EUROPEAN ETHYLENE PRODUCERS COMMITTEE

NEW TRENDS IN OLEFIN PRODUCTION

Prof. Kevin M. Van Geem

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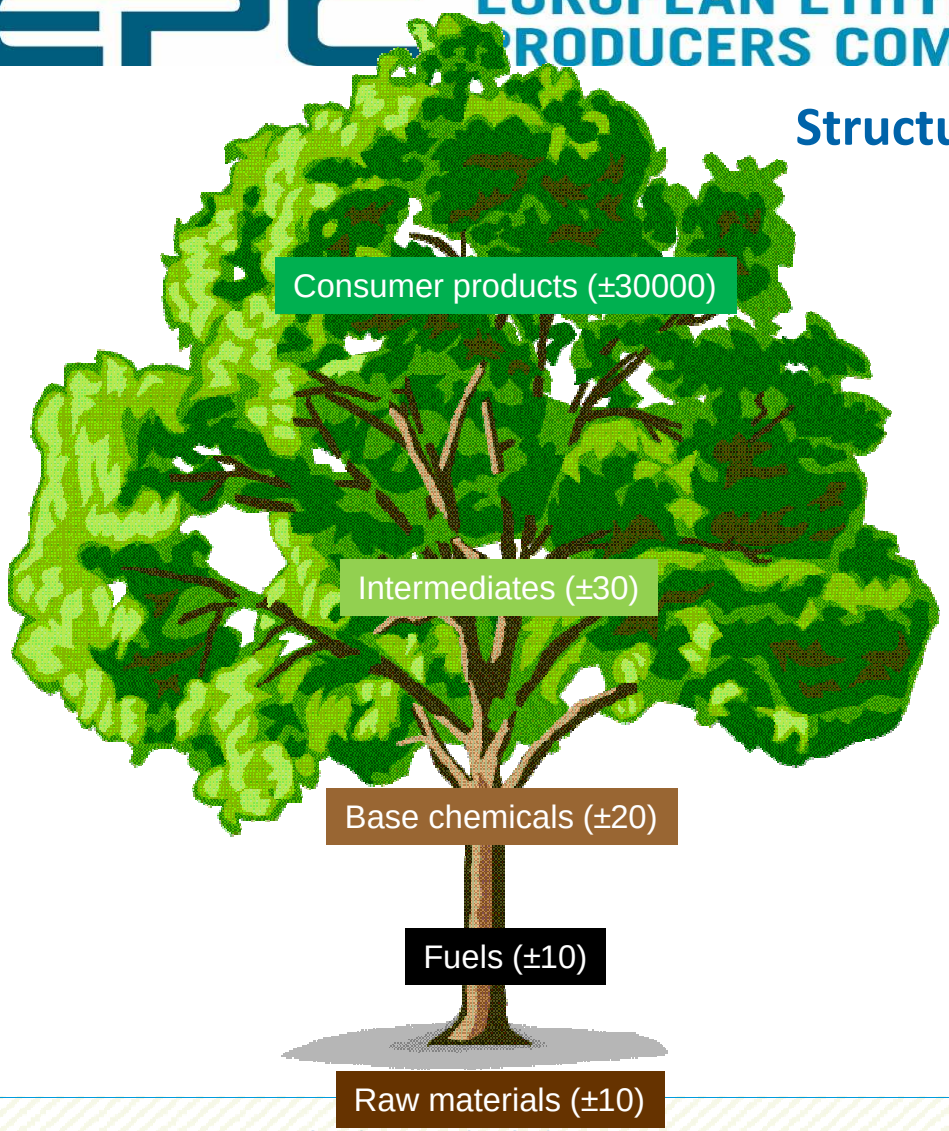
Structure of the chemical industry: chemistree



Plastics, electronic materials,
Fibers, solvents, detergents,
insecticides, pharmaceuticals

Acetic acid, formaldehyde,
Urea, ethene oxide,
Acrylonitrile, acetaldehyde,
Terephtalic acid

Ethene, propene, 1,3-butadiene,
Benzene, synthesis gas, ammonia
Methanol sulfuric acid, chlorine

LPG, gasoline, diesel
Kerosene

Oil, natural gas, coal, biomass,
Rock, salt, sulfur, air, water

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Emerging Technologies for Olefins Production [Synthesis]

Article 87B

EPC 2000

Robert Gartside
ABB Lummus Global Inc.

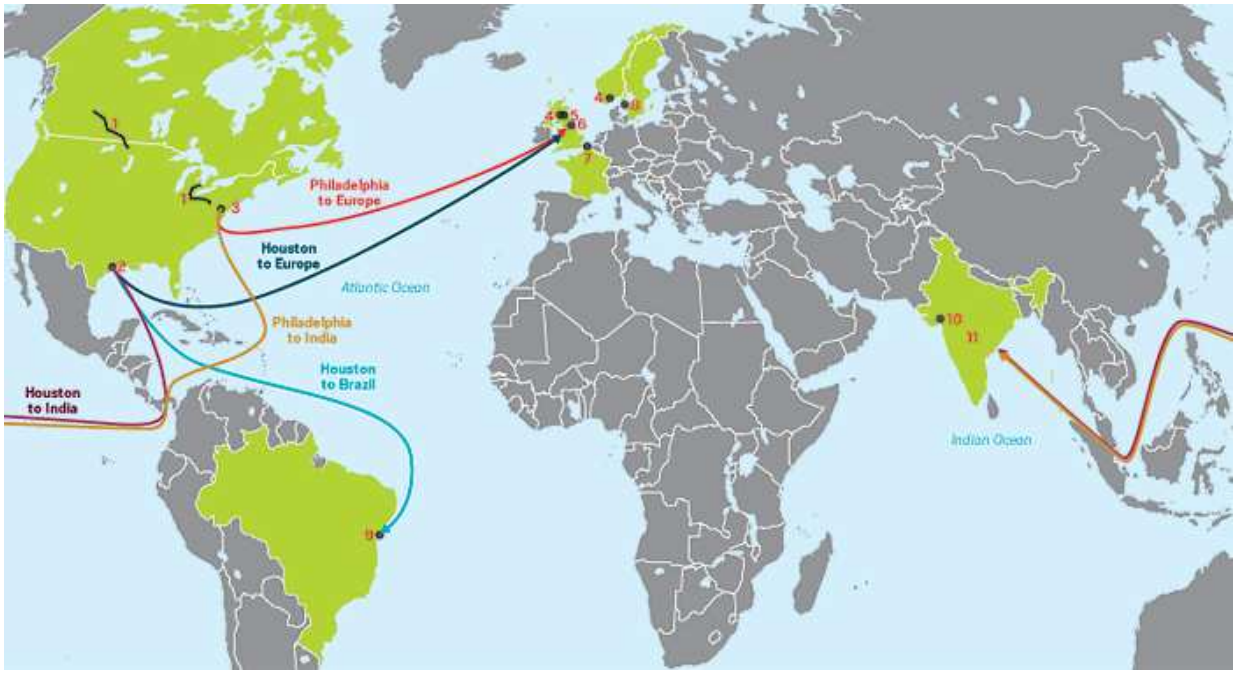
Thomas McCall
Kellogg Brown & Root

Eric Wagner
Technip USA Corporation

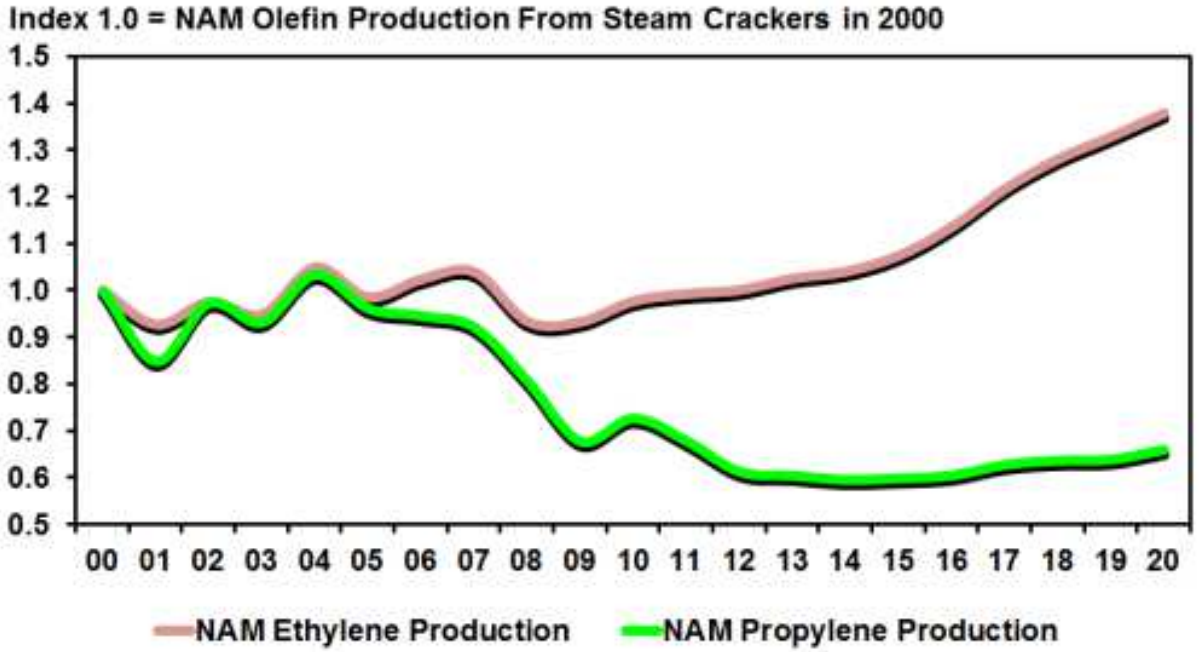
Mark Whitney
Stone & Webster Engineering Company

SHALE GAS

New Trends in Olefin Production
Ismaël Amghizar Laurien A. Vandewalle Kevin M.Van Geem Guy B.Marin
Engineering
Volume 3, Issue 2, April 2017, Pages 171-178



WHAT ABOUT PROPYLENE?



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HOT TOPIC

THE GREAT GAS GOLD RUSH

Cheap and abundant shale gas is changing how the chemical industry makes the ingredients of modern life. Chemists want to ensure that it's change for the better.

BY MARK PEPLOW

As the *Ineos Intrepid* cruised slowly through the sapphire waters of Norway's Frierfjord, chaperone tugboats sprayed jets into the sky to herald her arrival. In giant refrigerated tanks below decks, the ship carried 27,500 cubic metres of liquid ethane — enough to fill 11 Olympic swimming pools. *Intrepid* also brought a message, painted in giant capital letters along her side: "SHALE GAS FOR PROGRESS".

The vessel's arrival in March 2016 brought the first ever shipment of shale gas from the United States to Europe — and marked the start of a burgeoning business. More of these 180-metre-long 'Dragon'-class vessels have followed in her wake, forming a 'virtual pipeline' for ethane across the Atlantic Ocean. This gas, which is extracted from the ground through the hydraulic fracturing of shale deposits, isn't destined to fuel power stations or domestic stoves. Instead, it will be transformed into the chemical building blocks needed to make a panoply of products, including plastics, clothes, adhesives and medicines.

Intrepid's voyage is a striking demonstration of how cheap US shale gas is reshaping the chemical industry and changing the origin of

The *Ineos Insight*, carrying US shale gas, approaches port in Scotland in September 2016.

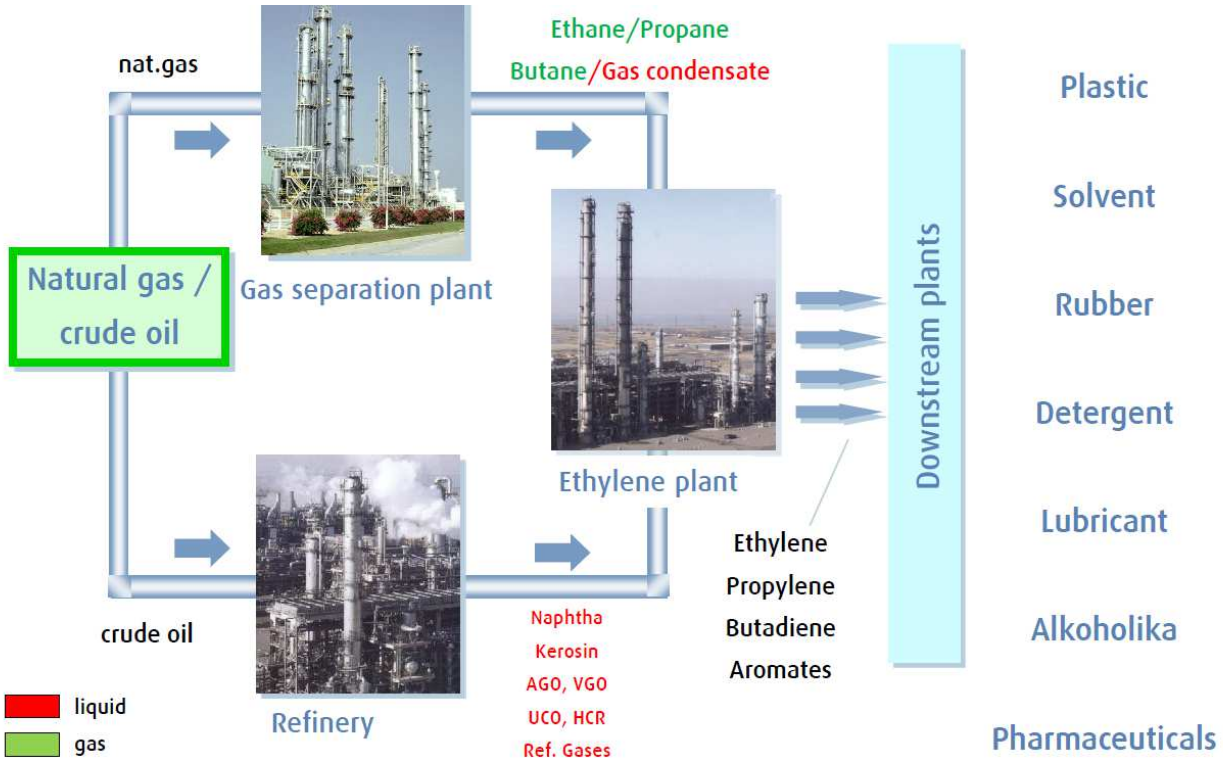
JEFF J MITCHELL/GETTY

Presentation outline

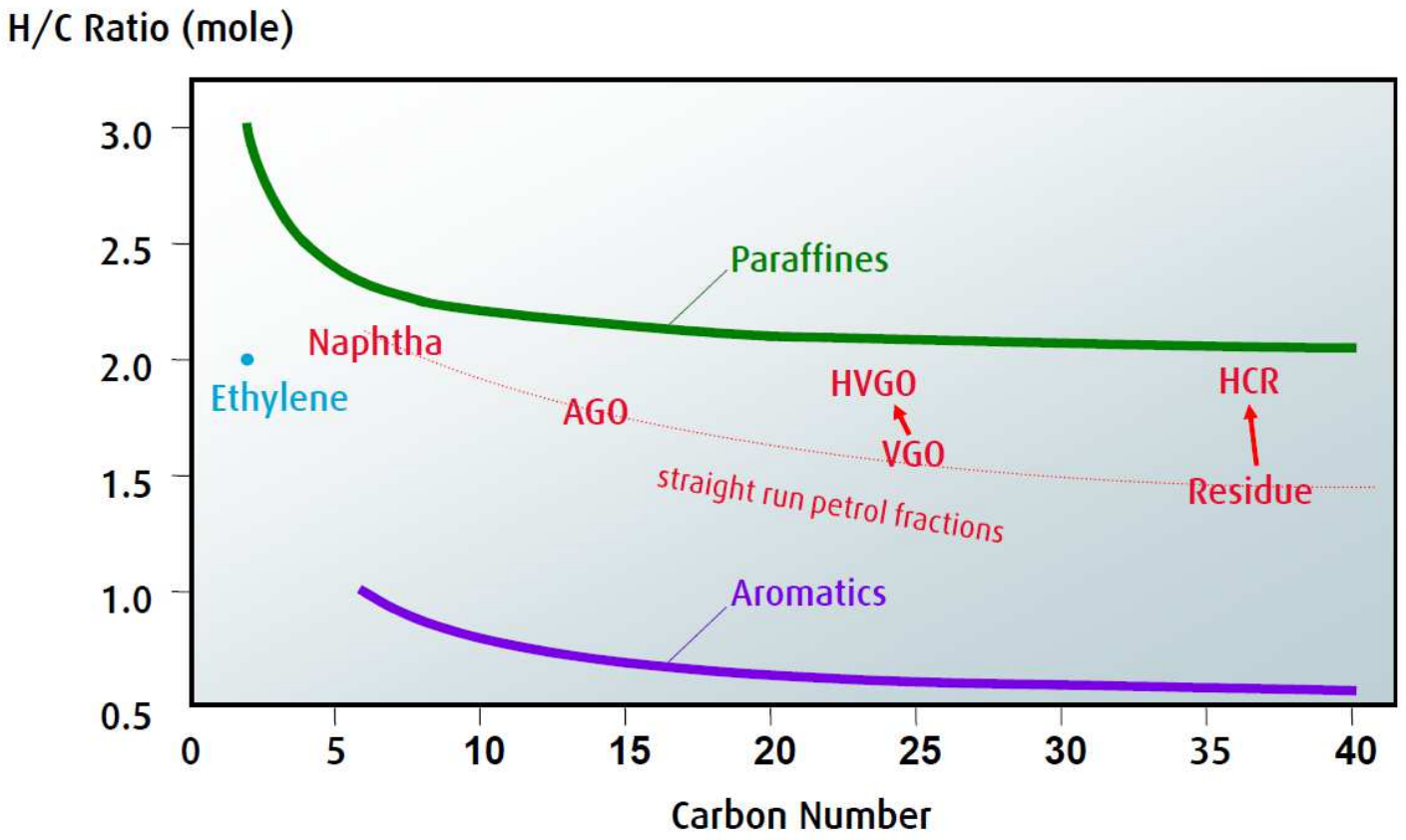
New trends in olefin production

1. Production technologies for olefins
2. How mature is steam cracking?
3. Electrification of the chemical industry

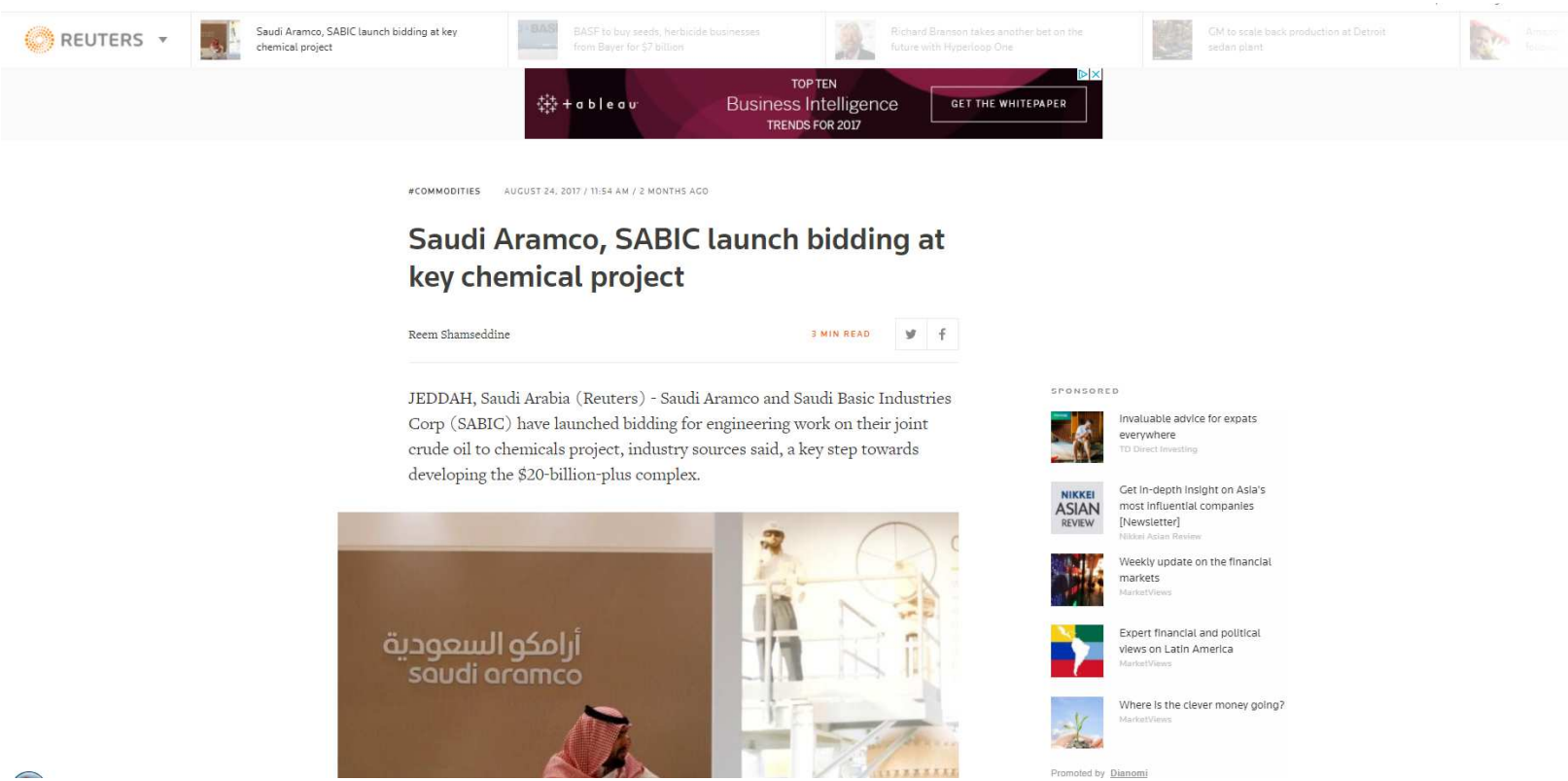
ETHYLENE PRODUCTION TODAY



FEEDSTOCKS RANGE FROM ETHANE TO HEAVY FRACTIONS



WHAT ABOUT CRUDE OIL?



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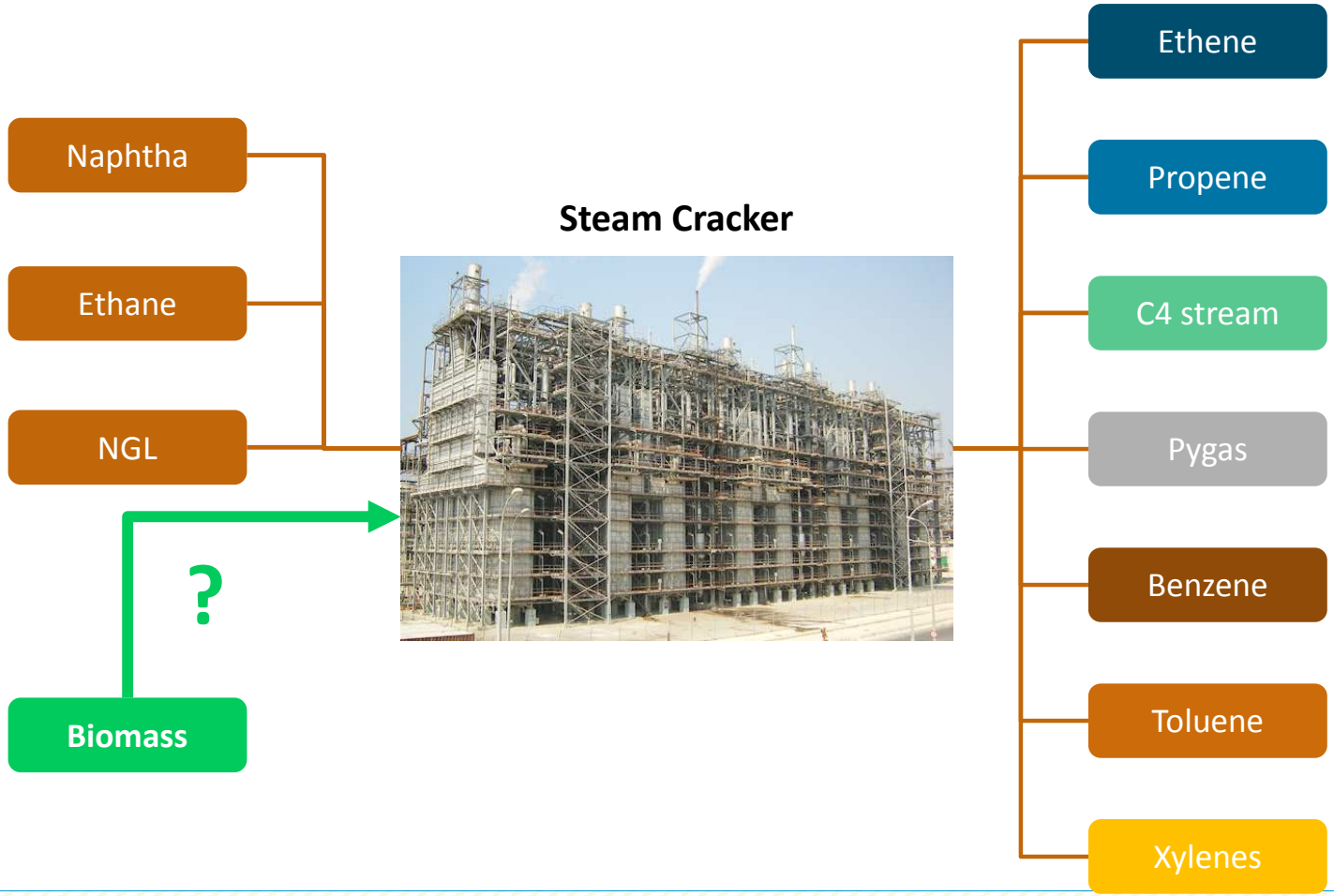

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Naphtha

Ethane

NGL

Steam Cracker

Ethene

Propene

C4 stream

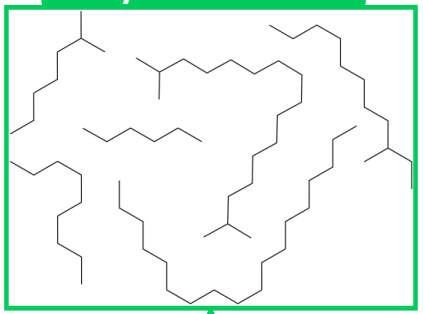
Pygas

Benzene

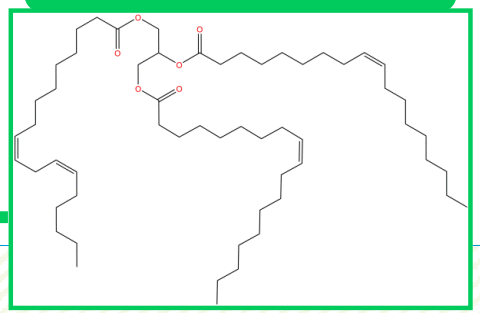
Toluene

Xylenes

Bio-derived Hydrocarbons



Triglyceride and fatty acid biomass



Catalytic upgrading:
Hydrodeoxygenation
Hydrocracking
Isomerization

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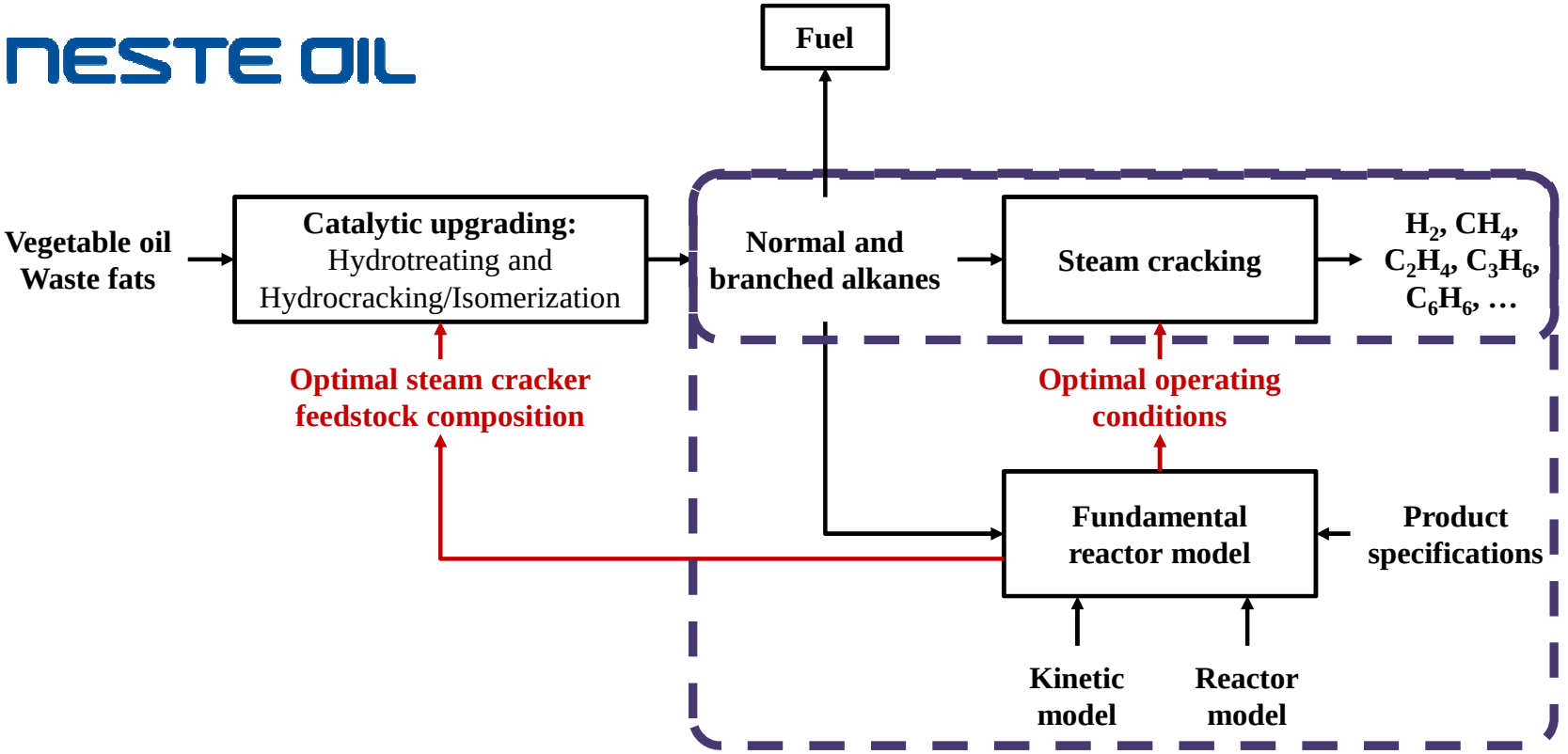
SCHEMATIC OVERVIEW

NESTE OIL



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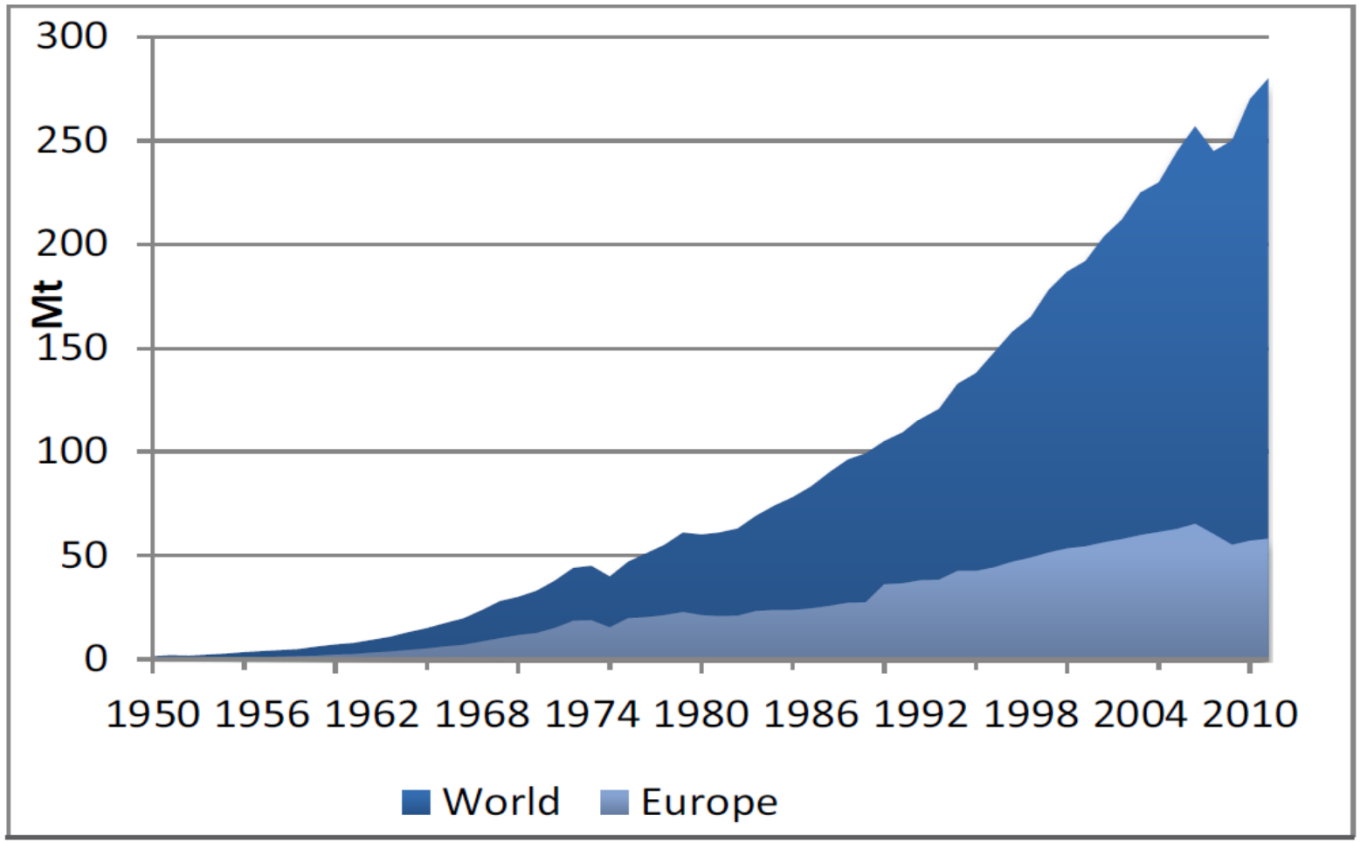
PLASTICS PRODUCTION KEEPS ON INCREASING



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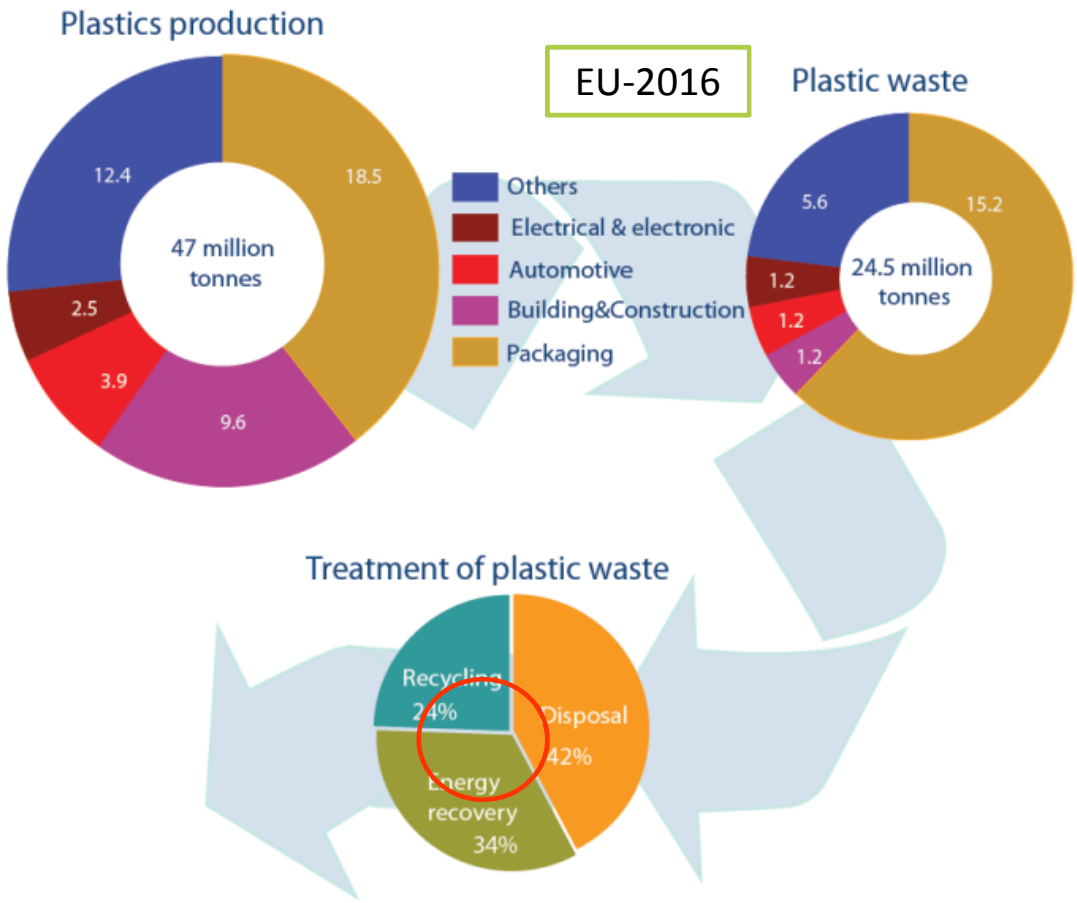

http://libraryeuroparl.wordpress.com/2013/11/07/plastic-waste/

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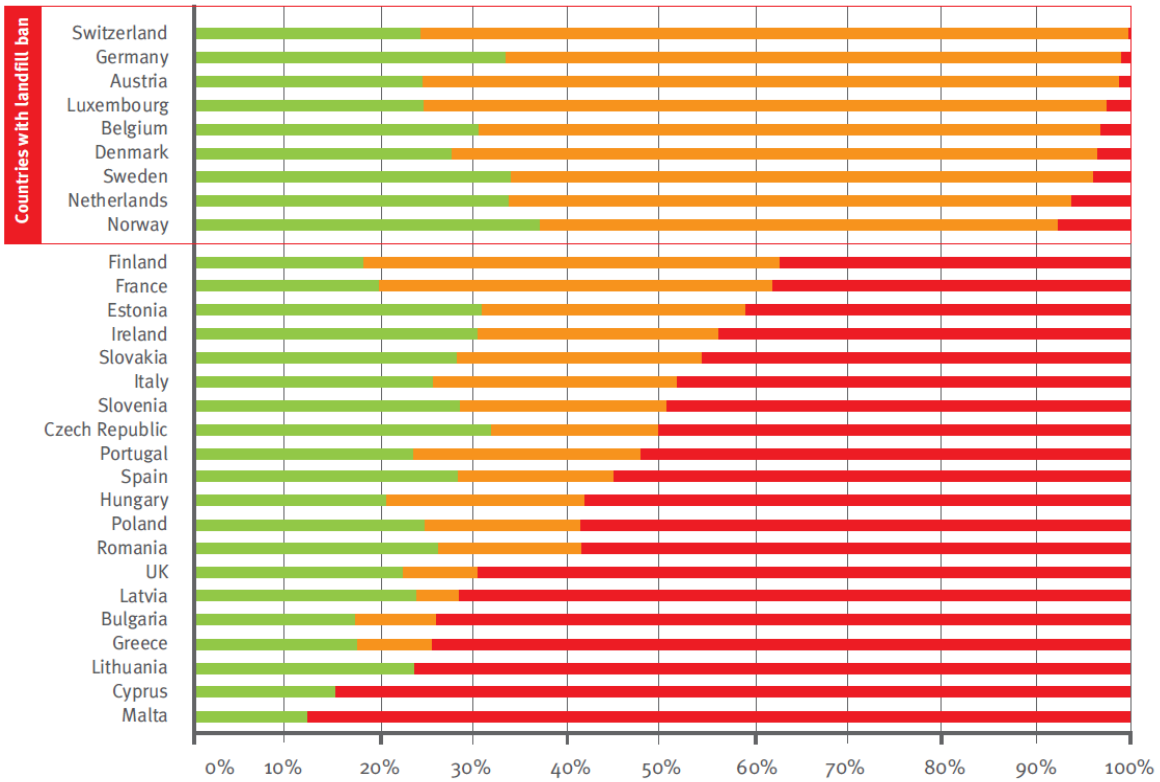
EU TARGET



Treatment of post-consumer plastics waste 2012
(EU-27 + CH/NO)
Source: Consultic

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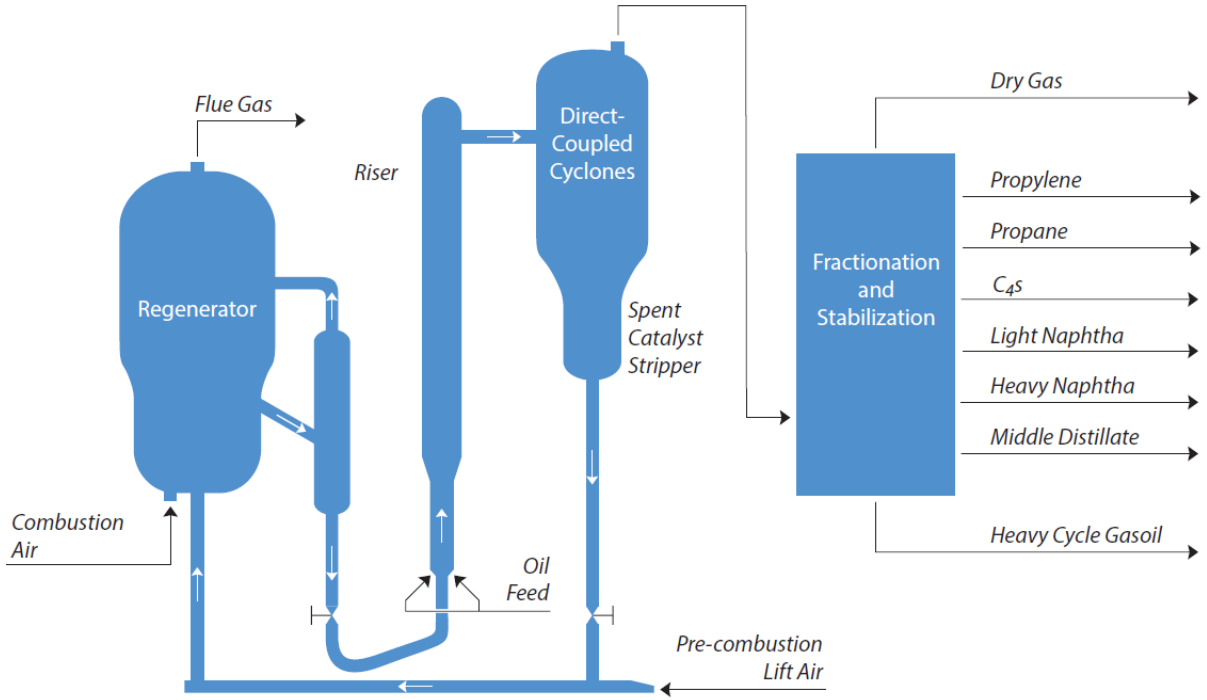
WHAT ABOUT FLUID CATALYTIC CRACKING?

Timeline of the use of zeolites in higher FCC olefins production

Year	Event
1970	ZSM-5 in FCC invented
1974	USY in FCC invented
1983	ZSM-5 commercialised in cracking
1986	Zeolite Beta in FCC invented
1990	First on-purpose olefins production via ZSM-5
1995	Indmax FCC process invented
2003	Indmax process commercialised



Benefits and drawbacks of zeolite catalysts

Catalyst	Pros	Cons
Ultrastable Y (USY)	More $C_3=/C_4=$; less coke	Poor stability
RE-USY	Improved stability vs USY	Limited olefin potential
ZSM-5	Excellent $C_3=$ yields	Poor conversion activity; additive dilution effect
Zeolite Beta	Enhanced $C_4=$	High cost; poor stability

Typical yield of olefins for the I-FCC process

	wt% of feed	wt% in C_2 & lighter
Ethylene	3–7	40–50
		wt% in LPG
Propylene	12–24	40–50
i-Butylene	4–5	8–12
Other butylene	5–12	20–25

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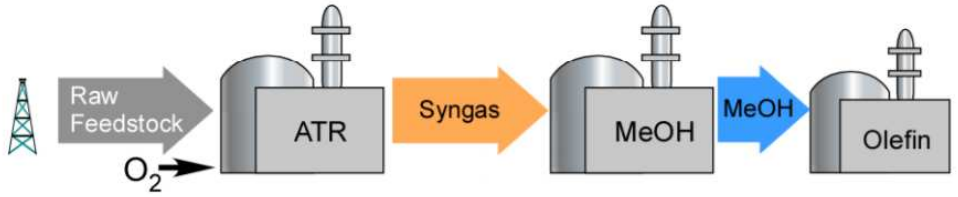
NEW TRENDS IN OLEFIN PRODUCTION

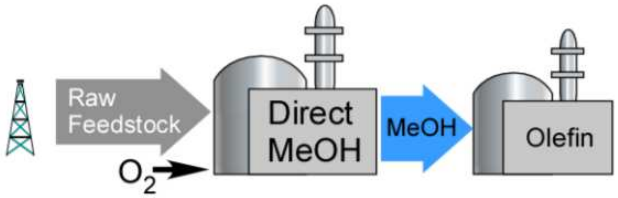
Abundancy of cheap methane from shale gas and stranded gas

→ Develop processes to **valorize methane** to higher hydrocarbons

Syngas / MeOH

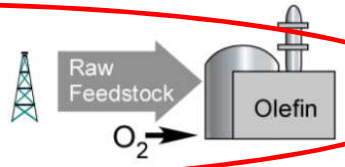


Avoid syngas



Oxidative Coupling of Methane

Avoid intermediates



Success for implementation will require:

- ✓ Breakthrough in catalysts, reactor design and separation processes
- ✓ Fundamental technology development
- ✓ Industry / government / academic partnerships

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OXIDATIVE COUPLING OF METHANE (OCM)

Recent history

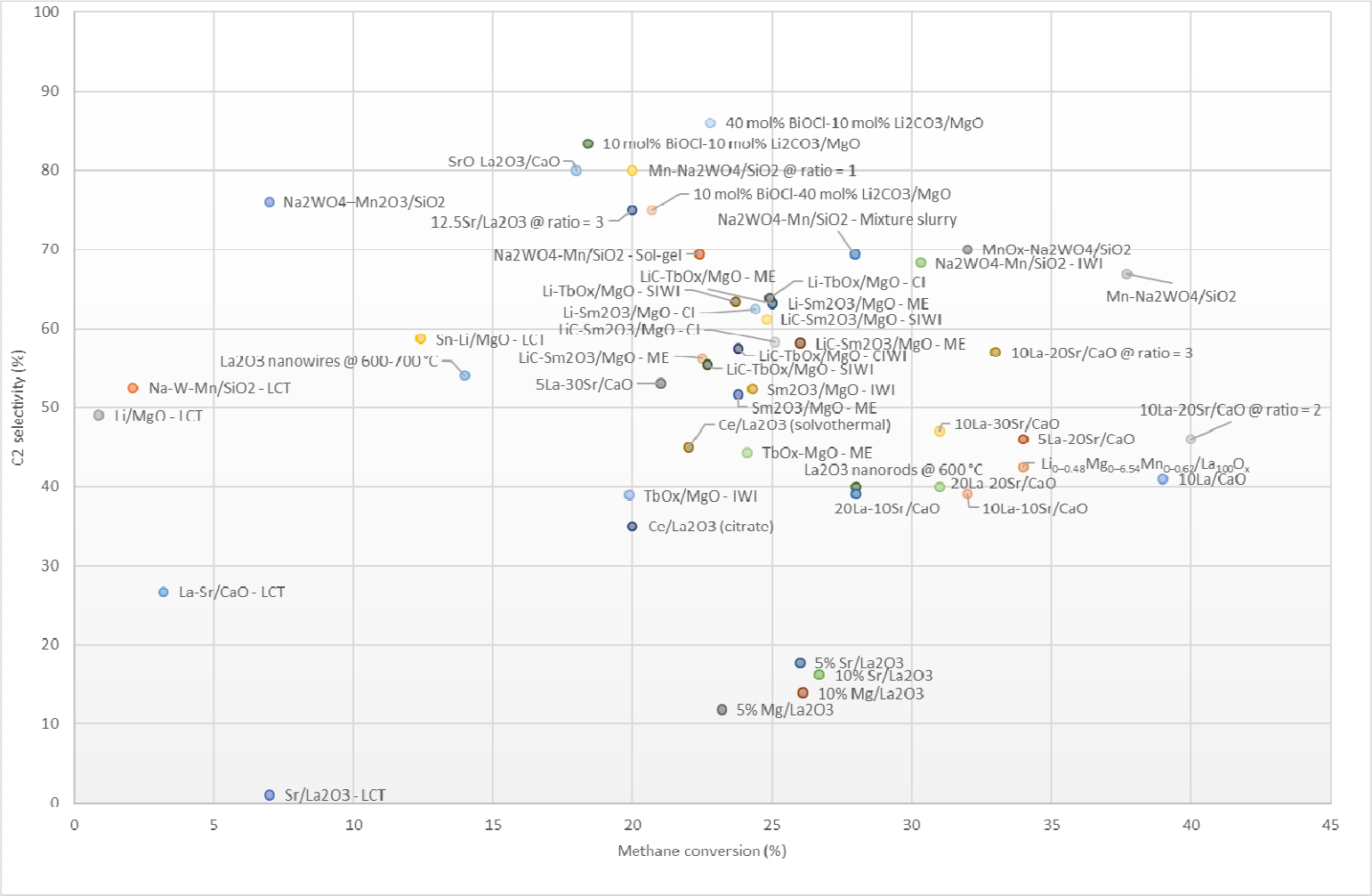
- **1982** Keller and Bhasin: pioneering work
- **2008** DOW Chemical awards “methane challenge grants”
- **2013** Small firms are developing technology for converting natural gas to fuel and chemicals
- **April 2015** Siluria Technologies successful start-up of demonstration plant for OCM

Demonstration unit for OCM in La Porte, Texas

Key challenges

- Strongly **exothermic** reaction(s)
- Inverse relationship between C2 hydrocarbon selectivity and CH4 conversion: **low C2 yields**

} Reactor design!


C2 selectivity (%)
Methane conversion (%)
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30
35
40
45
40 mol% BiOCl-10 mol% Li2CO3/MgO
10 mol% BiOCl-10 mol% Li2CO3/MgO
SrO La2O3/CaO
Mn-Na2WO4/SiO2 @ ratio = 1
Na2WO4-Mn2O3/SiO2
10 mol% BiOCl-40 mol% Li2CO3/MgO
12.5Sr/La2O3 @ ratio = 3
Na2WO4-Mn/SiO2 - Mixture slurry
Na2WO4-Mn/SiO2 - Sol-gel
MnOx-Na2WO4/SiO2
Na2WO4-Mn/SiO2 - IWI
LiC-TbOx/MgO - ME
Li-TbOx/MgO - CI
Li-TbOx/MgO - SIWI
Mn-Na2WO4/SiO2
Li-Sm2O3/MgO - CI
Li-Sm2O3/MgO - ME
LiC-Sm2O3/MgO - SIWI
LiC-Sm2O3/MgO - CI
Sn-Li/MgO - LCT
LiC-Sm2O3/MgO - ME
10La-20Sr/CaO @ ratio = 3
La2O3 nanowires @ 600-700 °C
LiC-TbOx/MgO - CIWI
LiC-TbOx/MgO - SIWI
Na-W-Mn/SiO2 - LCT
5La-30Sr/CaO
Sm2O3/MgO - IWI
Li/MgO - LCT
Sm2O3/MgO - ME
10La-20Sr/CaO @ ratio = 2
Ce/La2O3 (solvothermal)
10La-30Sr/CaO
5La-20Sr/CaO
TbOx-MgO - ME
La2O3 nanorods @ 600 °C
Li0–0.48Mg0–6.54Mn0-0.62/La100Ox
10La/CaO
20La 20Sr/CaO
TbOx/MgO - IWI
20La-10Sr/CaO
10La-10Sr/CaO
Ce/La2O3 (citrate)
La-Sr/CaO - LCT
5% Sr/La2O3
10% Sr/La2O3
10% Mg/La2O3
5% Mg/La2O3
Sr/La2O3 - LCT

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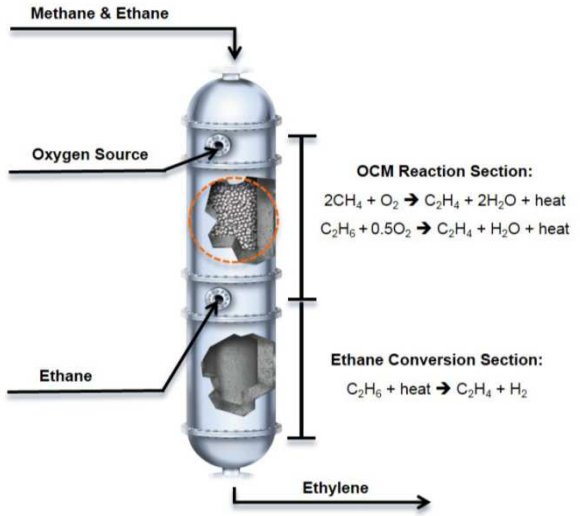
REACTOR DESIGN FOR OCM

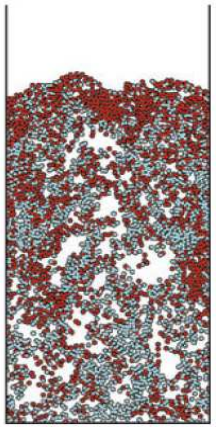
Conventional Fixed Bed



Limitations:

- Thermal control of the reactor is difficult:
- Potential formation of hotspots

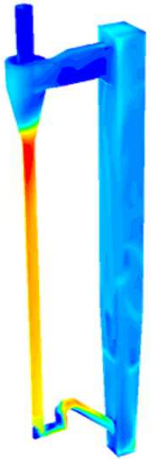
Static Fluidized Bed



Drag force

Gravitational force

Riser/Circulating Fluidized Bed



Advantages:

- Better heat and mass transfer

Limitations:

- Entrainment of particles at high gas flow rates
- Limited slip velocities (~ 1 m s^{-1})

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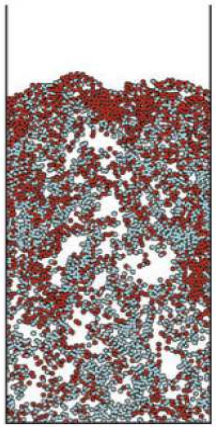
REACTOR DESIGN FOR OCM

Centrifugal instead of gravitational force field → Process intensification

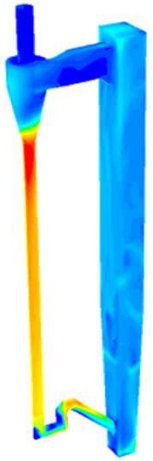
Static Fluidized Bed



Drag force

Gravitational force

Riser/Circulating Fluidized Bed

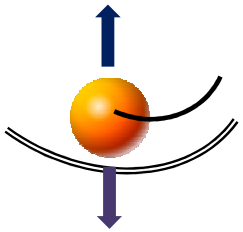


Limitations:

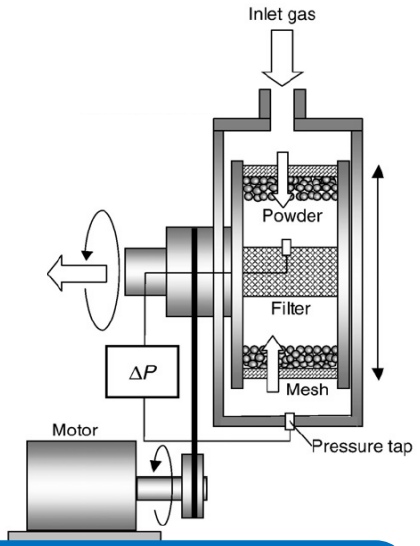
- Entrainment of particles at high gas flow rates
- Limited slip velocities (~ 1-2 m/s)

Rotating Fluidized Bed

Drag force



Centrifugal force



Advantages:

- Dense particle bed
- High gas feed flow rates
- Higher slip velocity
  → *better heat and mass transfer*

Limitation:

- Mechanical moving parts (abrasion)

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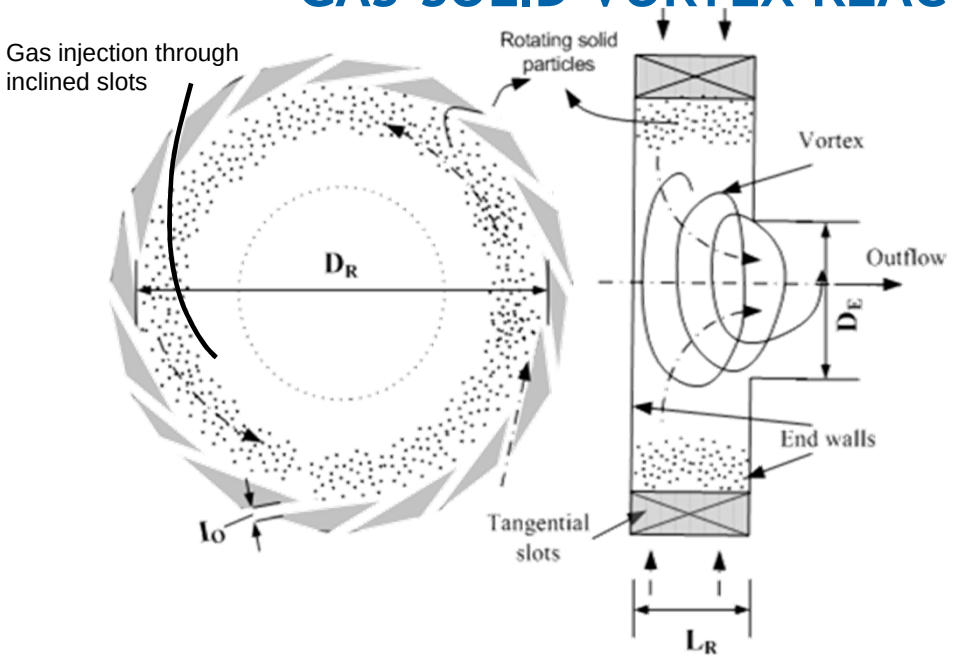
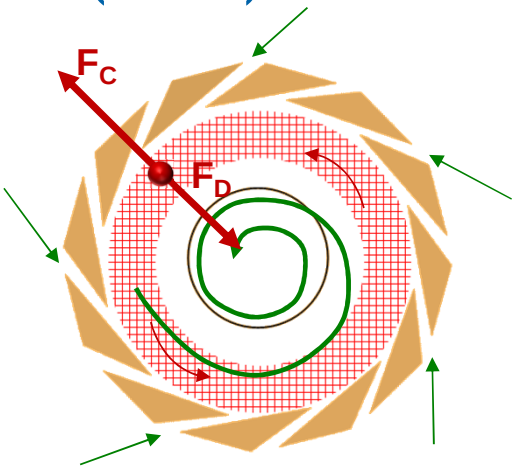
GAS-SOLID VORTEX REACTOR (GSVR)





Fluidized Bed in Vortex Reactor

Advantages:

- Dense particle bed
- High gas feed flow rates
  → *high throughput operation*
- Higher slip velocity
  → *better heat and mass transfer*

GSVR emerges as an excellent reactor choice to demonstrate the OCM process

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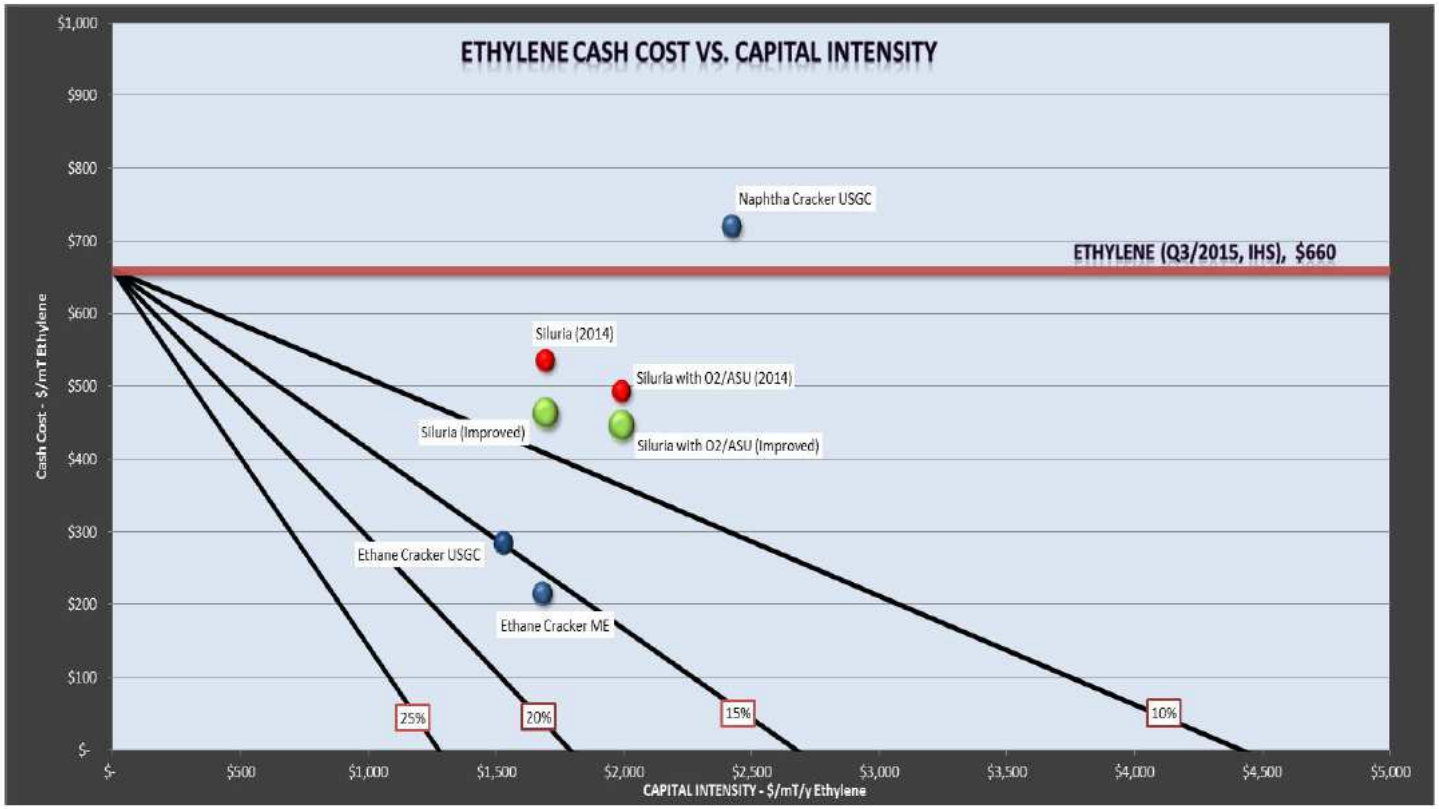
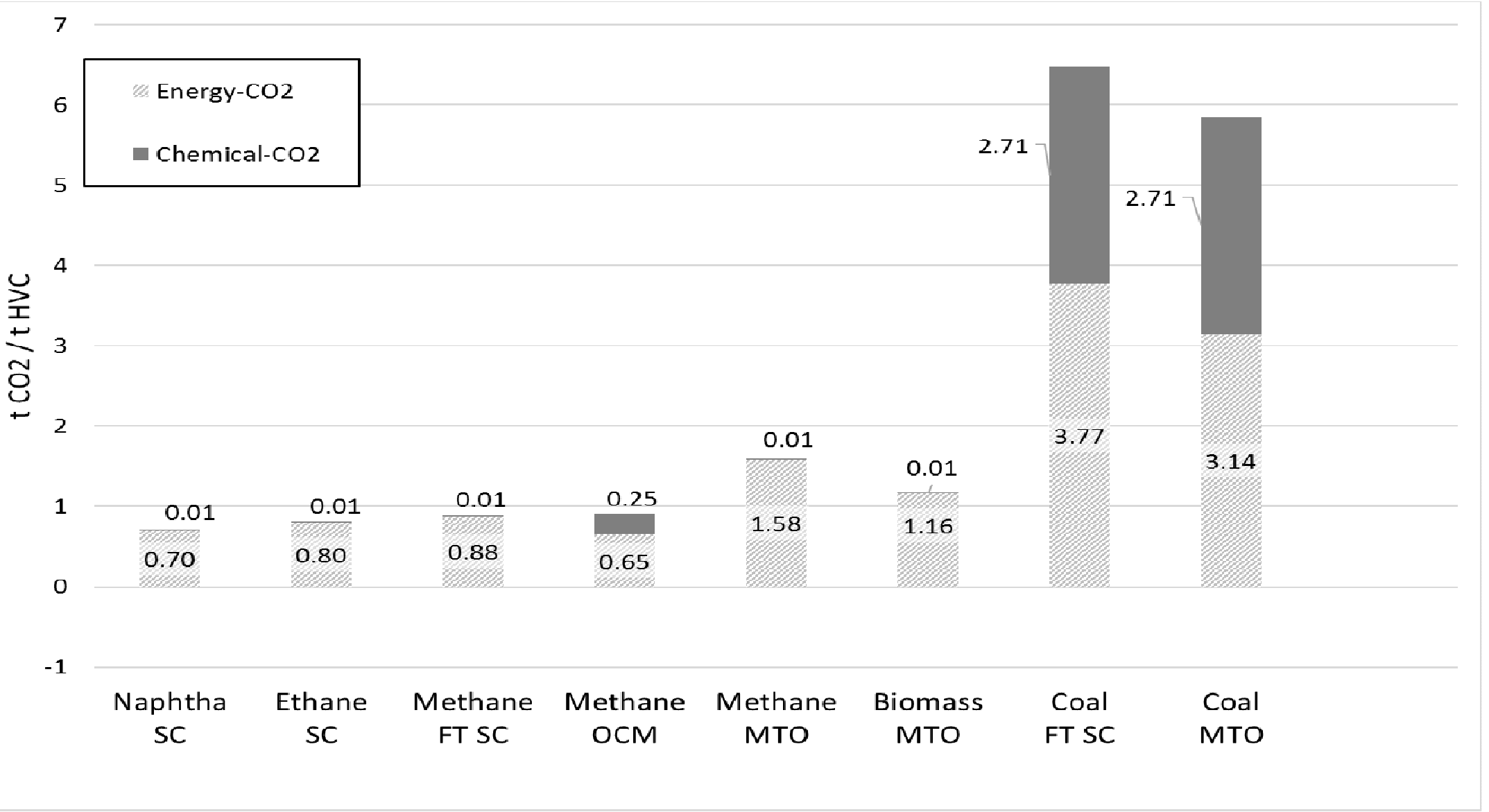


Improved Siluria's Cash Cost (based on new ranges from presentation)

- OCM only: $464/MT$_{C2H4}$ ($443-$485/MT$_{C2H4}$)
- OCM + ASU: $447/MT$_{C2H4}$ ($430-470/MT$_{C2H4}$)


Energy-CO2
Chemical-CO2
t CO2 / t HVC
7
6
5
4
3
2
1
0
-1
0.01
0.70
0.01
0.80
0.01
0.88
0.25
0.65
0.01
1.58
0.01
1.16
2.71
3.77
2.71
3.14
Naphtha SC
Ethane SC
Methane FT SC
Methane OCM
Methane MTO
Biomass MTO
Coal FT SC
Coal MTO

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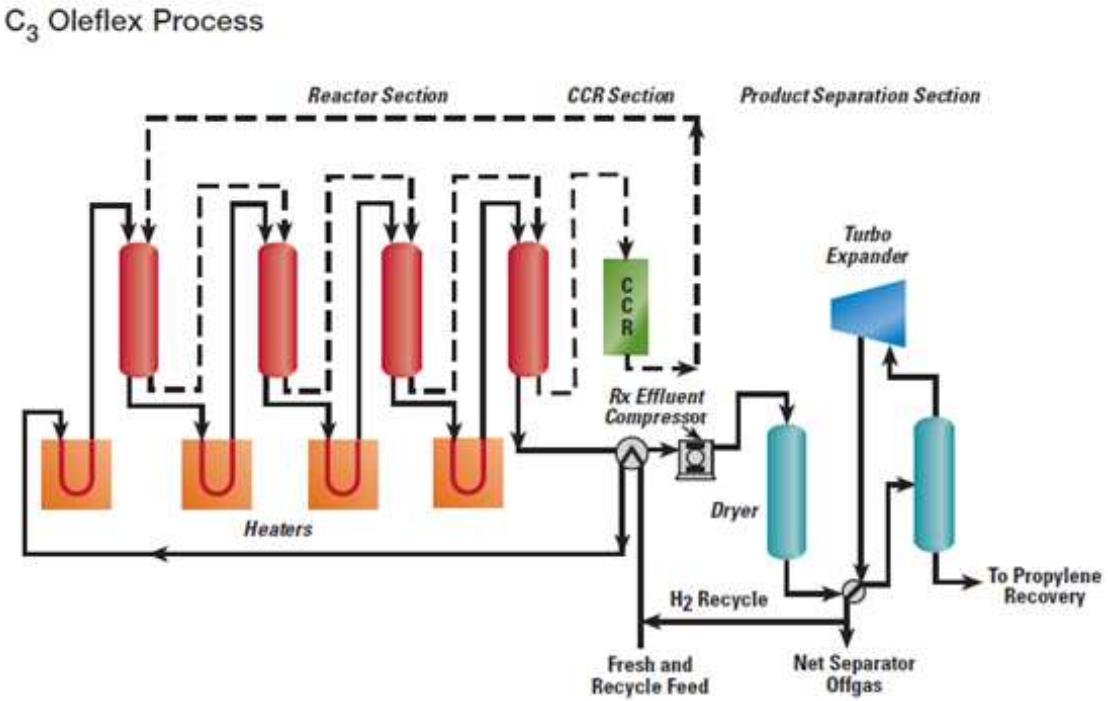
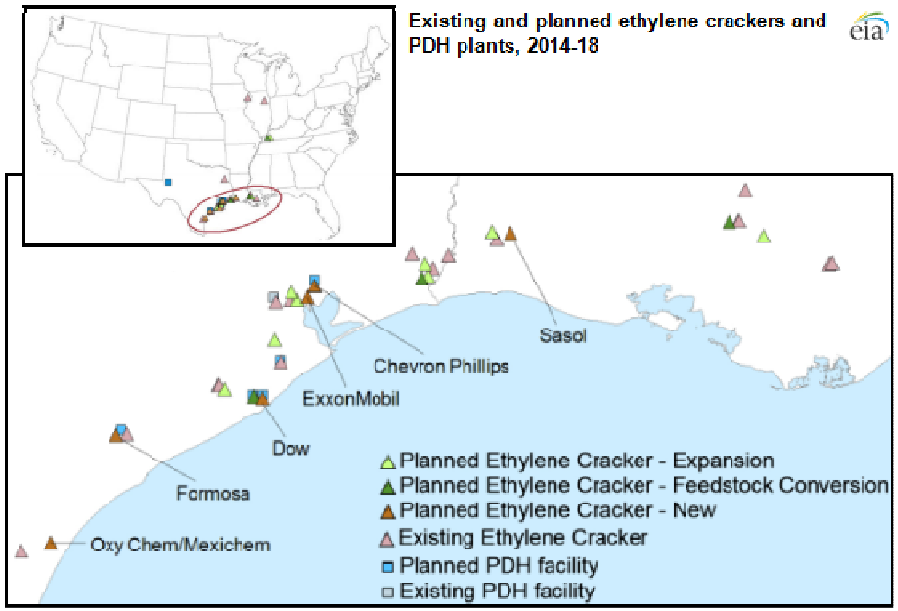
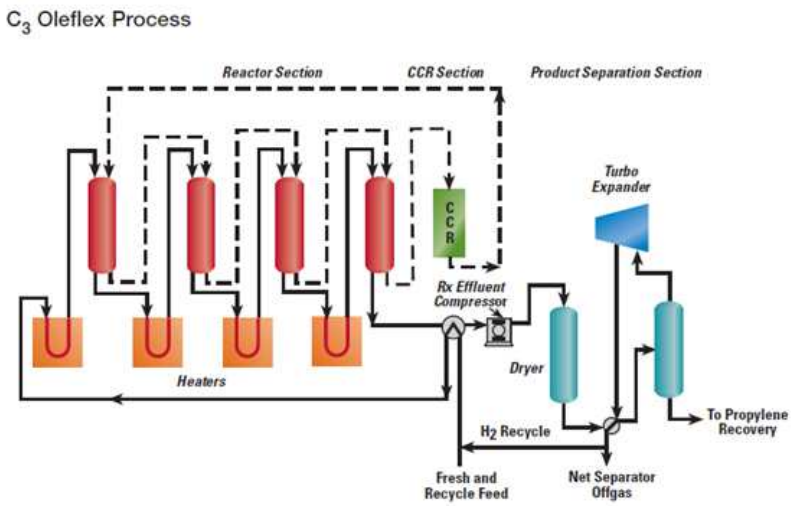
Pearl project Shell

PROPANE DEHYDROGENATION





A LOT OF ACTIVITY

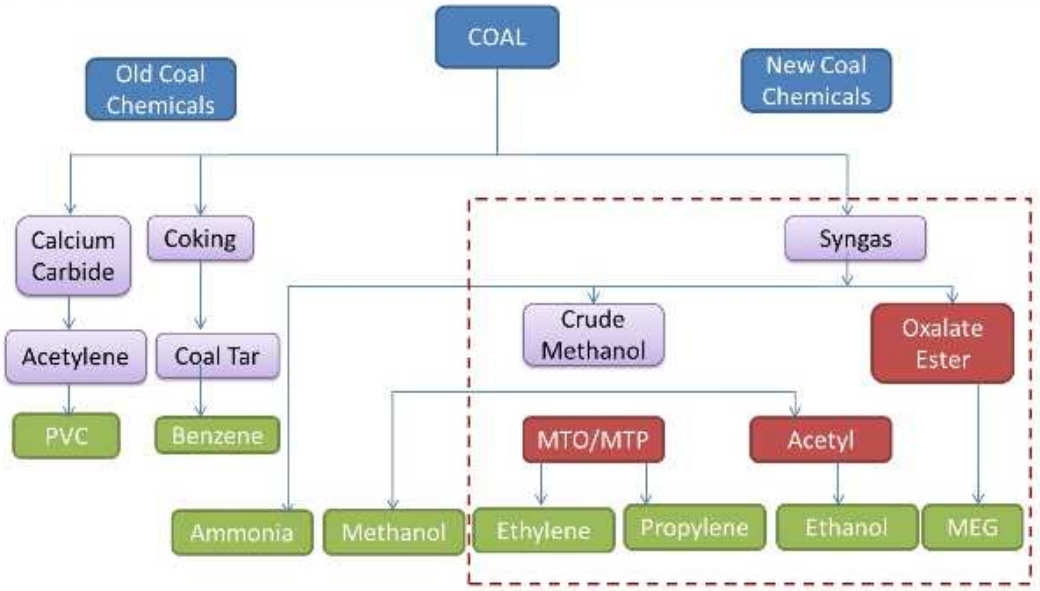


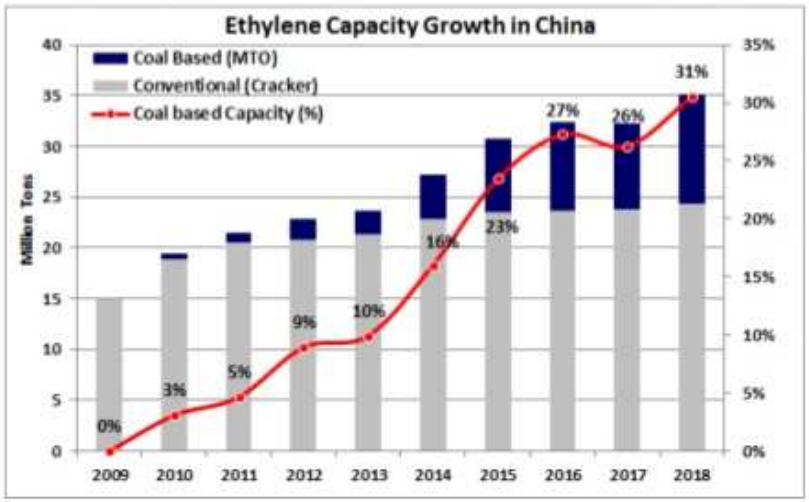
RECENT AND ONGOING PDH PROJECTS

Company	Location	Country	Capacity (tpa)	Start-up	Notes
Fujian Meide Petrochemical	Fujian	China	660,000	2014	
Jiangsu Haili Chemical	Dafeng City, Jiangsu	China	510,000	2014	UOP technology
Ningbo Haiyue New Material	Ningbo City, Zhejiang	China	600,000	2014	Lummus technology
Shaoxing Sanyuan Petrochemical	Nantong	China	450,000	2013	
Shaoxing Sanyuan Petrochemical	Shaoxing	China	450,000		
Tianjin Bohai Chemical Industry Group	Tianjin	China	600,000	2013	
Tianjin Bohai Chemical Industry Group	Tianjin	China	600,000		
Tianjin Bohua Petrochemical	Tianjin	China	600,000	2013–H1	Lummus technology
Yantai Wanhua Polyurethanes	Yantai, Shandong	China	600,000	2014–H2	
Zhangjiagang Yangzijiang Petrochemical	Zhangjiagang	China	600,000	2015	Phase 1
Zhangjiagang Yangzijiang Petrochemical	Zhangjiagang	China	600,000	2017	Phase 2
Zhejiang Julong	Pinghu, Zhejiang	China	450,000	2013	Phase 1. UOP technology
Zhejiang Julong	Pinghu, Zhejiang	China	750,000	2014	Phase 2. UOP technology
Zhejiang Shaoxing Sanjin Petrochemical	Zhejiang	China	450,000	2013	UOP technology
Egyptian Propylene & Polypropylene Co. (EPPC)	Port Said	Egypt	400,000	2010–Oct	
OPC (Oriental Petrochemicals Co.)	Gulf of Suez	Egypt	250,000	2015–H1	Uhde technology
Mehr Petro Kimia	Pars Special Economic Energy Zone, Iran	Iran	450,000	2013	Uhde technology
Kazakhstan Petrochemical Industries (KPI)	Atyrau	Kazakhstan	500,000		Lummus technology
Sibur	Tobolsk	Russia	510,000	2013	
Al-Waha Petrochemical	Al Jubail	Saudi Arabia	450,000	2009–May	
National Petrochemical Industrial Co (NatPet)	Yanbu	Saudi Arabia	400,000		
National Petrochemical Industrial Co (NatPet)	Yanbu	Saudi Arabia	400,000	2008–Dec	UOP technology
HMC Polymers	Mab Ta Phut	Thailand	300,000	2010	
Abu Dhabi Oil Refining (Takreer)	Abu Dhabi	UAE	500,000	2013–H2	UOP technology
Dow	Freeport, Texas	US	750,000	2015	UOP technology
Dow		US		2018	
Formosa Plastics USA	Point Comfort, Texas	US	600,000	2016	
Petrologistics	Houston, Texas	US	544,000	2010–Nov	

SOURCE: ICIS

WHAT ABOUT COAL?





Almost a third of China's ethylene production could soon be coal based if integrated process technology challenges are overcome

Presentation outline

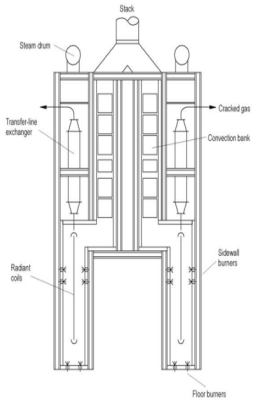
New trends in olefin production

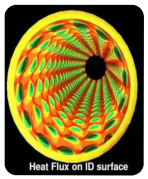
1. Production technologies for olefins
2. How mature is steam cracking?
3. Electrification of the chemical industry

WHAT CAN BE IMPROVED?

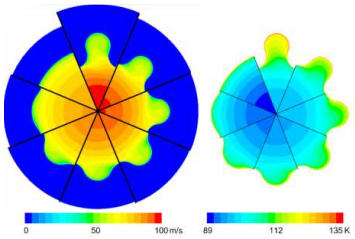
Renewable fuel characterization
- experimental activity
- kinetic mechanisms

Innovative Furnace System developments and integration
- oxy-fuel combustion
- coke formation
- emissivity coating
- 3D reactor testing





Advanced 3D modeling
- CFD RANS/LES
- Reactor optimization
- pilot plant simulation



Upscaling and Demonstration

EUROPEAN ETHYLENE PRODUCERS COMMITTEE

A SPIRE project

IMPROOF

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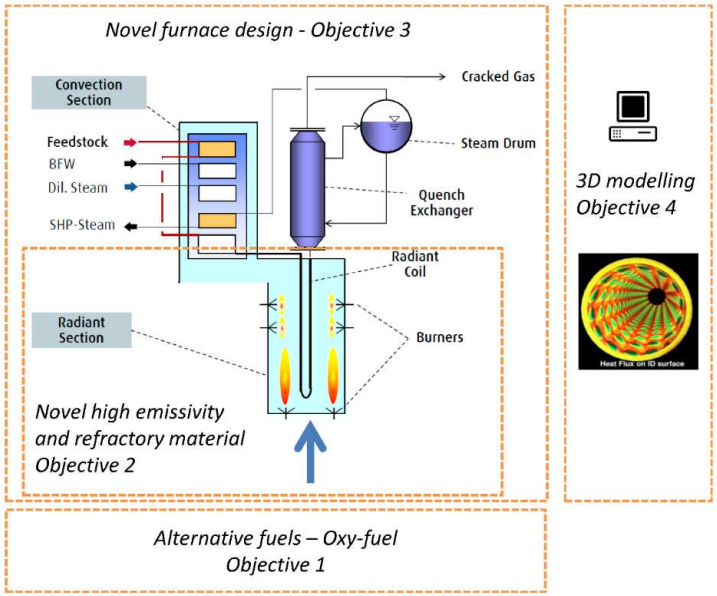
von KARMAN INSTITUTE FOR FLUID DYNAMICS

NEW TECHNOLOGIES RESEARCH CENTRE UNIVERSITY OF WEST BOHEMIA

TechnipFMC

CONCEPT AND OBJECTIVES



1. Novel combustion technology using alternative fuels and oxy-fuel combustion
2. Demonstrate the individual impact of novel emissive, reactor and refractory materials on pilot scale (TRL5)
3. Demonstrate the power of advanced process simulation (high performance computing and CFD) for furnace design and optimization
4. Demonstrate the technical economic and environmental sustainability of the IMPROOF furnace at TRL6
5. Coke formation reduction and real time optimization

3D COILS

3D geometries to enhance heat transfer by

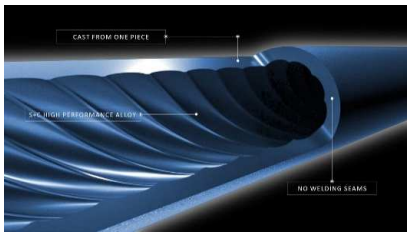
- Increased internal surface area
  - Fin-like structures

- Enhanced mixing
  - SCOPE (S+C)
  - Swirl Flow Tube (SFT)
  - MERT

Major drawback:
Increased pressure losses

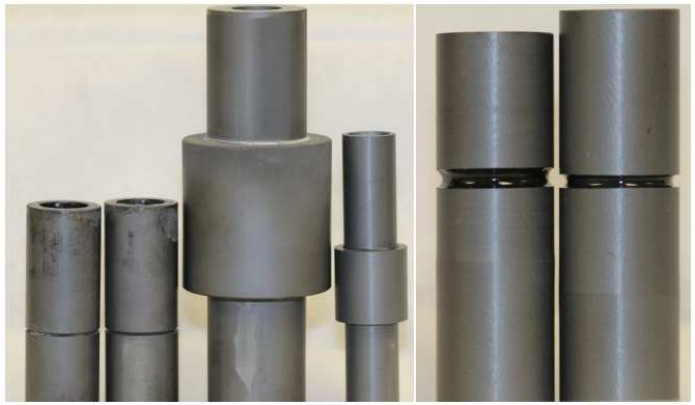
Models can help to descide on the optimal geometry

SFT®



SCOPE®

NEW TRENDS: HIGH TEMPERATURE RESISTANT MATERIALS



Higher temperatures & shorter residence times

Improved energy efficiency

Reduce catalytic coke formation

Problem of ceramics: producing coils

http://www.nrel.gov/docs/fy01osti/28265.pdf

Presentation outline

New trends in olefin production

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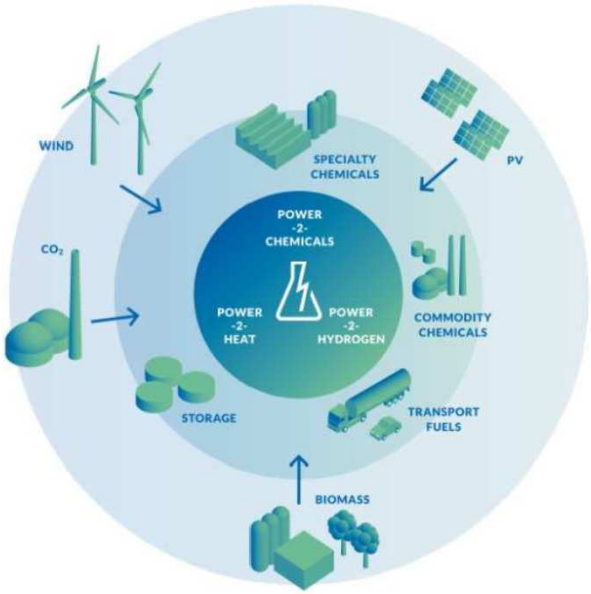
GOVERNMENT INITIATIVES

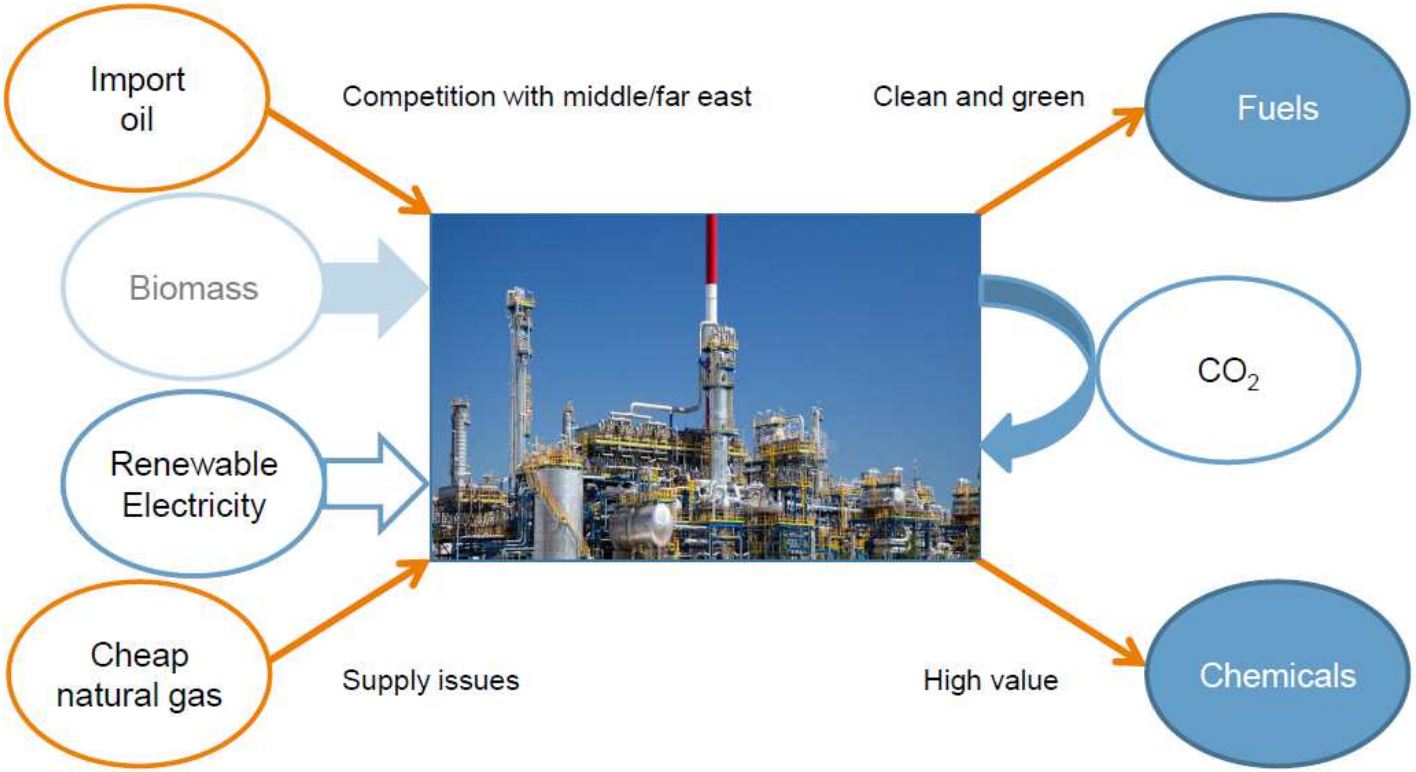
VoltaChem: Our mission



- Accelerate innovation and implementation of ***electrification & decarbonization*** in chemicals.
- Initiate and facilitate ***collaborative development*** *of technology and associated business models.*
- Addresses both the *indirect and direct use of electricity* within the chemical industry, involving stakeholders from ***chemicals***, ***energy & equipment supply***.

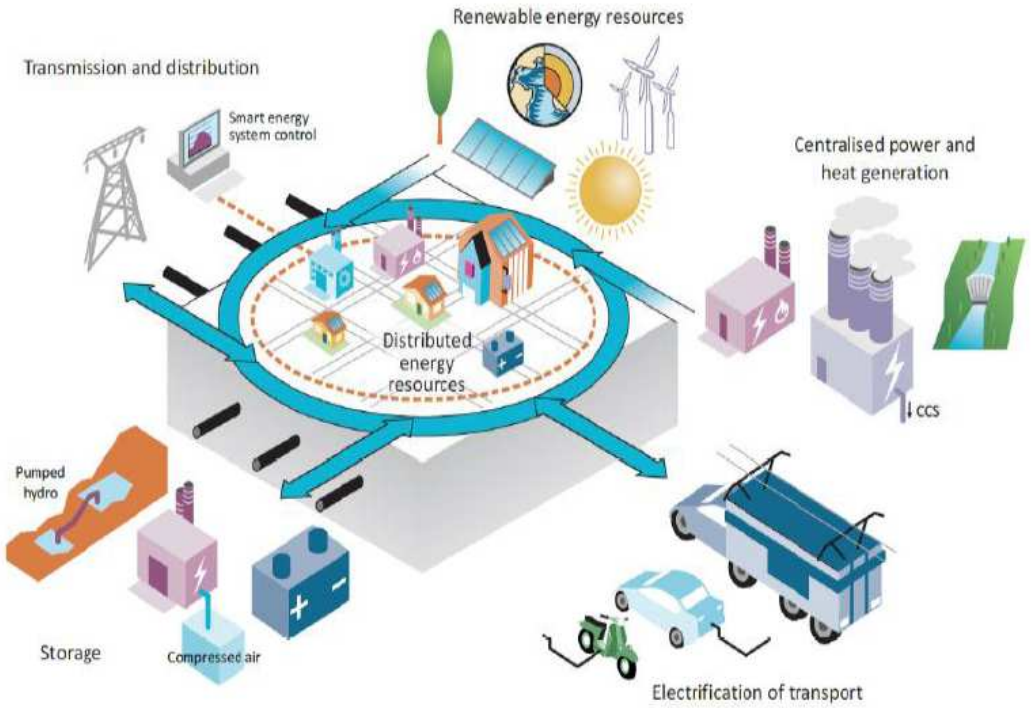
21-09-2015

THE PETROCHEMICAL INDUSTRY



THE ENERGY SYSTEM OUTLOOK

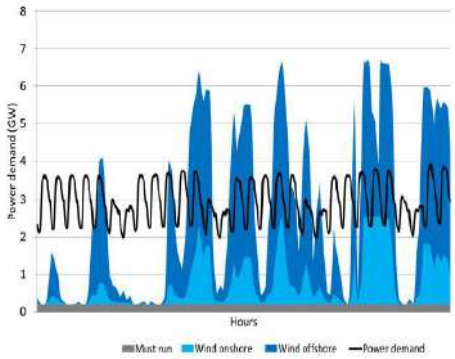
Electricity will play an increasingly important role in energy systems of the future, both in sustainable generation, smart distribution, and **smart end-use consumption**

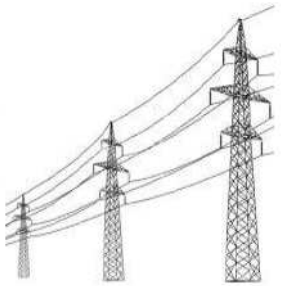


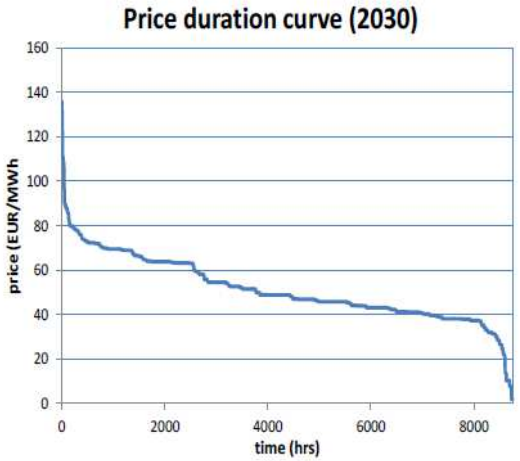
Source: Energy Technology Perspectives 2014 - Harnessing Electricity's Potential.

VARIABLE SUPPLY

Variability of supply and demand → Transport limitations → Variable price







Time **Place** **Price**

Sources: de Joode, 2014, NEV, 2015
Visie 2030, Tennet

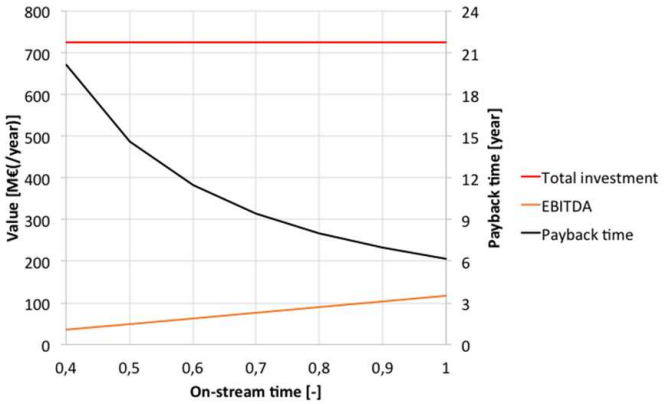
CHALLENGES FOR ELECTRIFICATION

Electrochemical conversions are currently economically not feasible:

Primary reason: High reactor CAPEX (expensive electrodes, you scale based on surface and not on volume, a lot of reactors are needed)

Important parameters:

- Electricity price
- On-stream time
- CO2 price has limited impact



CONCLUSIONS

New trends in olefin production:

1. the dominant technology for at least the coming 30 years
2. From a CO_2 point of view: New trends in olefin production lowest emissions per ton HVC
3. New innovations will allow to decrease emissions even further and increase selectivity

Alternative Technologies

1. Propane dehydrogenation: many new projects
2. Catalytic cracking of naphtha bright future
3. OCM: reactor technology and separation are challenging
4. Electrification not economically viable

EUROPEAN ETHYLENE PRODUCERS COMMITTEE

Thank you … for your attention !

New trends in olefin production

ACKNOWLEDGEMENT

Prof. Philip de Smedt

A SPIRE project

IMPROOF