

Technologies to Enhance Ethylene Production

SINOPEC Corp.

Yulong Li November 2021







Outline

Who we are

II SERT™ for Steam Cracking Furnace

III Related Catalysts & Technologies

IV Cold Oil Absorption Technology (COAT™)



Who we are

SINOPEC R&D Capability

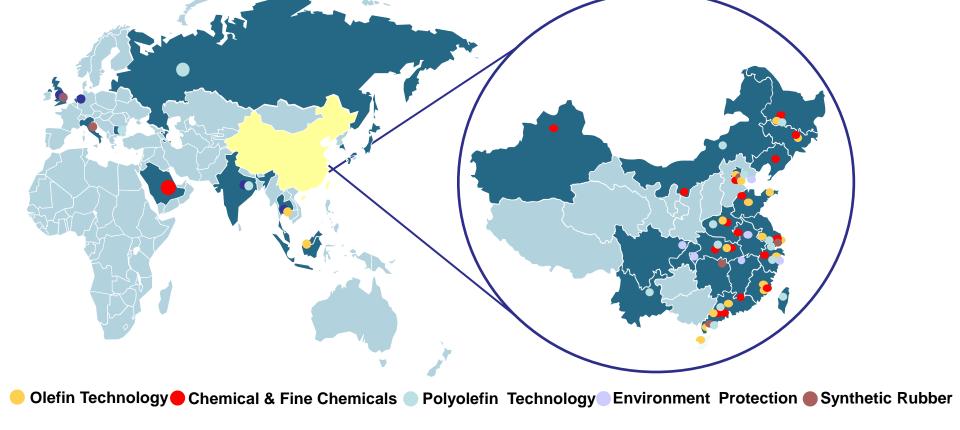
- ✓ SINOPEC has a complete system for scientific R&D, engineering and intellectual property management.
- √ 8 Research Institutes
- √ 5 Engineering companies (Sinopec Engineering Group)





Who we are

BRICI: Beijing Research Institute of Chemical Industry We provide technology & products package solutions!

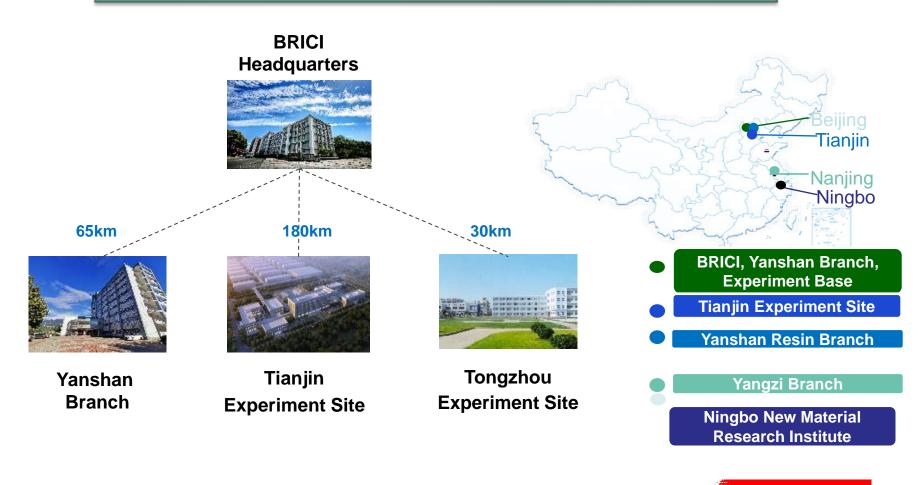




Who we are

We have multiple operation sites in China

Multiple-site operation for coordinated development





Outline

I Who we are

SERT™ for Steam Cracking Furnace

Related Catalysts & Technologies

IV Cold Oil Absorption Technology (COAT™)





SINOPEC Cracking Furnace



Concept of SERT™



Commercial Performance of SERT™



Summary

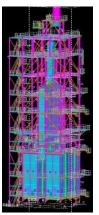


Sinopec Cracking Furnace

- Sinopec has plenty of experiences in cracking furnace design and development (CBL technology). The furnace capacity is up to 200 kta.
- The raw materials are from light feedstock, such as ethane and light hydrocarbons, to heavy feedstock as diesel and HVGO.
- Till now,113 furnaces have been built by using CBL technology. The total capacity is 11.3 Mt. The total number of Gas Furnace designed using CBL Technology is 23.
 Total capacity is 2.7 Mt.

Our new generation cracking technology CBL to realize value cracking and increase-feedstock-flexibility









Sinopec Technology Features of CBL Furnace

- Feed flexibility: From ethane to HVGO
 - DS injection: Single stage (light feed) / two-stage (heavy feed)
- Enhanced heat transfer technology:
 - Swirling Element Radiant Tube (SERT™)
 - High thermal efficiency: up to 94~96%
 - Longer operating days: increased more than 30%
- Radiant coil: High selectivity coil
- Coil hanging: Constant spring hanger
- Cracked gas quench: Linear quench cooler
- Firing
 - Combined hearth and side wall firing, hearth burner duty about 60~80%
 - 100% hearth firing
- I.D Fan: Inverter drive for fan speed control
- Low investment



Enhanced heat transfer technology



Challenges

- ✓ Harsh Reaction Conditions
- a) High temperature(**780~900°C**)
- b) Short residence time
- c) Lower hydrocarbon partial pressure
- ✓ Poor heat transfer
- a) Due to the flow boundary layer and coke
- b) Resulting in over temp. and shortened operating days



Targets

- ✓ Quick heat transfer through tube wall into the fluid body?
- ✓ Reduce coking?
- ✓ Extend Operating days?

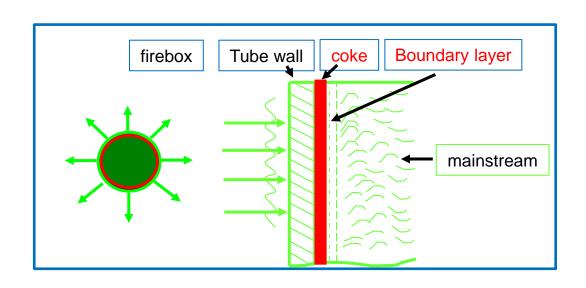
Swirling Element Radiant Tube technology (SERT™) for extending the furnace operating days



Heat transfer theory

•
$$q = -kA\frac{dT}{dy}$$

- ✓ To increase the heat transfer area, A
- ✓ To increase the temperature gradient, dT/dy
- ✓ To increase the heat transfer coefficient, k



- The coke layer and the boundary layer is the biggest resistance in pyrolysis Tube
- Thinning the boundary layer and reducing the coking rate is a difficult problem in pyrolysis technology.

•
$$\frac{1}{k} = r_{coil} + r_{boundary} + r_{coke}$$



 $r_{boundary} \downarrow, r_{coke} \downarrow \Rightarrow k \uparrow$



To change the flow pattern of the fluid body

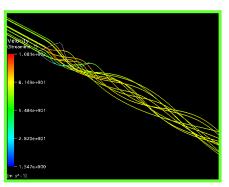
Thinner boundary layer

Reduced coking rate

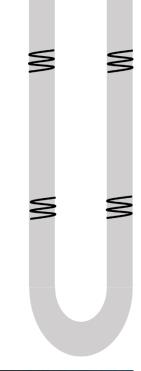
Reduce Tube Metal Temperature (TMT)

Extend run length









Swirling Element Radiant Tube technology (SERT™)

Hydrocarbon feedstock is impelled from plug flow to swirlling flow through it. Flow velocity along the tube perimeter is increasing and laminar boundary layer is getting thinner because of the scouring of hydrocarbon feedstock, and coke formation is reduced.





Development History of SERT™

Bench Scale Experiment

1995

Experiment

2004

Industrial Scale Commercial Promotion (2nd gen SERT™)

2015

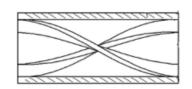
1999

Pilot Scale Experiment 2007

Commercial Promotion (1ST gen SERT™)



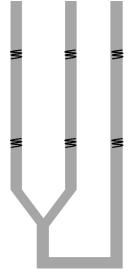




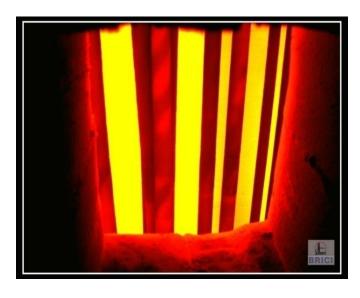


Case 1 Liaohua Petrochemical (Ba-115)

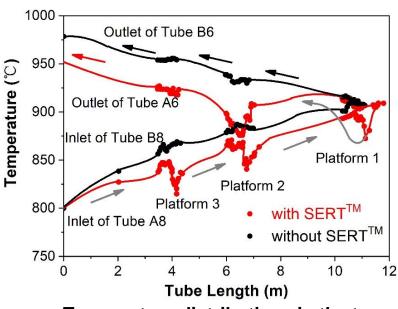
- CBL-I Cracking furnace with 1st gen SERT™
- Coil configuration: 2-1
- Capacity: 2 kta
- liquid feedstock: Naphtha



2-1 coil configuration



The SERT™ in the online furnace



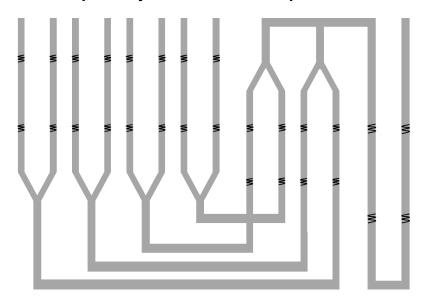
Temperature distributions in the two neighboring tubes

The coil surface temperature drop 20 °C

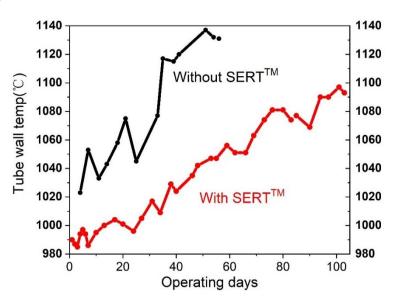


Case 2 Yanshan Petrochemcial (Ba-115)

- SRT-IV furnace with 1st gen SERT™ in whole furnace
- Coil configuration: 8-4-1-1
- Feedstock: Naphtha and Ethane
- Capacity: 100 kta, liquid feed or gas feed



8-4-1-1 Coil configuration

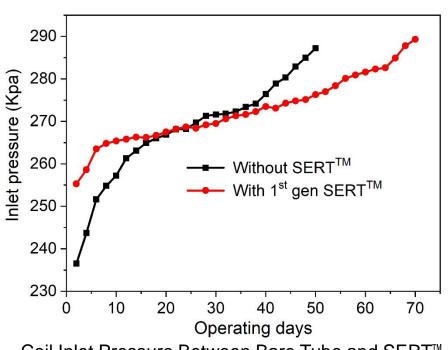


Tube Wall Temperature (TMT) Comparison

The operating days is extended twice



Case 2 Yanshan Petrochemcial (Ba-115)



Product Yield With or Without SERT™			
Product	SOR with SERT™	EOR with SERT™	Bare Tube
COT (°C)	822	822	822
Ethylene (wt%)	28.92	28.78	28.81
Propylene (wt%)	15.89	15.50	15.86
Butadiene (wt%)	4.77	4.83	4.71

Coil Inlet Pressure Between Bare Tube and SERT™

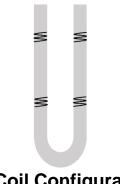
Pressure rise smoothly

Nearly no negative impact on product yield

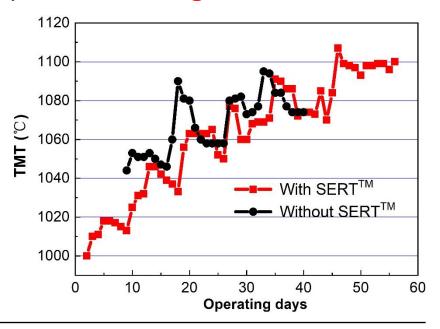


Case 3 BASF-YPC, Nanjing, China (Ba-116)

- SW-U furnace: whole furnace replaced with 1st gen SERT™
- Coil configuration: 1-1
- Capacity:60 kta, Liquid feed
- Feedstock: Naphtha



1-1 Coil Configuration



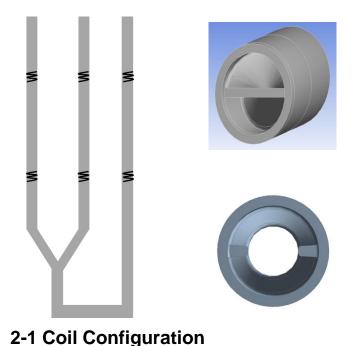
Operating cycle in a Bare Tube contrast to SERT™

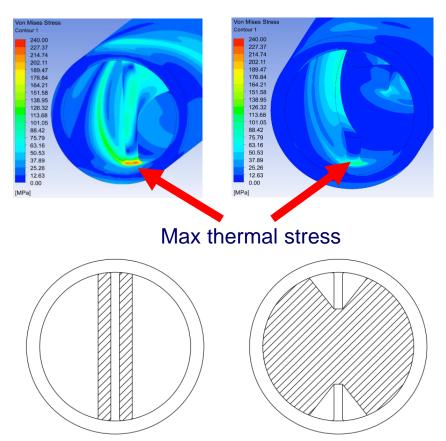
	SERT	Feed (kg/h)	COT(°C)	P/E	Operating days
BA116	NO	28679.5	825	0.574	40 (2008.07.14~08.22)
BA116	YES	29923.5	830	0.568	56 (2008.09.30~11.24)
Remark		105%			140%



Case 4 Yanshan Petrochemcial (Ba-112)

- CBL-III furnace with 2nd gen SERT™ in whole furnace
- Coil configuration: 2-1
- Feedstock: Naphtha
- Capacity:100 kta, liquid feed





The permeability of the SERT



Case 5 SSTPC 1,000 KTA Ethylene complex (SINOPEC-SABIC) (1st gen SERT™)



1. Feed: HVGO, NAP, C2/C3, LPG

2. Thermal Efficiency: 93.8-95.5%

3. Operating days

• **HVGO**: 96 days

• **NAP**: 120 days

• **C2/C3**: 122 days

4. Liquid furnace: CBL-III

5. Gas furnace: CBL-R

6. Capacity:

100 kta each

Total 11 cracking furnaces

7. Operated on Jan. 16, 2010



Case 6 ZHONGKE,800 KTA Ethylene complex (Sinopec-Sabic)

(2nd gen SERT™)

1. Feed: HVGO, NAP, C2/C3, LPG

2. Capacity: 80 KTA each, Total 7

furnaces, double firebox

30 kta ethane feed

15 kta gas feed

15 kta liquid feed

3. Operating days

HVGO: 78 days

NAP: 85 days

C3/C4: 93 days

• C2: 118 days

4. Thermal efficiency: 93.8-95.5%

5. Liquid furnace : CBL- VII

6. Gas furnace: CBL-R

7. Operated on Sep.20, 2020





SERT[™] in different Type Furnaces

Company	Furnace Type	Capacity (10KTA)	Opera. Days (NO USED)	Opera. Days (USED)	Remarks
Α	LUMMUS/SRT-IV(HC)	6	55	105	Coil replaced
В	LUMMUS/SRT-VI	10	40	79	Coil replaced
С	SINOPEC/CBL	8	-	75	New, 1070 °C
D	SINOPEC/CBL-III	6	60	99	Coil replaced
E	LUMMUS/SRT-IV(HS)	4	55	110	Coil replaced
F	S&W/SUC-80U	6	40	60	Coil replaced
G	SINOPEC/CBL	10	-	>100	New
Н	SINOPEC/CBL	10/15	-	>100	New
Q	SINOPEC/CBL	15/30	-	>80	New
J	SINOPEC/CBL	15/30	-	>80	New
K	S&W/SUC-40U	3.5	30	>80	Revamp
L	TECHNIP/GK-VI	5	50	100	Revamp



Economics

Case Description:

- 100,000 ton/yr SL-1 Furnace in Yanshan, Petro-Chemcial Company,
- Feedstock: Naphtha
- Same Operating Condition
- TMT is decreased by 20°C and operating days is extended twice than normal (60days -> 120days)
- Both fuel gas usage and steam production rate were decreased 1%-3%

Results:

Description	Benefit	Unit	Saving (1000\$)
Furnace Decoking Times	↓3	Times/Yr	+180
Furnace Operation Days	16	Days	+300
Fuel Gas Usage	\downarrow 6.4× 10 ⁴	Ton Nature Gas	+428
Steam Made	\downarrow		-340

Total Saving: \$268,000(Min)-\$568,000(Max)/Furnace per year)

^{*}Yield improvement was not considered in this evaluation



SERT™ Installed Commercial Furnace

- By the end of 2020, the 1st gen SERT[™] has been applied to 122 cracking furnaces, with a production capacity of 8.615 million tons of ethylene per year.
- The technology of 2nd gen SERT[™] has been applied 74 cracking furnace in total with a production capacity of 7.26 million tons of ethylene per year.
- At present, the longest operating time of the cracking furnace in which this technology is applied is 11 years.



To sum up:

- Lower cost! (comparing with other heat transfer technologies)
- Can be installed on current tubes or built the new cracking furnace
- Tubes with SERT™ can handle flexible feeds (naphtha, propane, etc.)

Feature	Without SERT™	With SERT™
Product yields	BASE	No negative effects
TMT	BASE	Reduce at least 20°C
Operating days	BASE	Increase at least 30%
Capacity	BASE	Increase about 7%
Pressure drop	BASE	Increase about 8%
Operation	BASE	No additional workloads

^{*} Under the same operation conditions, with insertion of the tube with twisted-tape



Outline

Who we are

II SERT™ for Steam Cracking Furnace

Related Catalysts & Technologies

Cold Oil Absorption Technology (COAT™)





Introduction to C1/C2/C3 Catalysts



C1 Low Temperature Methanation Catalyst



C2 Selective Hydrogenation Catalyst



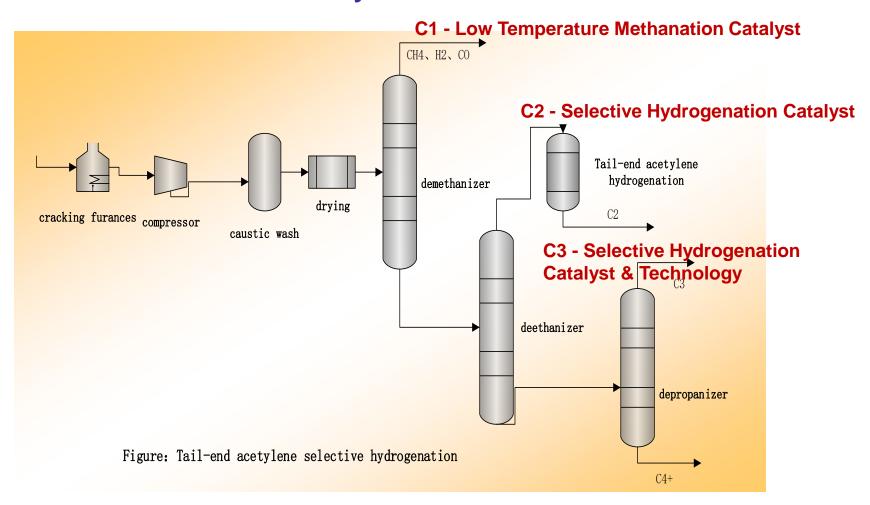
C3 Selective Hydrogenation Catalyst



Commercial Performance of C1/C2/C3 Catalysts



Introduction to C1/C2/C3 Catalysts



Sequential Separation process in ethylene Plant



Introduction to C1/C2/C3 Catalysts









C1 - Low Temperature Methanation Catalyst

- High activity in low temperature 150 ~ 200°C
- Adapting to various reactor and process
- Excellent operation flexibility & low cost

C2 - Selective Hydrogenation Technology

 Front-end Selective Hydrogenation Technology for Removal of Acetylene in Depropanizer Process

C2 - Selective Hydrogenation Technology

 Tail-end Selective Hydrogenation Technology for Removal of Acetylene in C2 Fraction

C3 - Selective Hydrogenation Technology

 Liquid-phase Selective Hydrogenation Process and Catalyst for the Removal of Methyl Acetylene and Propadiene in C3 Fractions



Introduction to C1/C2/C3 Catalysts

Research resource and equipments

- ✓ Professional research team and advanced equipments.
- ✓ Small scale, pilot scale and industrial sideline experiments can be performed in lab to test the catalyst performance.
- Catalyst industrial production company.





























C1 Low Temperature Methanation Catalyst: BC-H-10

Physical Properties		
Composition	Ni/Al2O3	
Appearance	Black granular	
Life	≥5 Years	

SOR	CUSTOMER	CAPACI TY/KTA
2008	Zhongyuan Petrochem.	200
2011	Guangzhou Petrochem.	200
2012	Tianjin Petrochem.	200
2012	Yangzi Petrochem.	300
2013	Sinopec-SK(Wuhan) Petrochem.	800
2013	Fujian Petrochem.	1100
2017	Shanghai Petrochem.	400
2020	Zhongke	80
2021	Fujian Gulei Petrochem.	800



Industrial Application

- Initial used in Zhongyuan plant since May 2008.
- Use the original Highpressure steam.



2

- Used in **Guangzhou** since April 2011.
- Change HS to MS for energy saving.

HS

3.53MPa, 385°C



MS

1.08MPa, 270°C

3

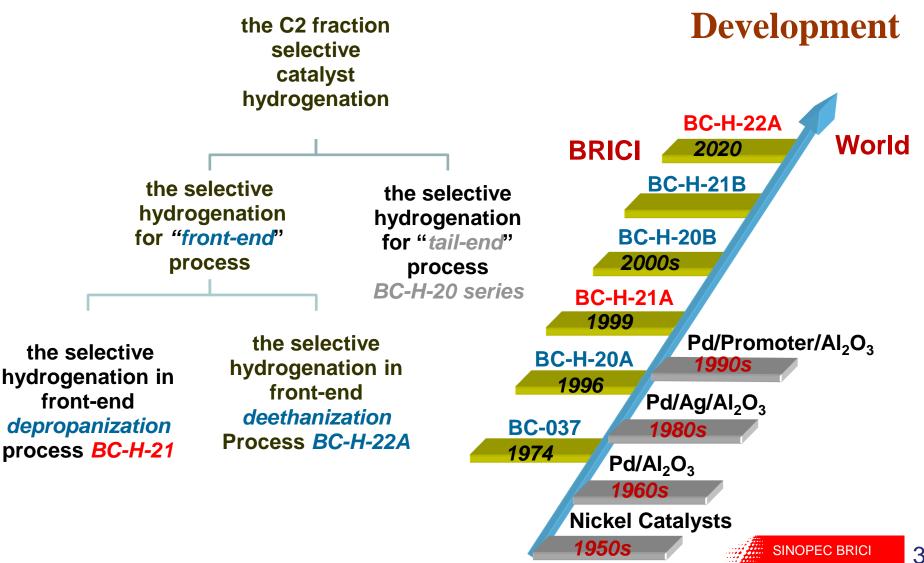
- 2012/9, used in Tianjin ethylene with the original HS.
- 2012/9, use in Yangzi petrochemical with the original SHS.

4

Many ethylene plants are planning to use.



C2 Catalysts





C2 Catalysts: BC-H-20B

Tail-end Acetylene Hydrogenation Catalyst

Physical Properties		
Appearance	yellowish gray granule	
Composition	Pd/Promoter /Al ₂ O ₃	
Regeneration Cycle	≥6 Months	
Lifetime	≥ 5 Years	



A Wider Range of Operating Conditions

Temperature: 40~95 °C (Inlet)

65~135 °C(Outlet)

Pressure: 0.9~3.0 MPa

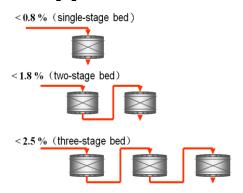
GHSV: (Adiabatic Reactor) 2300~6500 NM3/M3/h

(Isothermal Reactor) 8000~13000 NM3/M3/h

Advantages of BC-H-20B

- Allowing a wide range of operating conditions
- 2. High space velocity
- 3. Low pressure drop
- 4. High selectivity and excellent activity
- Less green oil produced and adhesion to the catalyst
- 6. Longer cycle of operation
- 7. Longer life

Inlet C₂H₂ concentration:





BC-H-20B Commercial Application

In China, BC-H-20B catalyst has been successfully used in 15 ethylene plants and 9 MTO plants until 2020.



Commercial Application Overseas (BC-H-20B)



C2 Catalysts: BC-H-21B

Front-end depropanization Acetylene Hydrogenation Catalyst

Physical Properties		
Appearance	yellowish gray granule	
Composition	Pd-Promoter /Al ₂ O ₃	
Lifetime	≥5 Years	

Operating Conditions of BC-H-21B

Inlet C2H2 Concentration: < 1.0 %(mol)

Outlet C2H2 Concentration: <0.5ppm

MAPD Conversion: > 50 %

Temperature: 55 ~ 120 °C

Pressure: 1.0~3.5MPa

GHSV: 8000~15000 hr⁻¹

Response to CO Range: 200 ~ 2000 ppm

Advantages of BC-H-21B

Higher stability during CO fluctuations to avoid runaways

High Selectivity

Less green oil production

Lower pressure drop, higher SV.

Wider operating conditions

Good stability

Appropriate activity, easy to startup

The key properties are better than other catalysts

- selectivity, catalyst life,
- CO fluctuation resistance,
- Lower pressure drop,
- higher space velocity



BC-H-21B Commercial Application

- ✓ Currently, our catalyst has been applied in 11 Ethylene plants in China.
- ✓ The most capacity of the ethylene project is 1,100 kta.











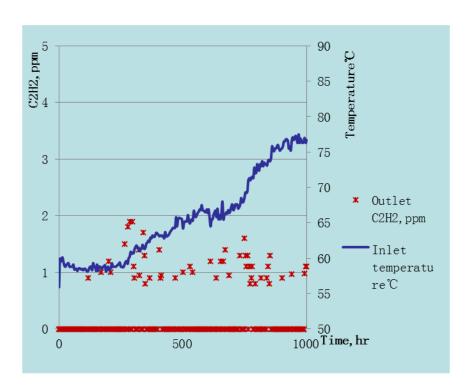




C2 Catalysts: BC-H-22A

Front-end deethanization Acetylene Hydrogenation Catalyst

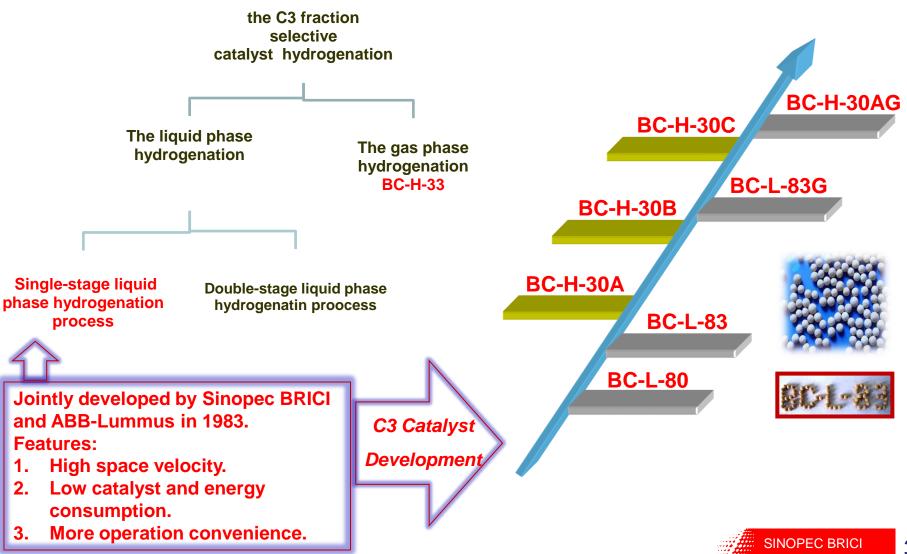
Physical Properties		
Appearance	yellowish gray granule	
Composition	Pd-Ag/Promoter /Al ₂ O ₃	
Lifetime	≥5 Years	



Sideline Test



C3 Catalysts





C3 Catalysts

Physical Properties			
Brand	BC-L-83 BC-H-30A BC-H-30B		
Appearance	yellowish granule		gray granule
Composition s	Pd/Al ₂ O	Pd-Promoter /Al ₂ O ₃	Pd/Al ₂ O ₃
Regen. Cycle	>6 months		
Life	5 years		

Operating Conditions		
Inlet MAPD: Inlet Temperature: Outlet Temperature: Pressure: LHSV: H2/MAPD:	1.4 ~ 2.8%(mol) 30 ~ 45 °C 50 ~ 65 °C 2.1 ~ 2.7 MPa 20 ~ 70 hr ⁻¹ 1.2 ~ 2.0	

	Advantages			
Brand	BC-L-83	BC-H-30A	BC-H-30B	
Feature	 High space velocity Low catalyst used High activity, selectivity, stability, less polymers formed Longer regeneration cycle and catalyst life More convenient operation used in single-stage, or double-stage. Energy saving, Remove propylene cooler propylene cooler 	 Higher selectivity Higher inlet MAPD	 50% reduced of Pd Higher Pd dispersion, higher activity Higher selectivity and propylene production Reduction is not needed before startup 	



C3 Catalysts Commercial Application







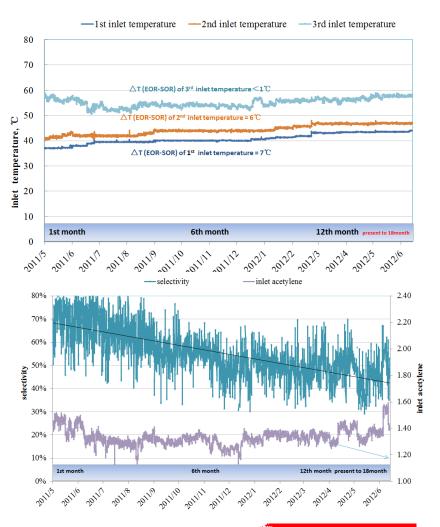
Commercial Case 1

ZHENHAI 1,000 kta Ethylene

C2 catalyst: BC-H-20B

Reactor: DC-401A/B	
GHSV	≈6000h ⁻¹
Flowrate	160~180ton/h
DC-401A regen (1st cycle)	12 months
DC-401B regen (1st cycle)	24 months
DC-401B (12th month)	

DC-401A regen (13 cycle)		12 1	12 months	
DC-401B regen (1st cycle)		24 n	24 months	
DC-401B (12th m	DC-401B (12th month)			
	1 st	2 nd	3 rd	
Inlet Temperature,°C	43	47	56	
Outlet Temperature,°C	75	73	67	
Inlet C2H2,%	1.4	0.7	0.2	
Outlet C2H2,%	0.7	0.2	< 0.3 ppm	
Average selectivity,%	60	50		
No CO injection!				





Commercial Case 1

ZHENHAI 1,000 kta Ethylene

C2 catalyst: BC-H-30A

Reactor style	Single bed (DC-402A/B)
Flow Rate, t/h	150~180
LHSV,h ⁻¹	60
Pessure,MPa	2.3—2.5
Regen. Cycle	12months
Inlet temperature,°C	36~42
Outlet temperature,°C	59~61
H2/MAPD	1.2~1.8
Inlet MAPD,%	1.9~2.5
Outlet MAPD,ppm	<500ppm
Average selectivity	>80%





Commercial Case 2

Sinopec-SK(Wuhan) 800KTA Ethylene

Catalyst used:

C1 catalyst: BC-H-10
 C2 catalyst: BC-H-21B

3. C3 catalyst: BC-H-30A



BC-H-10	BC-H-21B	BC-H-30A
Inlet CO: 0.3 vol%	Inlet C2H2: 0.5%-0.7%	Inlet MAPD: 1.4-2.0mol%
Outlet CO: < 1 ppmv	Inlet MAPD: 0.7%-1.0%	Outlet MAPD: <100ppm
Inlet Temperature: 170-175	CO: 800ppm-1000ppm	H2/MAPD: 1.3-1.8
	(Startup CO Max 2000ppm)	
Life: 2013-2020; 2020-now	Outlet C2H2: <1ppm	Inlet temperature: 36-42°C
SV: 3000-6000 h ⁻¹	Selectivity: 70%	Outlet temperature: <65°C
	Life: 4 years	SV: 30-90h ⁻¹



Outline

I Who we are

II SERT™ for Steam Cracking Furnace

Related Catalysts & Technologies

IV Cold Oil Absorption Technology (COAT™)





Introduction to COATTM



Technical Advantages



Commercial Performance



Introduction to COAT™

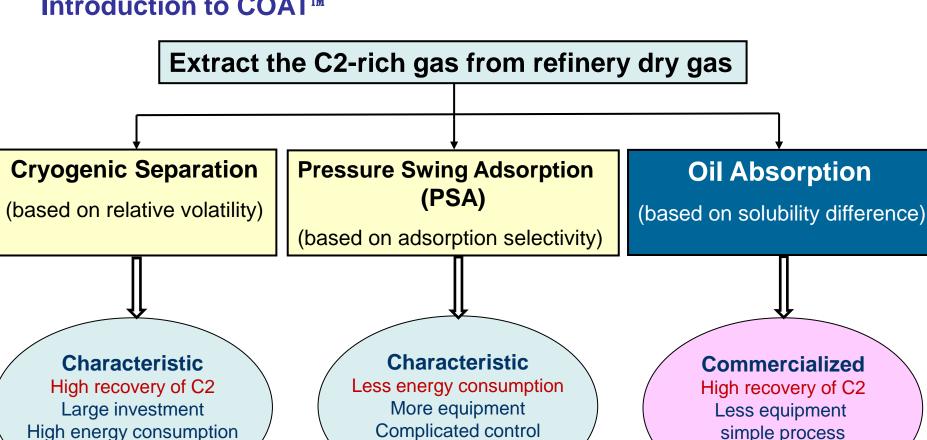
- Why to recover Refinery off-gas?
 - Most used as fuel gas
 - FCC dry gas, coking dry gas, PSA off-gas, etc.
 - ethylene and ethane content about 10~20%
- What will we recover? C2 fraction!
 - Higher value than burned



How to recover?



Introduction to COAT™



Short operating cycle

Operating Temperature -99 °C ~ -130 °C

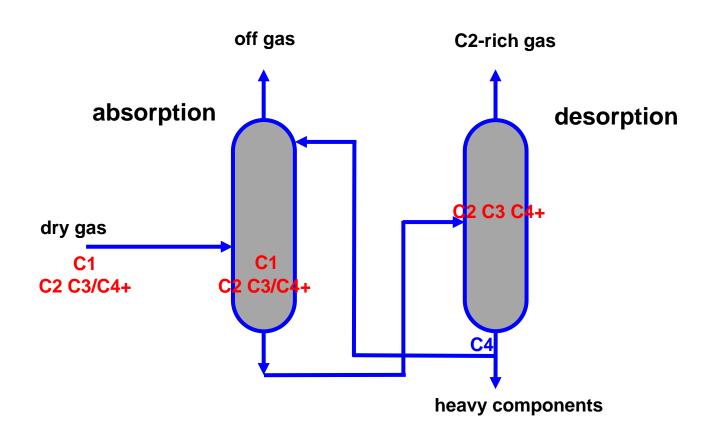
Complicated operation

Operating Temperature Above 0 °C (COAT™)

long operating cycle

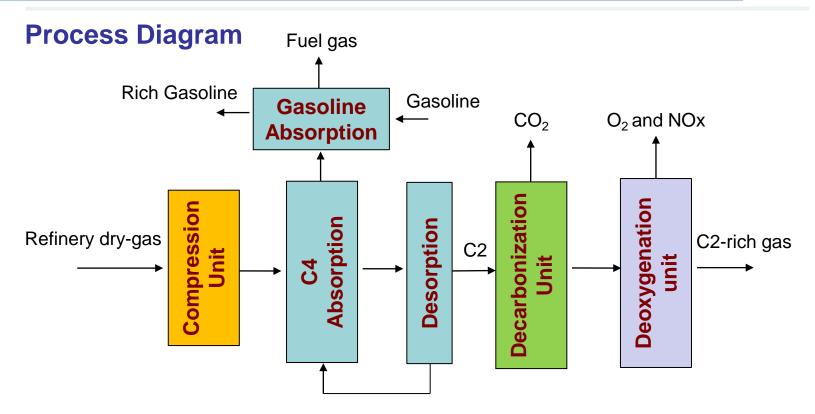


Advanced technology for recovery of C2 from refinery dry gas - Cold Oil Absorption Technology (COAT™)



The principle of COAT is the well-known 'Like Dissolves Like' Theory.





- ✓ C4 fraction is used to absorb C2+ fraction. The stabilized gasoline is used to recover the C4 fraction entrained by fuel gas.
- \checkmark H₂,CH₄,N₂,O₂,NO_x,CO,etc. are removed at the operating temperature **above 0**°C.
- ✓ The obtained C2-rich gas can be sent to caustic washing tower of ethylene unit.
- ✓ lithium bromide water absorption refrigerating equipment is used for cold water supply.



Technical advantages of COAT™

1. High recovery

✓ More than 93% of C2 can be recovered

2. Simple process

✓ Less number of equipment are needed

3. Stable operation

Simple operation, stable running and long operating cycle

4. High quality product

- ✓ Unique advantages in impurity removal; methane content is lower than 5%
- ✓ After treated by the deoxygenation unit, O₂<1ppmw, NOx<10ppbw</p>



Technical advantages of COAT™

5. Less energy consumption

✓ Both the lithium bromide absorption refrigerator and tower reboilers can be driven by the refinery surplus heat.

6. Wide range of application

✓ Adaptable to various types of refinery dry gas (i.e., FCC, atmospheric-vacuum distillation, delayed coking, catalyst reforming, ...), coal-chemical gas and even oilfield gas.

7. Low investment and Less floor space

- ✓ All equipment are not complicated.
- ✓ Occupied less floor space.

With so many advantages, COAT is reliable and has good prospects in application!



Commercial Application Case 1



100 kta COAT™ Unit in Qilu, Sinopec

- ✓ Qilu, SINOPEC:
 - COAT™ unit built in 2011
 - supplied high quality C2-rich gas.
- ✓ Ethylene recovery rate is 93%
 - >80% ethylene and ethane
 - Oxygen content is lower than 1PPM
- ✓ ROI is less than 2 years.
- Continue running smoothly and stably

^{*}The capacity is based on the feed stock.



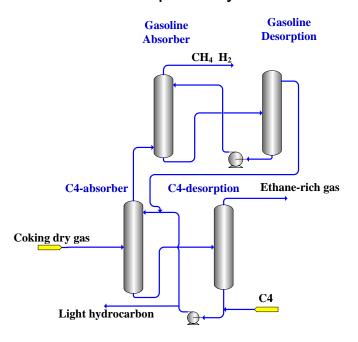
Commercial Application Case 2



220 kta COAT™ Unit in Qilu, Sinopec

*The capacity is based on the feed stock.

- ✓ Qilu, SINOPEC
 - Recovery of delayed coking dry gas
 - Started up in July 2015.





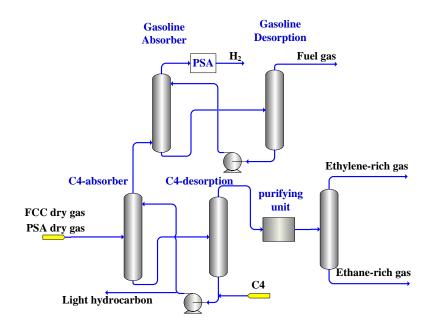
Commercial Application Case 3



230 kta COAT™ Unit in FREP, Fujian

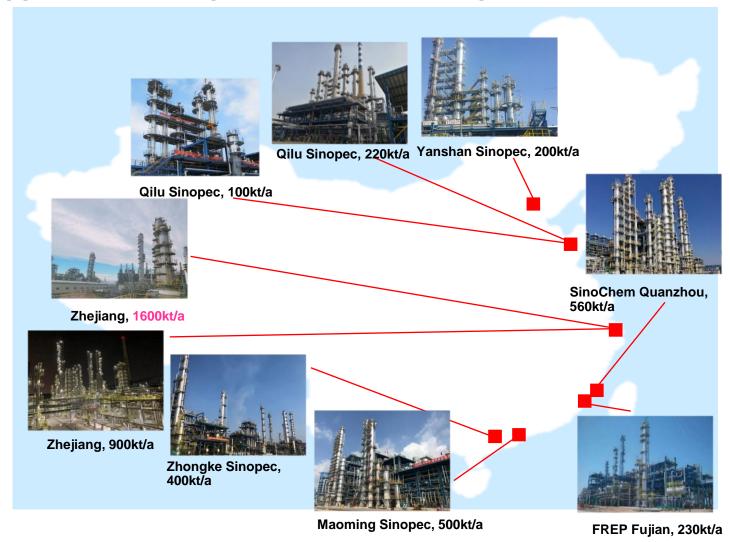
*The capacity is based on the feed stock.

- ✓ Fujian Refining & Petrochemical Company Limited
 - Recovery of FCC, PSA dry gas and other dry gases
 - Started up in October 2015.





Application Examples - 9 units under operation





Other Application Cases - 7 units under construction

NO.	Applied Enterprises	Capacity(kta)	Phase
1	Tianjin, Sinopec	250	Under construction
2	Guangdong, Petrochem	350+600	Under construction
3	Hainan, Sinopec	630	Under construction
4	Shandong Yulong Petroleum Chemical Company., Ltd	650+900	Under construction
5	Ningbo Zhongjing Petroleum Chemical Company., Ltd	1000	Under construction
More			

^{*}The capacity is based on the feed stock.

Innovation, Development Cooperation & Win-Win Thank you

China Petrochemical Technology Co., Ltd. (SINOPEC TECH) zhaoran.chji@sinopec.com

Sinopec Beijing Research Institute of Chemical Industry (Sinopec BRICI) wangcs.bjhy@sinopec.com



