Lovraj Kumar Memorial Trust Workshop (India)

Recovery of Ethylene and Production of Ethyl Benzene/Styrene from FCC Off-gas

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CB&I Technologies

Agenda

- Introduction
- LPR Technology
- EB Technology
- SM Technology
- Summary






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- FCC/RFCC offgas is typically used as fuel gas
- FCC/RFCC offgas contains valuable olefins (ethylene / propylene) which could be recovered
- Recovered Ethylene free-up polymer grade ethylene for other purpose
- CB&I Technology offers complete ethylene recovery process
  - Pretreatment
  - Low Pressure Recovery (LPR) process for dilute as well as high purity ethylene
- Recovered ethylene (high purity or dilute) is used to produce Ethyl Benzene
  - CB&I/UOP EB*One* Process
  - CDTech EB
- Ethyl Benzene is dehydrogenated to Styrene
  - Classic SM
  - Smart SM

- Olefin-rich streams from which ethylene and propylene can be recovered
- Saturated streams that can used for feedstock to an ethylene unit

Olefin-rich Streams:

- ***FCC Offgas***
- ***Indmax™ FCC Offgas***
- ***Coker Offgas***

→ ***Ethylene***, ***Ethane***, ***Propylene***, ***C_3+***

Saturated Streams:

- ***Crude Unit***
- ***Reformer***
- ***Hydroprocessing***

→ ***Hydrogen***, ***Ethane***, ***C_3+***

Example of Olefin-rich Refinery Offgas

Composition	wt%	kta
Hydrogen	2.7	6.8
Methane	25.7	64.2
Nitrogen	19.2	48
Carbon monoxide	0.8	2
Carbon dioxide	0.1	0.3
Hydrogen Sulfide	0.2	0.5
Oxygen	0.2	0.5
Ethylene	21.6	54
Ethane	21.7	54.2
Propylene	4.8	12
Propane	1.4	3.5
C_4+ Hydrocarbons	1.6	4
Total	100	250

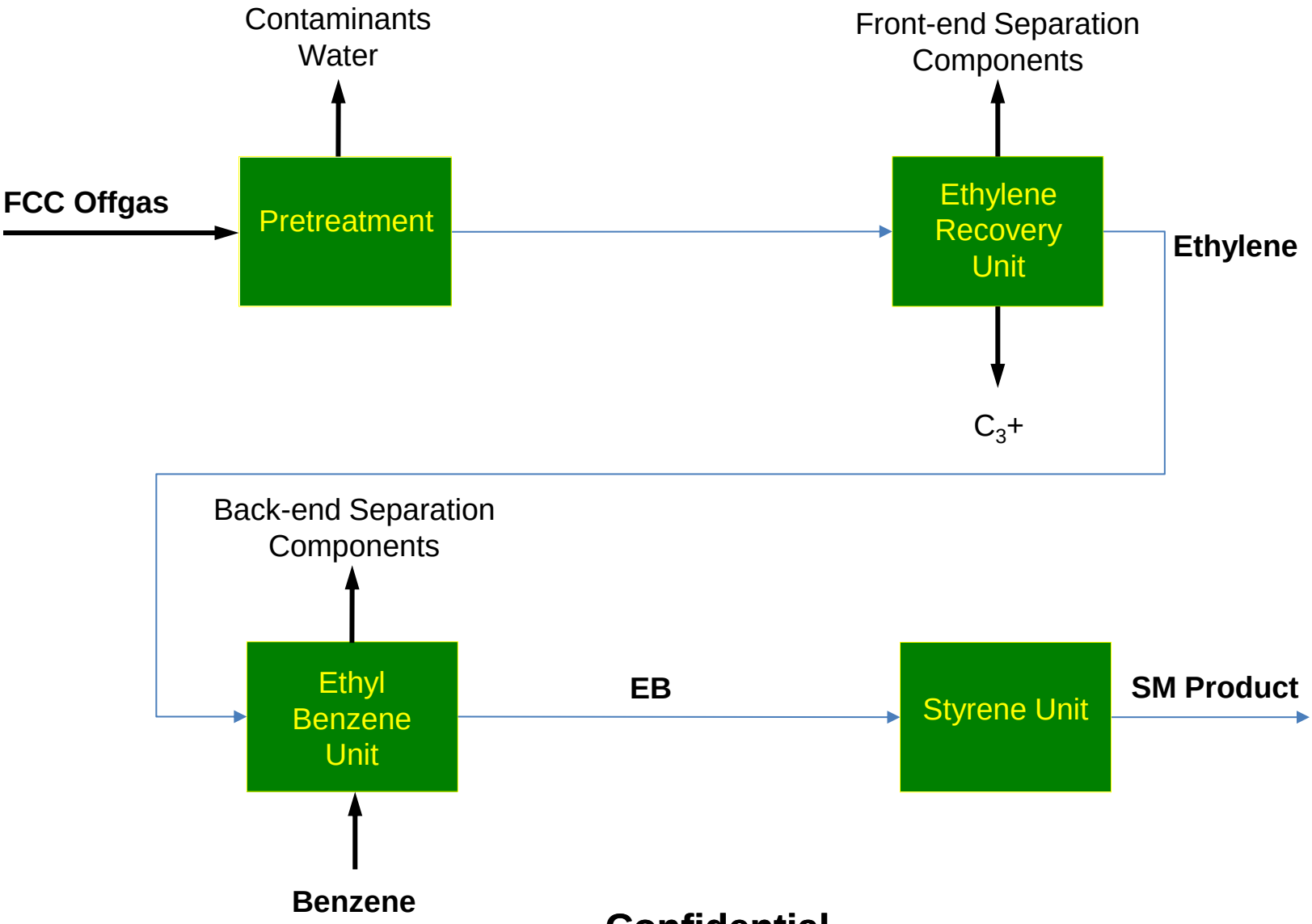
- Coker & (R)FCC mixed gas
- High levels of lights, removed by cold distillation
- Other contaminants removed by feed treatment

Ethylene $54 million / yr
Propylene $13.2 million/yr

Ethane $9.6 million / yr
Propane $1.5 million/yr

High value olefin upgrade available

General Overall Configuration



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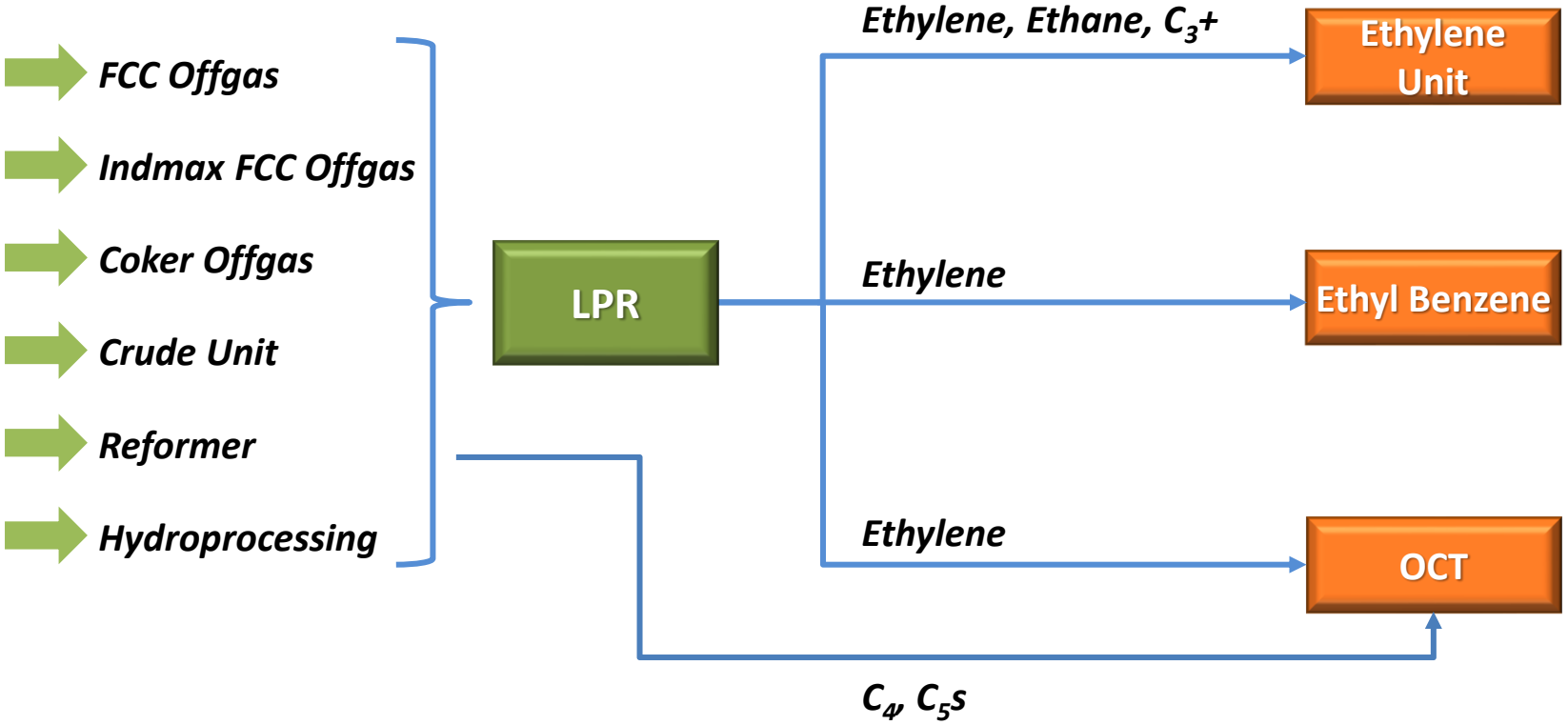
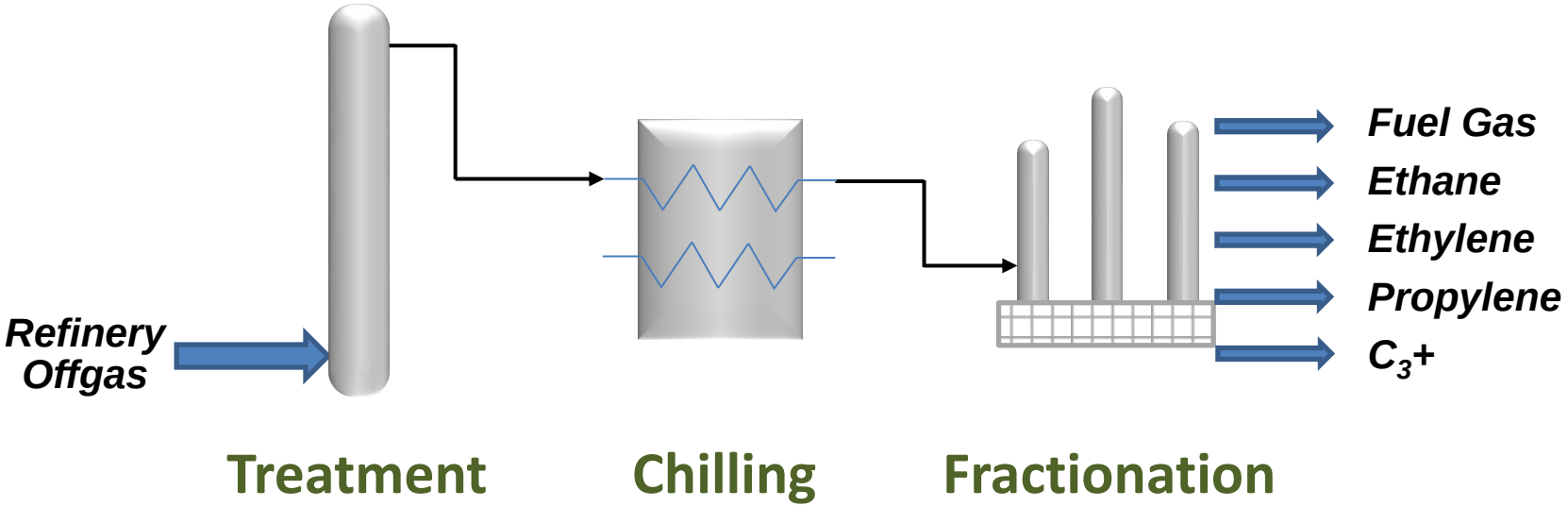
Low Pressure Recovery (LPR) Process

- Low Pressure Recovery (LPR) of refinery offgas integrates with many downstream units





- Process configuration optimized based on:
  - Feedstock composition and contaminants
  - Product requirements
  - Integration with downstream units

LPR Configuration Options for EB Process

- Two possible configurations
  - Dilute Ethylene Recovery
  - High Purity Ethylene Recovery
- Dilute ethylene is fed to CDTech EB process which can handle up to 5% - 100% purity ethylene
- High Purity ethylene is fed to CB&I/UOP EB*One* process
- Dilute ethylene production scheme requires only feed treatment and de-ethanization of offgas feed
- For high purity ethylene feed treatment, offgas chilling, demethanization and de-ethanization is required

- Impurities removal based on experience
  - Ethylene / EB
  - Olefins Conversion Technology (OCT)
  - Fluid catalytic cracking
  - Coking
- Treatment considers all impurities
  - Carefully planned and robust approach
- Emphasis on safe process design

Inherently Safe Process

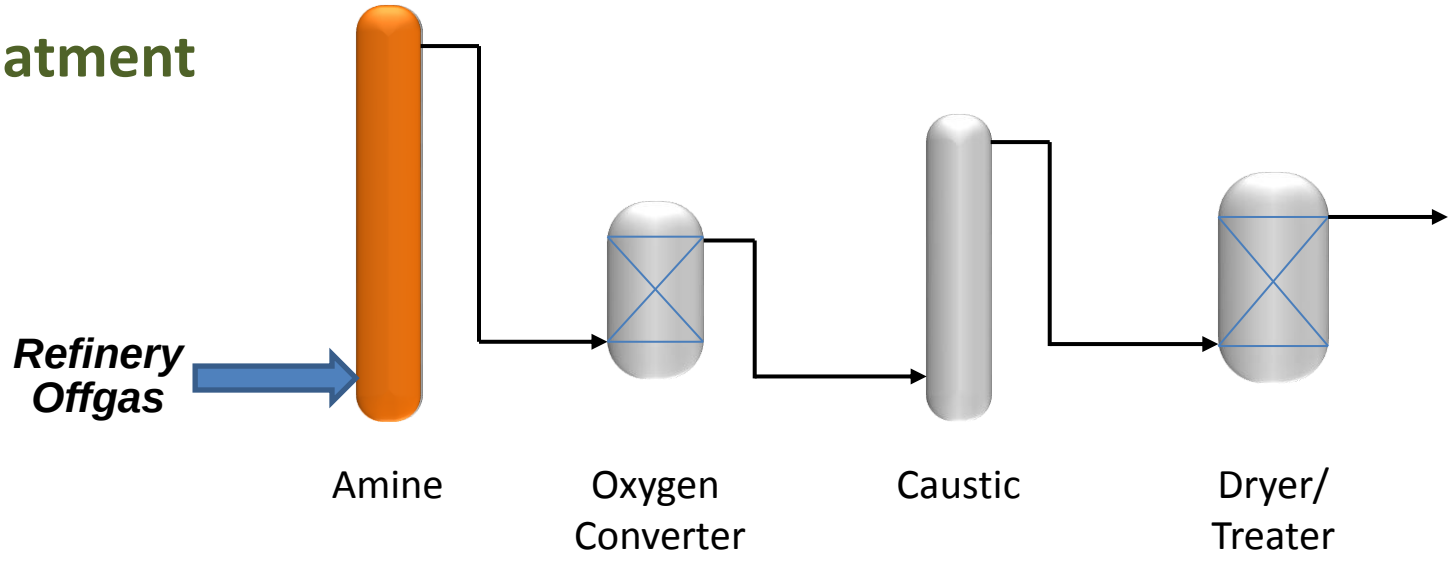
Treatment

Potential Safety Hazard
NOx
Oxygen
CO

Catalyst Poisons	
Arsine	HCl
Phosphines	HCN
Chlorides	Lead
Sodium	Mercury

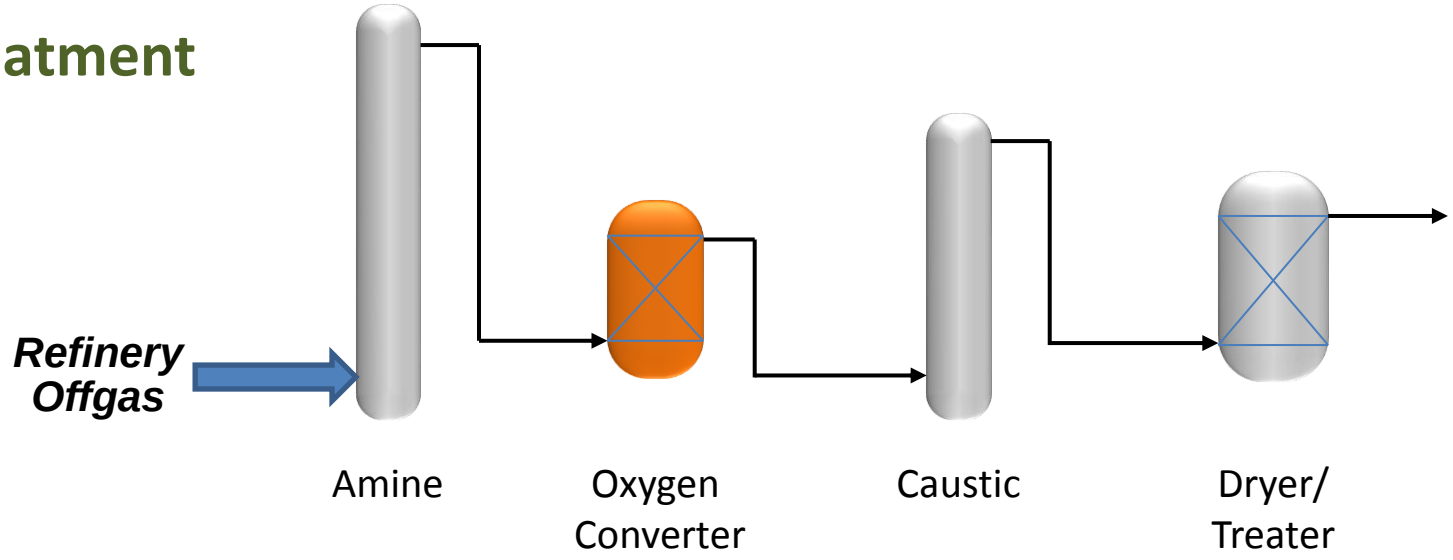
Product Quality	
Acetylene	H_2S
Ammonia	MAPD
Amines	Mercaptans
Butadiene	Methanol
CO_2	Nitriles
COS	SOx

Treatment



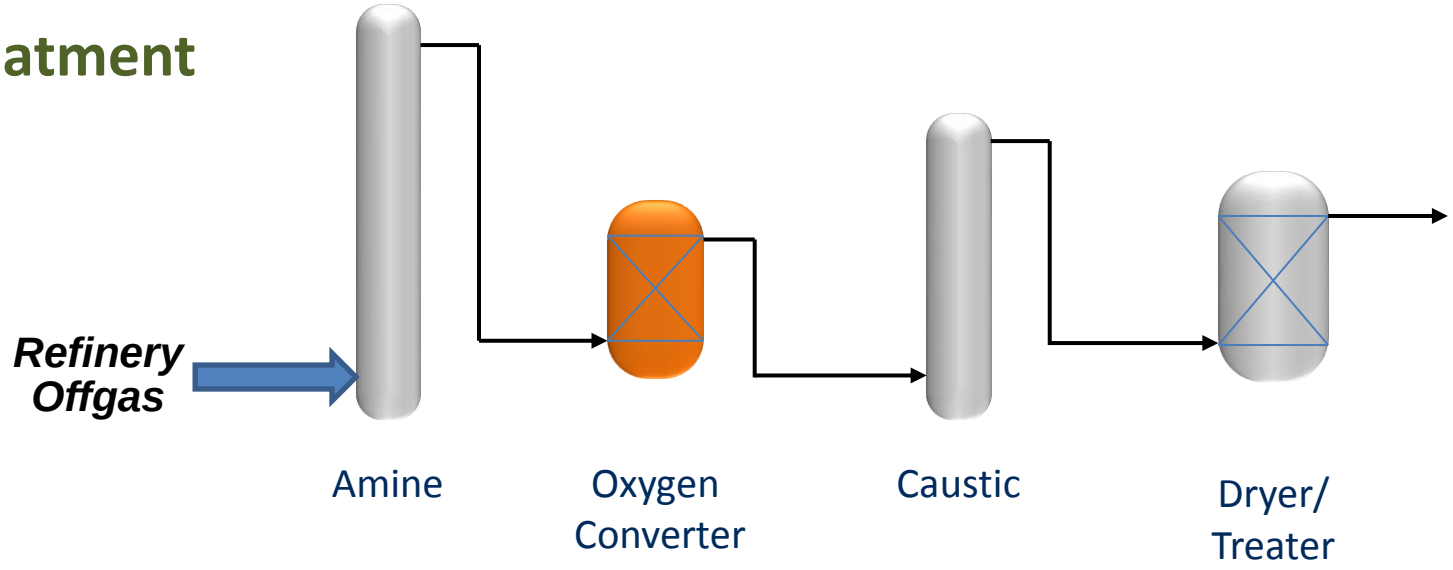
- Amine wash system – for bulk removal of acid gas
  - Often already part of refinery

Treatment



- Fixed bed nickel or copper based catalyst
- Regenerated on site
- Hydrogen present in offgas utilized in reaction
  - No hydrogen makeup required

Treatment



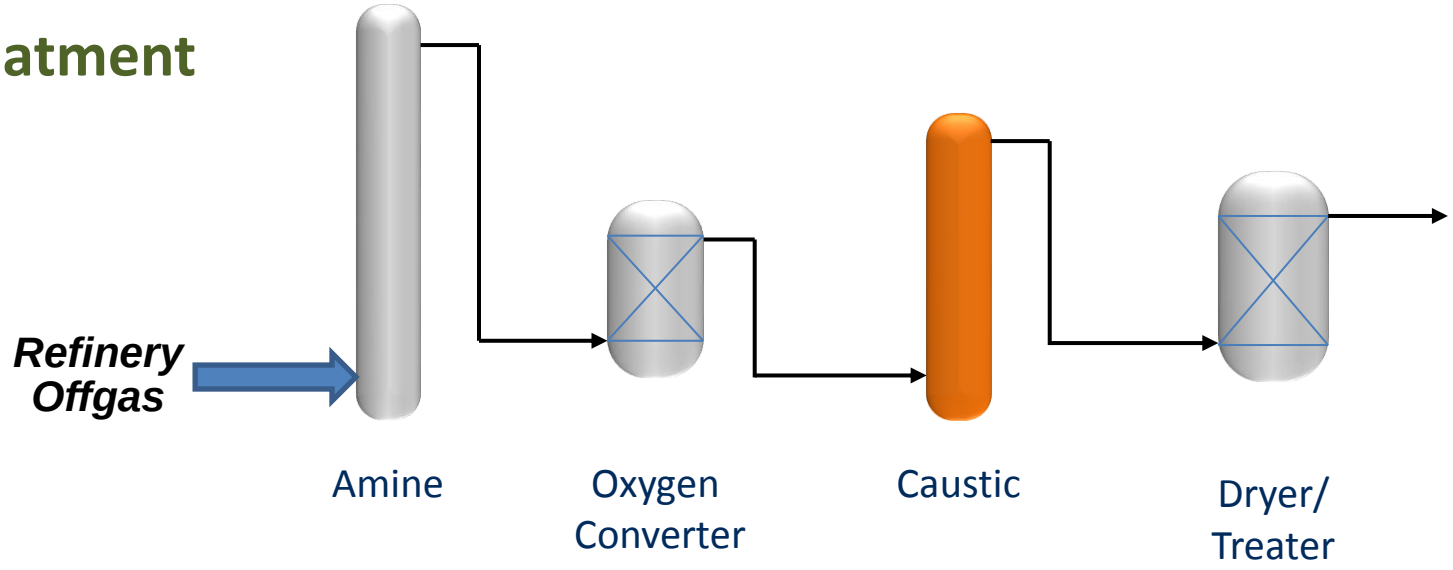
$Oxygen + H_2$ ➔ Water

$NOx + H_2$ ➔ Ammonia + Water

$Acetylene + H_2$ ➔ Ethylene + Ethane

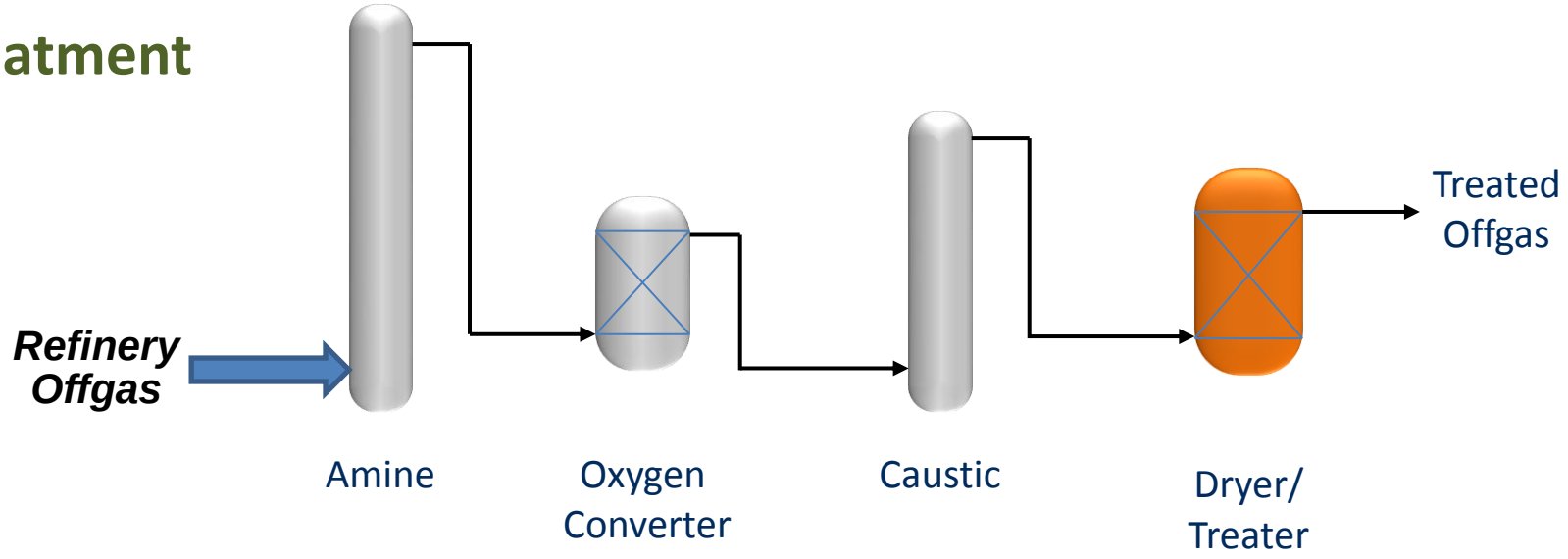
Easily Removable Compounds

Treatment



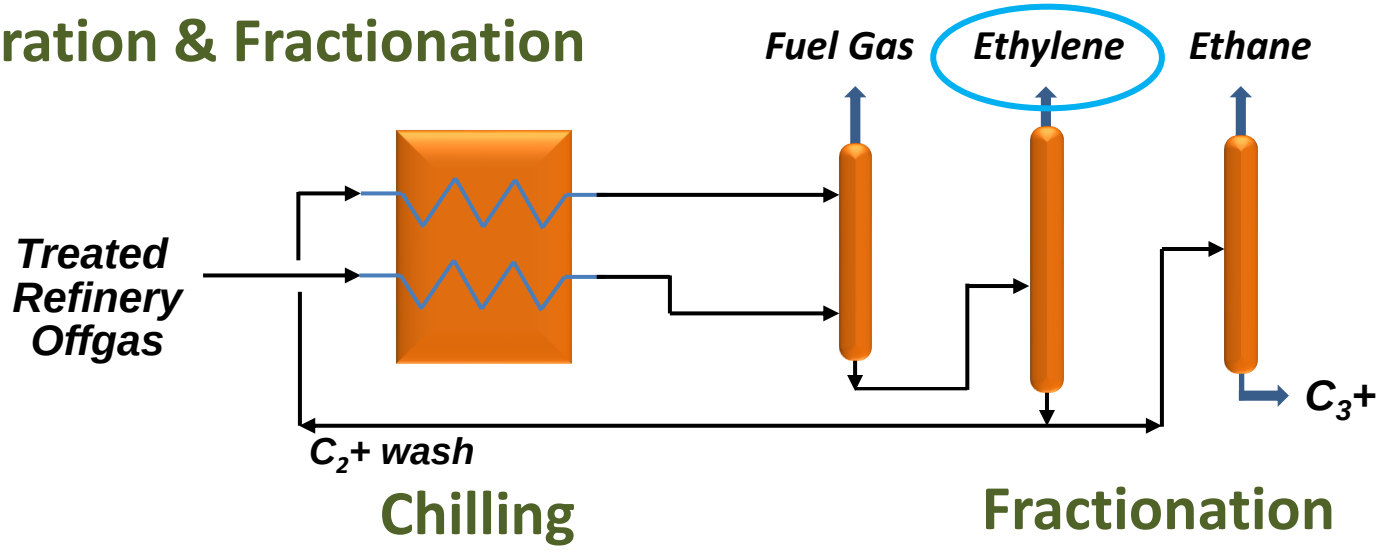
- Removal of trace acid gases
  - H_2S <1 ppm
- Wash to remove residual salts, halides

Treatment

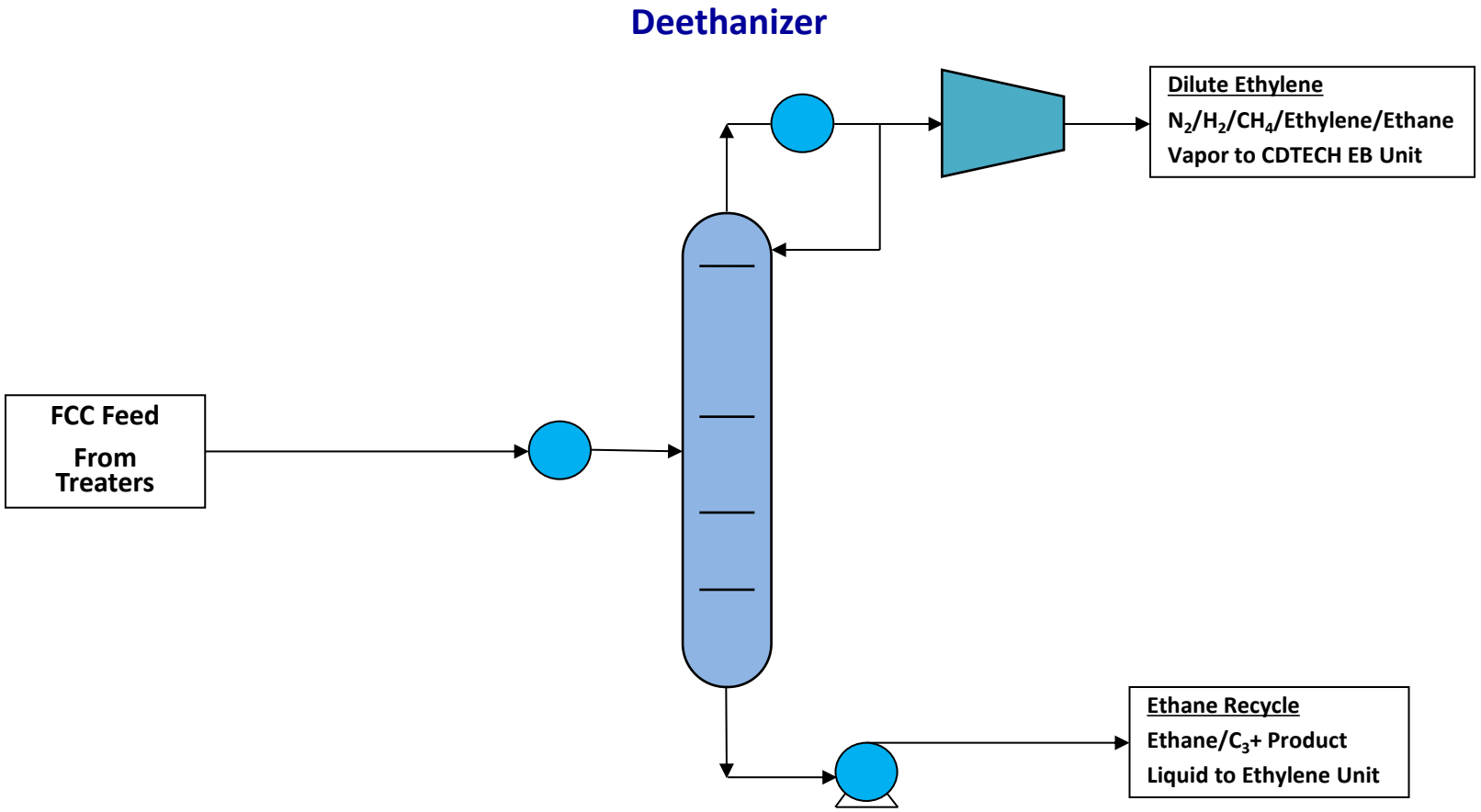


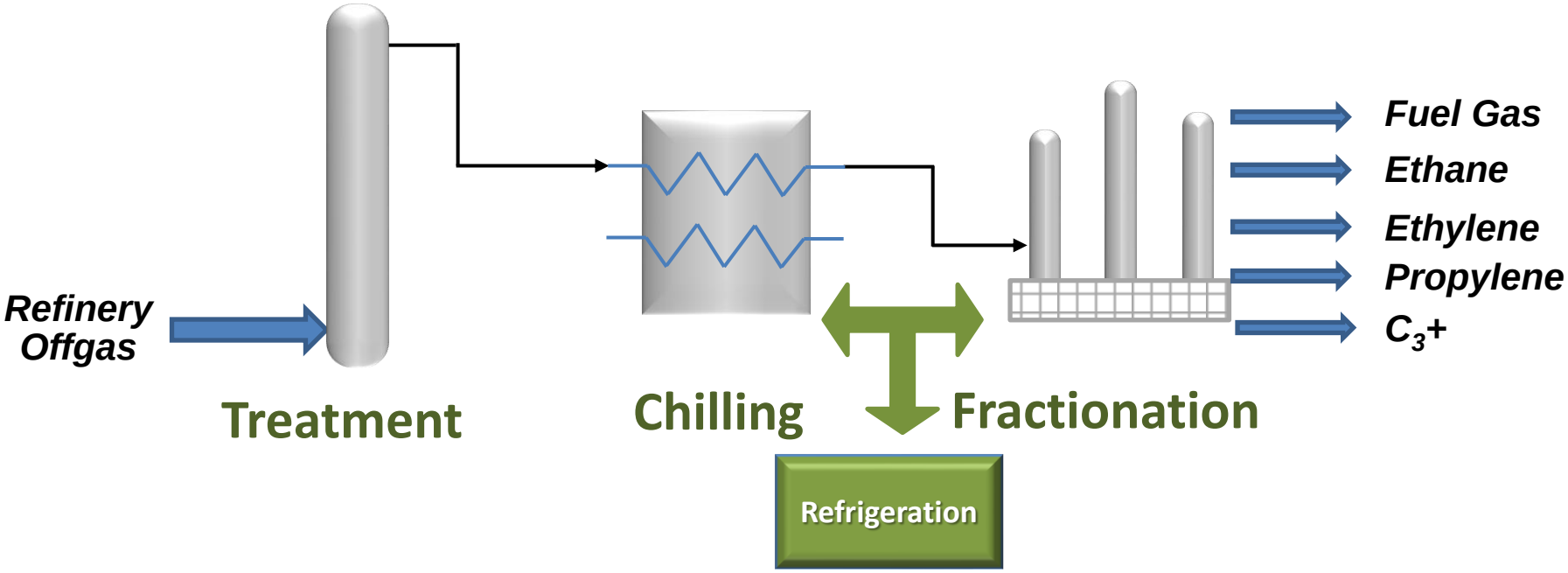
- Removes:
  - Ammonia
  - Amine
  - Mercaptans
  - Water, etc.
- Activated alumina, molecular sieve or a combination

Refrigeration & Fractionation



- Absorber demethanizer temperature selected to avoid NOx issues
  - Internally accumulated wash
- Ethylene recovered
  - Feed to Ethyl Benzene Unit
  - OCT feed with refinery C_4s and C_5s
- Optional ethane recovery





- Integrated with the ethylene plant
  - BR, EBR, C_2R and C_3R
- Binary refrigeration (for stand-alone units or expansions)
  - Single machine, down to -140°C

Refinery Offgas Recovery Experience

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Refinery Offgas Recovery Experience

- More than 40 years of experience with refinery offgas recovery of olefins
- 15 plants
  - 17 to 232 kta ethylene
    - from 160 to 714 kta of offgas
  - 9 integrated with ethylene cracker
  - 4 integrated with OCT for propylene
  - 2 stand-alone for ethylene

EB/SM Process

Styrene Market

- Total installed capacity – 27 to 28 MM MTA
  - Total capacity grew at a rate of 4 to 5% per year till 2007
  - Market consolidation
    - Smaller/older units shut down from 2008 to 2011
    - Major players divested assets (e.g., Dow, BASF)
- Since late 2012, margins have returned to pre financial crisis level
  - But total installed capacity is still close to pre crisis level
  - Producers interested in expansions or grassroots designs
- CB&I/UOP EB-SM technology can provide cost effective expansions and grassroots design
  - More than 30 grassroots EB-SM plants since 1990
  - Recent activities – expansions to achieve higher plant capacity and to improve cost of production

EB*One*

Liquid-Phase, Fixed-Bed
Uses polymer-grade ethylene

Classic SM

Lowest cost of production
Best for new unit design

CDTECH *EB*®

Catalytic Distillation
Accepts dilute ethylene feed

SMART SM

Oxidative reheat for
low-cost capacity expansion

EB*One*

Liquid-Phase, Fixed-Bed
Uses polymer-grade ethylene

CDTECH *EB*®

Catalytic Distillation
Accepts dilute ethylene feed

- Ethylene feedstocks
  - Polymer grade
  - Chemical grade
    greater than 55 mol.% ethylene with ethane
  - Dilute
    less than 55 mol.% ethylene with hydrogen, methane, ethane and other light gasses

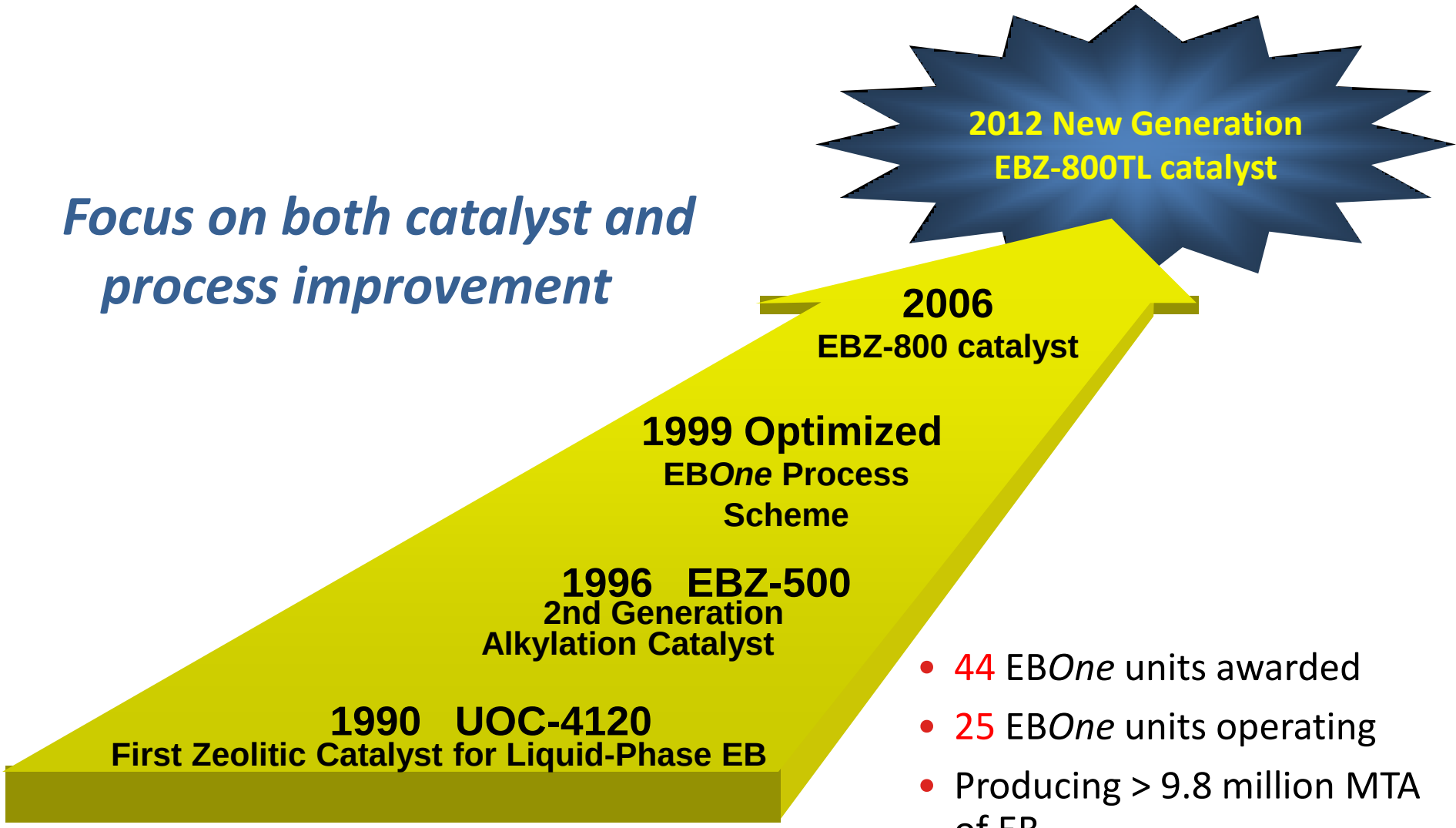
EB*One*

Liquid-Phase, Fixed-Bed
Uses polymer-grade ethylene

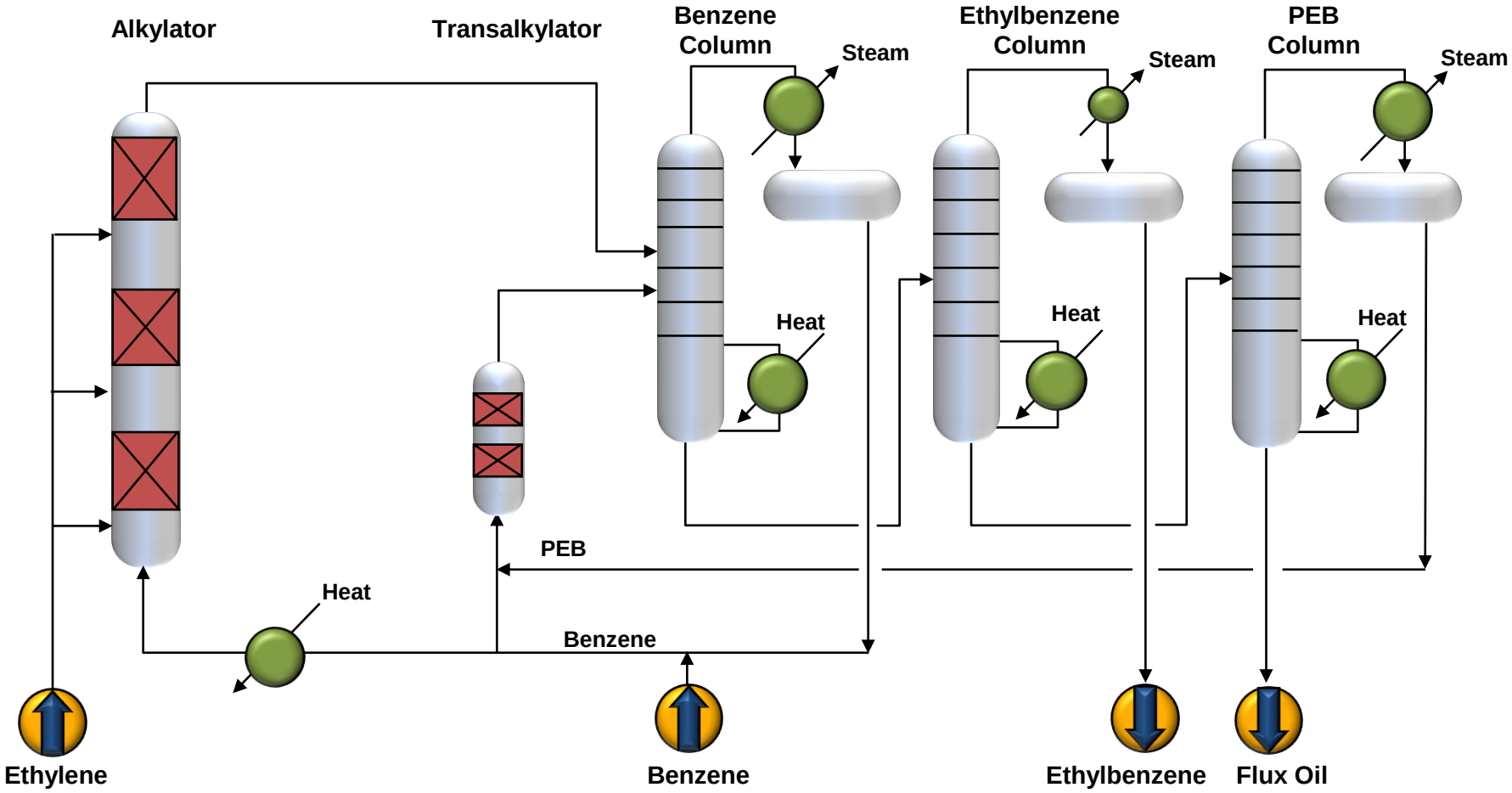
- EB*One* is a combination of several improvements and is the result of 300 operating years of commercial experience and continuous process evolution since 1990

Continuous EB Technology Innovation

Focus on both catalyst and process improvement



- 44 EB*One* units awarded
- 25 EB*One* units operating
- Producing > 9.8 million MTA of EB



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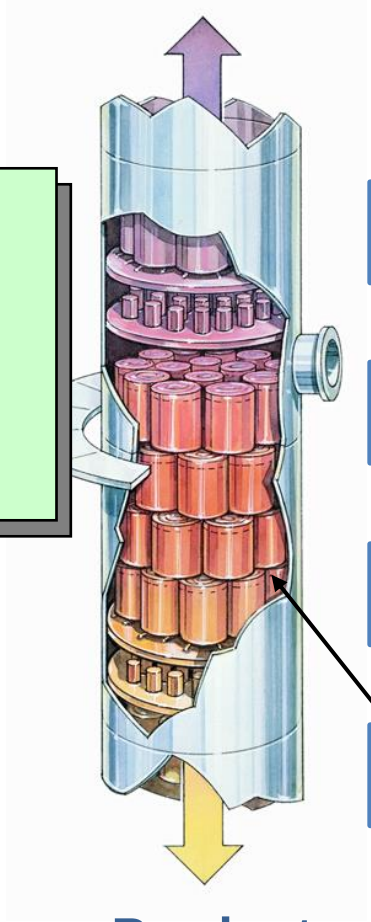
- High performance, proven catalyst system
  - Latest formulation of alkylation catalyst
  - NiGUARD technology effectively removes basic nitrogen compounds from the feed
  - Allows processing of recycle benzene from styrene plant
- Highly optimized simple flow scheme and design basis
  - Minimizes capital cost and cost of production
  - Low benzene recycle
- Most commercial operating experience
  - Long term operating experience incorporated in the new designs

Olefin and Benzene

CDTECH *EB*®

Catalytic Distillation
Accepts dilute ethylene feed



- Combined distillation/reaction
- Heat removal by vaporization
- Low temperature isothermal operation
- Continuous removal of reaction products

Product

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- Ethylene feedstock: 100 to 5% purity
- Low ethylene feed pressure: 20 barg
- Lowest commercially proven B/E ratio
- Successful operation since December 1996
- Catalyst quantity: dependent on feedstock
- Greater revamp possibilities for large capacity expansions

- High yield: 99.7+ wt.%
- High EB product purity
- Zeolite catalyst system
- Long catalyst run-lengths
- High energy efficiency

- Over four decades of experience in development and licensing of EB technology
- EB*One* liquid-phase technology
  - 43 project awards, 1,250,000 MTA largest capacity
  - 25 plants in operation
  - Durable high performance catalyst
- CDTECH EB technology
  - Six project awards > 800,000 MTA largest capacity
  - Five plants have been put into operation
  - Optimum for dilute ethylene feedstock

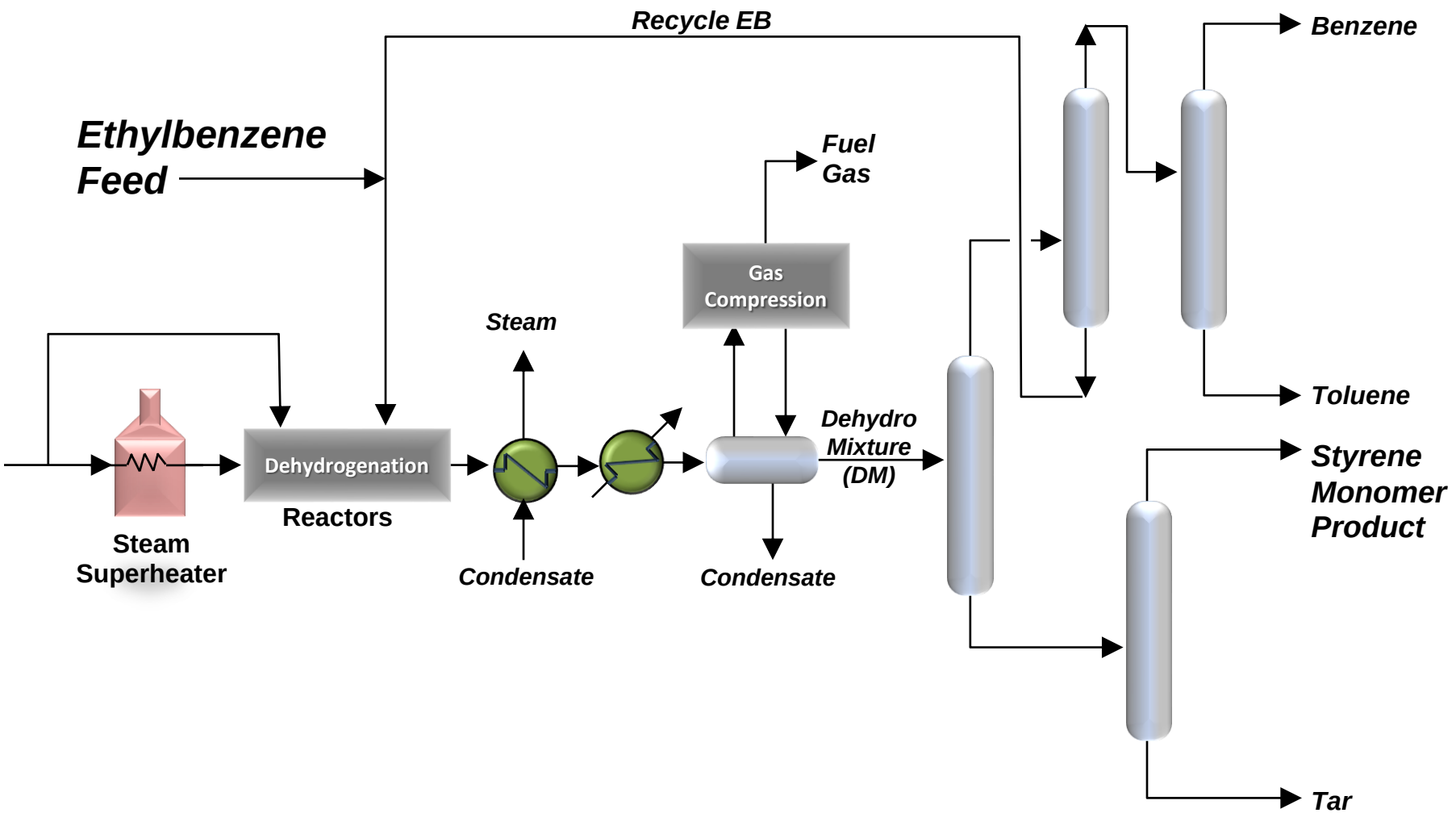
"Classic" SM Technology

Classic SM

Lowest cost of production
Best for new unit design

- Includes an integrated unique reactor design
  - Outstanding mechanical reliability
  - Excellent low S/O mixing/flow distribution
  - Minimum void volume
- Selection of optimum styrene catalyst
  - Low steam-to-oil operation
  - High activity, selectivity and stability
- Patented azeotropic heat recovery system
  - Non-compressive
  - Less live steam required to achieve reactor steam to oil ratio

"Classic" SM Process Scheme



The Industry Standard

- Patented azeotropic distillation system
  - Net steam requirement equivalent to S/O ratio of 0.65 wt. (3.8 molal)
- Low steam-to-oil ratio = 1.15 wt. (6.8 molal)
- Optimum distillation scheme
- SM product purity of 99.95 wt.%
- Reliable operation
  - Proven reactor design
  - Minimum fouling
- Efficient heat integration

“Azeo 2”

Styrene’s next generation of the azeotropic distillation

"Azeo 2" – The New Standard

- New azeotropic distillation system
- Lowers net steam requirement equivalent to S/O ratio = 0.50 wt. (2.95 molal)
- Lowers reactor steam-to-oil ratio = 1.0 wt. (5.9 molal)
- Optimum distillation scheme
- Can achieve SM product purity of 99.95 wt.%
- Reliable operation
  - Proven reactor design
  - Minimum fouling
- Efficient heat integration

SMART SM

Oxidative reheat for
low-cost capacity expansion

- Oxidative reheat technology
- Increased single pass EB conversion

- Oxygen addition
- Removal of hydrogen shifts equilibrium towards styrene
- Heat of oxidation reheats process gas to required temperature for next dehydrogenation stage

EB	$\leftrightarrow$	SM + H_2 - heat	(Dehydrogenation)
H_2 + 1/2 O_2	$\rightarrow$	H_2O + heat	(Oxidation)

- Utilization of state-of-the-art styrene catalysts such as Clariant's Styromax and UL (ultra-low steam-to-oil) catalysts
- Superior mechanical design of hot end in reaction area
- Azeo and Azeo 2 heat recovery schemes
- Low investment and operating cost
- "Classic" and SMART technology revamp options

- Classic SM technology
  - Most widely used SM technology in the world
  - 63 project awards, 36 units in operation
  - Highest conversion and selectivity
  - Uniquely integrated reactor system
- SMART SM technology
  - Low investment cost revamp option
  - 14 project awards, 10 units in operation
  - Innovative oxidation reheat technology minimizes plant modifications and achieves higher plant expansion capacities

Summary

- Valuable olefins (ethylene and propylene) could be recovered from FCC/RFCC offgas streams using LPR process
- Recovered ethylene can be used to produce Ethylbenzene and Styrene
- LPR process configuration can be selected to produce either dilute ethylene or high purity ethylene
- Dilute ethylene can be used as a feedstock for CDTech EB process
- High Purity ethylene can be used as a feedstock for CB&I/UOP EB*One* process
- Integrated LPR/EB/SM unit configuration cold be optimized based on the site specific conditions to yield maximum benefits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