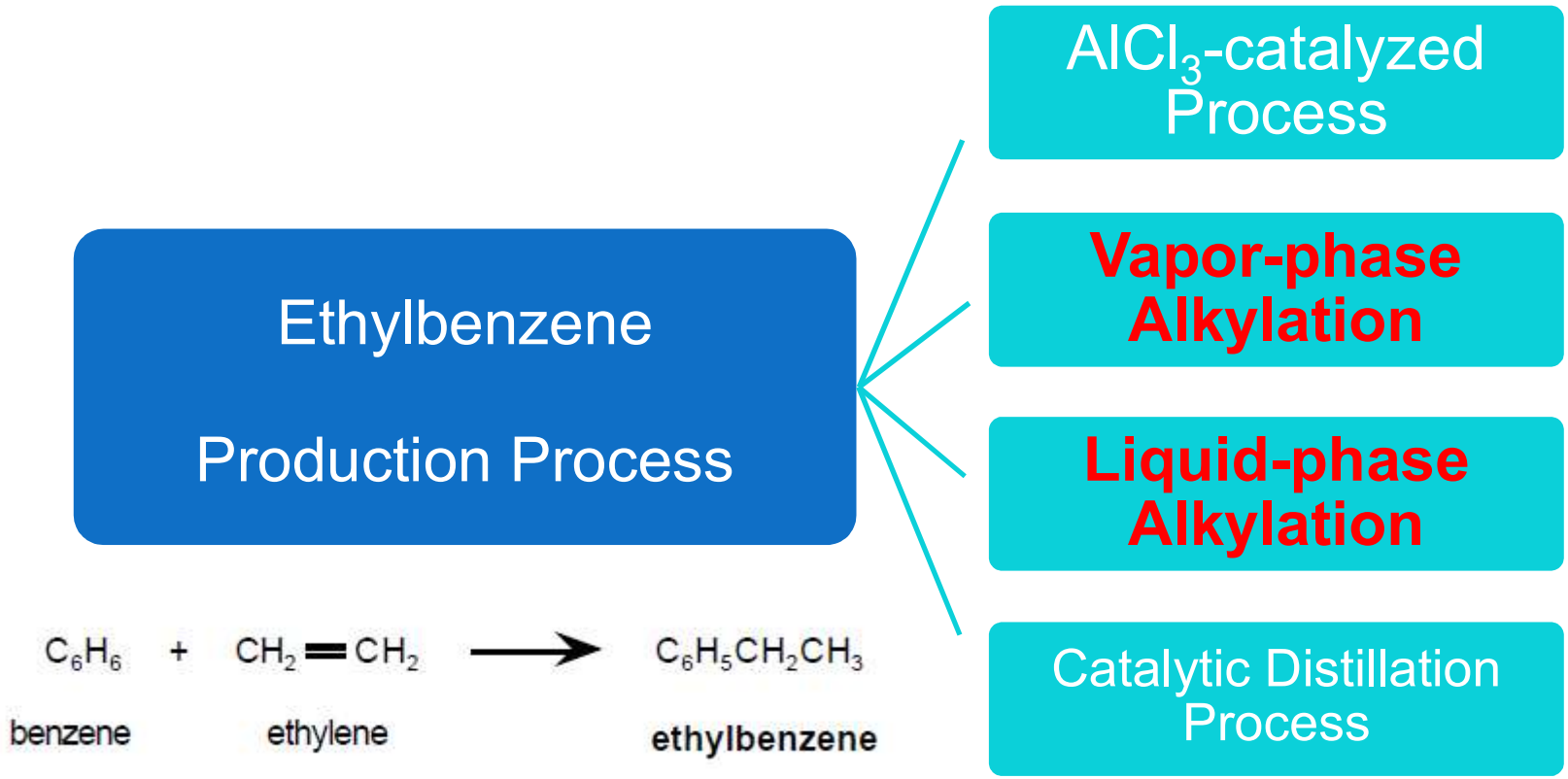





Electronics/Commodity

1. Introduction

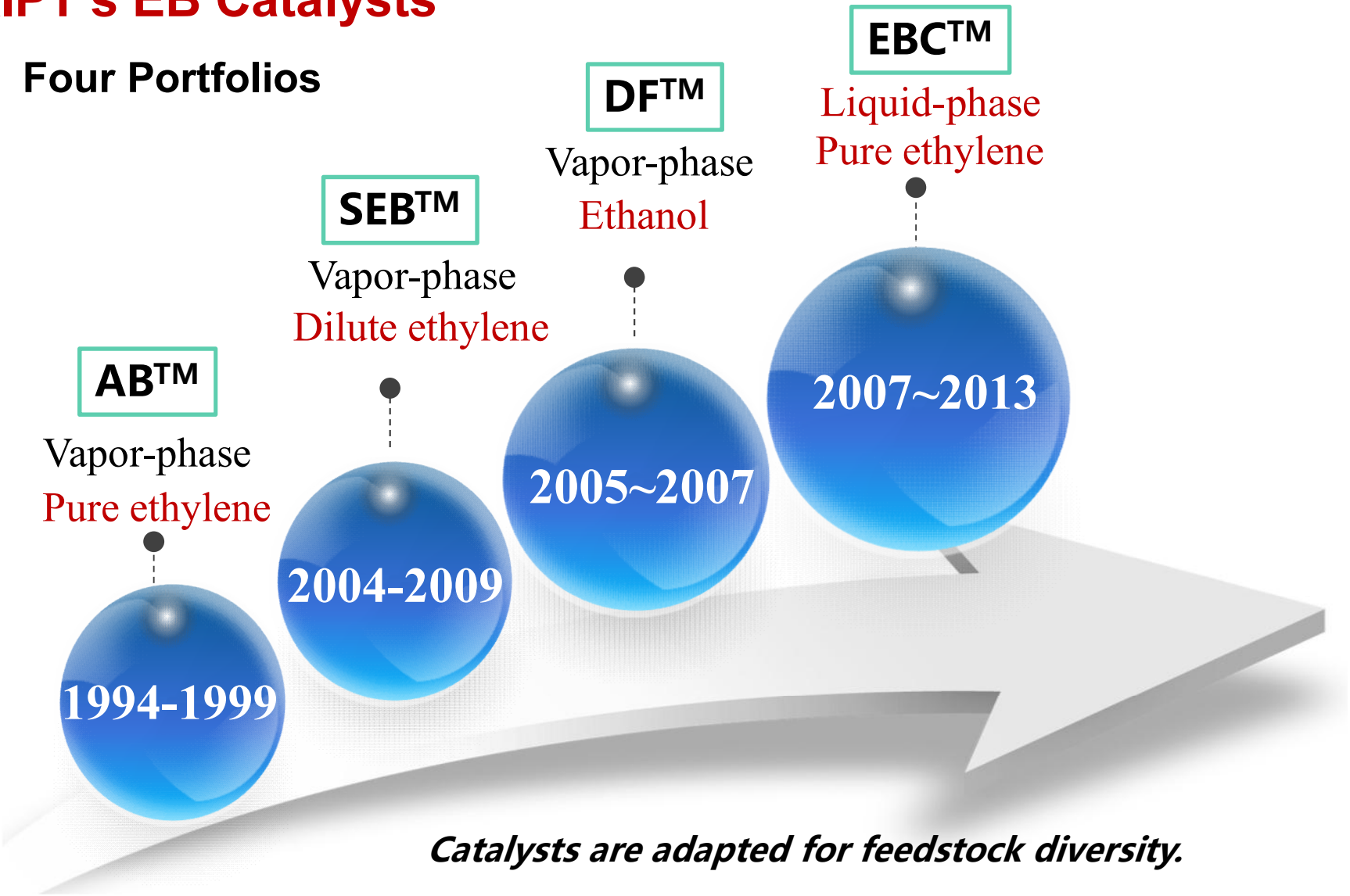
Commercial Processes for EB Production



1. Introduction

SRIPT's EB Catalysts

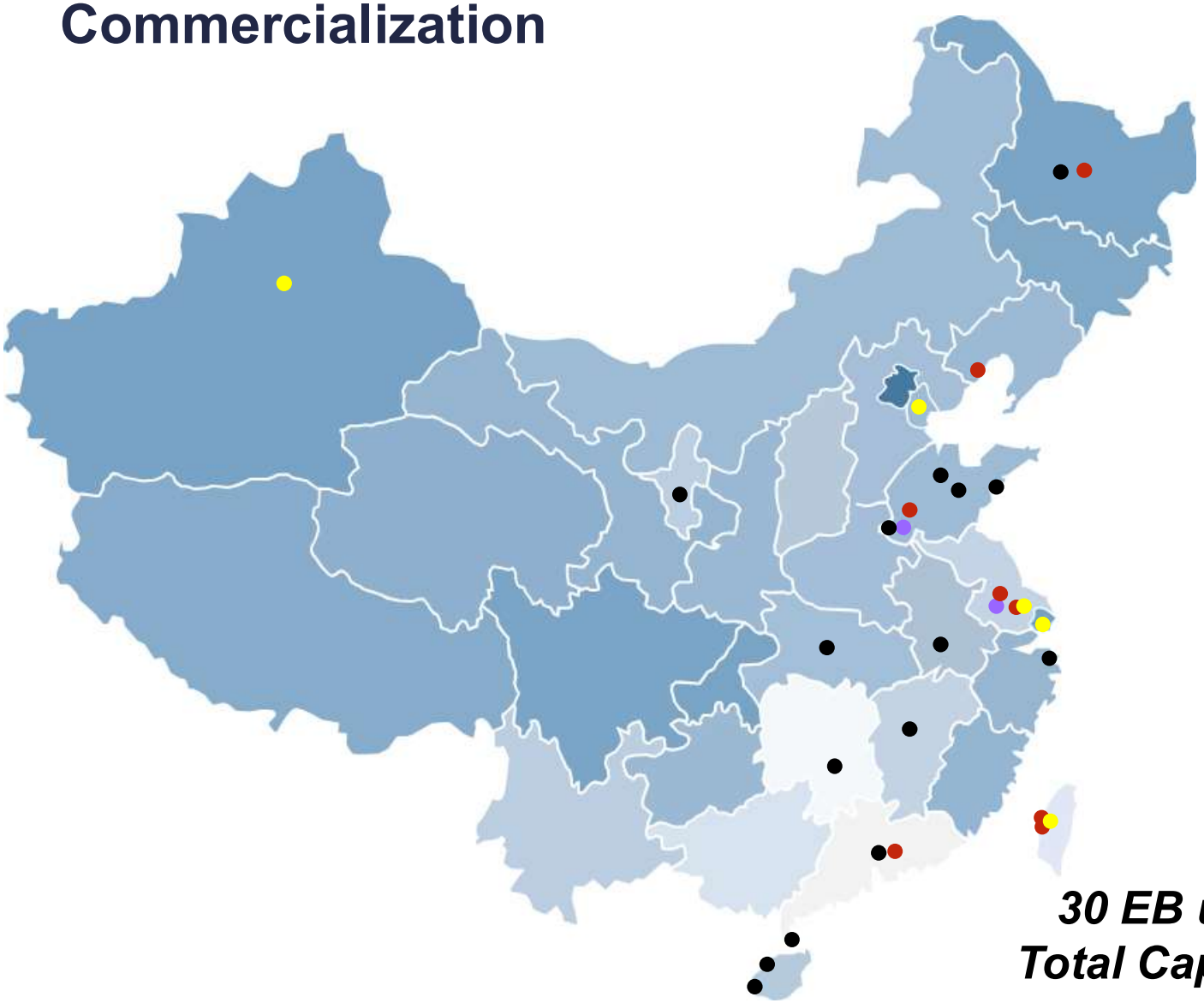
Four Portfolios



Catalysts are adapted for feedstock diversity.

1. Introduction

Commercialization



- AB™
- SEB™
- DF-AS™
- EBC™

30 EB units applied
Total Capacity 520 KTA

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1 Introduction

2 **Vapor-Phase EB Catalyst**
(Pure Ethylene)

3 Vapor-Phase EB Catalyst
(Dilute Ethylene)

4 Liquid-Phase EB Catalyst

2. Vapor-Phase EB Catalyst
(Pure Ethylene)

Vapor-phase alkylation catalysts adapting pure ethylene

- Catalyst brand:
  - AB-97™, AB-12™
- Applicable tech. sources
  - Badger, Sinopec
- Catalyst features:

Items	AB-97™	AB-12™
Inlet temperature (℃)	385~395	**370~380**
B/E ratio(mol/mol)	6.0~7.0	**5.5~6.0**
Ethylene conversion (%)	≥99.6	**≥99.8**
Cycle length (month)	≥12	**≥24**
Service lifetime (month)	≥36	**≥48**

2. Vapor-Phase EB Catalyst
(Pure Ethylene)

Vapor-phase trans-alkylation catalysts

■Catalyst brand:

- AB-97-T™, AB-12-T™

■Applicable tech. sources

- Badger, Sinopec

■Catalyst features:

Items	AB-97-T™	AB-12-T™
Inlet temperature (℃)	420~450	**410~440**
DEB conversion (%)	≥60	**≥65**
EB selectivity (%)	≥99	**≥99**
Cycle length (month)	≥18	**≥24**
Service lifetime (month)	≥36	**≥48**

2. Vapor-Phase EB Catalyst
(Pure Ethylene)

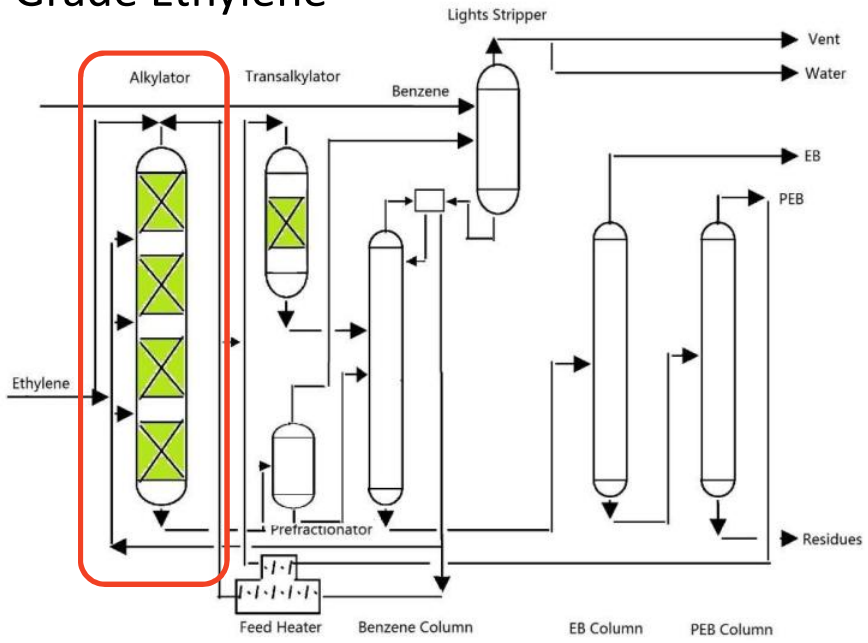
8 EB units applied

No.	Location	Capacity KTA	Tech. Source	Unit Startup Year	Catalyst Appl. Year
1	Liaoning	60	Badger	1996	1999
2	Heilongjiang	60	Badger	1997	2002
3	Guangdong	80	Badger	1997	2002
4	Jiangsu	15	Sinopec	2003	
5	Jiangsu	160	Sinopec	2007	
6	Shandong	215	Sinopec	2015	
7	Taiwan	350	Badger	2002	2015
8	Taiwan	250	Badger	1998	2016
		Total: 1,190			

Application Cases

Case 1

- **Unit Conditions**
  - Tech. Source: Badger (3rd Generation process)
  - Tech. Type: Vapor-Phase/Polymer Grade Ethylene
  - Capacity: 350 KTA EB
  - Reactor diameter: ϕ2200mm
  - Startup time: 2002.02



- **Application of AB-12**
  - Since 2015.10

Problems of Alkylation

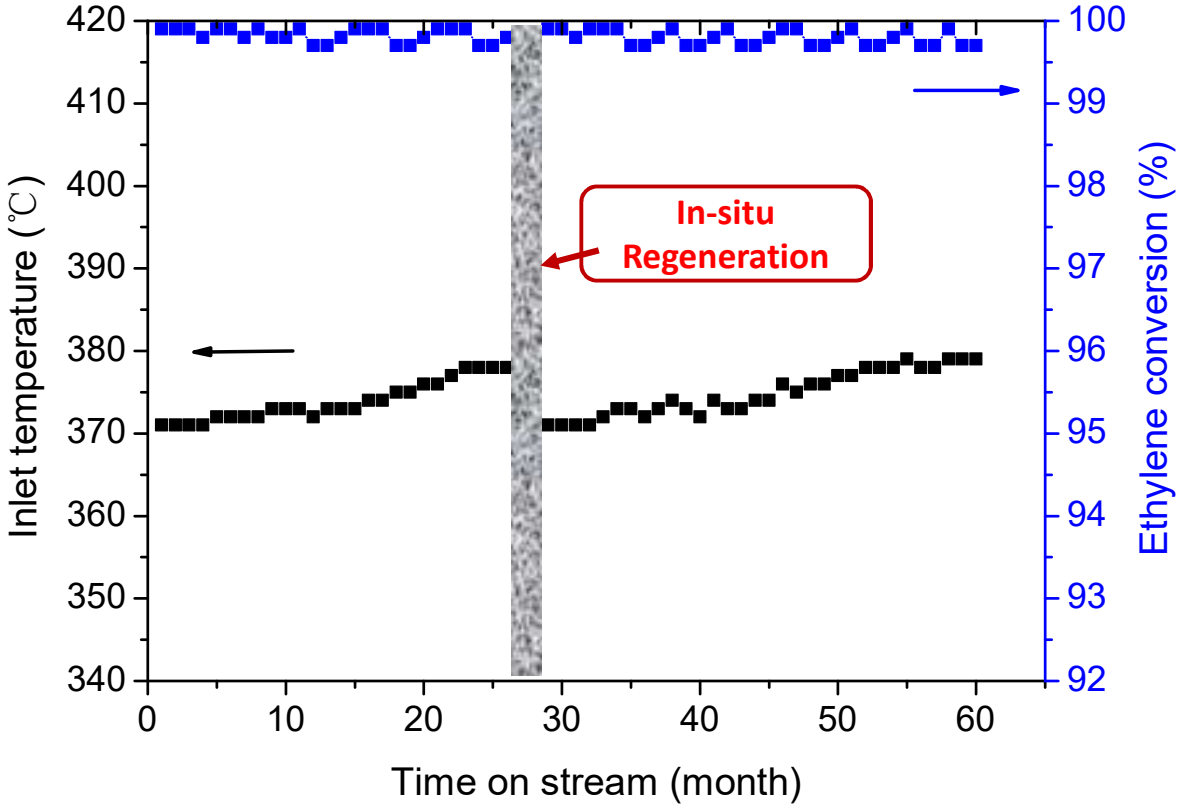
(before the year 2015)

Unit load	Xylene content	EB quality	Consumption of raw materials
Up to 100%	> 1500 ppm	< 99.2%	
↓		↓	
Activity of catalyst		**Selectivity of catalyst**	

A more ACTIVE & SELECTIVE alkylation catalyst was required!

Catalyst Replacement by AB-12™

- **In Oct. 2015, the unit was re-started with AB-12™ loaded in the alkylator.**



- Inlet temperature is stable
- Conversion of ethylene is higher than 99.6%
- The catalytic properties can be maintained after regeneration
- Unit ran steady for 60 months efficiently.

Solution for the Problems

- **Catalyst replacement**
- **Assist with optimizing the operation conditions**
- **Suggestions on improving catalyst regeneration process**

	Unit load	Xylene content	EB quality	Consumption of raw materials
Ref. Cat.	Up to 100%	> 1500 ppm	< 99.2%	
AB-12™	Up to 110%	< 1200 ppm	> 99.6%	Bz ↓ 2.2 kg $C_2^=$ ↓ 2.0 kg

Economic Benefits

Items	Improvement	Estimated Additional Retained Profit* (M USD)
Benzene consumption, kg/tEB	↓ 2.2	0.66
Ethylene consumption, kg/tEB	↓ 2.0	0.70
Xylene/EB, ppm	↓ 300~500	1.00
Product EB purity, %	↑ 0.4	
EB output, %	↑ 10	6.11
Total	-	**8.47**

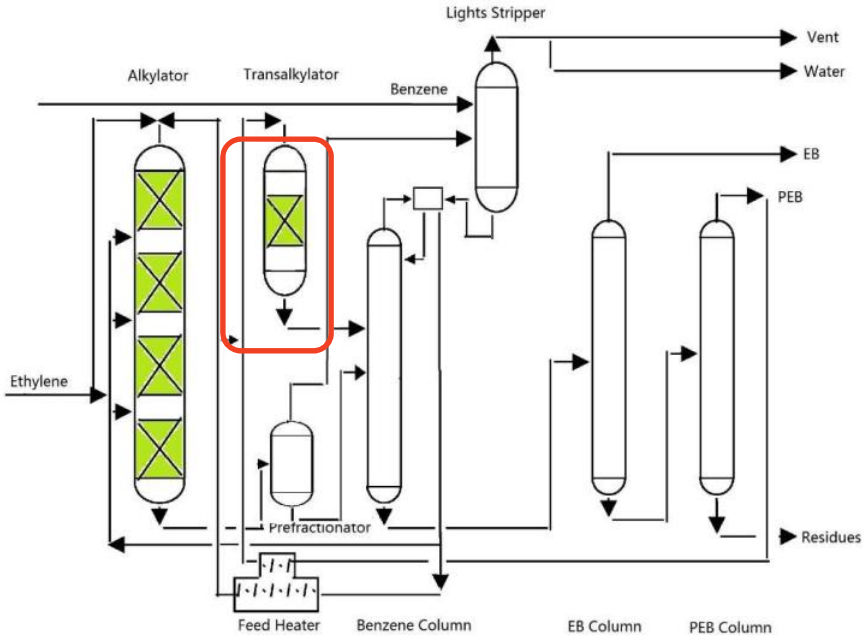
*The benefits from the energy saving by AB-12 and AB-12-T are even excluded here.

*More than **8 Million USD/a** additional retained profits for the 350 KTA EB unit !*

Application Cases

Case 2

- **Unit Conditions**
  - **Transalkylator**
  - Reactor diameter: φ2700mm
  - Startup time：2002.02
  - Catalyst: AB-12-T



- **Troubles encountered before 2017**
  - **Low DEB conversion**
  - **High reaction temp.**
  - **High content of heavy aromatics**

A more Active and Selective trans-alkylation catalyst was needed!

Catalyst Replacement by AB-12-T™

Performance Comparison

(run for 1 month)

Item	Ref.	AB-12-T	Comparison
Inlet Temp., °C	416.1	**415.4**	**↓ 0.7**
DEB conv, %	78.32	**82.82**	**↑ 4.50**
Sel. to EB, %	99.21	**99.58**	**↑ 0.37**

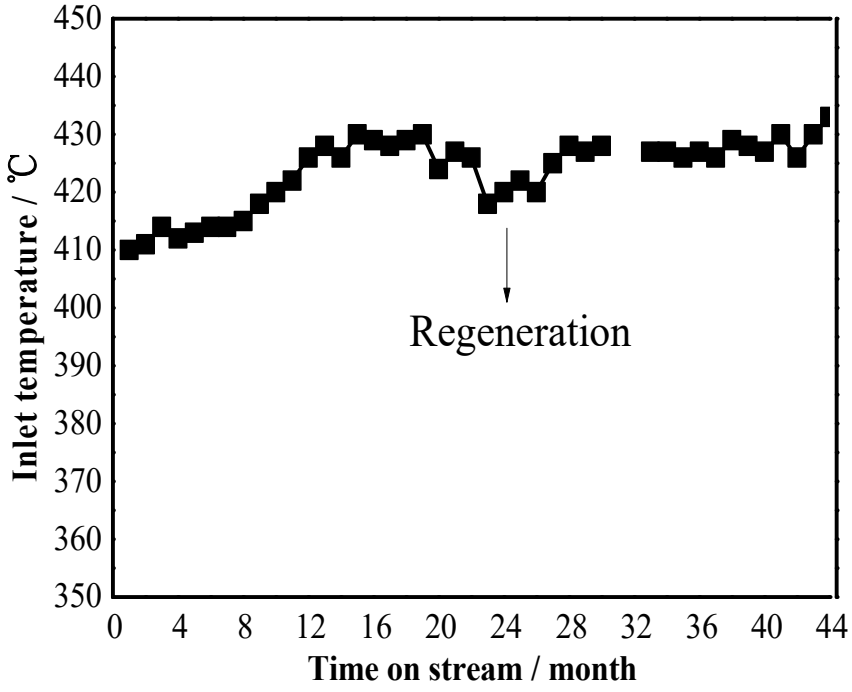
(run for 12 months)

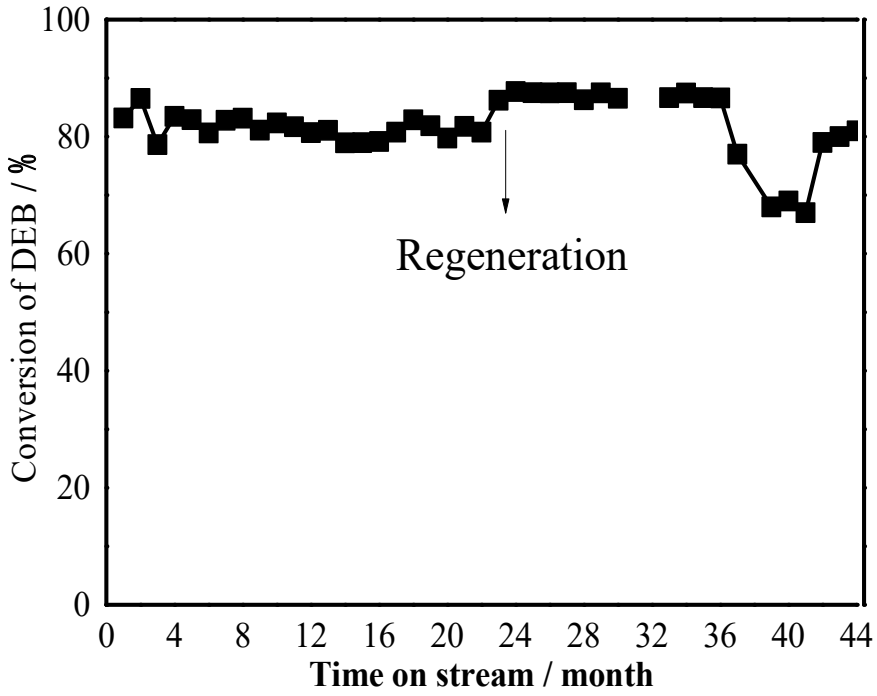
Item	Ref.	AB-12-T	Comparison
Inlet Temp., °C	426.5	**422.1**	**↓ 4.1**
DEB conv, %	75.18	**82.05**	**↑ 6.87**
Sel. to EB, %	99.35	**99.61**	**↑ 0.26**

Heavy aromatics are greatly reduced on AB-12-T™

Catalyst Replacement by AB-12-T™

Running Data (2017.11~2021.7)

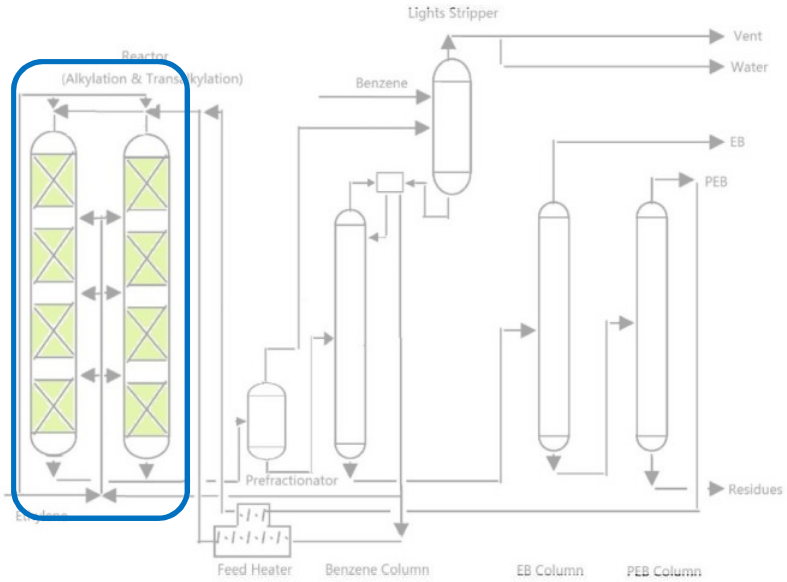




- Inlet temp. rises very slowly.
- DEB conv. is maintained at about 65~85%.
- Cycle length of AB-12-T was running smoothly for 24 months

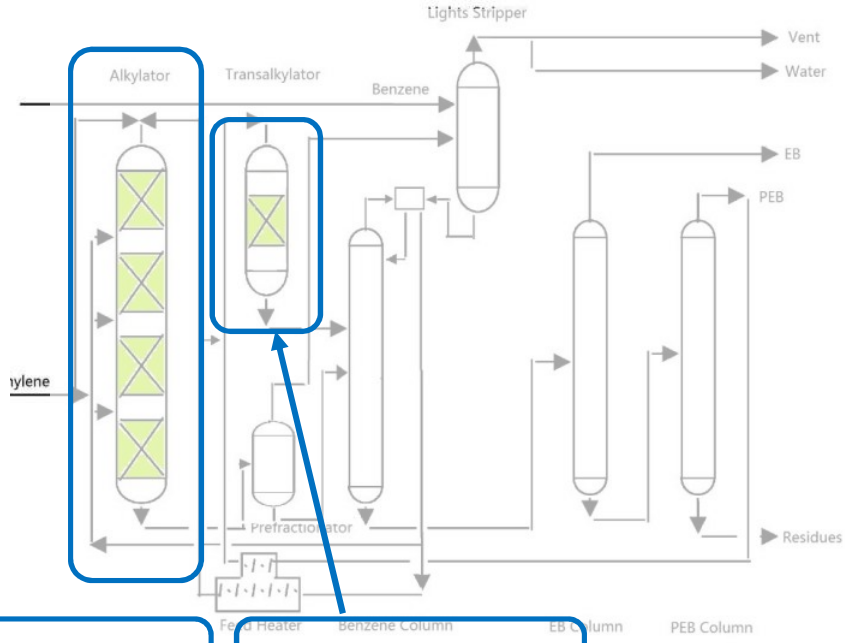
Win the trust of clients

EB Unit No.1: 250 KTA



Jun. 2016

EB Unit No.2: 350 KTA

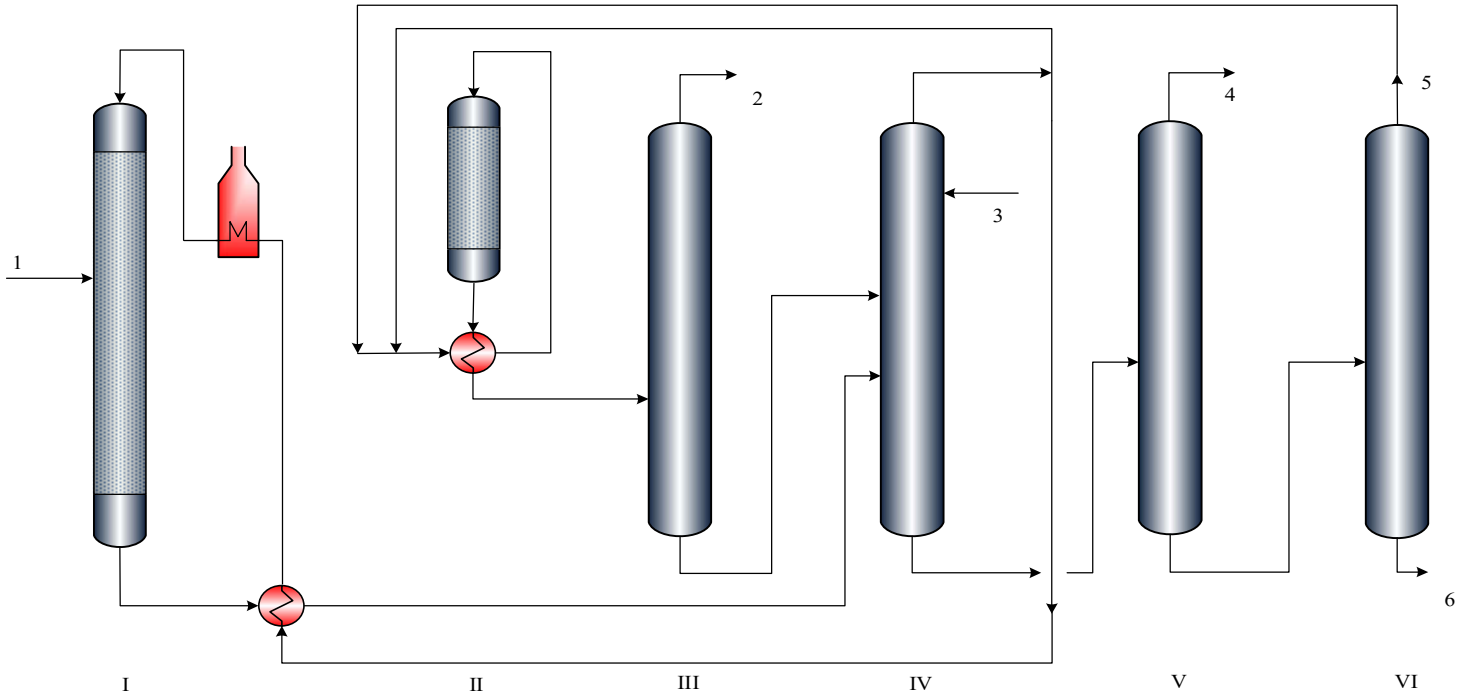


Oct. 2015

Nov. 2017

AB series catalyst completely substituted the old catalyst and brings benefits to them

Sinopec's Vapor-phase EB Process



1.Ethylene; 2.Off-gas, 3.Benzene; 4.EB; 5.Diethylbenzene; 6. High boiling production.
I. Alkylation reactor； II. Transalkylation reactor; III. Stabilizer; IV. Benzene column; V. EB column; VI. Diethylbenzene column.

The simplified process diagram for vapor phase EB process with polymer grade ethylene

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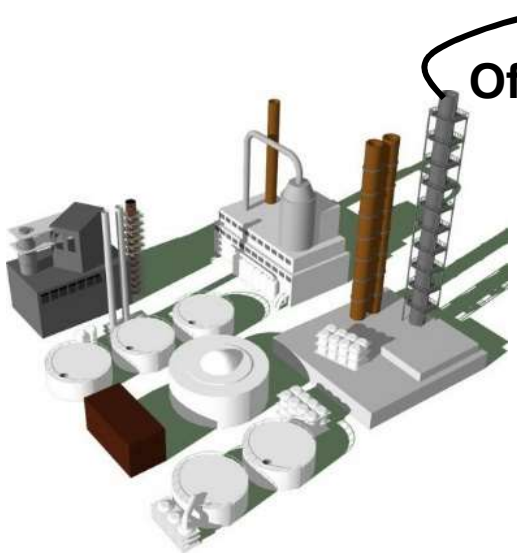
3. Vapor-Phase EB Catalyst
(Dilute Ethylene)

Dilute Ethylene: An abundant resource from refinery units



Refinery Units

Off-gas

FCC/DCC off-gas

Fuel
(Wasted)

Chemicals

EB/SM ➔ SAN/ABS/PS

Ethylene content, FCC: 10~20 wt% / DCC: 20~40 wt%

Sinopec has the whole technology chain from FCC/DCC to down-stream products.

3. Vapor-Phase EB Catalyst
(Dilute Ethylene)

- Catalyst brand:
  - SEB-08™ (B/E = 6.0~7.0, mol/mol)
  - SEB-12™ (B/E = 5.0~5.5, mol/mol)
- Applicable tech. sources
  - Sinopec, Other internal tech.
- Catalyst features:
  - Usage of a refinery off-gas (FCC/DCC)
  - Low materials cost of EB production
  - High ethylene conversion (≥ 99.5%)
  - High selectivity (≥ 99%)
  - Low xylene content (600~800 ppm)
  - Long cycle length and service lifetime (≥1 year, ≥2 years)

3. Vapor-Phase EB Catalyst
(Dilute Ethylene)

15 EB units applied

No.	Location	Capacity KTA	Tech. source	Appl. Yr.
1	Hainan	85	Internal Co.	2009
2	Shandong	90	**Sinopec**	2011
3	Guangdong	85	**Sinopec**	2011
4	Hunan	127	**Sinopec**	2012
5	Anhui	106	Internal Co.	2013
6	Heilongjiang	106	Internal Co.	2013
7	Guangdong	64	**Sinopec**	2013
8	Shandong	20	Internal Co.	2014
9	Hainan	127	**Sinopec**	2015
10	Shandong	40	Internal Co.	2015
11	Zhejiang	300	**Sinopec**	2016
12	Jiangxi	85	**Sinopec**	2017
13	Shandong	80	Internal Co.	2017
14	Shandong	65	Internal Co.	2018
15	Gansu	65	Internal Co.	2018
16	Henan	120	**Sinopec**	2021
17	Guangdong	400	**Sinopec**	2021
18	Anhui	400	**Sinopec**	2022
		Total: 2,365		

Application Case

- **Plant Location:**
  - **China**
- **Unit Conditions**
  - Tech. source: DCPI
  - Designed capacity: 84.8 KTA
  - Startup time: 2006.12
- **Catalyst**
  - 2006 – Reference Catalyst
  - **2009 – SEB-08™ (SRIPT)**
  - **2014 – SEB-12™ (SRIPT)**

Problems

(before the year 2009)

A part of ethylene was wasted

Xylene content was high

EB quality was not good enough

Raw Material Consumption was high

Energy Consumption was high

Catalyst was frequently regenerated

Activity

Selectivity

Stability

The problem of reference catalyst

Catalyst Replacement by SEB-series

Item	Ref. Cat.	SEB-08	SEB-12
Average $C_2^=$ conversion, %	81.2	**97.2**	**99.4**
Annual EB yield, actual/design, %	83.5	**95.5**	**107.7**
B/E, mol/mol	6.5	**6.5**	**5.2**
Xylene/EB, ppm	1500	**850**	**550**
Cycle length, month	6	**12**	**17**

All the aforementioned problems are solved by:

- **Catalyst replacement**
- **Assistance to improve the pre-treatment process of feedstock**
- **Assistance to optimize the reaction conditions (temp., B/E ratio, etc)**

Economic Benefits

Items	Improvement*
Ethylene conversion (EB yield)	↑ 14.6%
Cycle length	↑ 100~200%
Xylene/EB	↓ 400 ppm
Benzene consumption	↓ 6%
Energy consumption	↓ 27%

*The benefits are calculated between SEB-12 and the Reference Catalyst.

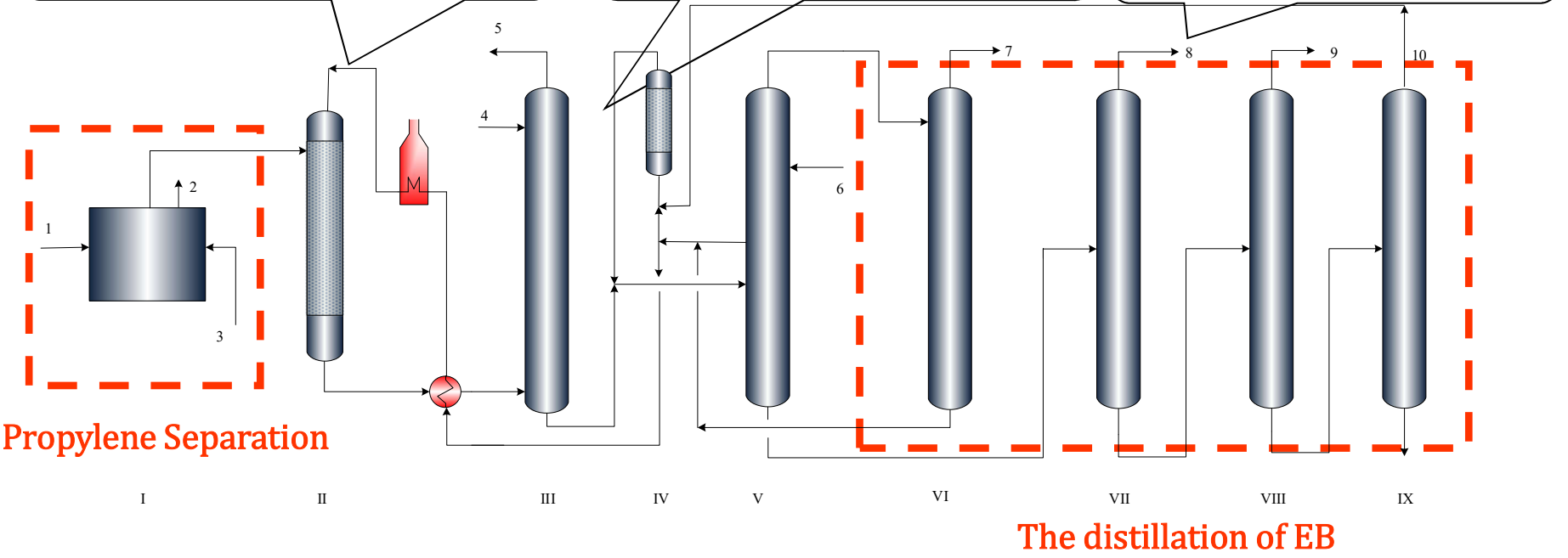
*More than **5.95 Million USD/a** additional retained profits for the 84.8 KTA EB unit!*

Sinopec's SGEB EB Process with Dilute Ethylene

Conversion of ethylene ≥96%
Cycle of regeneration >1 year

Low transalkylation temperature
（170-240℃）

Purity of EB≥99.8%
Content of xylene ≤800ppm



I. The preprocessing for dry gas； II. Alkylation reactor； III. Off-gas absorber；IV. Transalkylation reactor； V. Benzene column；VI. Removal column of non aromatic；VII. EB column； VIII. Phenypropane column； IX. Diethylbenzene column.

The simplified process diagram for vapor phase EB process with dilute ethylene

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1 Introduction

2 Vapor-Phase EB Catalyst
(Pure Ethylene)

3 Vapor-Phase EB Catalyst
(Dilute Ethylene)

4 **Liquid-Phase EB Catalyst**

4. Liquid-Phase EB Catalyst

- Alkylation Catalyst: **EBC-1™ & EBC-3™**
  - Lower reaction temperature, lower B/E ratio
  - High ethylene conversion
  - More selective to (mono-)EB
  - Traces of xylene, less residues
  - High EB product purity
- Trans-alkylation Catalyst: **EBC-2™**
  - High DEB & TEB conversion
  - High selectivity to EB
  - High space velocity
  - Low PEB/benzene ratio
  - Flexible reaction temperature

EBC-1/3
Quadlobe ϕ1.1 m
>70 N/cm

4. Liquid-Phase EB Catalyst

4 EB units applied

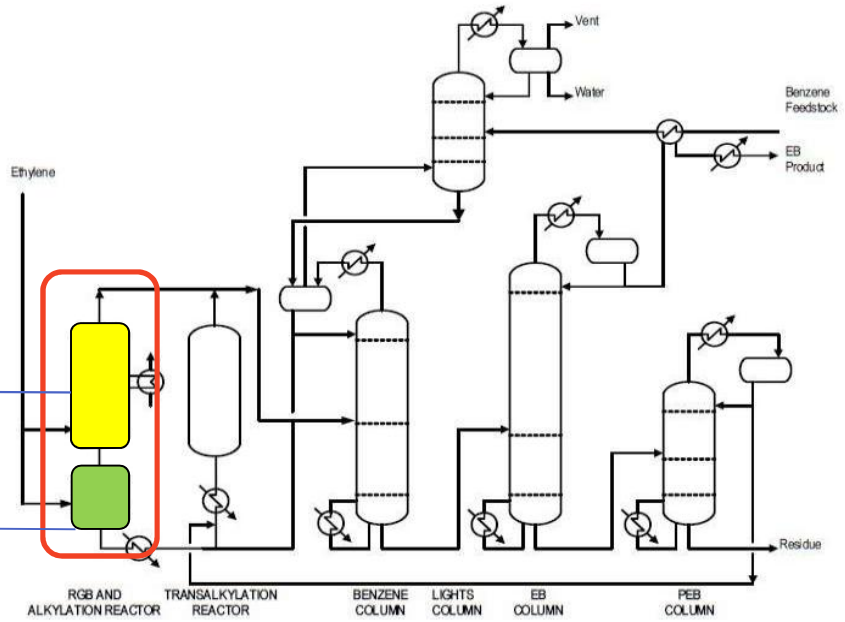
No.	Location	Capacity, KTA	Appl. Year	Catalyst
1	Client 1	320	2013	EBC-1™
2	Client 2	840	2017	EBC-1™
3	Client 3	530	2018	EBC-1™
4	Client 4	690	2020	EBC-3™

Application Cases

Application Case (840KTA)

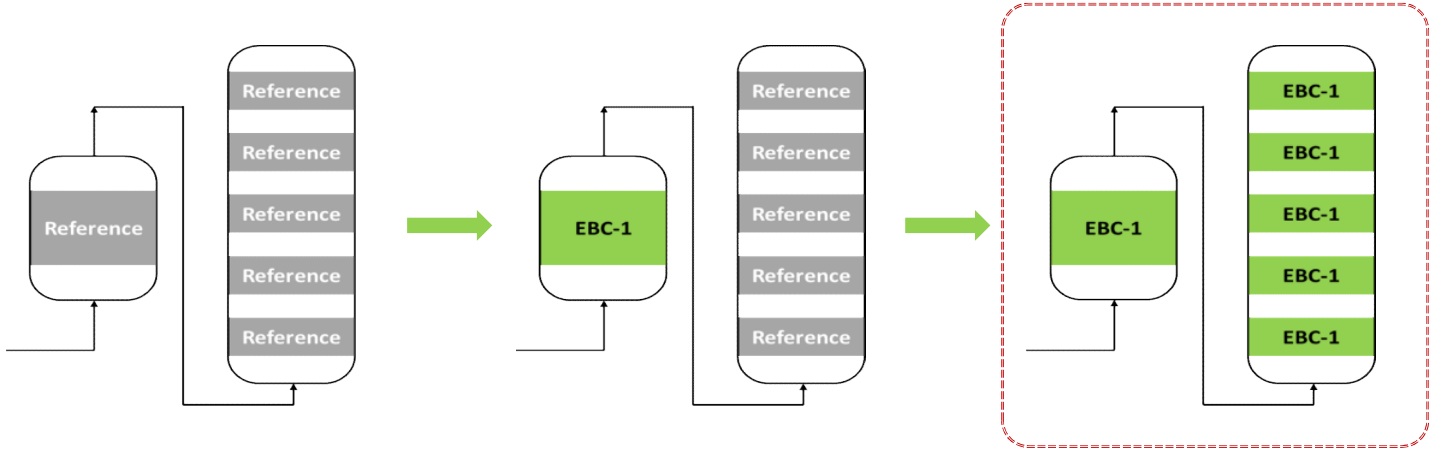
2019.6
EBC-1™ in Main Alkylator

2017.6
EBC-1™ in RGB



Application Cases

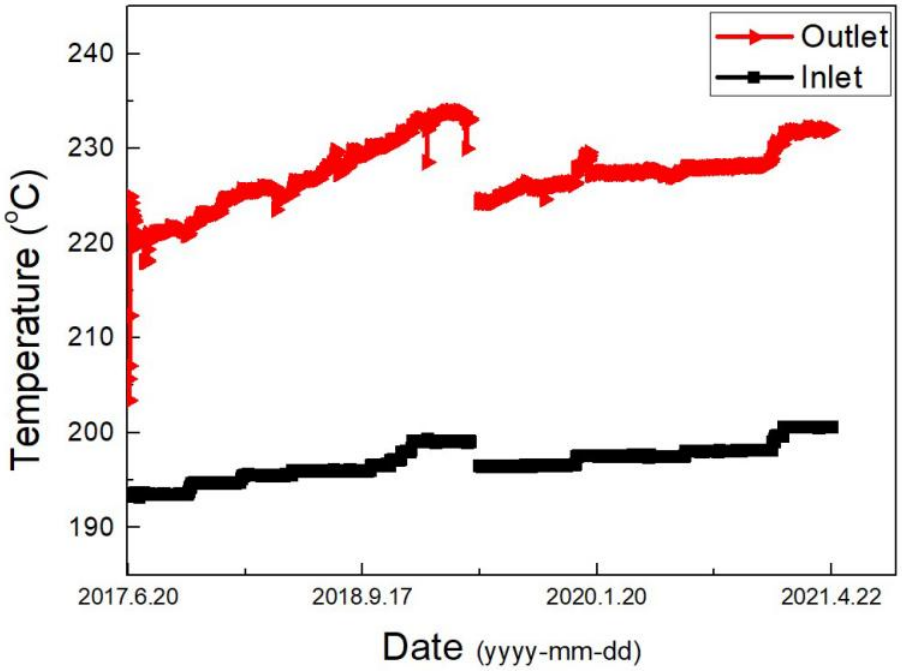
Application Case (840KTA)



Since Jul. 2017 **Since Jul. 2019**

Activity and Stability of EBC-1

Application Case (840KTA)

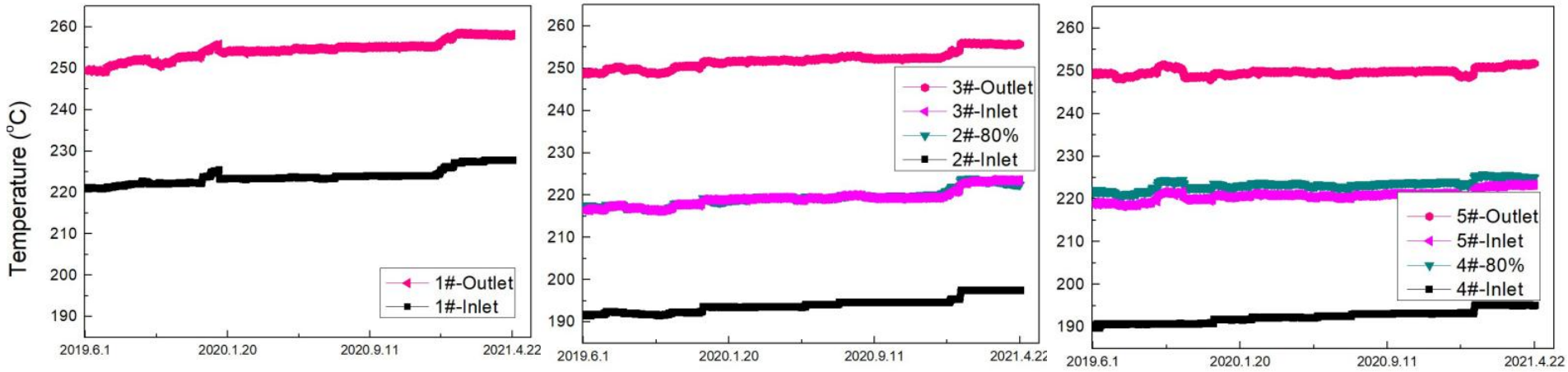


- 48 months since startup, RGB temperature rise is steady.
- Inlet temp. is stable at 193~198 °C.
- Hot spot is stabilized at around 60%.
- Stable ethylene conversion (100%)

Activity and Stability of EBC-1

Application Case (840KTA)

Bed 1# Bed 2#&3# Bed 4#&5#



- 24 months since startup,
- Inlet temp. is stable at 190~195 °C.
- RGB temperature rise is steady.
- Hot spot is stabilized at around 50~80%.

The EBC-1 catalyst ensures the stable operation for EB units

Application Cases

Main Alkylator + RGB

Conponents / %	Ref. (B/E = 3.2)	EBC-1 (B/E = 2.9)
N-A	1.053	0.305
Bz	62.203	60.236
TL	0	0
EB	31.964	35.134
X	0	0
PB	0	0
BB	0.005	0.003
DEB	4.381	4.053
TEM	0.322	0.228
Residues	0.072	0.041

EBC-1: Higher selectivity to EB; less by-products

Application Cases

Main Alkylator + RGB

Catalyst		Ref.	EBC-1
Inlet Temp. (℃)	RGB	196.3	196.5
	Bed2#	195.4	**192.2**
	Bed4#	190.8	**190.8**
Unit Load (%)		94	98
Total Ethylene WHSV (hr^{-1})		0.97	1.13
B/E molar ratio		3.2	**2.9**
Residue Content (kg/ton·EB)		2.76	**2.30**
Product EB purity (%)		>99.9	>99.9

EBC-1 is more active and selective



Thanks for your attention!

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