Successful Operation of the First AlkyClean® Solid Acid Alkylation Unit

June 29, 2017
AIChE Lecture Dinner Meeting

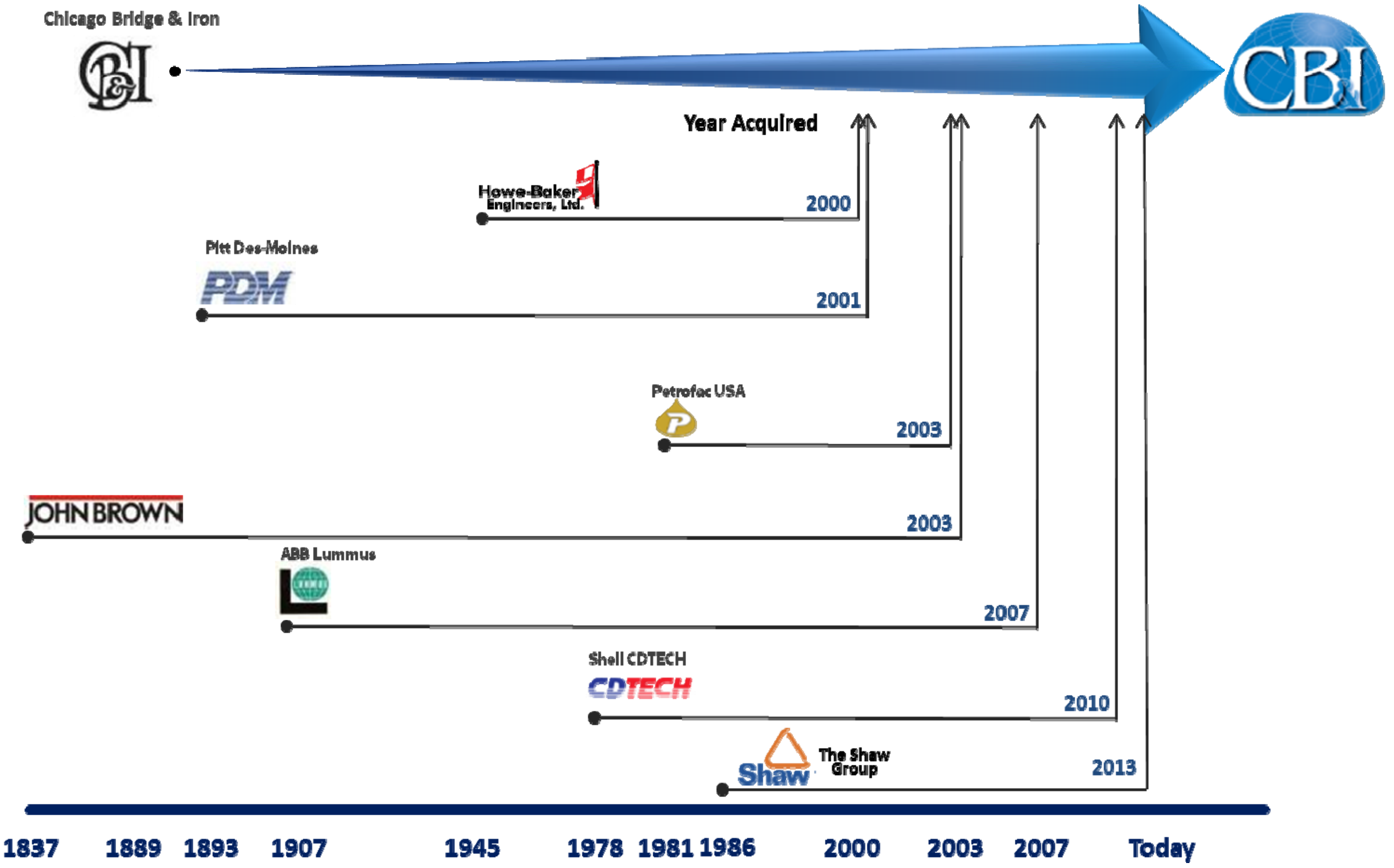
A World of **Solutions**

OVERVIEW

- Leading provider of technology and infrastructure for the energy industry
- 125+ years of experience and expertise in reliable solutions
- $19.3 billion backlog (Mar. 31, 2017)
- More than 40,000 employees worldwide
- Relentless focus on safety: 0.00 LTIR (Mar. 31, 2017)

CORE VALUES

CB&I HISTORY



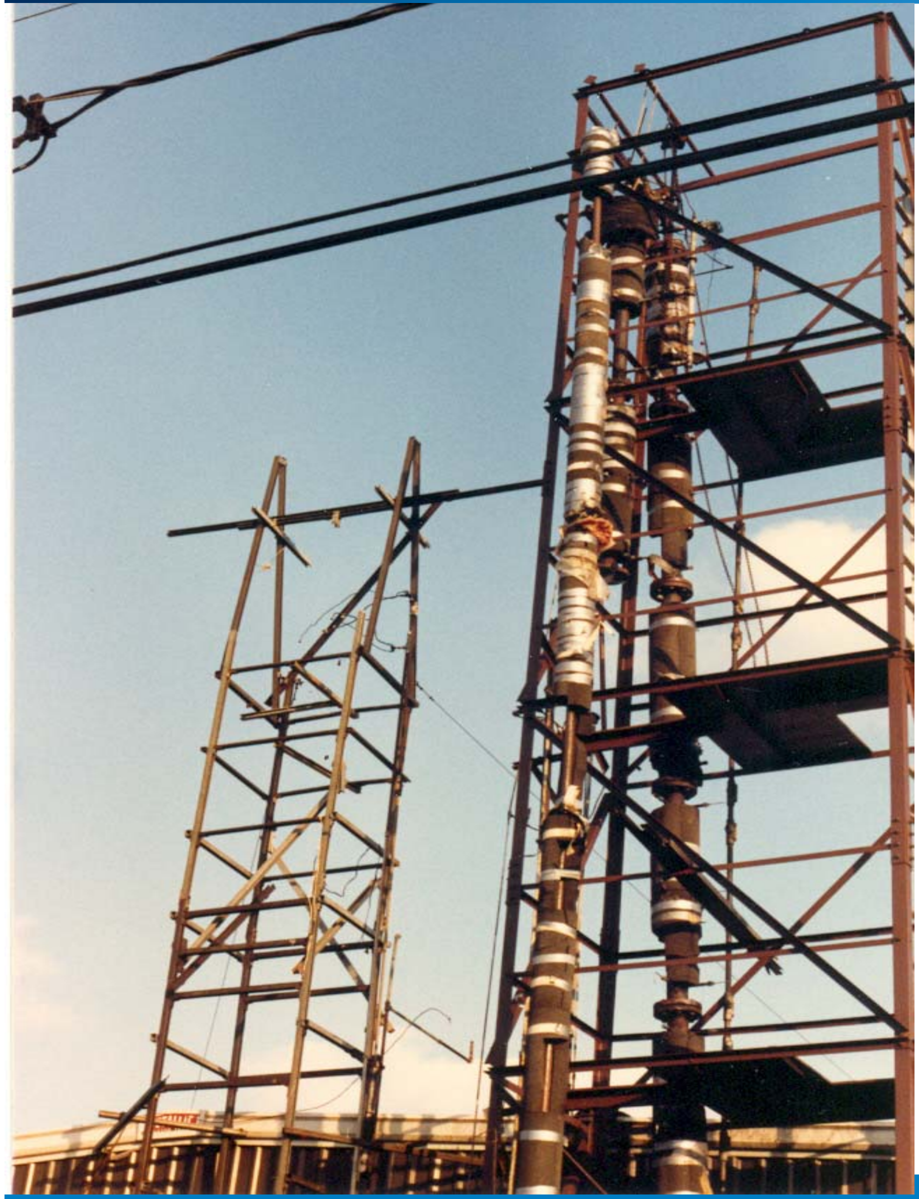
Chicago Bridge & Iron
Year Acquired
Howe-Baker Engineers, Ltd.
2000
Pitt Des-Moines
PDM
2001
Petrofac USA
2003
JOHN BROWN
2003
ABB Lummus
2007
Shell CDTECH
CDTECH
2010
Shaw
The Shaw Group
2013
1837
1889
1893
1907
1945
1978
1981
1986
2000
2003
2007
Today

CDTECH in the Beginning – Ingenuity at Work!

Site of Technology's birth in 1977:

Larry Smith's Laundry Room

Pasadena, Texas



South Houston Site –

Commercial Development Unit

(CDU)

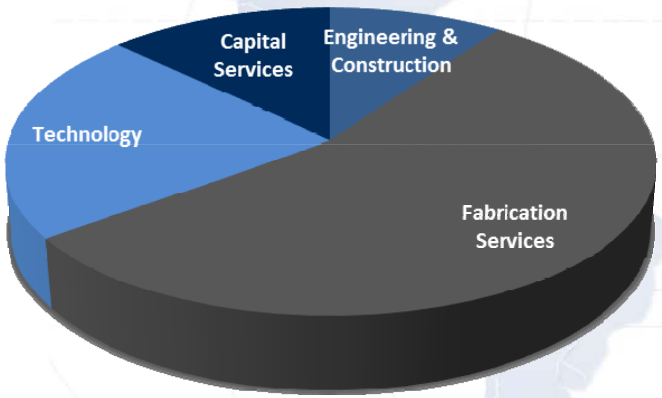
State of the Art

Research Facilities in

Pasadena, Texas

BREADTH OF SERVICES

2017 Q1 Operating Income



Technology

- Licensed technology
- Proprietary catalysts
- Technical services

Engineering & Construction

- Engineering
- Procurement
- Construction
- Commissioning

Fabrication Services

- Fabrication & erection
- Process & modularization
- Pipe fitting and distribution
- Engineered products
- Specialty equipment

Capital Services

- Program management
- Maintenance services
- Remediation and restoration
- Emergency response
- Environmental consulting

TECHNOLOGY OVERVIEW

Capabilities

- Petrochemical, gas processing and refining technologies
- Proprietary catalysts
- Consulting and technical services

Differentiation

- Most complete portfolio of olefins technologies
- World leader in heavy oil upgrading technologies
- Breadth of technologies provides complete solutions

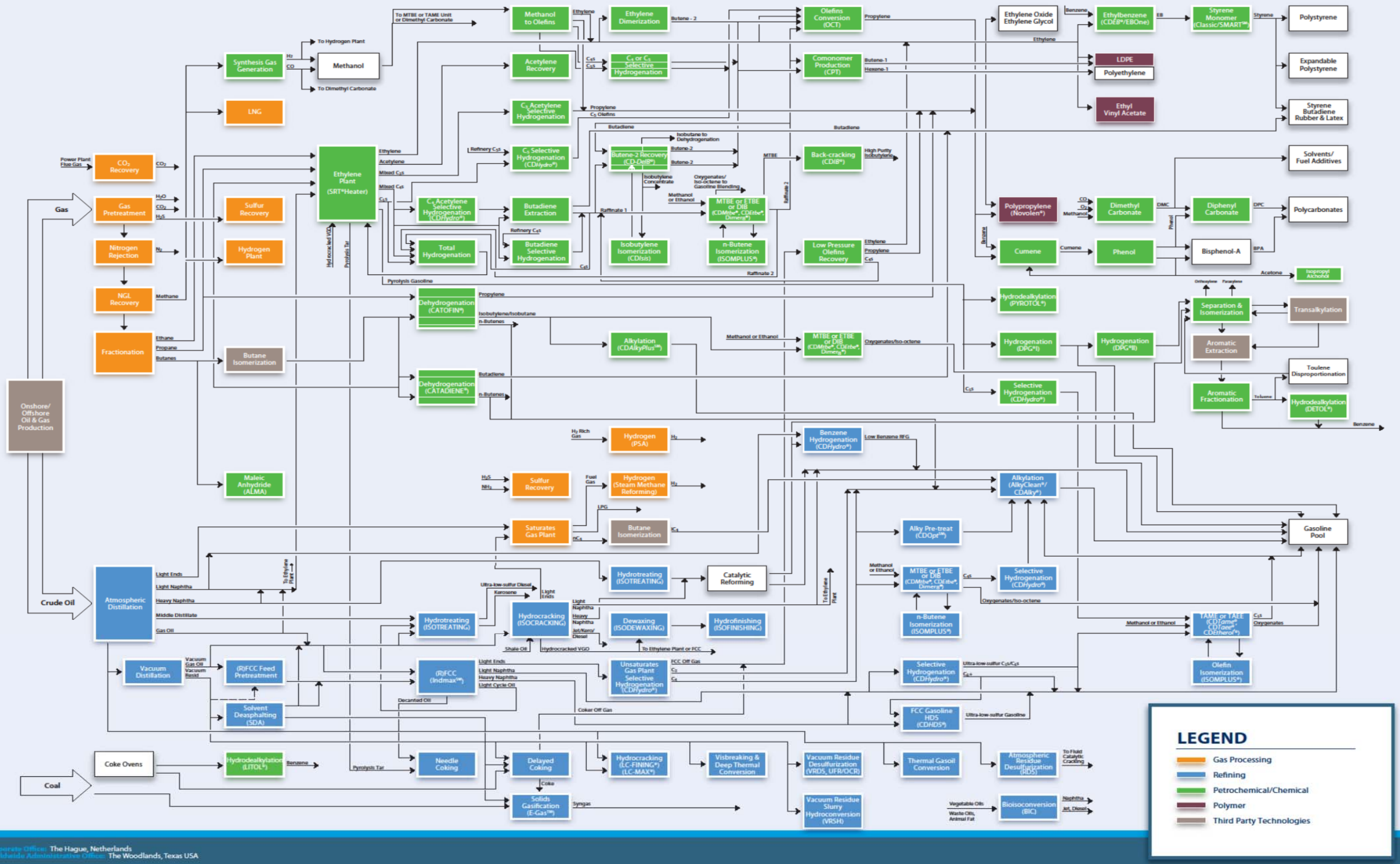
Commitment to Technology: R&D

Chevron Lummus Global, Chevron, Richmond, CA
Lummus Novolen Technology, BASF Site, Ludwigshafen, Germany
Technology Development & Manufacturing Center, Pasadena, TX

Over 3500 Patents

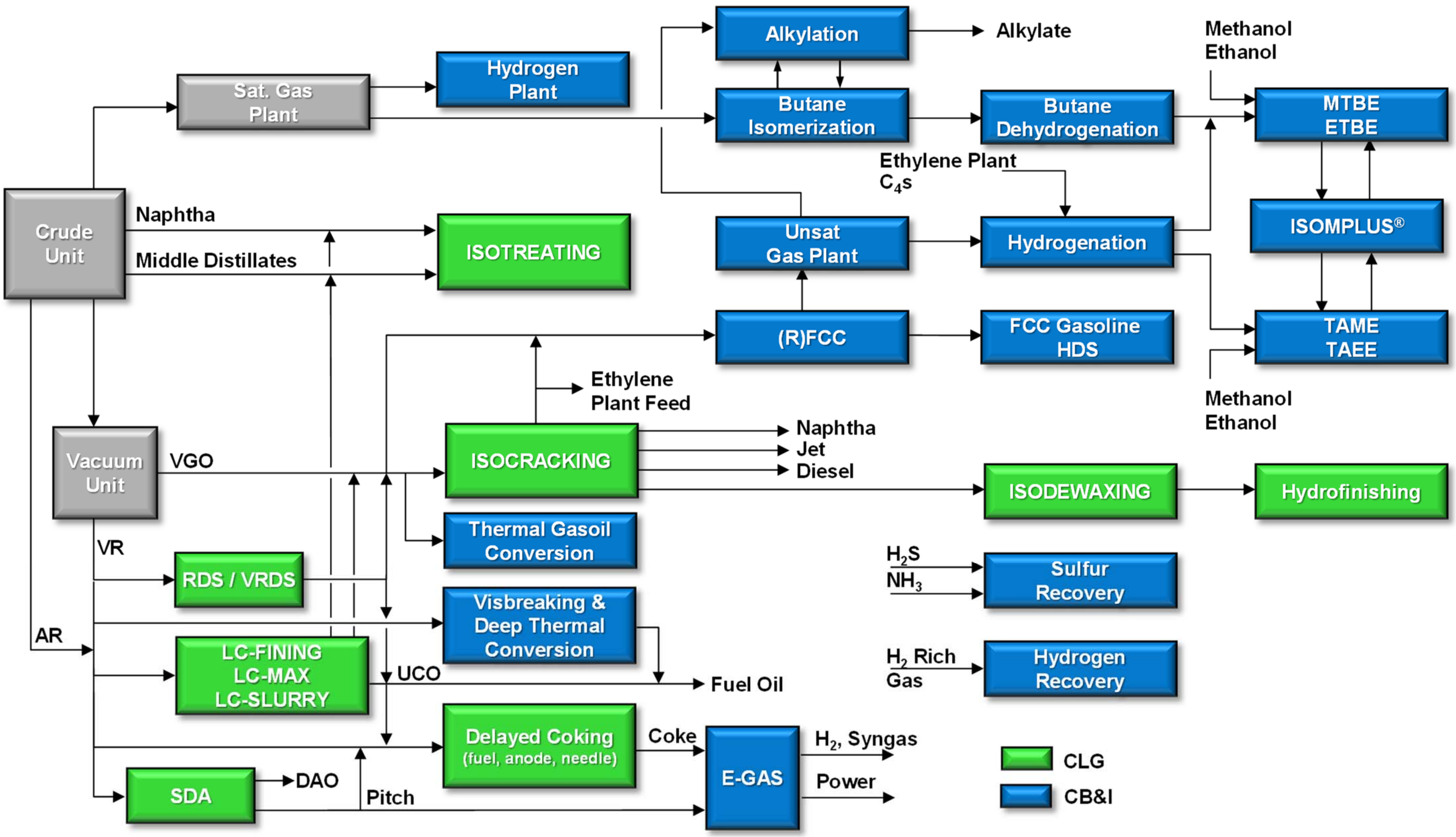
Core Values: Safety, Ethics, Teamwork and Innovation

Lummus Process Technologies



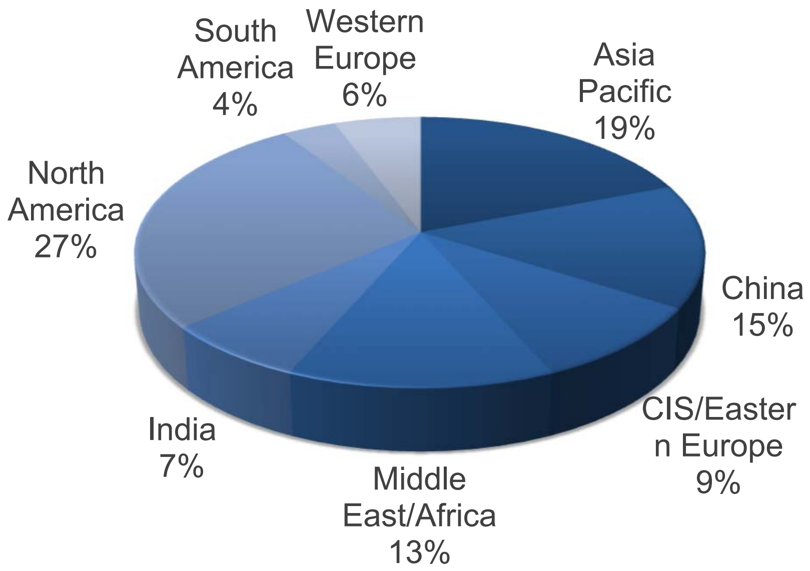
www.CBI.com

Refining Portfolio



Global Technology Awards 2005-2015

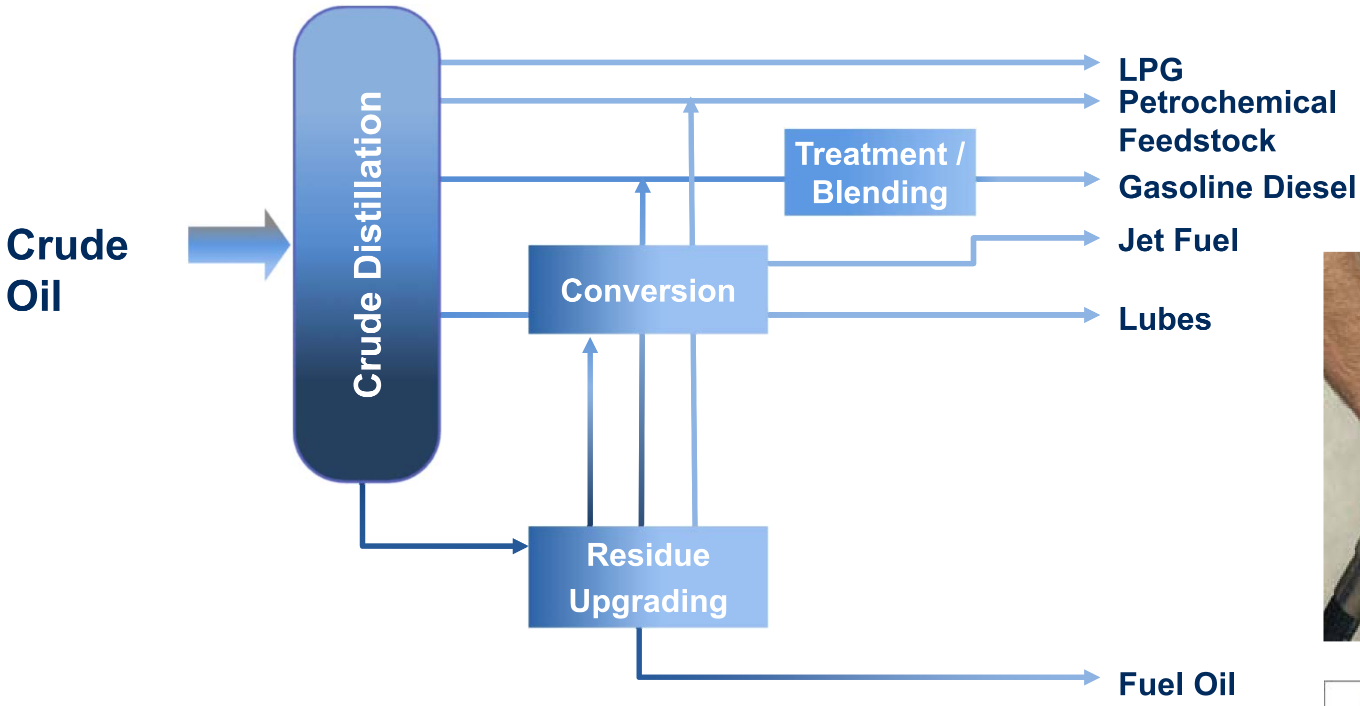
- 2005-2015 Technology Awards



Technology	Awards
Ethylene	39
OCT/CPT	36
MTO/LPR	18
Ethylbenzene/Styrene	19
Butadiene Extraction	24
CATOFIN® Dehydrogenation	15
Cumene/Phenol	6
Polypropylene	19
Other Petrochemical	11
Ethers	19
Gasoline HDS	28
Delayed Coking	23
FCC	36
Alkylation	6
ISOCRACKING®	39
ISOTREATING®	27
Lubes (dewaxing/hydrofinishing)	25
RDS/VRDS/OCR/UFR	18
Visbreaking	15
Other Refining	11
Sulfur	66
Hydrogen	63
Gas Processing	32
Coal/Petcoke Gasification	6

(as of 12/2015)

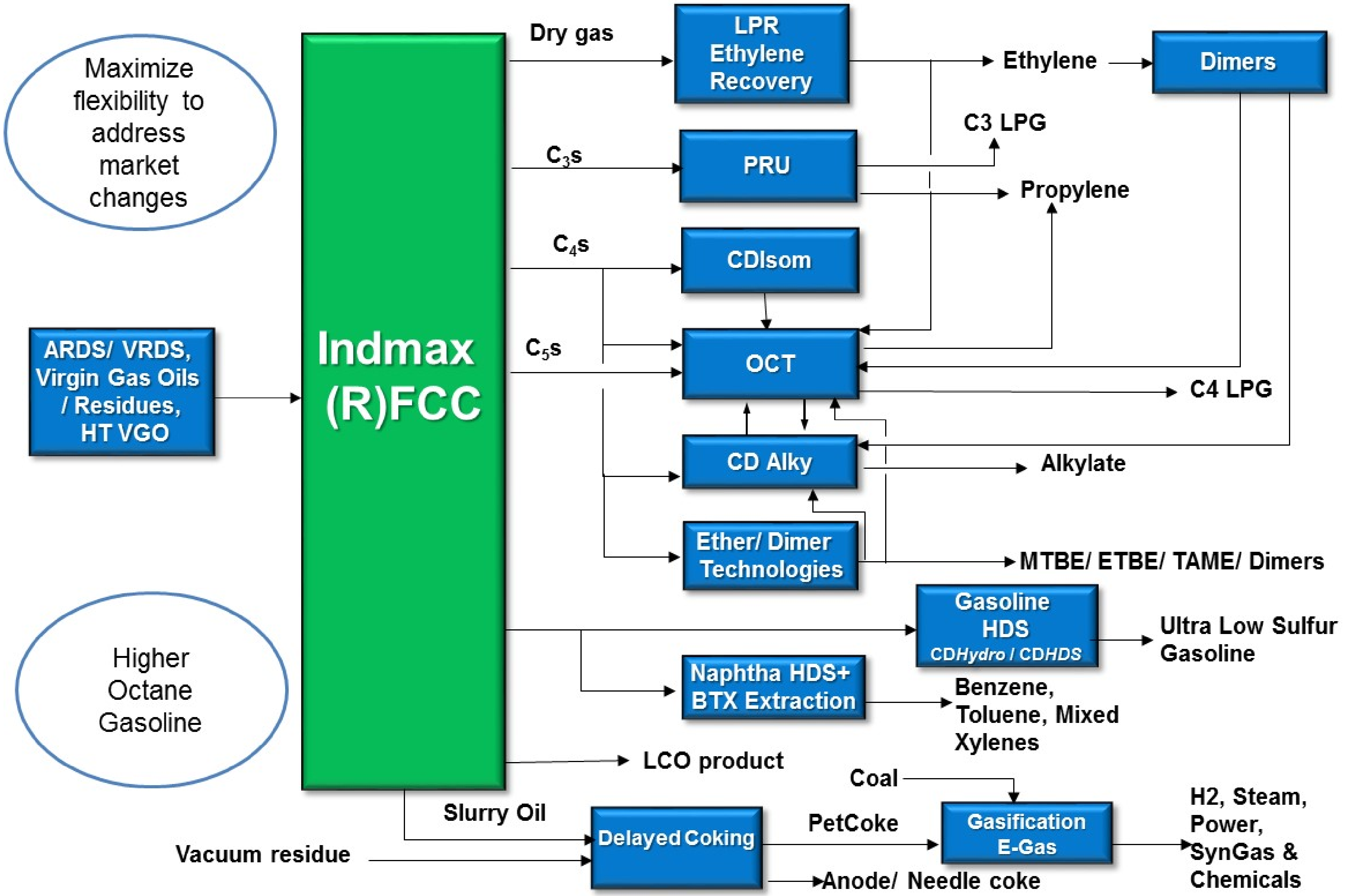
Refining Technologies



Key Technologies

- **Conversion Processes:** Hydrocracking, Fluid Catalytic Cracking (FCC), Alkylation, Dewaxing, Reforming
- **Residue Upgrading Processes:** LC-FINING, Residue Desulfurization, Delayed Coking, Visbreaking
- **Treatment Processes:** Hydrotreating, Hydrodesulfurization (HDS)

CB&I's Innovative Technology Bundling



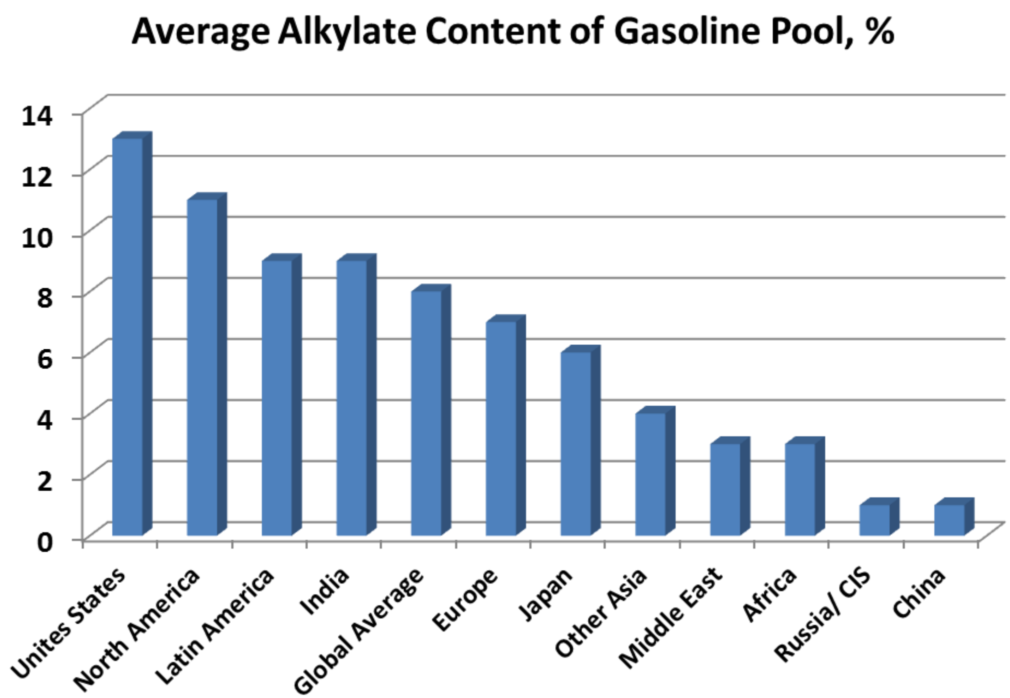
What is Driving the Demand for Octane?

- Global Fuel Demand Increasing, Including Gasoline
- High Octane Components Being Removed from Gasoline Pool
- Tighter Government Mandates
- Higher Performance Engines Requirements
- Overall Octane Deficit

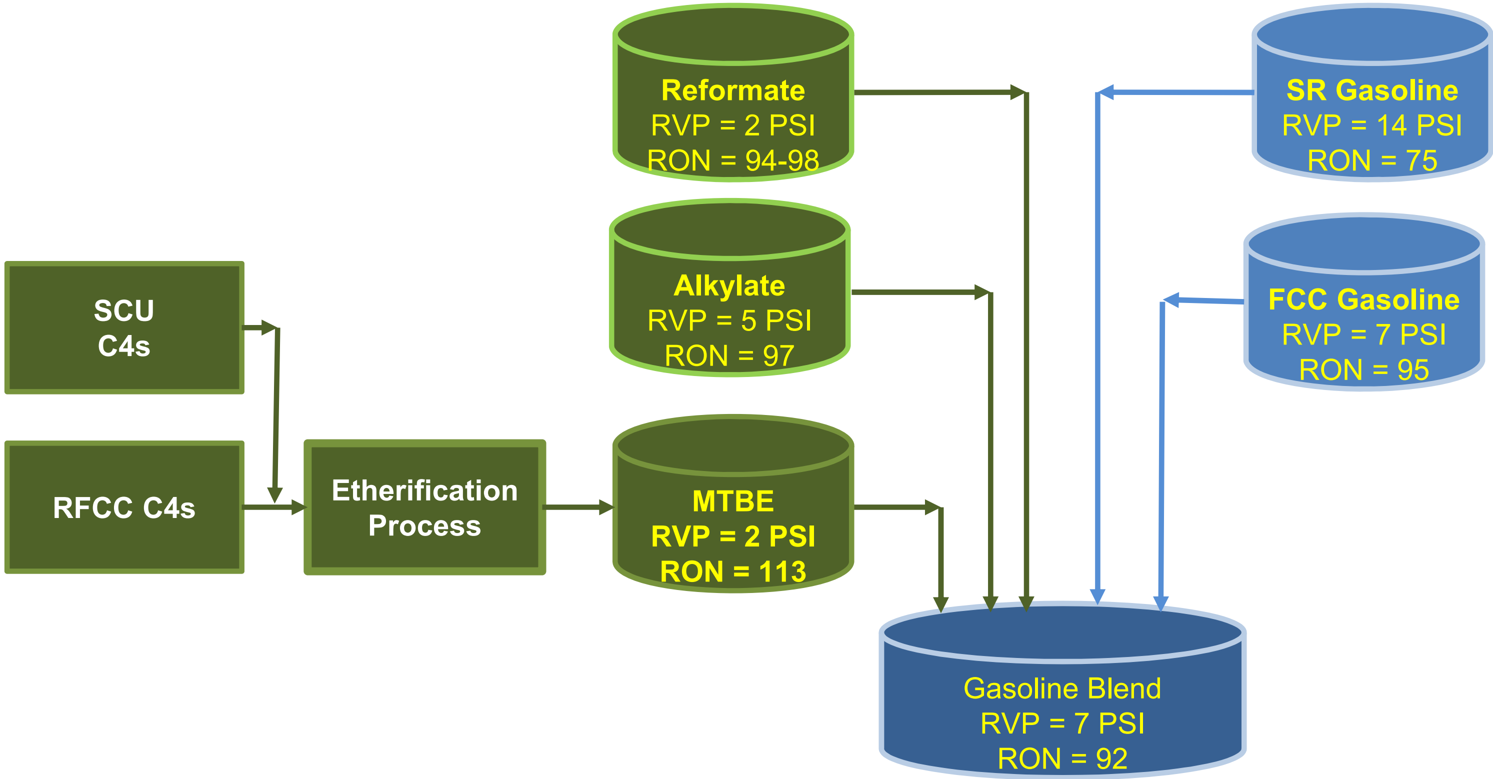
	China V	US Tier 3	California CaRFG3	Euro 5
Sulfur, ppm	10	10	15	10
Olefins, %	24	*10*	4	18
Aromatics, %	40	*25*	22	35
Benzene, %	1	*0.62*	0.7	1
RVP, kPa Winter/Summer	85/65	*7.0 psi ~48 kPa*	7.0 psi ~48 kPa	60
Effective	Jan. 1, 2018	Jan. 1, 2017	Jan. 1, 2012	Jan. 1, 2009

How Do We Address the Octane Balance Competitively?

- Blend options for meeting the octane demand
  - Reformate
    - High aromatics content
    - Associated yield loss at high severity operation
  - Ethers (except US)
    - Acceptable, up to the oxygen content limit
  - Bio-ethanol
  - Iso-octane/ Iso-octene
    - No volume gain on olefin
  - Alkylate
    - The 'Preferred' blend component
    - No olefins or aromatics, low Sulfur, low RVP



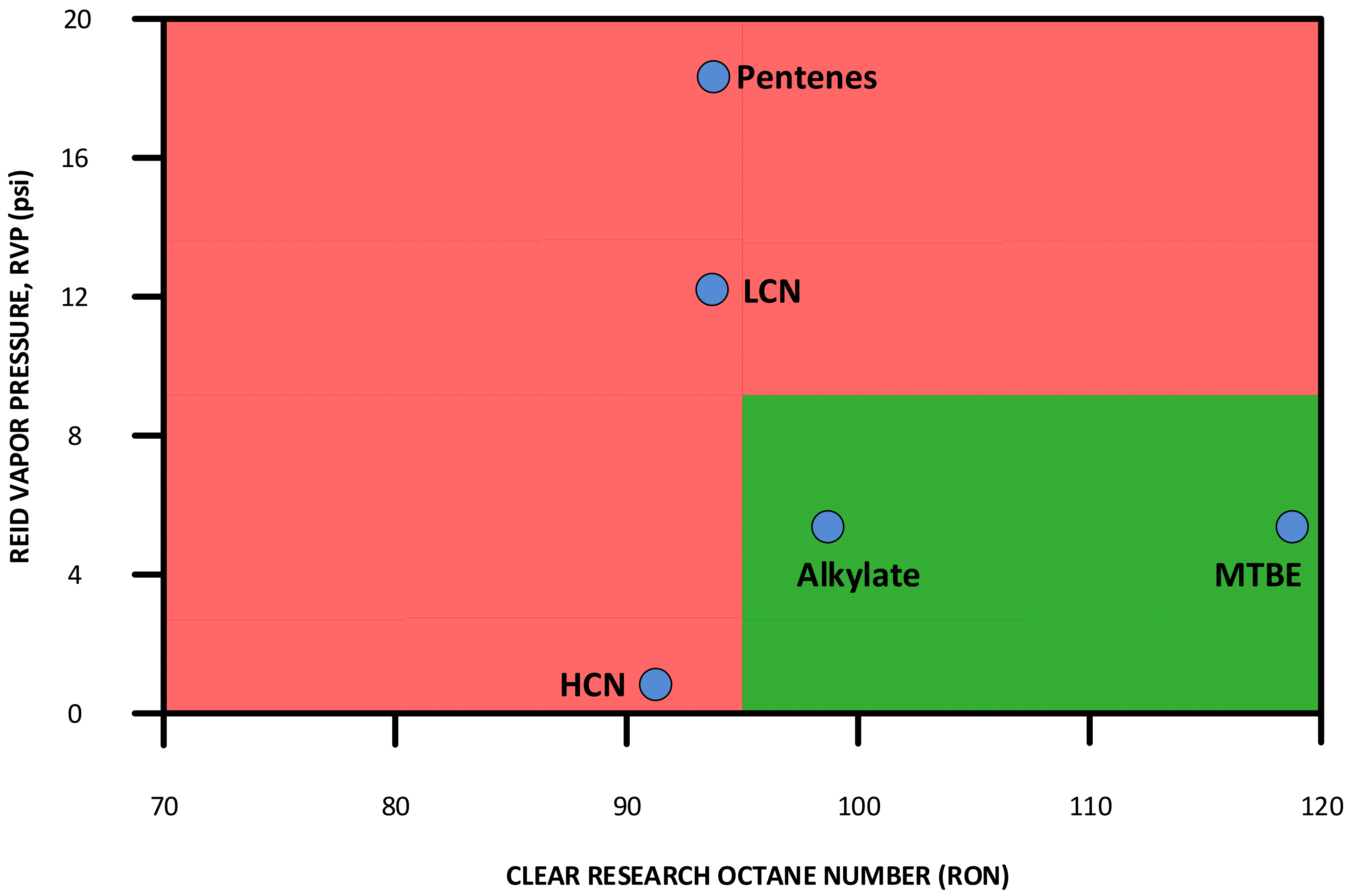
Octane Balance in a Refinery



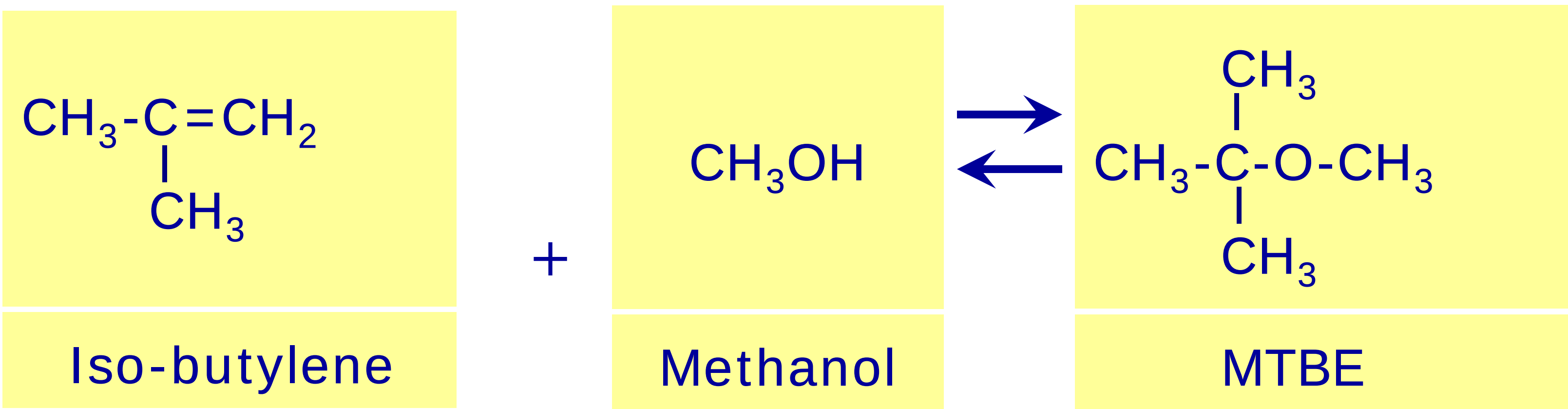
- Octane Loss must be compensated by using higher value octane boosters – reformate, alkylate, MTBE
- Typical value of octane : ~US$ 1 / bbl / octane point
- *Example*:
  - 75,000 BPSD FCC gasoline, 1 RON point octane loss

Cost of 1 RON Point = US$ 23 million, <u>every</u> year

Blending Properties of Some Gasoline Blending Stocks



Main Reaction



CD*Alky* Sulfuric Acid Alkylation Chemistry

- **Primary Alkylation Reaction**

C3 Olefin Alkylation:

iC_4 + C3= → C7 Alkylate

$2iC_4$ + C3= → C3 + C8 Alkylate

C4 Olefin Alkylation:

iC_4 + C4= → C8 Alkylate

2,2,4-trimethylpentane (TMP)	**RON: 100**
2,3,3 TMP	**RON: 106**
2,3,4 TMP	**RON: 109**

C5 Olefin Alkylation:

iC_4 + C5= → C9 Alkylate

$2iC_4$ + C5= → iC5 + C8 Alkylate

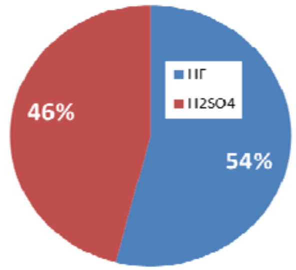
- **Undesirable Side Reactions**
  - **Polymerization** — $xC_4H_8 \rightarrow C_{4x}H_{8x+2}$
  - Hydrogen Transfer — $2\ iC_4H_{10} + C_5H_{10} \rightarrow C_8H_{18} + C_5H_{12}$
  - Disproportionation — $2\ C_8H_{18} \rightarrow C_7H_{16} + C_9H_{20}$
  - Cracking — $C_xH_{2x+2} \rightarrow C_yH_{2y} + C_{x-y}H_{2(x-y)+2}$
  - Contaminants, i.e., Oxygenates, Butadiene, Mercaptans, Aromatics
- **By-Products**
  - Acid Soluble Oil (ASO)
    - Esterification — $C_4H_8 + H_2SO_4 \rightarrow$ MBS mono-butyl sulfate
      2 MBS $\rightarrow H_2SO_4 +$ DBS di-butyl sulfate
    - **Polymerization** — $xC_4H_8 \rightarrow C_{4x}H_{8x+2}$
  - SO2 — $H_2SO_4 + C_xH_y\ (ASO) \rightarrow 2H_2O + SO_2 + C_xH_{y-2}$

➢ **Strategy:** **Minimize undesirable side reactions with Colder Reaction Temperatures**

For C4= & C5= operating at LOW TEMPERATURE is even more CRITICAL!

Traditional Commercialized Alkylation Options

- **HF Alkylation**
  - High quality alkylate, low acid consumption, good feedstock flexibility
  - Extremely hazardous; not preferred anymore
  - Some refiners are considering shutting down existing units due to risk profile
  - Public pressure is growing due to safety and environmental risks



World's Alkylation Capacity

- **Sulfuric Acid (SA) Alkylation**
  - The alkylation technology of choice for refiners at this time
  - Currently the best choice in balancing the safety/operability issues with benefits of high quality alkylate (particularly at low temperatures)
  - **CD*Alky*®** has become the technology of choice for sulfuric acid alkylation

CD*Alky* Commercial Experience

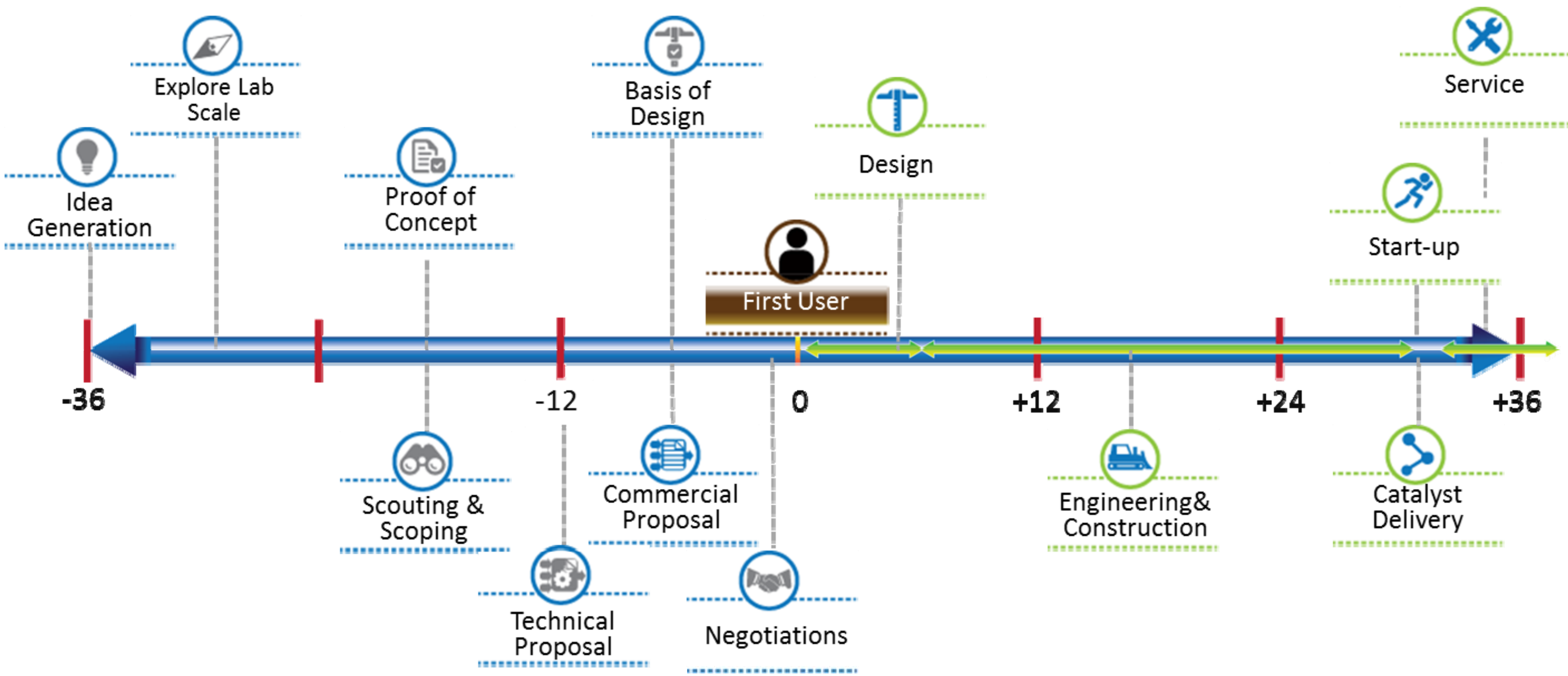
- **CD*Alky*® Has Become the Alkylation Technology of Choice:**
  - **~120 kBPD Alkylate Capacity by 2020**

Licensee	Capacity		Start-up	Awarded	Feedstock
	BPD	KTA			
Sincier, PRC (1)	5,000	200	2013	2012	C4 Raffinate
Haiyue, PRC (1)	15,000	600	2014	2011	C4 Raffinate
Tianheng, PRC (1)	5,000	200	2014	2012	C4 Raffinate
YuTianHua, PRC	6,800	265	2017	2014	C4 Raffinate
S-Oil, Korea (2)	16,000	624	2018	2014	C4s
Pertamina, Indonesia (2)	7,400	290	2019	2016	FCC C4s
Undisclosed, USA (2)	23,000	900	2020	2016	FCC C5s
Zhejiang Pet. Co. (ZPC), PRC	14,000	555	2018	2016	C4 Raffinate
Yanchang, PRC	5,000	200	2019	2016	C4 Raffinate
PetroChina Location 1, PRC	12,000	420	2018	2017	C4 Raffinate
PetroChina Location 2, PRC	5,000	200	2018	2017	C4 Raffinate
PetroChina Location 3, PRC	6,500	250	2018	2017	C4 Raffinate

Footnotes: (1) Exceeded all performance guarantees
(2) Operate conventional sulfuric acid alkylation unit

One of the top 5 finalists for the 2015 Kirkpatrick Chemical Engineering Achievement Award

Development Timeline – Looking ahead 5-7 years



Emerging Commercialized Alkylation Options

- **Ionic Liquid (IL) Alkylation**
  - Ionic Liquid alkylation was commercialized in a 100 KTA unit in China (2013)
  - Potentially removes some of the safety and hazard issues:
    - This needs to be confirmed particularly in co-catalyst preparation
  - Capital intensive: $130 MMUSD for 100 KTA (complex IL/HC separation)
  - High utility consumption: 50% more than sulfuric acid alkylation
  - Chlorides in the alkylate product: Post-treatment unavoidable
  - Reported alkylate quality value falls short of a technology breakthrough

- **Solid Acid Catalyst Alkylation**
  - Inherently safer than liquid acid technologies, particularly HF
  - Optimized for low to average alkylate capacities
  - CB&I and Albemarle successfully commercialized the first solid acid alkylation technology in China in 2015 using AlkyClean® technology (capacity 2,700 BPD)
  - AlkyClean technology is the first and only commercialized solid acid alkylation technology in the world

ALBEMARLE®

- **Challenges with HF Alkylation Units**:
  - – Safety issues
  - – Environmental issues
  - – Operational issues

- **Revamps & Grassroots Solution offered by CB&I and Albemarle** :

  An environmentally friendly and competitive Solid Acid Catalyst technology to replace HF alkylation technology: *AlkyClean*

HF Alkylation

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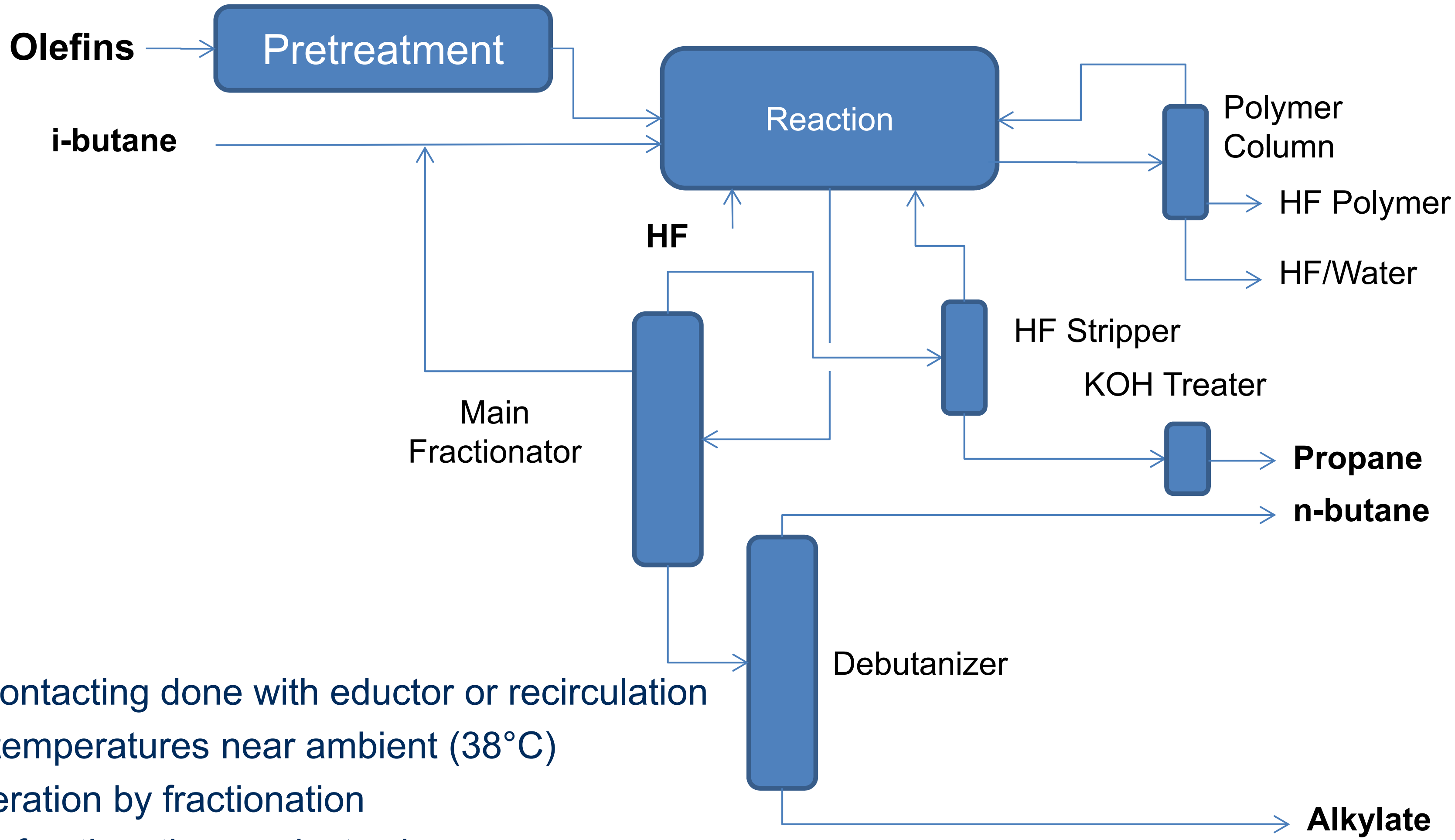

- Acid/HC contacting done with eductor or recirculation
- Reaction temperatures near ambient (38°C)
- HF regeneration by fractionation
- Numerous fractionation product schemes
- Product and by-product clean-up required

HF Alkylation: Safety Issues

Incident at Gumi, S-Korea

- September 27, 2012
- Unloading of HF to Storage Tank
- 5 people died
- 18 people injured
- > 3000 people evacuated
- Difficult to approach
- Difficult to decontaminate
- Agricultural damage
- Vehicle damage
- Livestock affected

HF Alkylation: Environmental Issues

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- Avoiding HF Release
- Minimizing HF Handling:
  - Transportation
  - Storage/Inventory
  - Regeneration
- Minimizing Waste Disposal
- Minimizing Impact of Other Refinery Units Incidents:
  - Potential major impact
  - Torrance refinery

➢ **Costly & Continuous Mitigation Required**

HF Alkylation: Operational Issues

- Inherent Drawbacks of HF Alkylation:
  - Expensive materials used to avoid/minimize corrosion
  - Corrosion, Plugging likely in isoStripper due to HF breakthrough
  - Breakthrough of HF with products/by-products
  - Post-treatment of products required
- Maintenance & Turnaround:
  - Frequent turn-around needed
  - Time on stream reduced significantly
  - Safety Risks
- Production:
  - Yield Loss due to the production of Acid Soluble Oil (ASO)
- Operability:
  - Operation more difficult compared to other refining units

ALBEMARLE®

- Commercially proven with over 1 year of successful operation
- Inherently Safer and Environmentally Friendly
  - No liquid acid used in the process
  - No corrosion
  - No safety risks through exposure
- Significant Operational Risks Reduction
  - Eliminate HF safety risks
- Very Easy to Maintain and Operate
  - Simple & robust operation: Fixed beds
  - No corrosion
- High Product Quality
  - Higher octane alkylate
  - No Acid Soluble Oil

AlkyClean Process Simplified Block Flow Diagram

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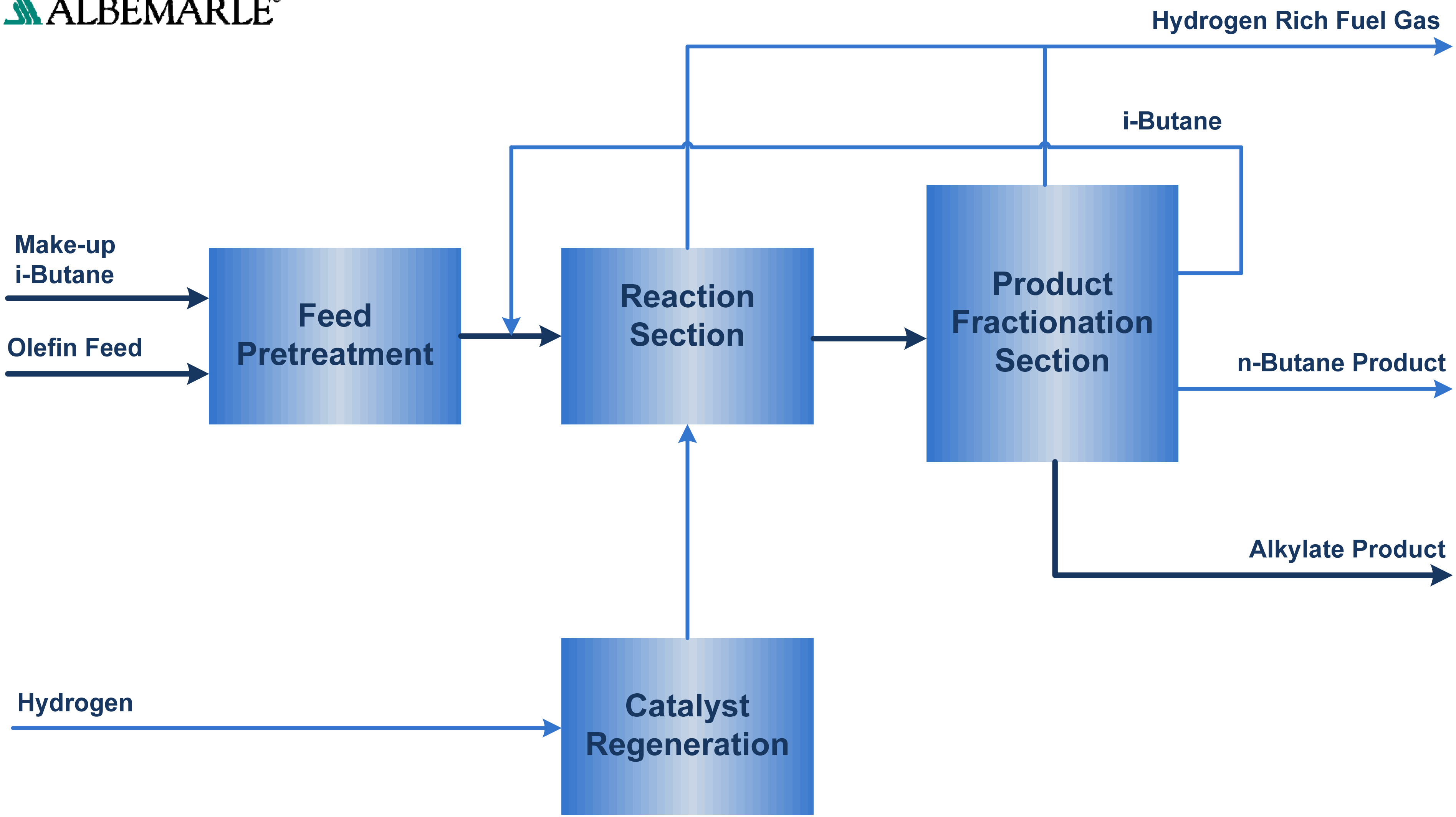

AlkyClean Differentiators

- **Only** Solid Acid Alkylation Process **Commercially Proven**
- Catalyst Supplier Albemarle:
  - Leader in catalyst manufacturing
  - Leader in catalyst development
- Optimized Catalyst Regeneration System:
  - Longer catalyst cycle/life
- Tolerant to Feed Contaminants by Design
  - Process design
  - Catalyst

ALBEMARLE®

- Reactor Type: Fixed Bed Reactor …
  - Well Know & Easy to Operate
- Catalyst Type: AlkyStar™
  - Zeolite Based Catalyst
  - Noble Metal Function
- Catalyst Regeneration Scheme: Maintain Catalyst Activity…
  - Regular & Cyclical at the Alkylation Conditions
  - Occasional Regeneration at Higher Temperature

AlkyClean Development – A Brief History

ALBEMARLE®

- **CB&I and Albemarle Catalysts**:
  - Cooperation since 1996
  - Bench scale pilot unit in Amsterdam

- **First Licensee : Shandong Wonfull, Zibo, China**
  - 100 KTA alkylate capacity
  - CB&I executed process design package in 2013
  - Start-up: August 2015

- **AlkyClean Awards**
  - 2016 Presidential Green Chemistry Award from the U.S. EPA

AlkyClean References: Shandong Wonfull, Zibo, China

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Shandong Wonfull Specifics

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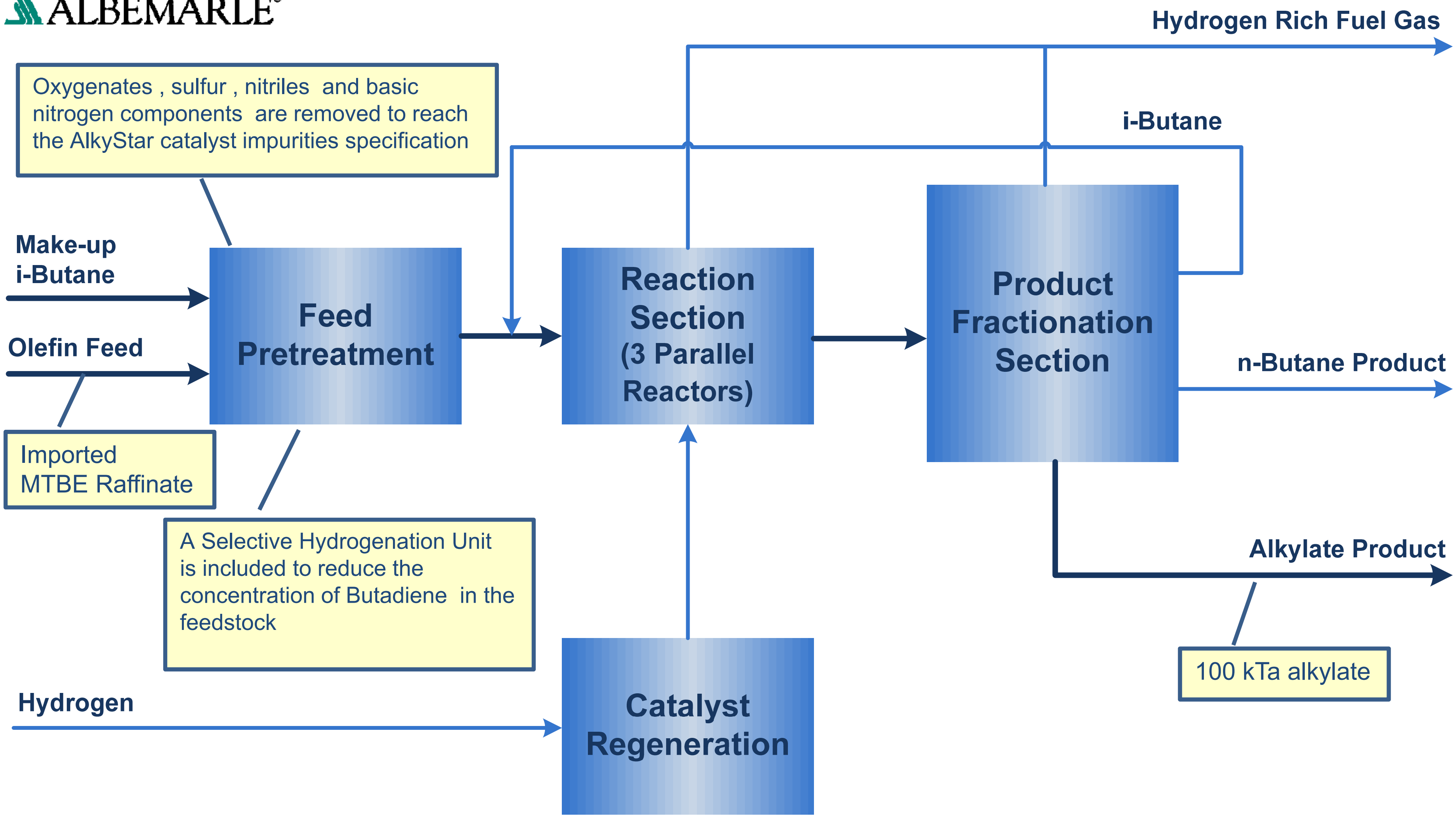

Reactor Regeneration Optimization

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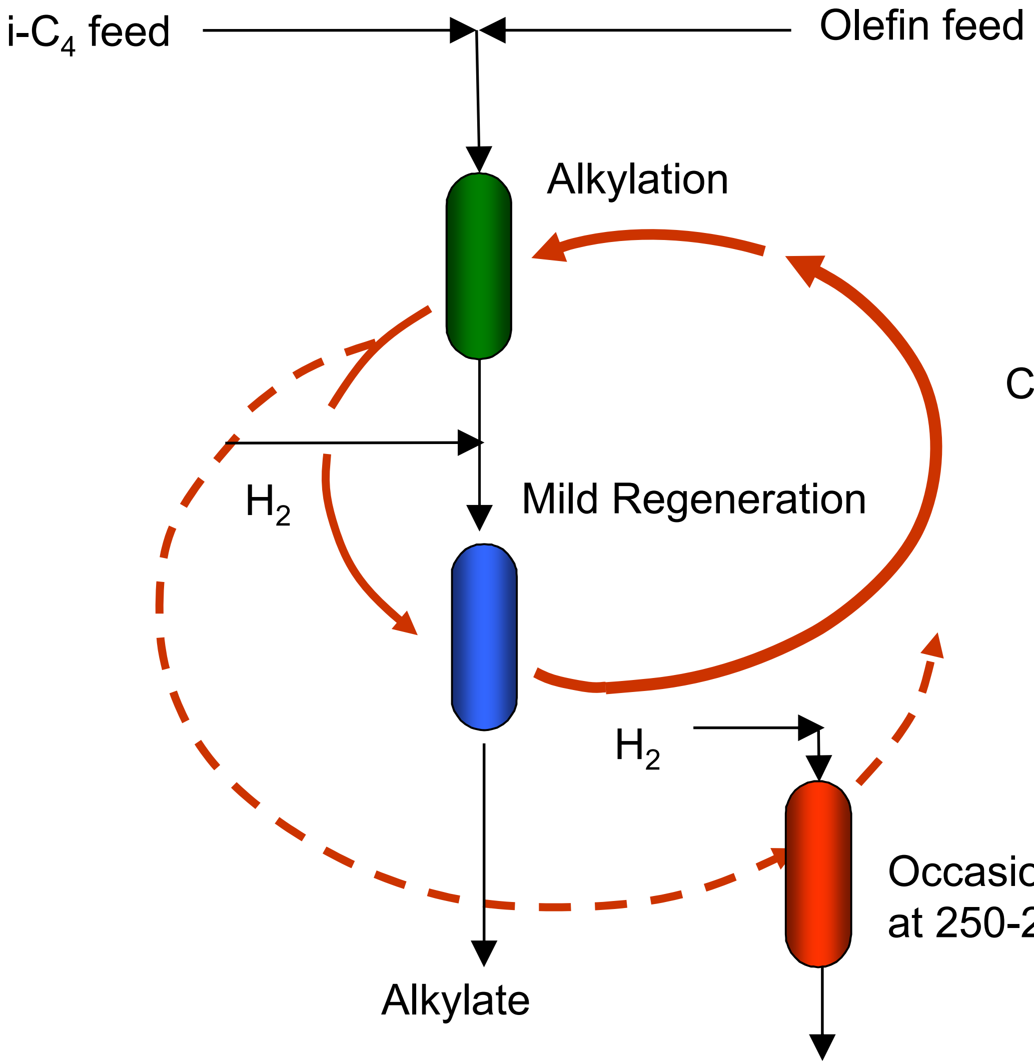


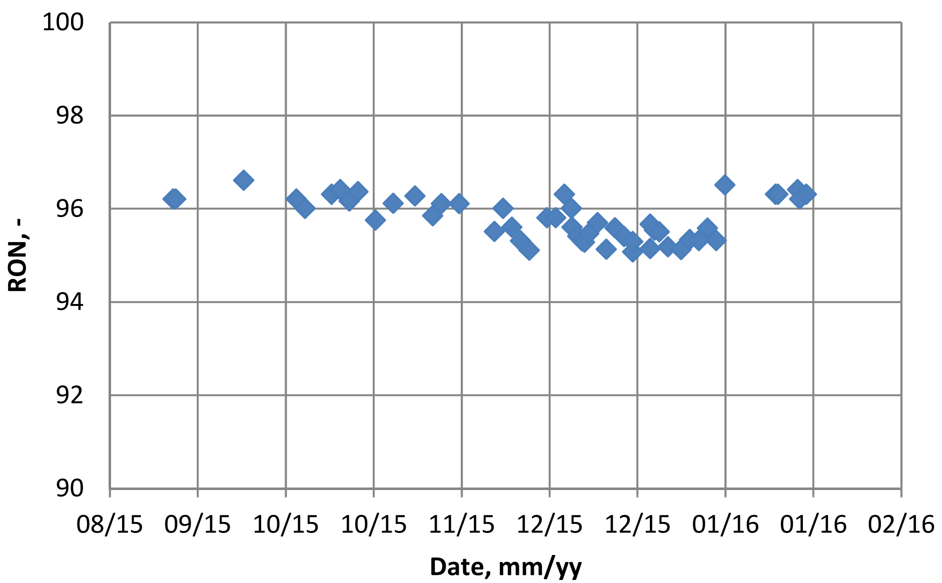
Continuous Operation at 50 to 90°C

Occasionally H_2 Regeneration at 250-275°C

Shandong Wonfull: AlkyClean Product Quality

ALBEMARLE®

RON	95-97
Sulfur	< 1 ppm
RVP	< 50 kPa
ASTM D-86 FBP	< 208°C



Feedstock / Operating Conditions Comparison

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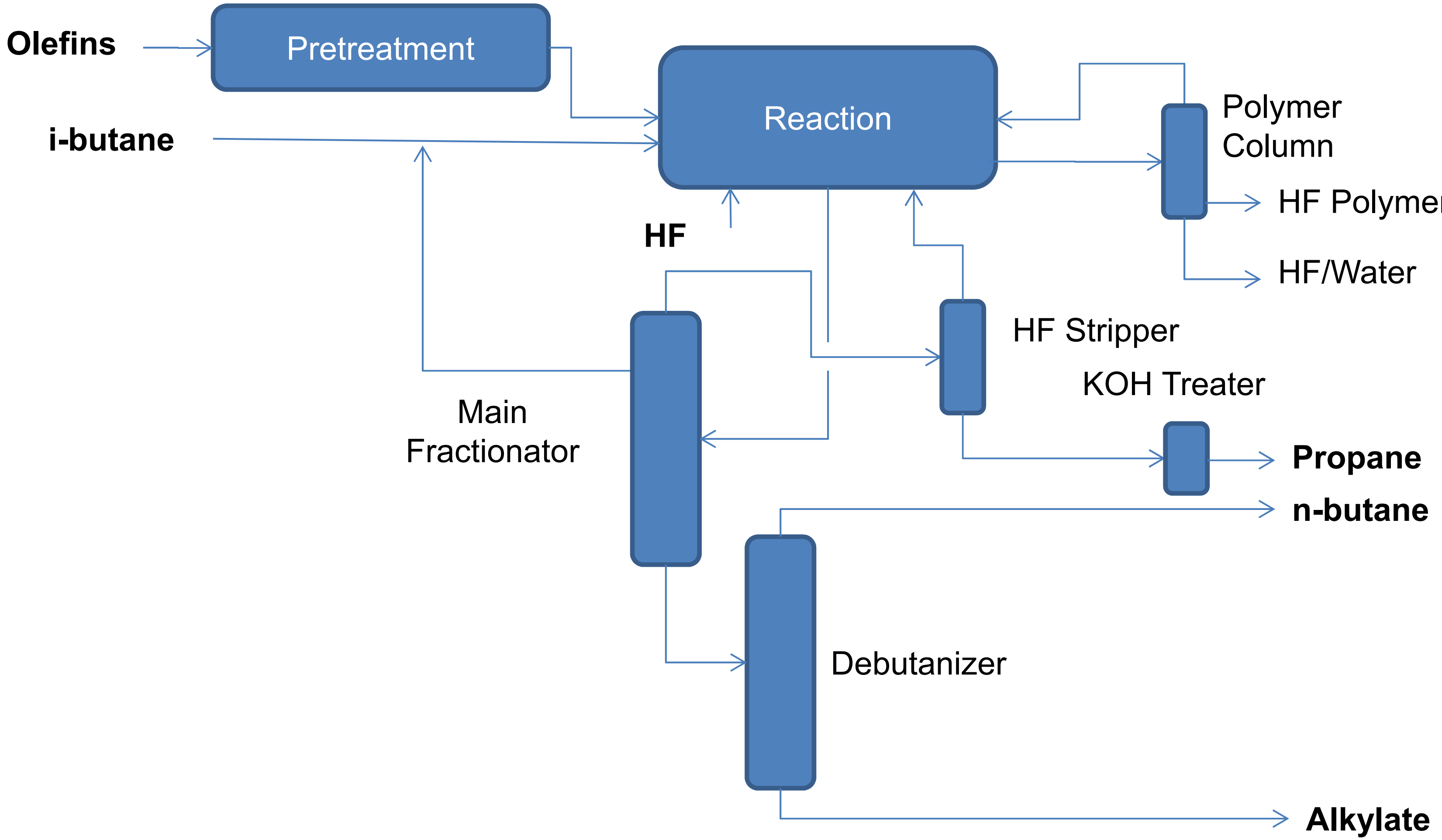
Operating Conditions Comparison			
	AlkyClean	HF Acid	Sulfuric Acid
Operating Temperature, °C	50-90 °C	32-38 °C	-3 - 10 °C
Feed I/O (External)	15 - 20 / 1	12 - 15 / 1	8 - 10 / 1

Feedstock olefin variation sensitivity			
	AlkyClean	HF Acid	Sulfuric Acid
Butene-2	Base	Base	Base
Butene-1	Base	Base - 4.0 RON	Base
Iso-Butene (25 vol%)	Base - 0.5 RON	Base - 0.5 RON	Base - 1.0 RON
Propylene (30 vol%)	Base - 1.0 RON	Base - 1.0 RON	Base - 1.5 RON


Olefins
Pretreatment
i-butane
Reaction
Polymer Column
HF Polymer
HF/Water
HF
HF Stripper
KOH Treater
Main Fractionator
Propane
n-butane
Debutanizer
Alkylate

- Feed Pretreatment requirements similar

Feed Pretreatment Requirements		
	HF Alkylation	**AlkyClean**
Mercaptan Removal	Recommended	Recommended
Water Removal	Recommended	Recommended
Selective Hydrogenation	Recommended	Recommended
Hydro-Isomerization	Recommended	Not Needed

- ➢ Feed Pretreatment section can be reused
- ➢ If Hydro-Isomerization function exists, catalyst cost is reduced

- Differences between HF Alkylation and AlkyClean

Reaction Condition Comparison		
	HF Alkylation	**AlkyClean**
Reaction Temp	Ambient	50 - 90 °C
Heat Removal	Cooling Water	Cooling Water
Acid/Hydrocarbon contacting/separation	Required	Not Applicable
Acid volume	Required	Not Applicable

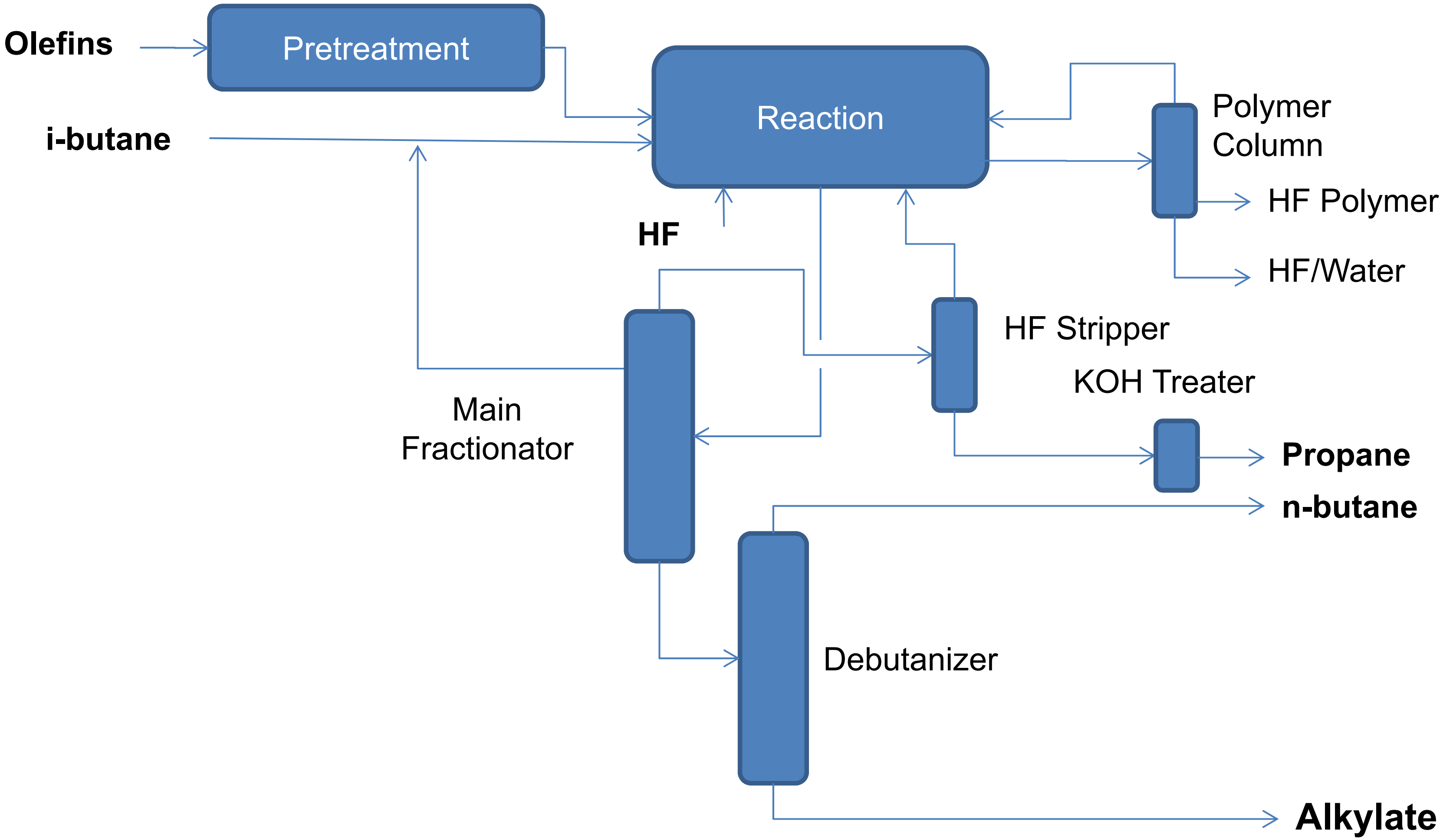
➢ Reaction Section replaced by AlkyClean reactors and associated equipment

HF Alkylation Revamp to AlkyClean: Fractionations & Treaters

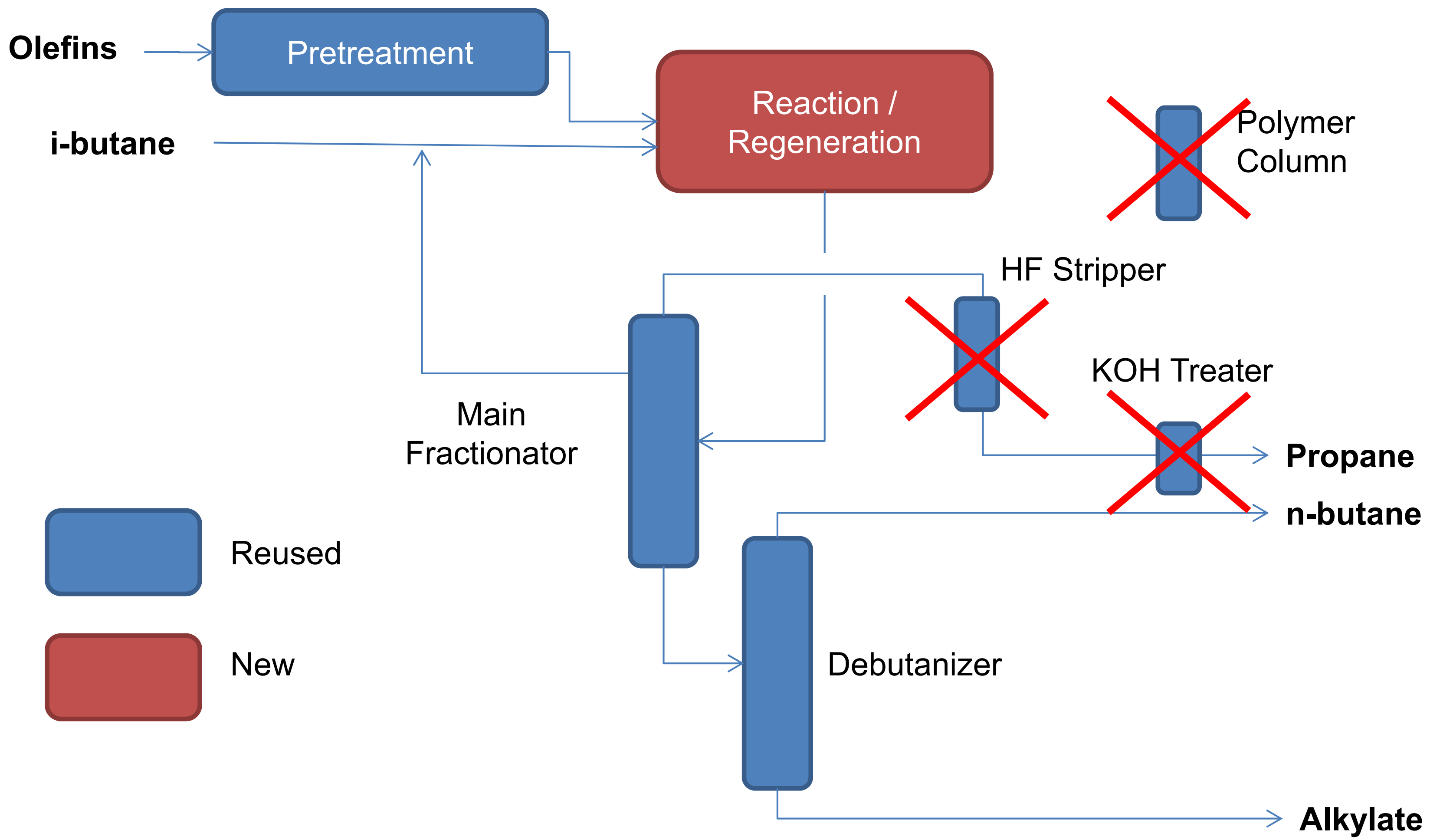
- HF IsoStripper:
  - Slightly Lower I/O ratio: 12-15 vs. 15-20
  - IsoStripper Trays may be replaced-High Capacity Trays

- HF Product Treaters:
  - HF Stripper is not required
  - KOH Treater is not required

- HF Regeneration:
  - HF polymer (rerun) column is not required


Olefins
Pretreatment
i-butane
Reaction
Polymer
Column
HF Polymer
HF/Water
HF
HF Stripper
KOH Treater
Main
Fractionator
Propane
n-butane
Debutanizer
Alkylate

AlkyClean® Revamp



- Feed Pretreatment Section: **Reuse**
- HF Regeneration Section: **Decommission HF polymer (rerun) column**
- HF Reactors Section: **Decommission Reactor Section to AlkyClean Reactors**
- HF Product treaters: **Decommission HF Strippers & KOH Treaters**
- HF Alkylate Fractionation: **Reuse and/or Revamp**

HF Alkylation Revamp to AlkyClean: Incentives

ALBEMARLE®

• Safety:	**Peace of Mind**
• Product quality:	**Higher**
– No ASO = Higher Yield	
– Higher RON, due to insensitivity for Butene-1	
– Impact of products on downstream units	**None**
• Continuous cost of HF mitigation:	**Eliminated**
• Maintenance Cost:	**Eliminated**
– No replacement of expensive materials	
– No corrosion issues	
– Less frequent shutdowns & turn around	
• Operating costs:	**Similar**
– Catalyst instead of HF acid processing	

Conclusions

ALBEMARLE®

- CB&I and Albemarle Successfully Developed & Commercialized **The World's First Solid Catalyst Alkylation Process: AlkyClean**
- AlkyClean Technology is **Proven** & **Demonstrated**:
  - **High Alkylate Product Quality**
  - **Economically Viable**
- Can easily Revamp HF Alkylation Units to AlkyClean
- AlkyClean Process Utilizes a Commercialized **Solid Acid Catalyst**, and therefore:
  - Is an Inherently **Safer** Alkylation Technology
  - Releases Refiners of **HF Safety**, **Environmental** and **Operational** issues
  - Provides Refiners with **Peace of Mind**