Resource-Efficient Catalytic Technologies for Shale Gas Upgrading

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Shale Gas Monetization Workshop
Montgomery, TX

March 27, 2014

Outline

- The global chemical industry
- Emerging feedstocks for making chemicals
- The need for resource-efficient technologies
- Examples with LCA analyses
- Concluding remarks

Growth of Global Chemical Industry

Figure 1. Chemical Industry Output: Developed Regions*

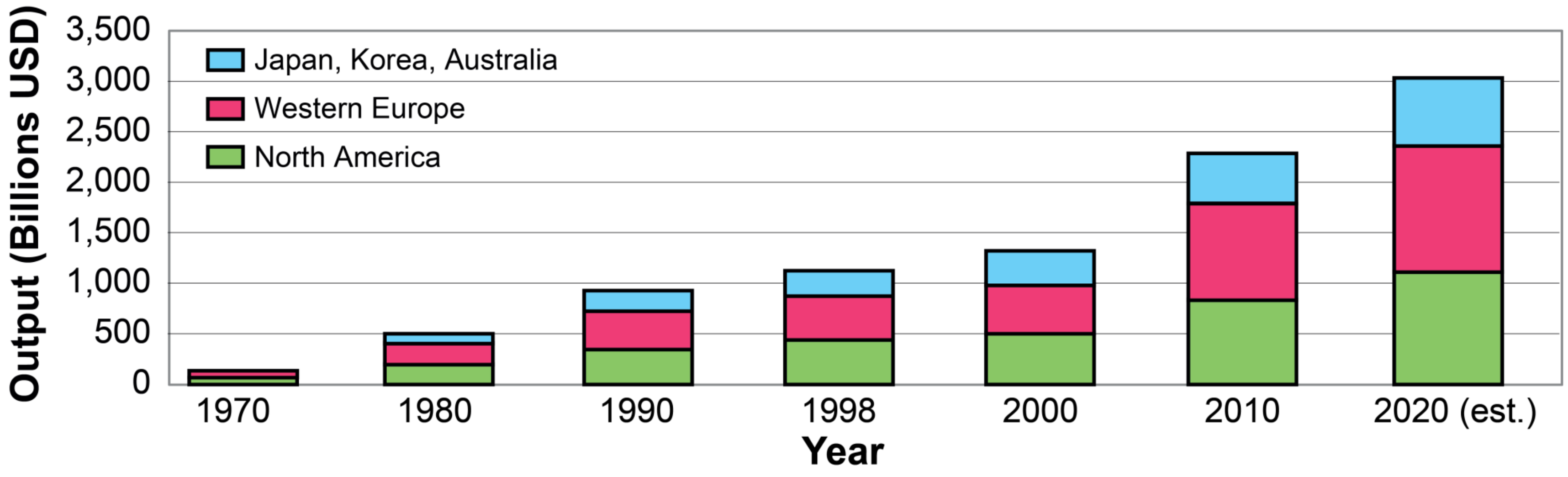
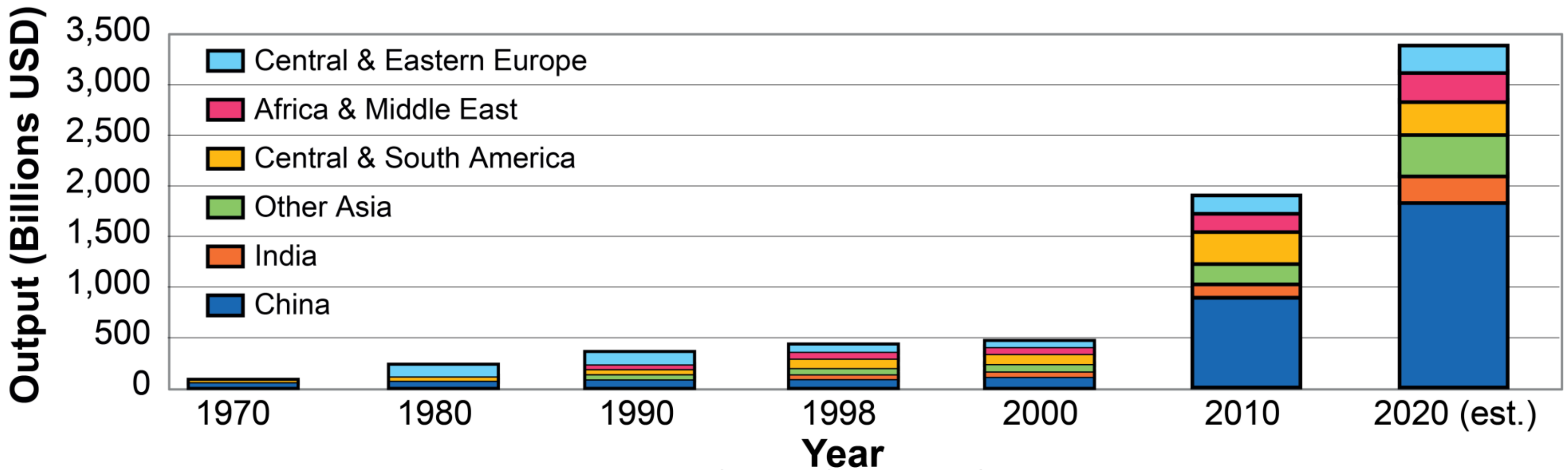
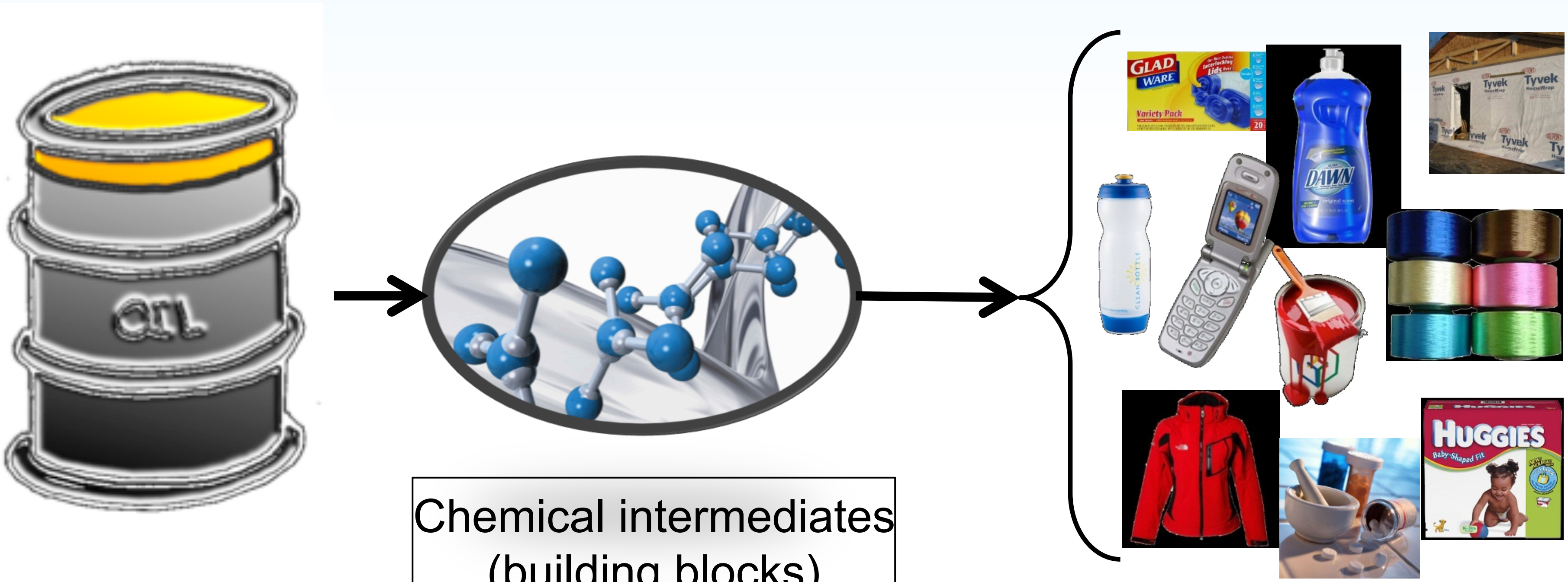


Figure 2. Chemical Industry Output: Developing Regions* & Countries with Economies in Transition



[Global Chemical Outlook, UN Environment Programme, 2012]

Petrochemicals

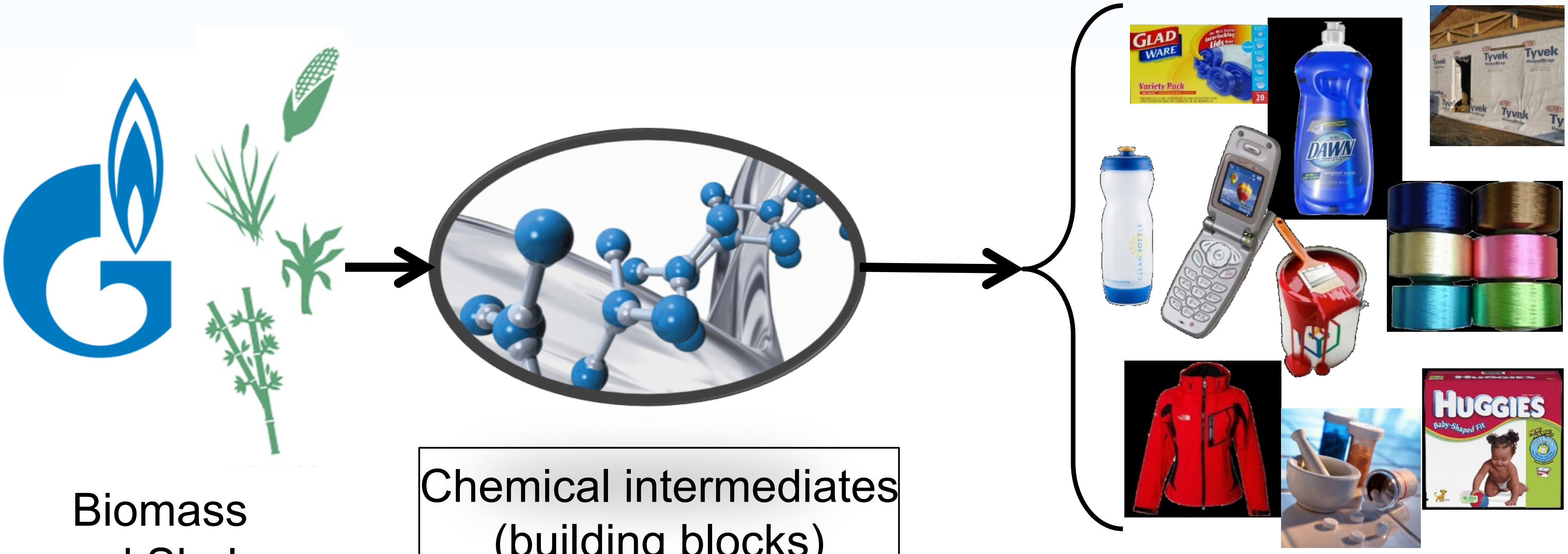


Chemical intermediates
(building blocks)

Consumer
goods

- <10% of crude oil used to make chemicals
- Chemicals more profitable than fuels

Natural Gas and Biomass as Alternate Feedstocks



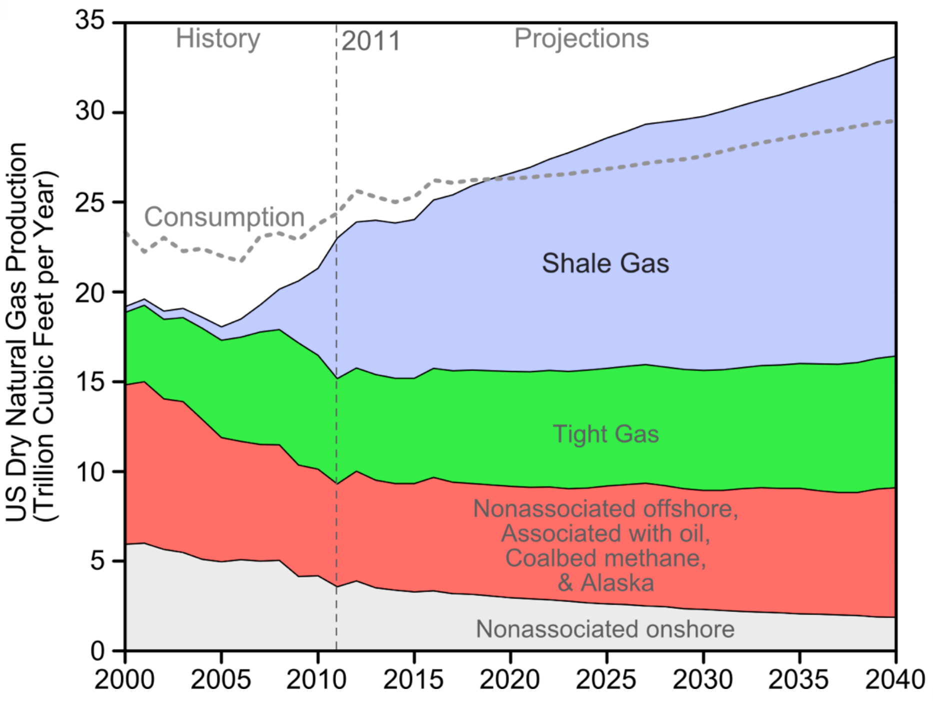
Biomass and Shale Gas

Chemical intermediates (building blocks)

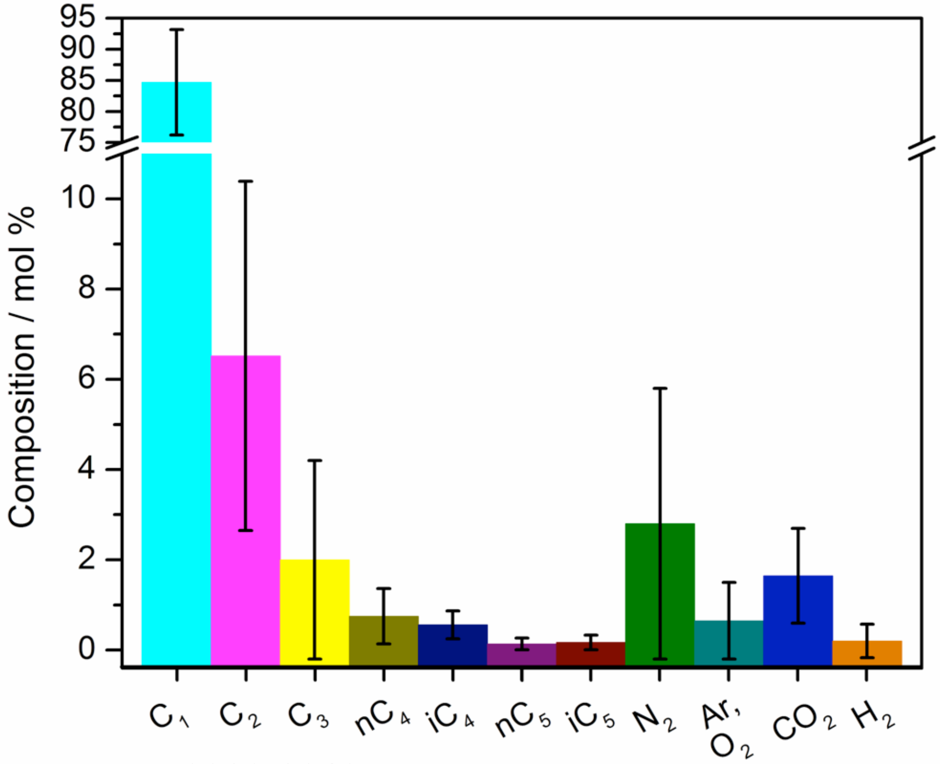
Consumer goods

- US natural gas production up ~28% since 2006, thanks to increased shale gas production [EIA, 2013]
- Biomass abundant for making chemical intermediates

Natural Gas Production by Source



Typical Shale Gas Composition



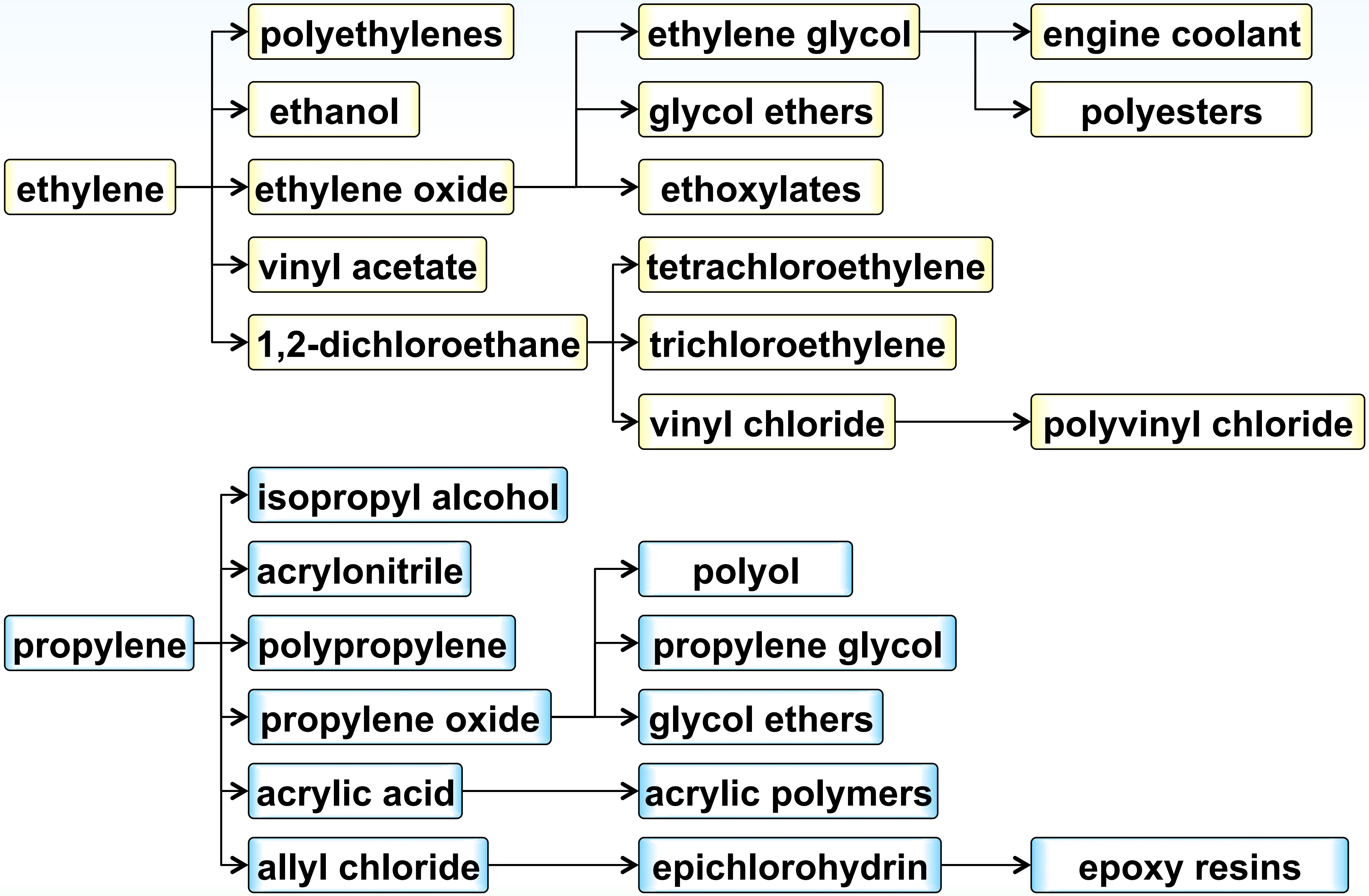
[Energy Information Administration, 0383-2013]

Proposed Expansion of U.S. Ethylene Production Capacity, 2013-2020

Company	Location	Proposed capacity, MMTY
Chevron Phillips	Baytown, TX	1.5
Exxon Mobil	Baytown, TX	1.5
Sasol	Lake Charles, LA	1.4
Dow	Freeport, TX	1.4
Shell	Beaver Co, PA	1.3
Formosa	Point Comfort, TX	0.8
Occidental/ Mexichem	Ingleside, TX	0.5
Dow	St. Charles, LA	0.4
LyondellBasell	Laporte, TX	0.4
Aither Chemicals	Kanawha, WV	0.3
Williams/Sabic JV	Geismar, LA	0.2
Ineos	Alvin, TX	0.2
Westlake	Lake Charles, LA	0.2
Williams/Sabic JV	Geismar, LA	0.1
Total		**10.2**

[Energy Information Administration 0383-2013]

Traditional C_2 and C_3 Utilization Schemes

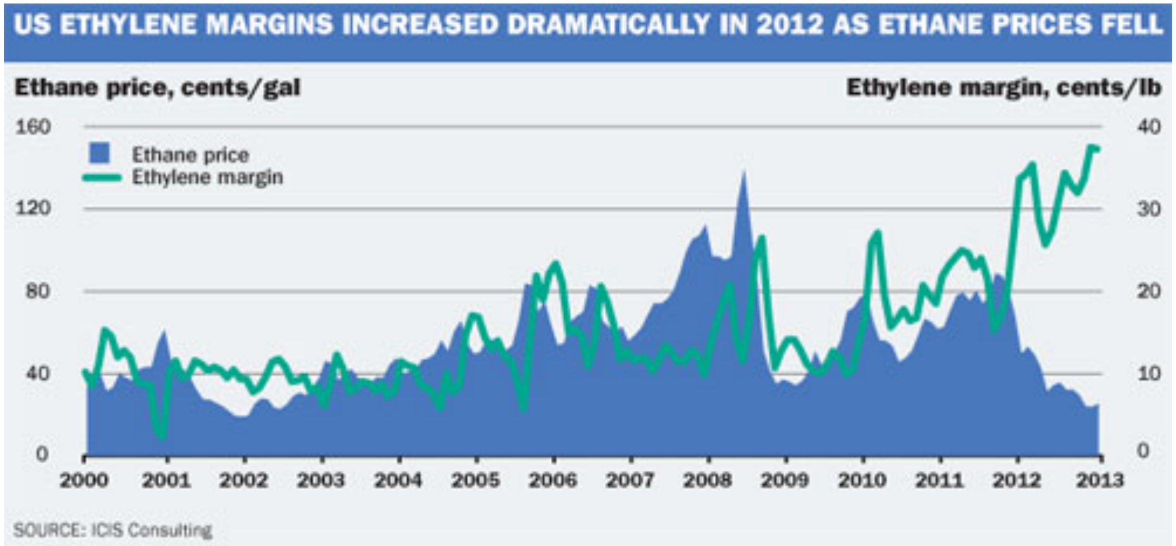


- ethylene
  - polyethylenes
  - ethanol
  - ethylene oxide
    - ethylene glycol
      - engine coolant
      - polyesters
    - glycol ethers
    - ethoxylates
  - vinyl acetate
  - 1,2-dichloroethane
    - tetrachloroethylene
    - trichloroethylene
    - vinyl chloride
      - polyvinyl chloride
- propylene
  - isopropyl alcohol
  - acrylonitrile
  - polypropylene
  - propylene oxide
    - polyol
    - propylene glycol
    - glycol ethers
  - acrylic acid
    - acrylic polymers
  - allyl chloride
    - epichlorohydrin
      - epoxy resins

[Adapted from Siirola, *AIChE J.* **2014** *60* 810]

NGLs as “Emerging Feedstocks”?

- Low price of ethane favor increased use of ethane as cracking feedstock



US ETHYLENE MARGINS INCREASED DRAMATICALLY IN 2012 AS ETHANE PRICES FELL

SOURCE: ICIS Consulting

- Many commercial routes to chemicals from ethylene, propylene already in use

So where are the R&D opportunities?

NGLs as “Emerging Feedstocks”?

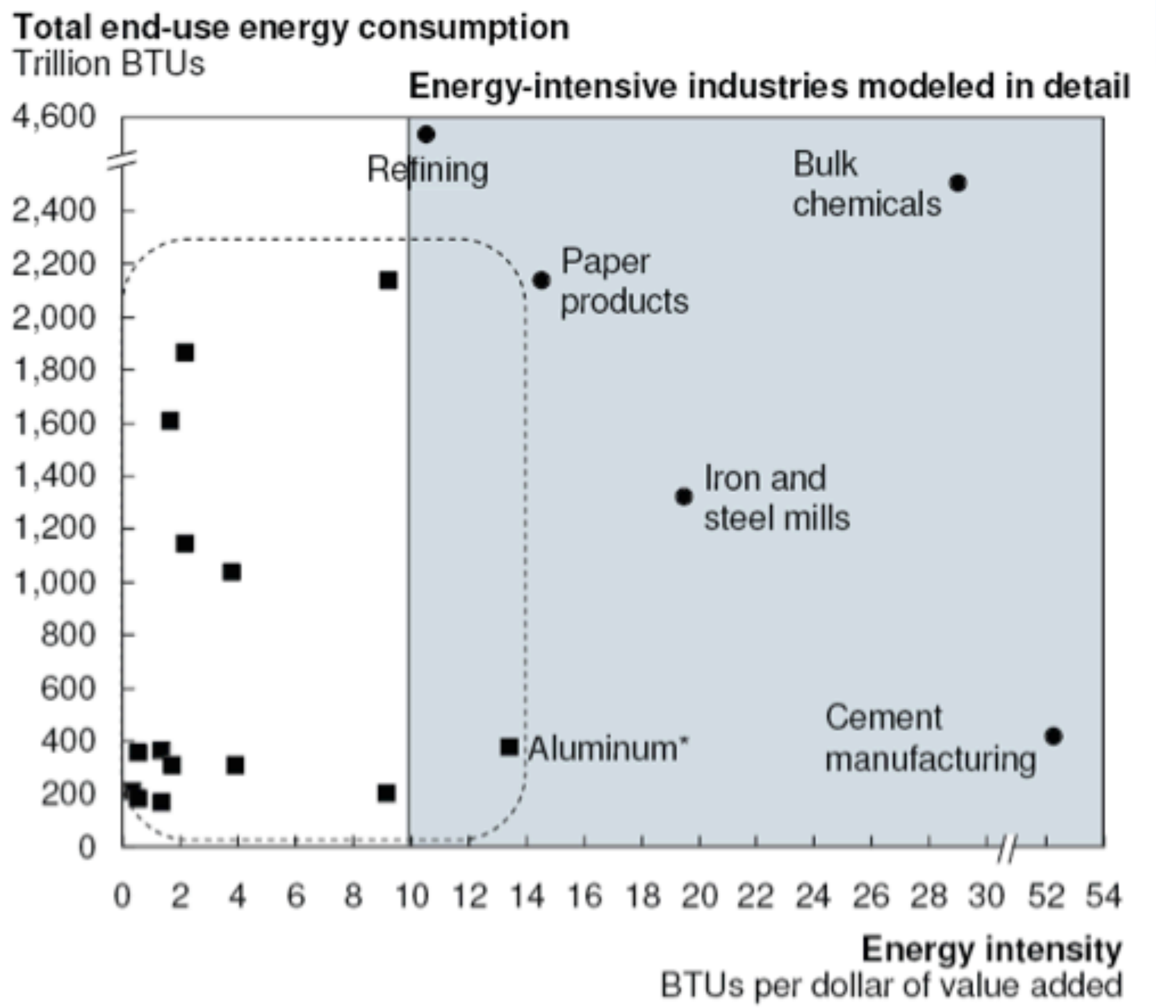
New technologies targeted:

- New more efficient catalysts/processes with lower carbon footprint
  - **Ethylene oxide, propylene oxide**
  - **Hydroformylation**
  - Higher olefins
  - Dimethyl carbonate
- New, selective catalysts/processes for *direct* conversion of propane
  - Acrylic acid, acrylonitrile
  - Alkane metathesis

Comparing environmental impact of chemicals from shale gas vs. petroleum feedstock

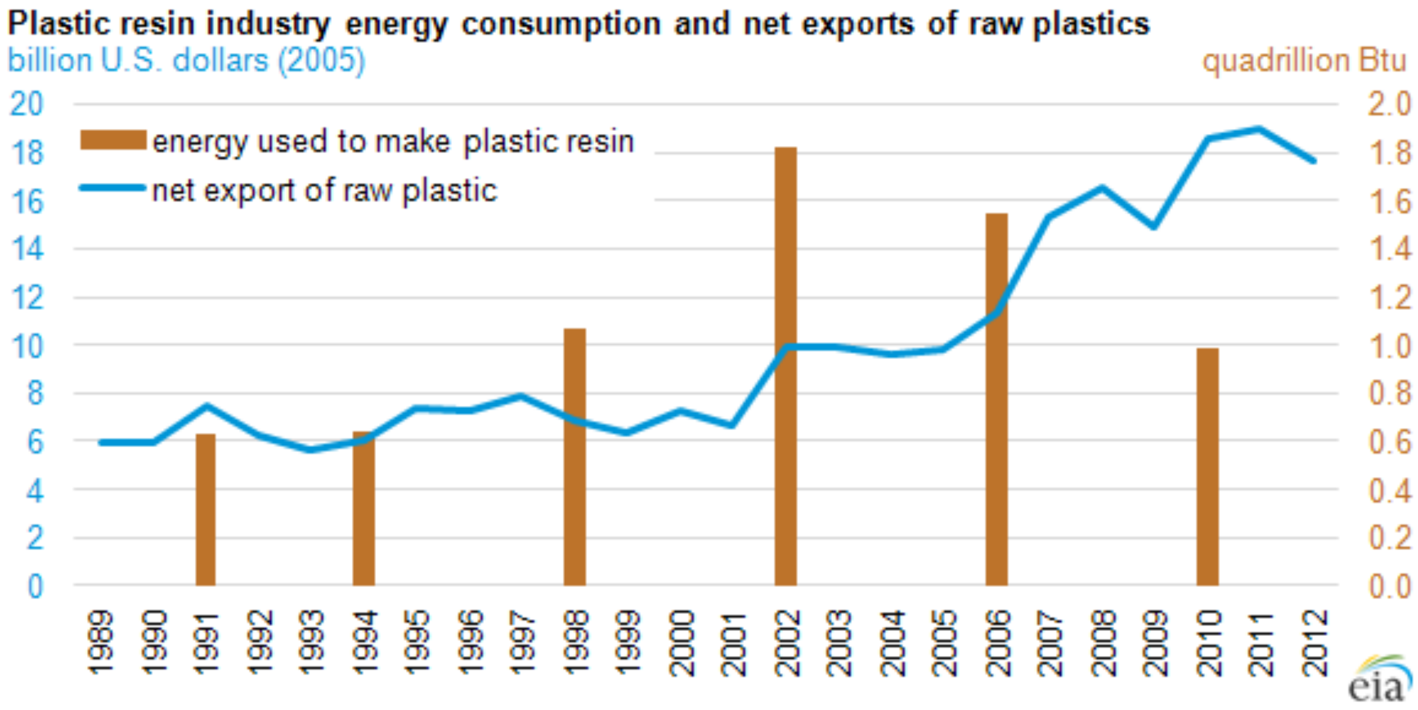
- Recent LCA studies: GHG impacts of shale gas compare to conventional for power generation [Weber, Env. Sci. Tech. 2012 46 5688]
- Issues not captured in published LCAs:
  - Reconciling/attributing underestimation of methane? [Brandt, *Science* **2014** *343* 733]
  - Groundwater contamination issues [Jackson, *PNAS* **2013** *110* 11250; Warner, *PNAS* **2012** *109* 11961]
  - Regulatory, social, political considerations
- Policy issues likely driven by power/fuels considerations, not chemicals

Energy Intensity of Chemical Industry Provides Opportunity for Process Improvements



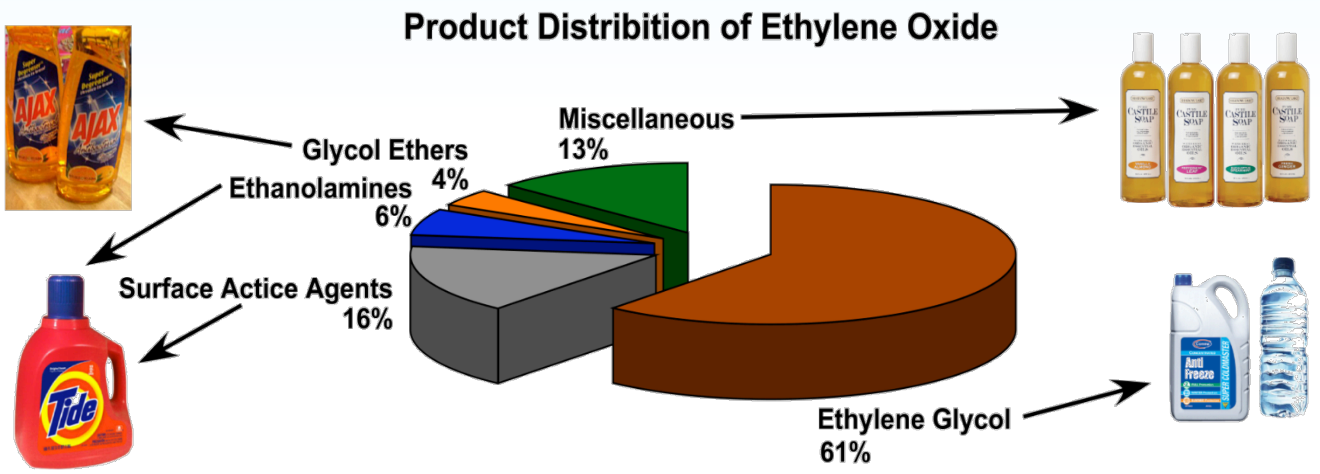
[EIA-AEO 2008. McKinsey Analysis]

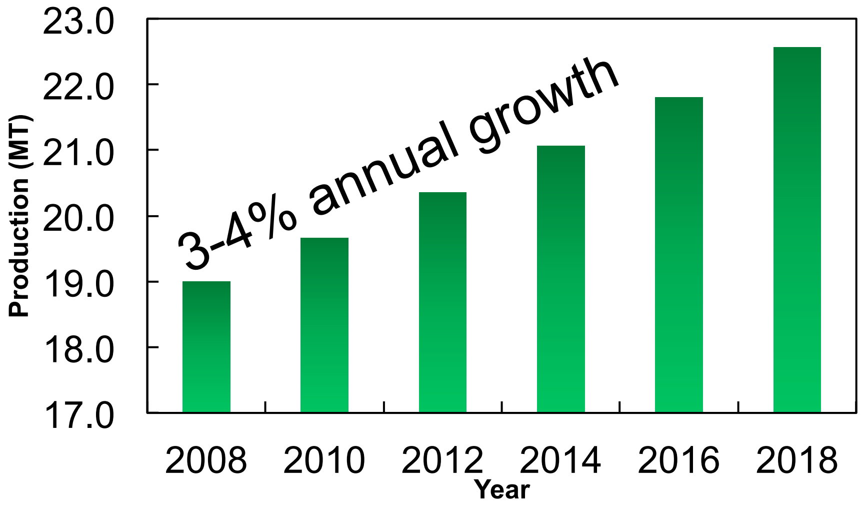
Global demand, inexpensive natural gas are increasing domestic plastic production



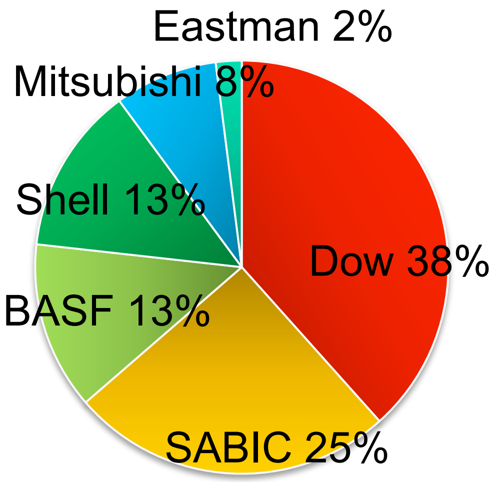
[Source: EIA, *Feb 14, 2014*]

Ethylene Oxide


Product Distribution of Ethylene Oxide

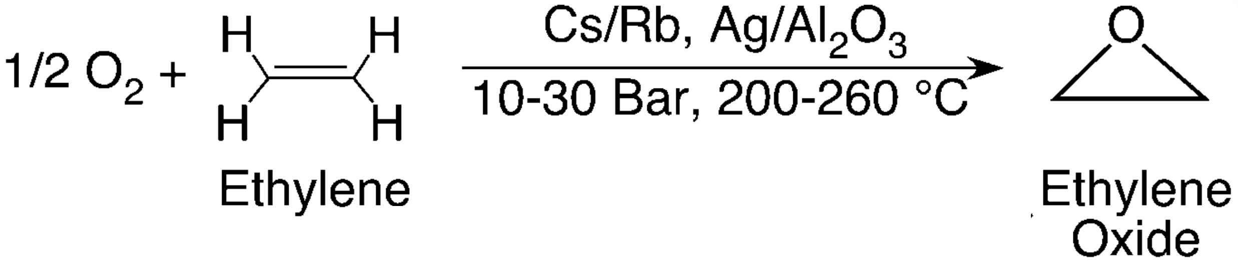


Ethylene Oxide Market Size



EO Manufacturers' Market Share

Conventional EO Production



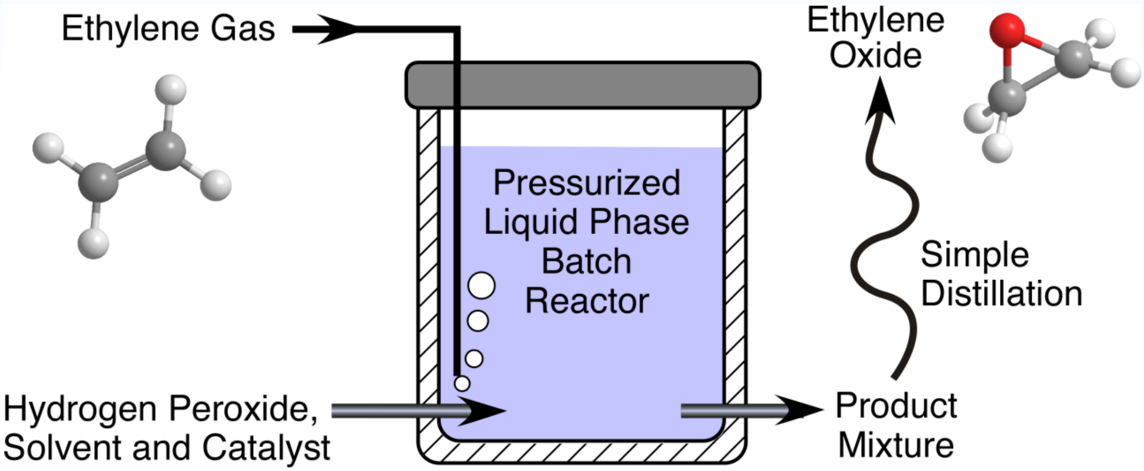
Up to 15% loss to burning
($2 Billion Loss)

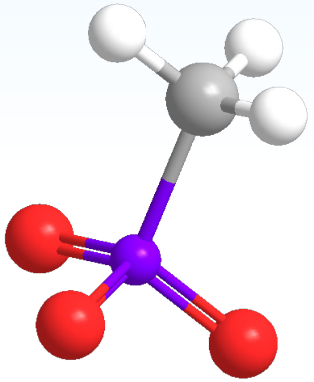
3.4 Million MT/year of CO_2 produced as byproduct, equivalent to the pollution caused by 900,000 cars

Current EO technology has large carbon footprint!

Industrial Organic Chemistry. 4th ed.; Wiley-VCH: Washington D.C., 2003.

Alternative Process with Total EO Selectivity





MTO (CH_3ReO_3)

$$\underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Hydrogen Peroxide}}{H_2O_2} \xrightarrow[\text{45 bar, 20-40 }^{o}\text{C}]{\text{Methyl Trioxorhenium, PyNO}} \underset{\text{Ethylene Oxide}}{C_2H_4O} + H_2O$$

- 99+% EO selectivity
- No CO_2 as byproduct
- No O_2 in gas phase

- Developed at the KU Center for Environmentally Beneficial Cataysis (CEBC)
- *ACS Kenneth Hancock Award for Green Chemistry* to Madhav Ghanta

H.-J. Lee, M. Ghanta, D. H. Busch and B. Subramaniam, *Chem. Eng. Sci.*, 2010, **65**, p.128-134

M. Ghanta, B. Subramaniam, H.-J. Lee and D. H. Busch, *AIChE J.*, 2013, **59**, p.180-187

Conventional vs. CEBC Process

Metric	Conventional Process*	CEBC Process
Pressure, bar	10 to 20	50
Temperature, °C	200-300	20-40
Metal /price $/lb	**Ag**: $461/lb	**Re**: $3,000/lb
Ethylene Conversion[1]	<10% per pass	No such limitations
EO Selectivity[2]	80-90%	99+%
CO_2 byproduct	10-20%	No CO_2 detected
Productivity [g EO/h/(g Ag or Re)]	2.2 - 4.1	1.61 - 4.97

- H_2O_2 fully utilized toward EO formation on MTO catalyst
- Costs on par with conventional process[3]

[1] Buffum, J. E. et. al., U.S. Patent No. 5,145,824, **1992**

[2] M. Ghanta, B. Subramaniam, H.-J. Lee and D. H. Busch, *AIChE J.* **2013** *59* 180

[3] M. Ghanta, T. Ruddy, D. Fahey, D. Busch and B. Subramaniam, *Ind. Eng. Chem. Res.* **2012** *52* 18

CEBC EO Process Conditions Similar to Propylene Oxide Technology

Process Attribute	**Dow/BASF PO Technology**	**CEBC EO Process**
Solvent	Methanol	Methanol
Oxidant	H_2O_2	H_2O_2
Catalyst	Heterogeneous (TS-1)	Homogeneous (MTO)
Pressure	30-50 bars	50 bars
Temperature	25-40°C	25-40°C

- But, TS-1 is not active for ethylene epoxidation
- Opportunity to develop heterogeneous catalysts
  - W, Nb, Ce are cheaper (< \$100/lb) compared to Re (~\$3,000/lb)

H_2O_2-Based Epoxidation with W- and Nb-based Catalysts: Previous Work

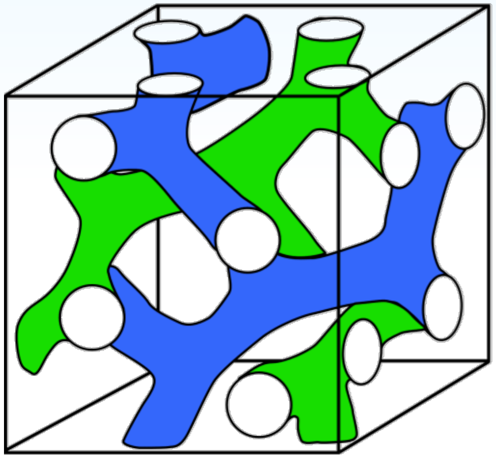
	Substrate Epoxidized	Temperature (°C)	Time (h)	Epoxide Yield (%)
[1]W complex – MCM-41[1]	*cis*-Cyclooctene	50	12	66.5
Nb-MCM-41[2]	Cyclohexene	45	12	58
Nb-MCM-41[3]	Cyclooctene	90	24	65
Nb-SBA-15[4]	Cyclohexene	40	40	32.5

- Are W and Nb-based catalysts applicable for selective ethylene epoxidation?
- What is the reaction mechanism? What is the extent of metal leaching?
- Is the H_2O_2 utilized selectively for forming EO? Does H_2O_2 decompose?

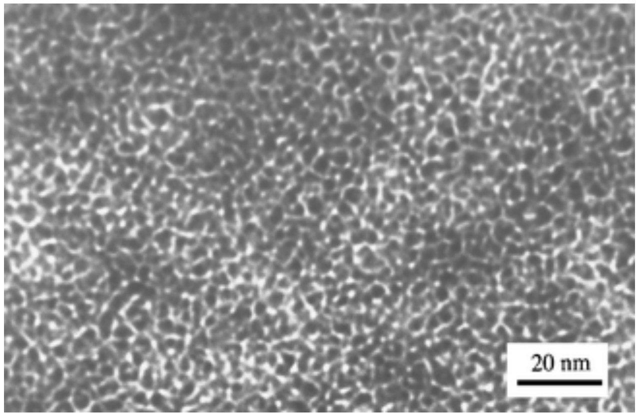
[1] D. Hoegaerts, B.F. Sels, D.E. de Vos, et. al., *Catal. Today* **2000** *60* 209
[2] I. Nowak, B. Kilos, M. Ziolek, et al., *Catal. Today* **2003** *78* 487
[3] J.M.R. Gallo, I. S. Paulino, U. Schuchardt, *Appl. Catal. A-gen.*, **2004** *266* 223
[4] M. Ziolek, P. Decyk, I. Sobczak, et al., *Appl. Catal. A-gen.*, **2011** *391* 194

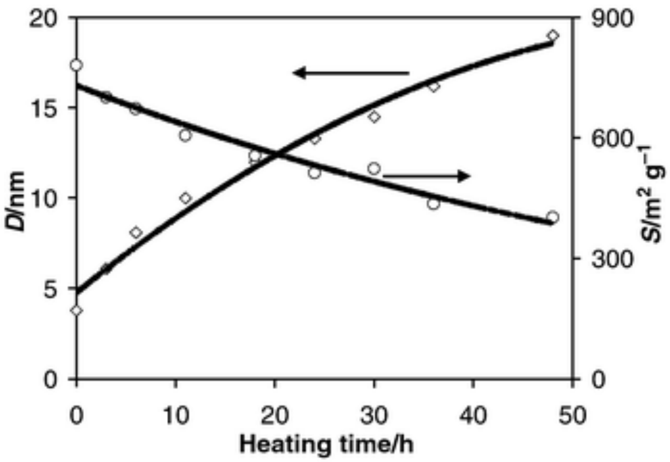
Metal-Loaded Catalysts

- KIT-6[1] silicates used to incorporate W and Nb
  - W[2] and Zr[3] successfully incorporated
- TUD-1[4] used to incorporate Ce



KIT-6





[1] T. W. Kim, F. Kleitz, B. Paul and R. Ryoo, *J. Am. Chem. Soc.* **2005** *127* 7601.

[2] A. Ramanathan, B. Subramaniam, D. Badloe, U. Hanefeld and R. Maheswari, *J. Porous Mater.* **2012** *19* 961.

[3] A. Ramanathan, B. Subramaniam, R. Maheswari and U. Hanefeld, *Microporous & Mesoporous Materials* **2013** *167* 207.

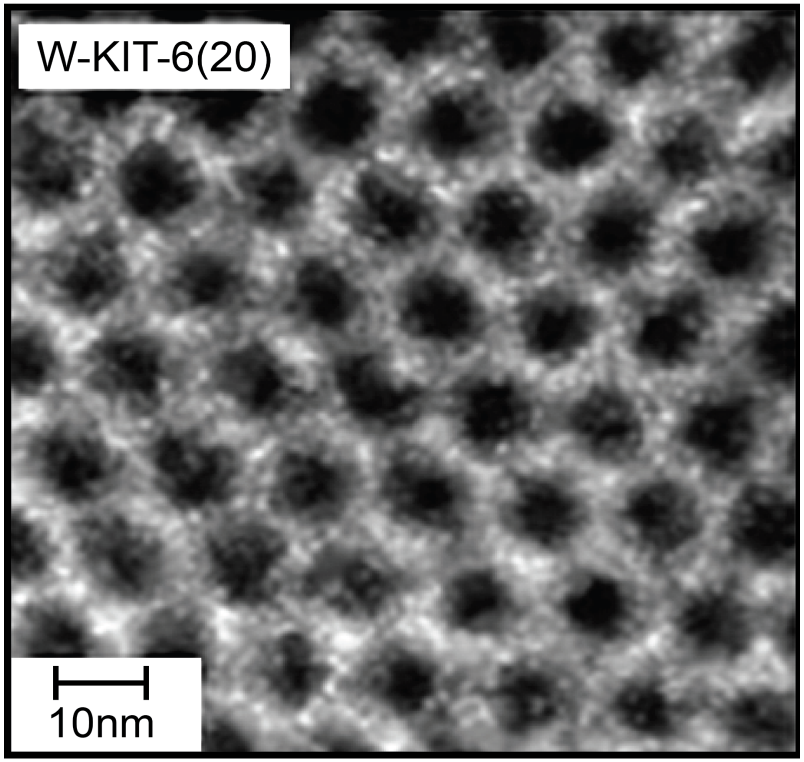
[4] J. C. Jansen, Z. Shan, L. Marchese, W. Zhou, N. von der Puil and T. Maschmeyer, *Chem. Commun.* **2001** 713.

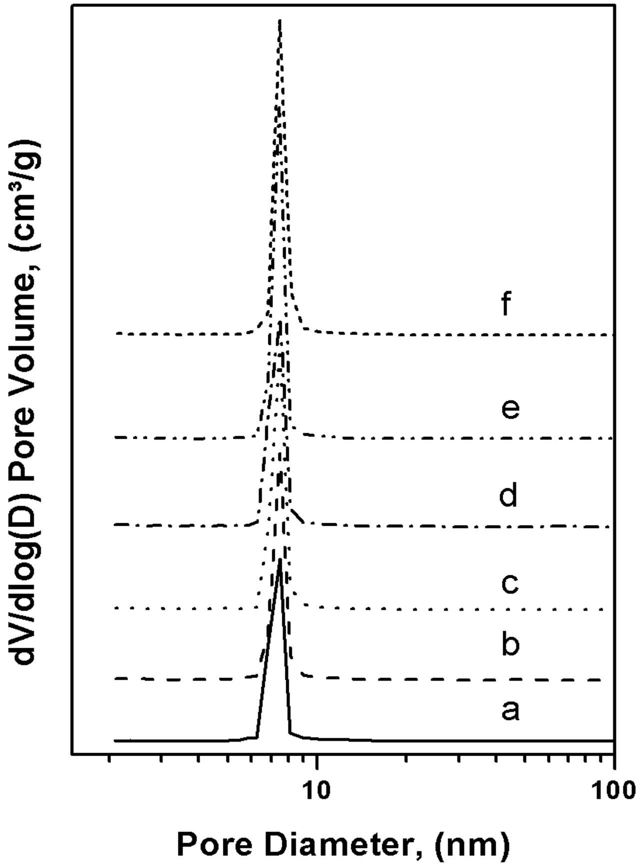
Textural Properties Confirm Mesoporosity

Sample	W-KIT-6[1]	Nb-KIT-6	Ce-TUD-1
Metal wt%	2.6-15.2	1.5-10.9	2-24.9
S_{BET} (m^2/g)	927-625	997-804	749-173
$V_{p,\ BJH}$ (cm^3/g)	1.44-1.09	1.46-1.12	0.65-0.91
$d_{P,\ BJH}$ (nm)	6.3-6.9	9.3	3.9-16.7
Total acidity NH_3 mmol/g	0.26-0.48	0.27-0.75	--

[1] A. Ramanathan, B. Subramaniam, D. Badloe, U. Hanefeld and R. Maheswari *J. Porous Mater.* **2012** *19* 961.

TEM Confirms Ordered Mesoporous Structure

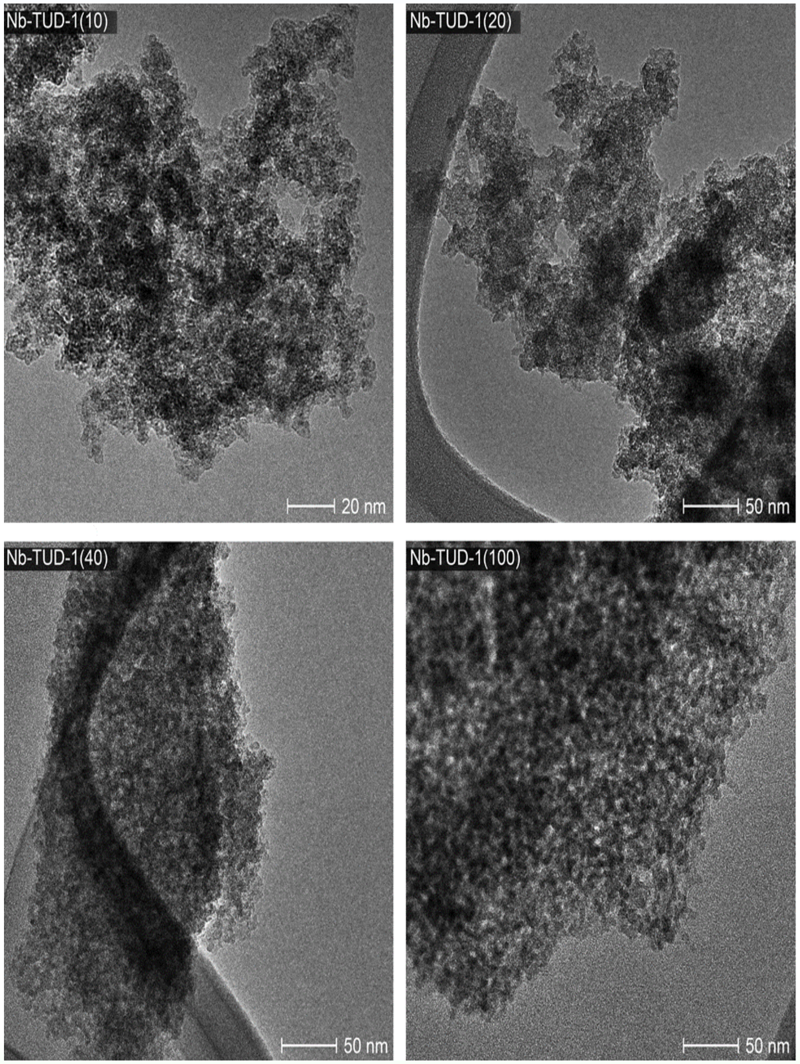




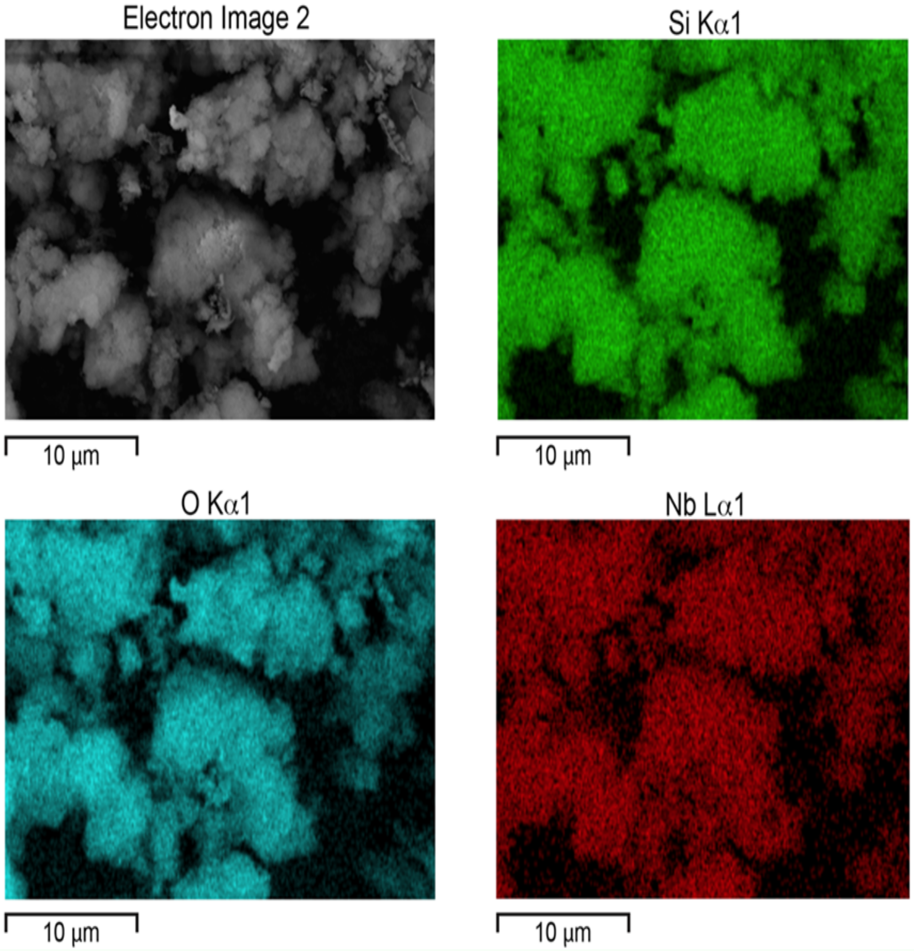
W-KIT-6, Pore size: 6.3-6.9 nm

A. Ramanathan, B. Subramaniam, D. Badloe, U. Hanefeld and R. Maheswari, *J. Porous Mater.*, **2012** *19* 961.

Disordered Worm-hole Morphology of Nb-TUD-1 and Uniform Distribution of Nb-species

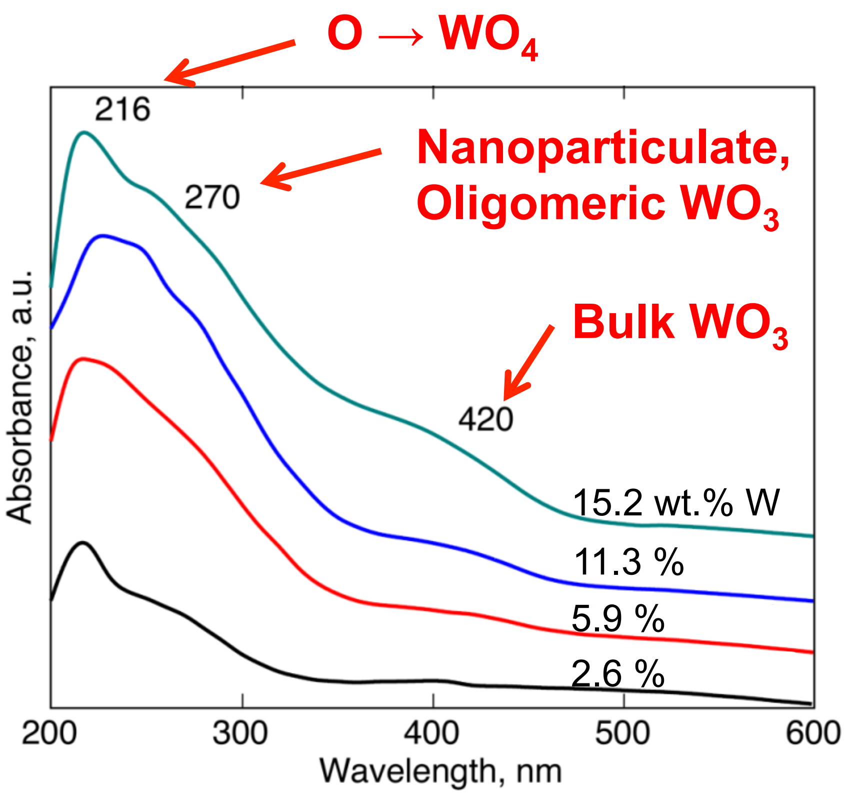


SEM of ~12wt% Nb-TUD-1



DR-UV-Vis Spectra Reveal Different Types of Metal Incorporation

W-KIT-6

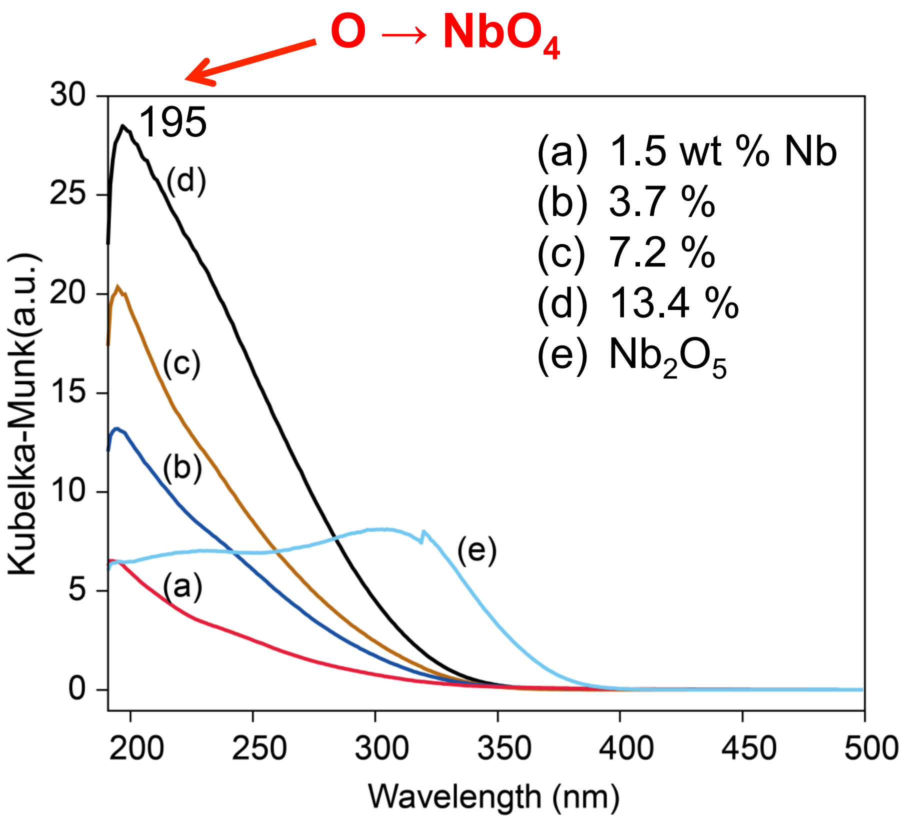


O → WO_4

Nanoparticulate, Oligomeric WO_3

Bulk WO_3

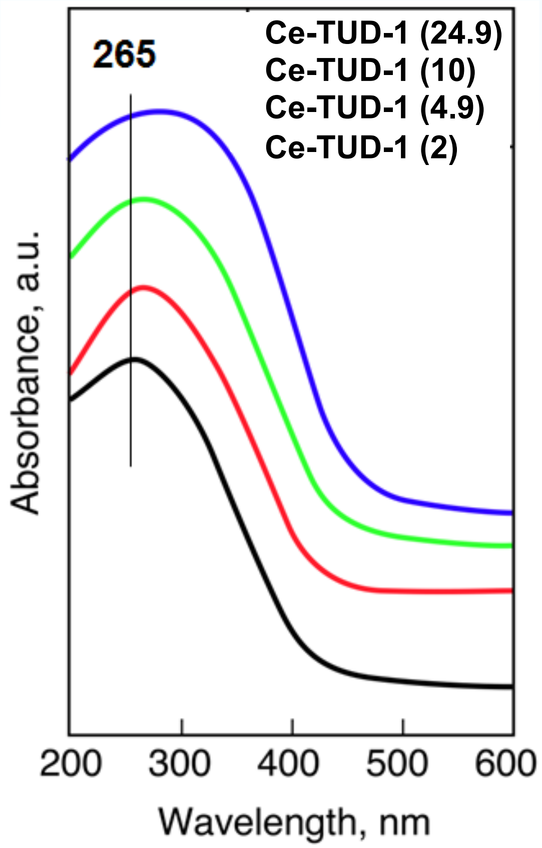
Nb-KIT-6

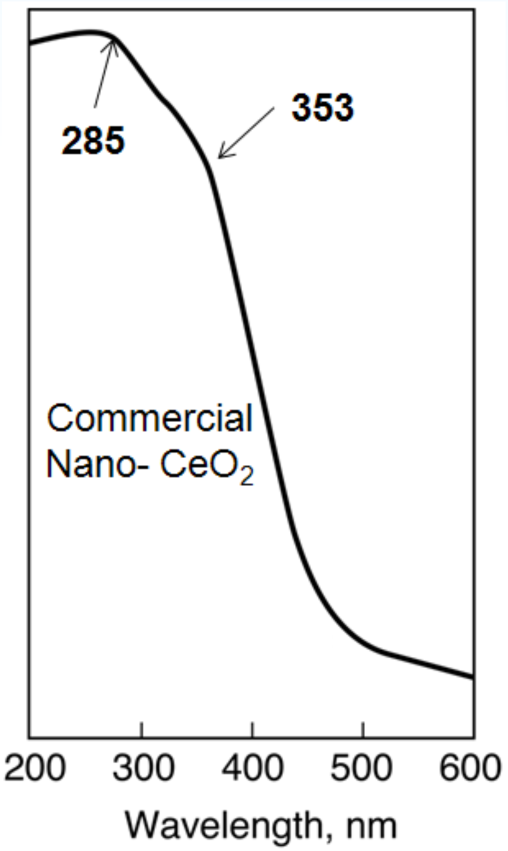


O → NbO_4

A. Ramanathan, B. Subramaniam, D. Badloe, U. Hanefeld and R. Maheswari, *J. Porous Mater.* **2012** *19* 961.

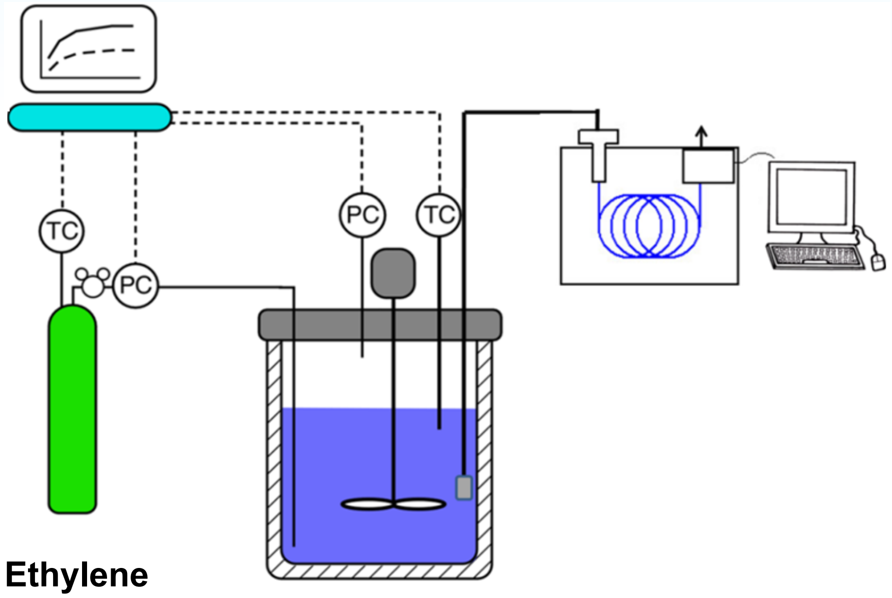
Cerium Coordination: DR-UV-Vis



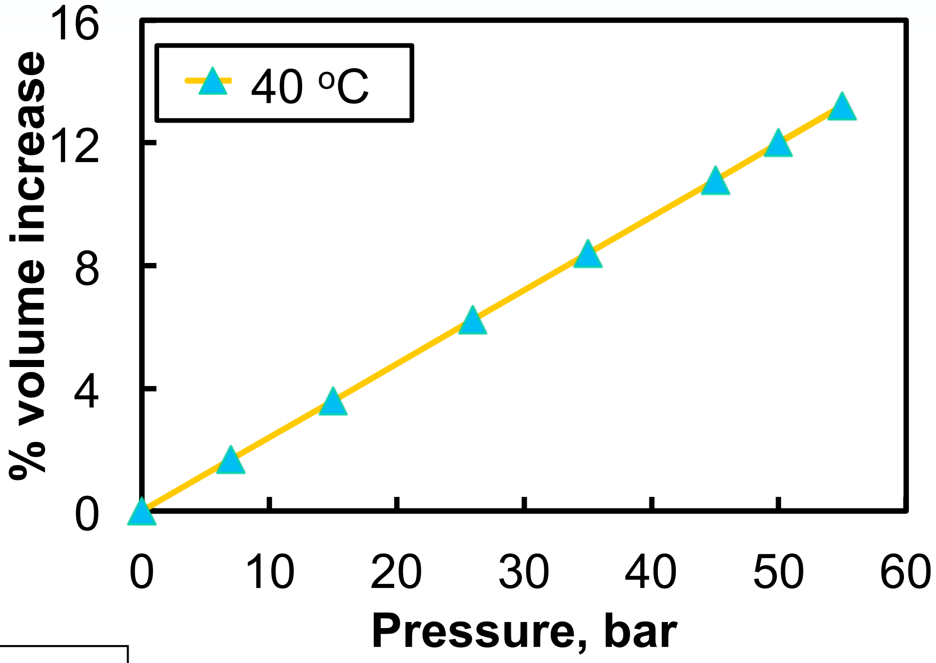


- 265 nm: $O^{2-} \rightarrow Ce^{3+}$ charge transfer transition
- 285 and 353 nm: nano-CeO_2

Catalyst Evaluation with Pressure-tuned Ethylene Solubility



T_c = 9.4 °C, P_c = 50.76 bar



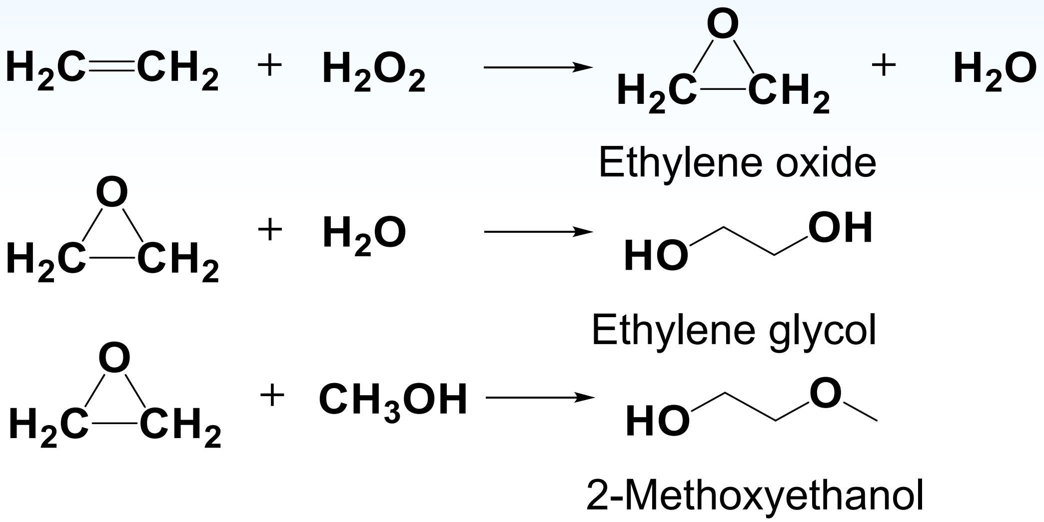
- P = 50 bar; T = 35 °C; Stirrer speed = 1400 rpm;
- 50 wt% H_2O_2/H_2O (oxidant) = 8 g;
- Methanol (solvent) = 20 g; Batch time = 5 h.
- Catalyst amount = 300 - 500 mg (metal + support).

Ethylene mole fraction at 50 bar: **0.163**

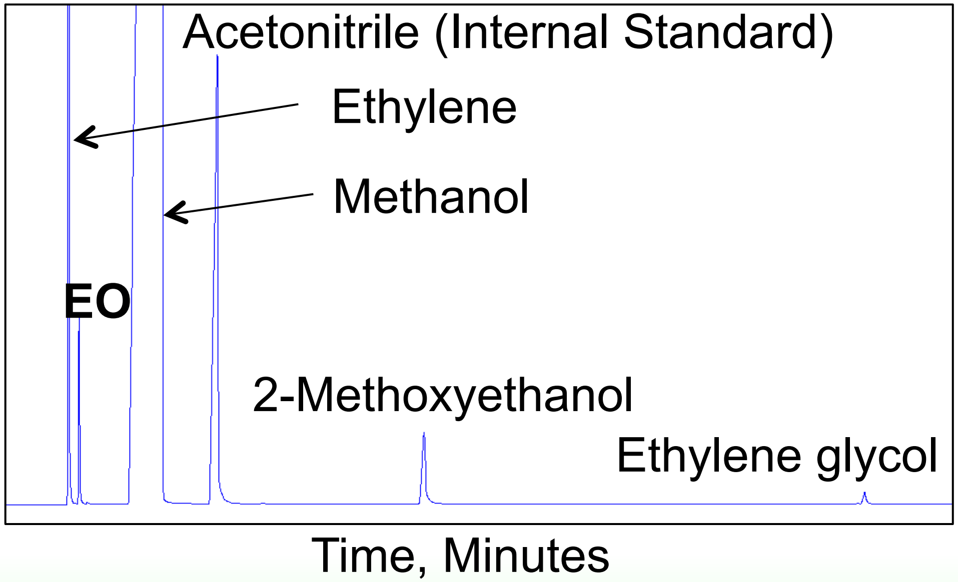
Ethylene-expanded liquid phase

H.-J. Lee, M. Ghanta, D. H. Busch and B. Subramaniam, *Chem. Eng. Sci.*, 2010, **65**, p:128-134

Observed Reactions



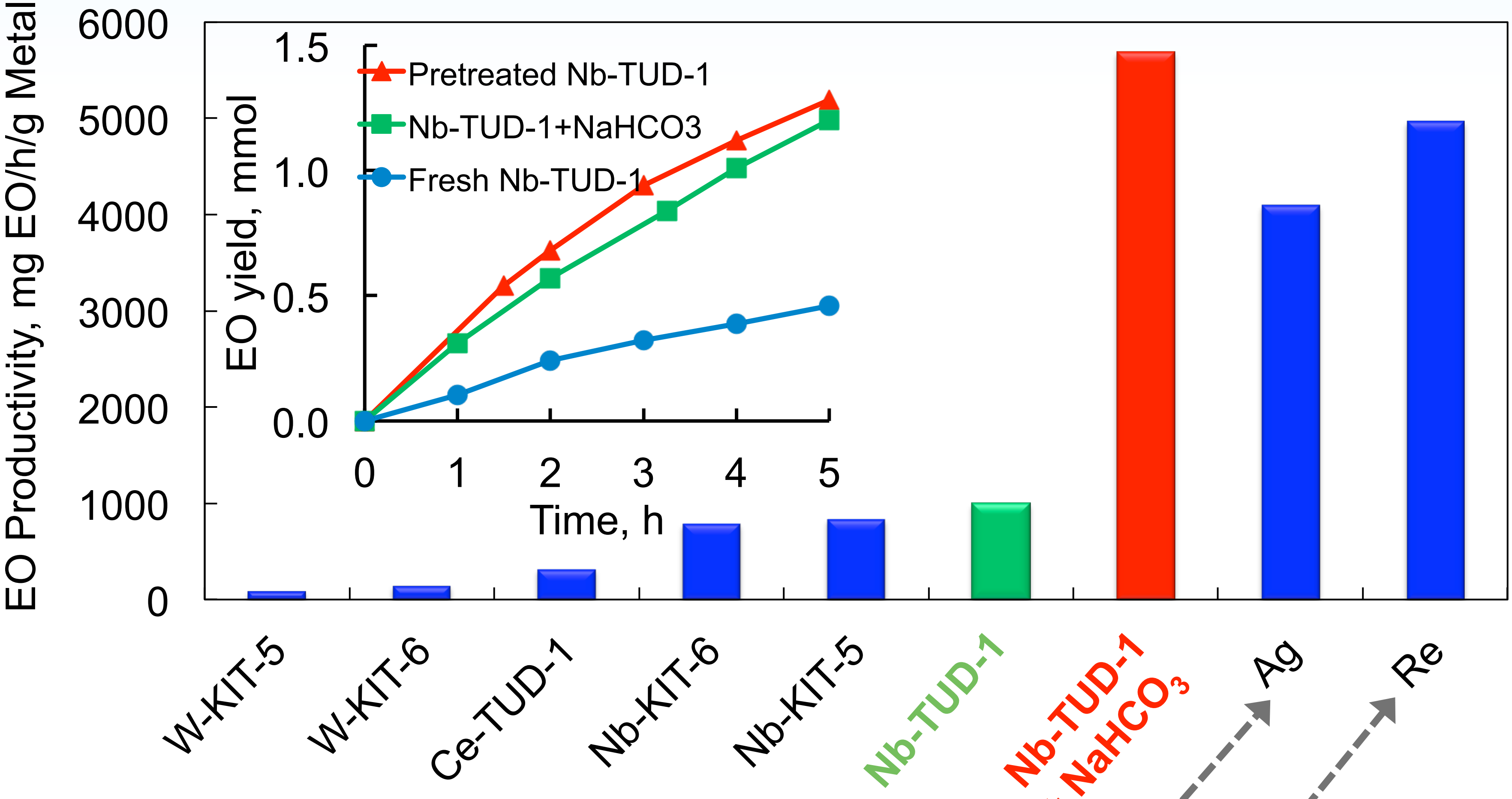
$$2\ H_2O_2 \longrightarrow O_2 + 2\ H_2O$$



H_2O_2 analysis:
Ceric Sulfate Titration

Metal content:
ICP-OES

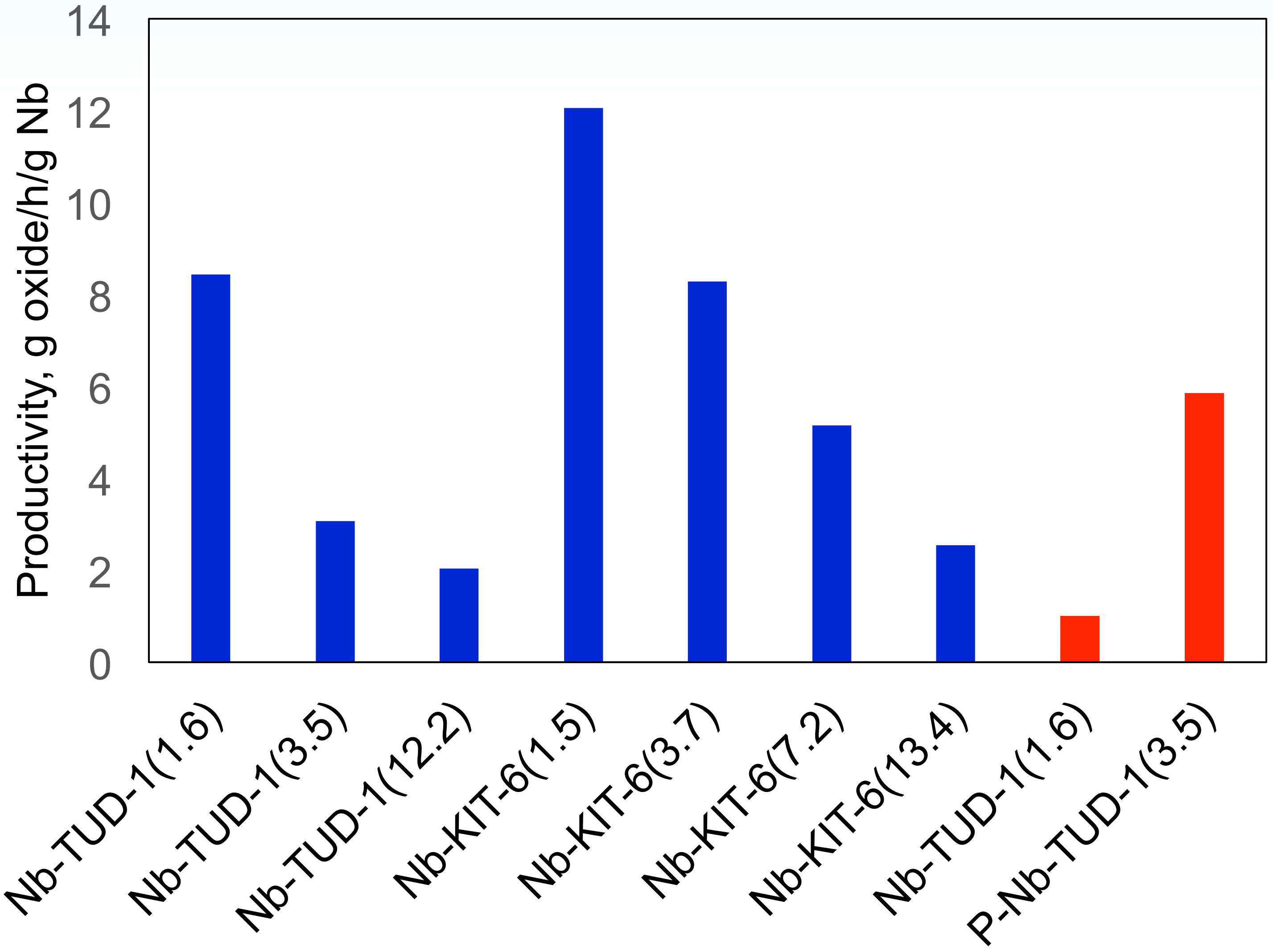
Metal-exchanged Mesoporous EO Catalysts



Ag catalyst for commercial process

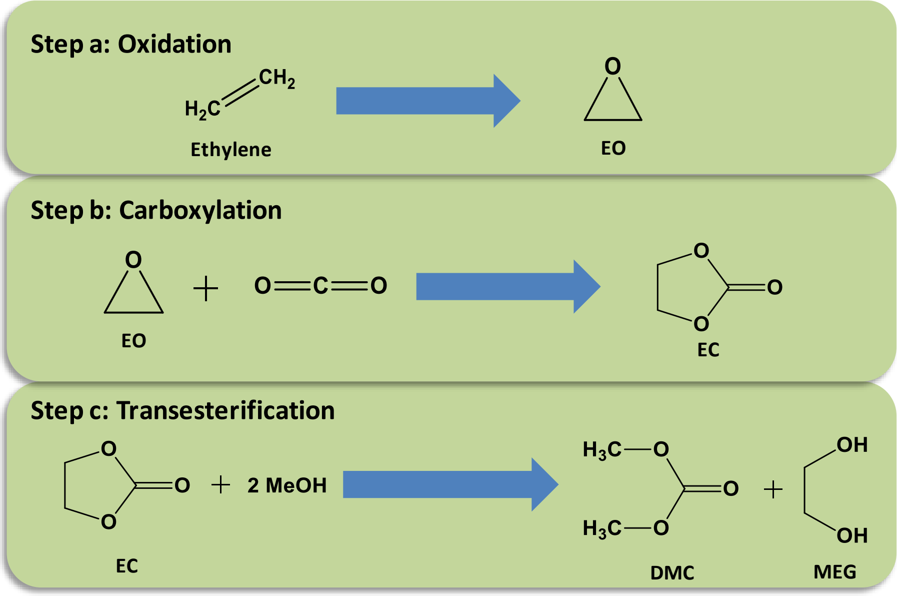
Re catalyst for CEBC process

Nb-TUD-1 and Nb-KIT-6 Active for *Propylene* Epoxidation as Well



Dimethyl Carbonate Production

- EO can be further carboxylated and transesterified to dimethyl carbonate
  - Non-phosgene route using CO_2 and methanol
- Potential for “one-pot” synthesis



Epoxidation Summary

- Homogeneous ethylene epoxidation with MTO catalyst and H_2O_2 as oxidant demonstrated.
  - Mild conditions: (20-40)°C, ~50 bar; Benign solvents.
  - Virtually total epoxide selectivity ~ 99+%; No CO_2 byproduct.
  - EO productivity comparable with Ag-catalyzed process
  - Lower environmental footprint

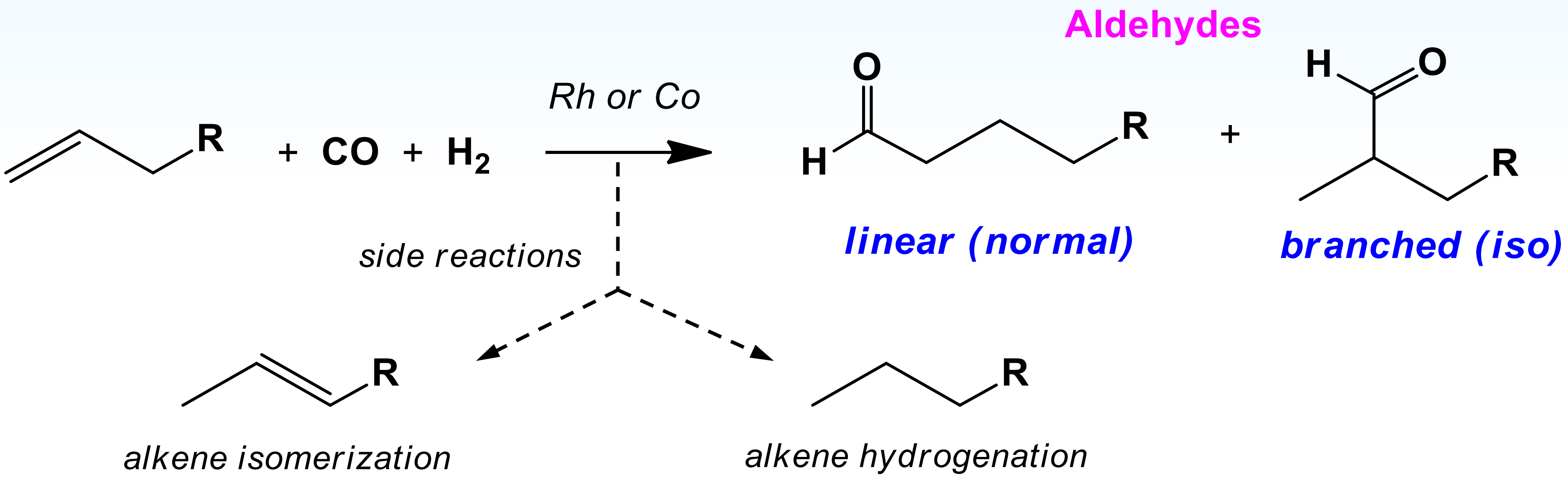
Epoxidation Summary

- W, Nb-KIT-6 and Ce-, Nb-TUD-1 catalysts are shown to be active for ethylene epoxidation with H_2O_2 as oxidant. No CO_2 formation.
- EO productivity on Nb-TUD-1 (~4,500 mg EO/h-g metal) superior to those observed on Re-based and conventional Ag catalysts

Ongoing Work

- Strategies to further reduce metal leaching and H_2O_2 decomposition
- Computational studies of reaction pathways and metal leaching
- Continuous epoxidation with Nb-TUD-1 catalysts
- Potential applications to mixed ethane/ethylene feeds

Industrial Relevance of Hydroformylation



Hydroformylation Product
(> 15 billion pounds/year)

Chemical Intermediates

Plasticizers

Detergents

Surfactants

Wiese, K.-D. and D. Obst Catalytic Carbonylation Reactions **2006** *18* 1-33.

Industrial Hydroformylation: Current Status

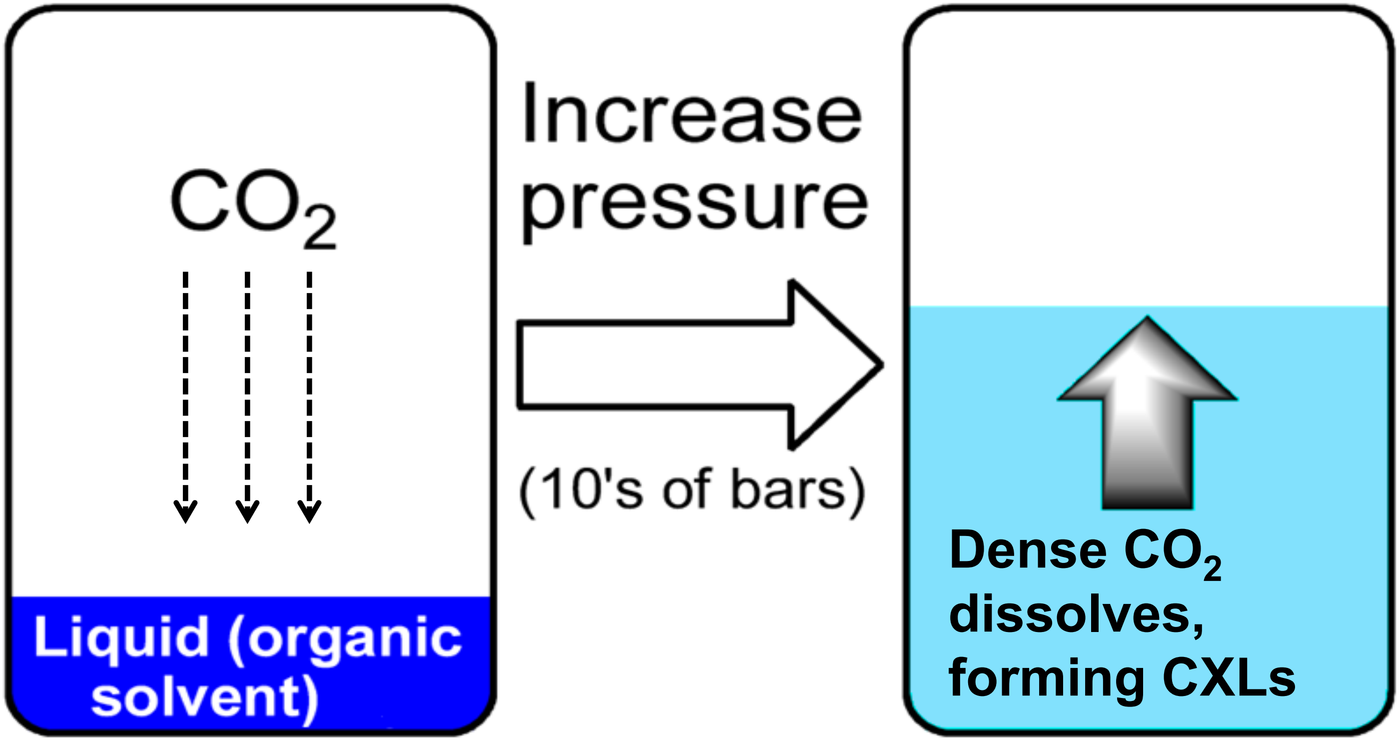
	Lower olefins (C_3 and C_4)	Higher olefins (C_5- C_{13})
Catalyst	Rhodium-Based	Cobalt-Based
Conditions	90 –130 °C; 15 – 40 bar	140 – 200 °C; 50 – 300 bar
TOF (h^{-1})	550 – 770	20 – 35
S_a (aldehydes)	> 95 %	75 –90 %
n/iso	4 - 5	2 - 3
Metal cost ($/lb, year 2012)	~ 20,800 [www.kitco.com]	~ 12 [www.metalprices.com]

A Rh-based hydroformylation process for higher olefin with high TOF, *n/i* and catalyst recovery is desirable.

Substrate: 1-Octene **Desired Product: *n*-nonanal**

[P. van Leeuwen, Homogeneous Catalysis, 2004]

CO_2-Expanded Liquids (CXLs) Provide Unique Properties



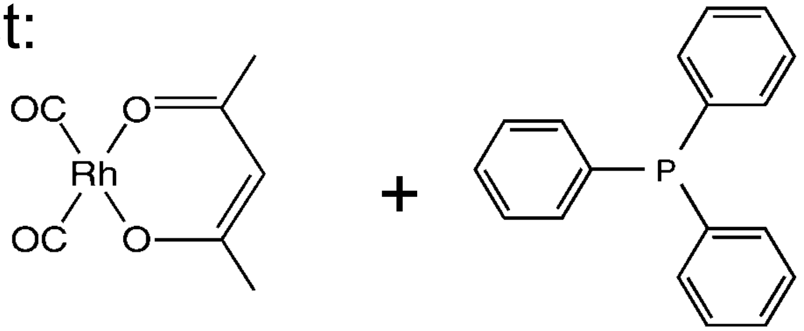
[Subramaniam and Akien, *Current Opinion in Chem. Eng*. **2012** *1* 336]

CO_2-expanded Liquids (CXLs) Enhance Hydroformylation Rate and Regio-Selectivity!

Total P	System	TOF, hr^{-1}	*n/i*
64 bar	Syngas Only	195	4
	6 bar Syngas + CO_2	290	11
	6 bar Syngas + N_2	180	5

T = 60 °C, 1-octene/Rh/P = 2136/1/200

Catalyst:



Jin *et al*., AIChE J., 52, 2575 (2006)

Syngas Solubility in Neat Solvent and in CXLs

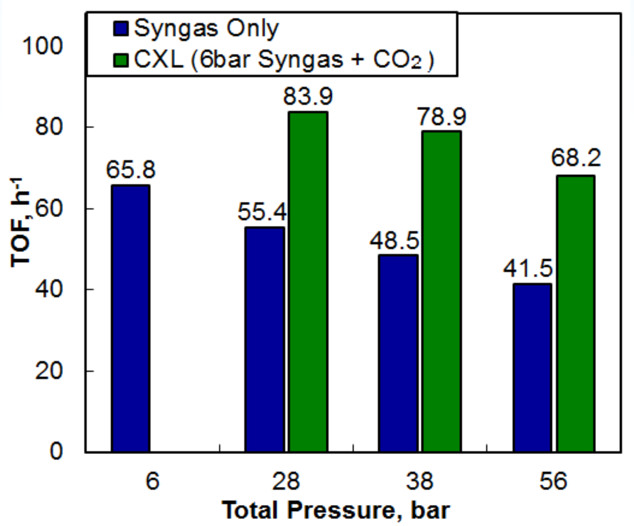
	Syngas Only			**CXL (6 bar syngas + CO_2)**		
P, bar	x, H_2	x, CO	H_2/CO	x, H_2	x, CO	H_2/CO
6	0.0011	0.0019	0.60	-	-	-
25	0.0048	0.0079	0.60	0.0012	0.0019	0.62
38	0.0073	0.0124	0.59	0.0013	0.0021	0.65
56	0.0105	0.0177	0.59	0.0016	0.0022	0.72

- H_2 and CO solubility increased with syngas pressure
- H_2/CO ratio had little change

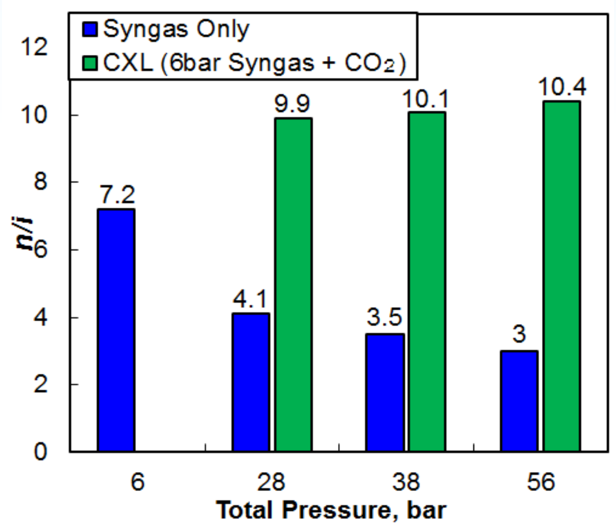
- H_2 and CO solubility increased a little with CO_2 pressure
- H_2/CO ratio increased in CXL

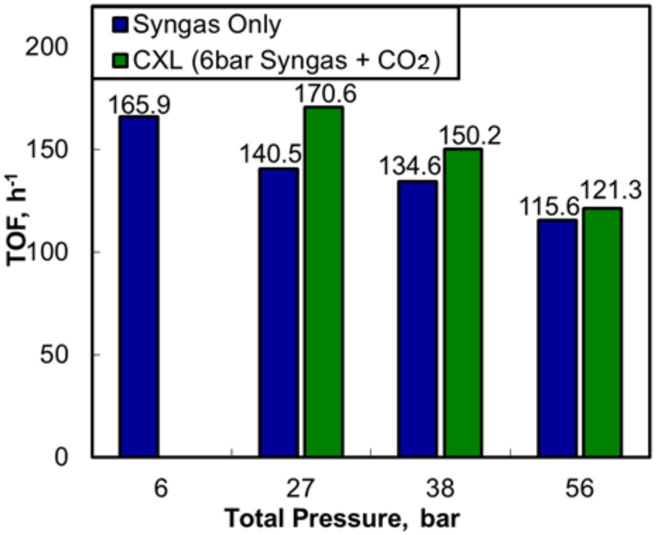
T = 50 °C. In 1-octene reaction mixture. H_2/CO ratio in syngas feed = 1. Standard deviations less than 5% for all data points.

CXLs Enhance TOF and n/i

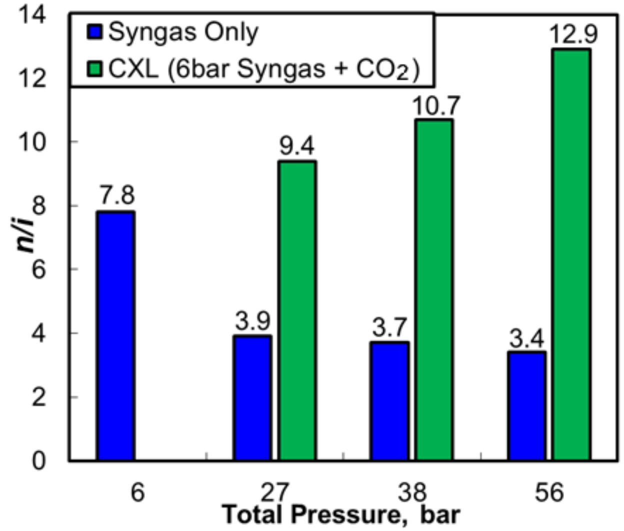


50 °C



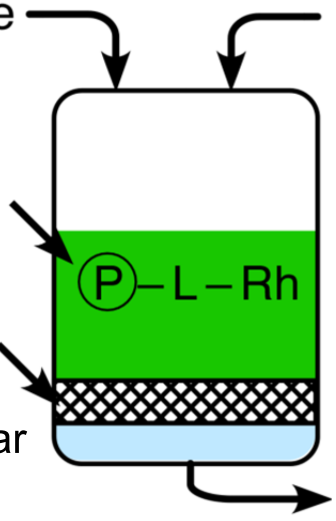


60 °C



1-octene/Rh/P = 988/1/205; Solvent: toluene

Continuous Hydroformylation Using Nanofiltration Membranes



1-Octene

Syngas

Soluble “bulky” polymer catalyst

Ⓟ–L–Rh

Nano-filtration membrane

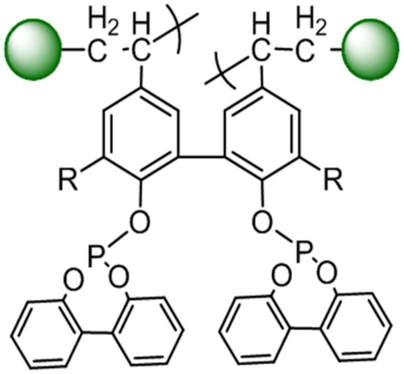
(max T = 50 °C,
280 Dalton molecular
weight cut-off)

Product stream

(Desired filtration pressure: **> 30 bar**)

(Rh, P contents analyzed by ICP-AES)

Polymer ligand:

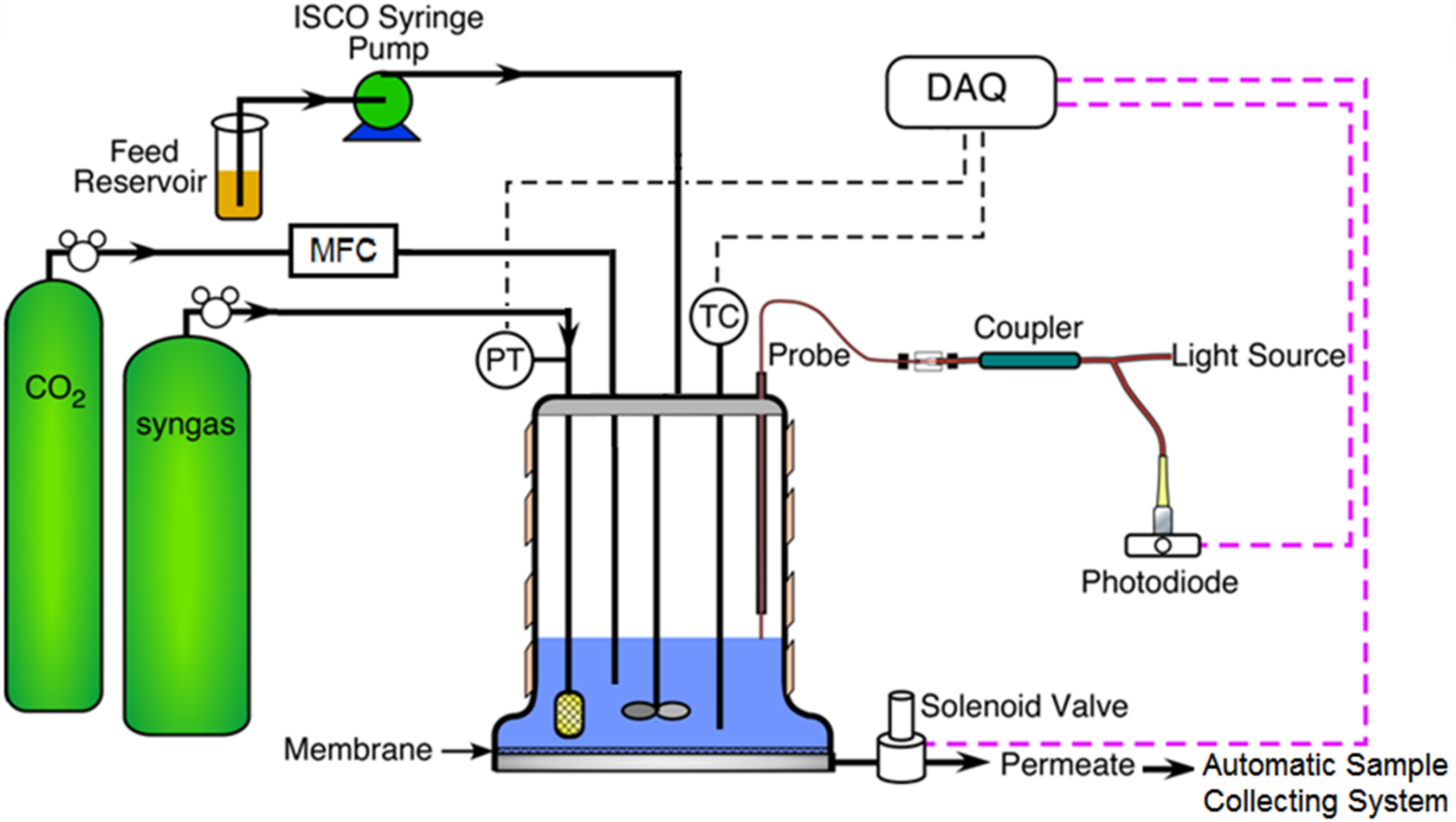


JanaPhos

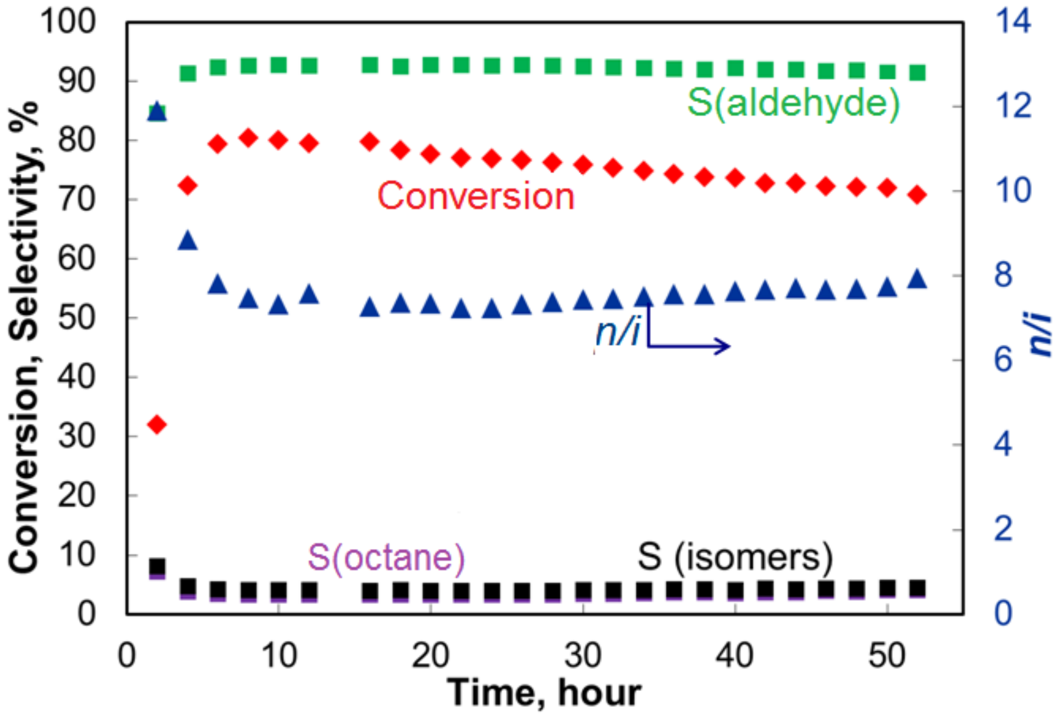
P loading: 0.65 mmol/g
MW: ~ 12,190 g/mol
PDI: ~ 1.3

[R. Jana *et al.*, *Org. Lett.* **2009** *11* 971]

Continuous CXL Reactor with Level Control



Continuous Hydroformylation in CXL Successfully Demonstrated

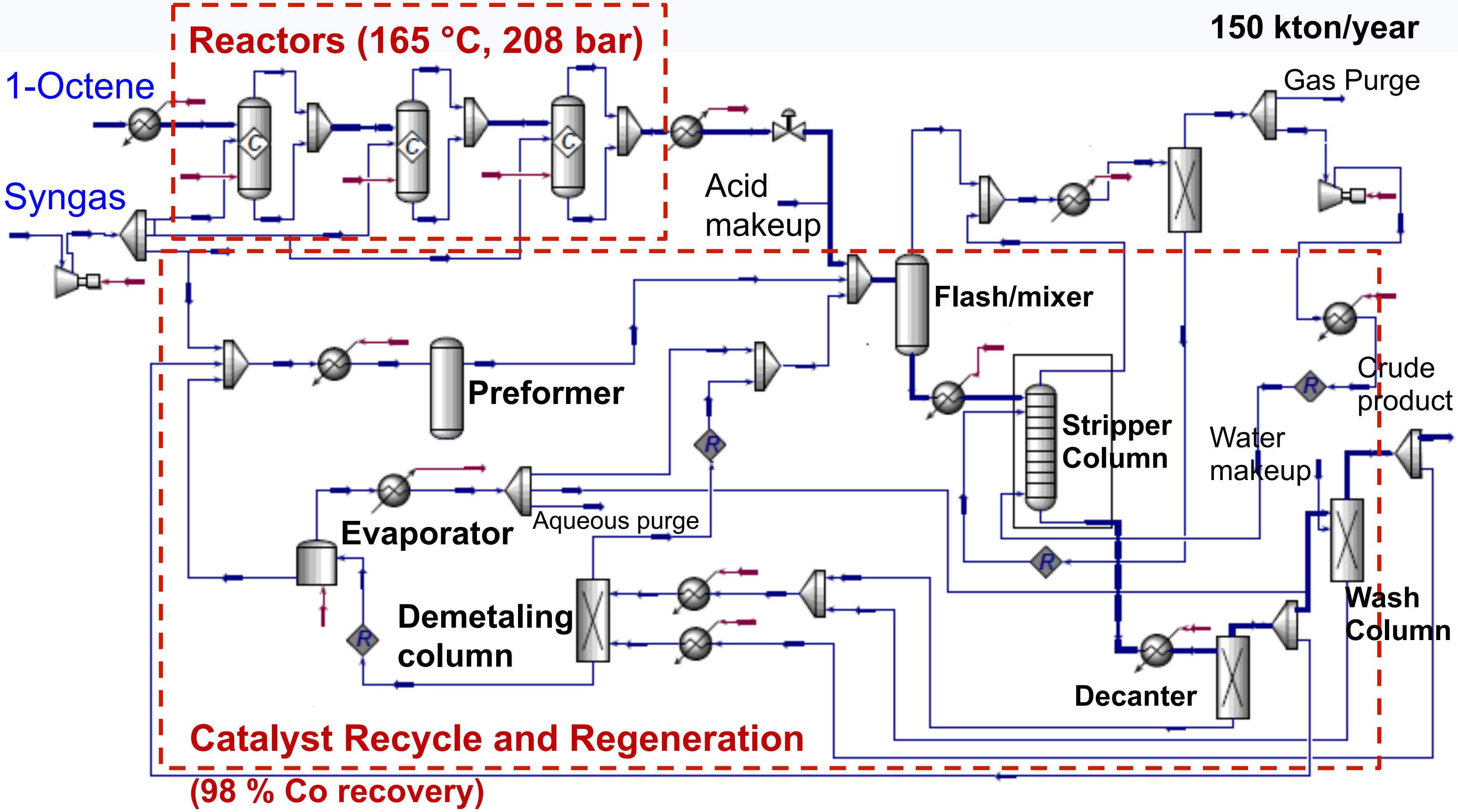


T = 50 °C; 6 bar syngas, 30 bar CO_2

TON after 52 hours: 17,351
Total lost in 52 h: Rh ~ 5%; P ~ 4.6%

	Syngas Only	**CXL**
Time, h	22	52
Pressure	30 bar	6 bar syngas + 30 bar CO_2
LHSV, g 1-octene/ g Rh/h	272	472
Conversion	~ 50%	~ 72%
n/i	~ 3.5	~ 8
TOF, h^{-1}	~ 125	~ 340

Conventional Octene Hydroformylation Process (Co-Catalyzed)

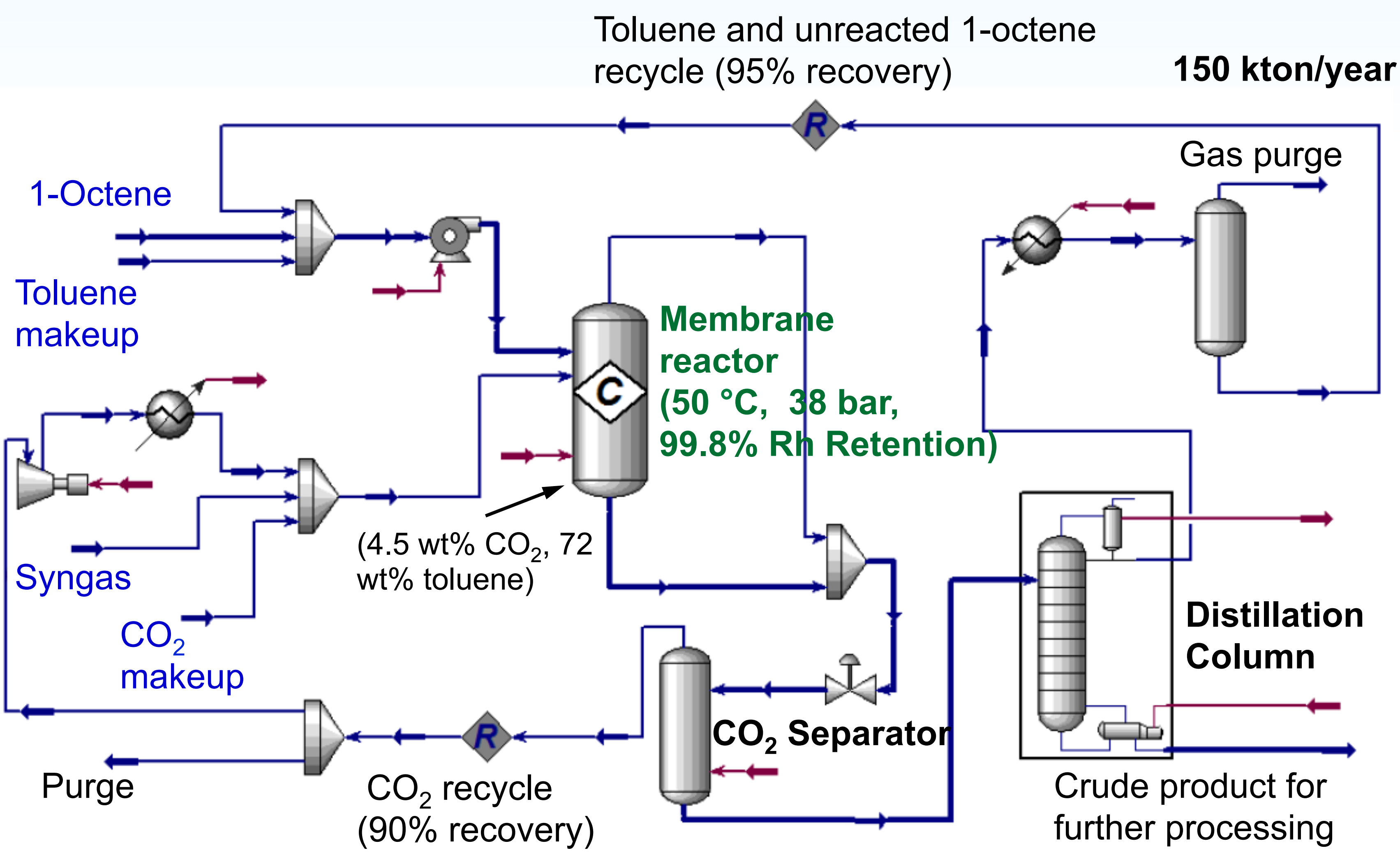

Reactors (165 °C, 208 bar)

150 kton/year

Catalyst Recycle and Regeneration (98 % Co recovery)

US 5,306,848; US 5,600,031; US 5,434,318; US 5,457,240; US 5,237,105; US 5,410,090 A; EP 0343819 A1

Conceptual CEBC CXL Hydroformylation Process



Toluene and unreacted 1-octene recycle (95% recovery)

150 kton/year

Gas purge

1-Octene

Toluene makeup

Membrane reactor (50 °C, 38 bar, 99.8% Rh Retention)

Syngas

CO_2 makeup

(4.5 wt% CO_2, 72 wt% toluene)

Distillation Column

CO_2 Separator

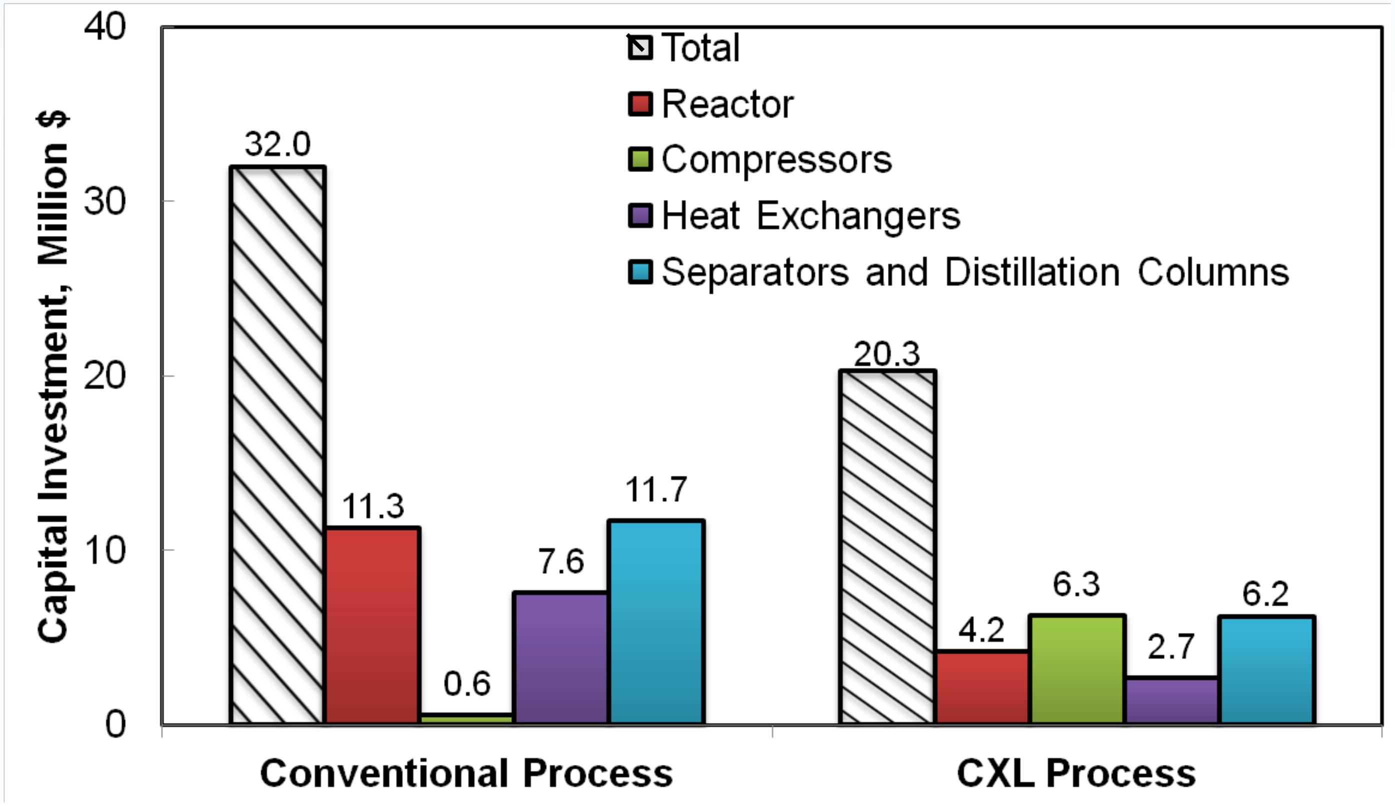
Purge

CO_2 recycle (90% recovery)

Crude product for further processing

∗Minimum toluene for catalyst dissolution: 33 wt%

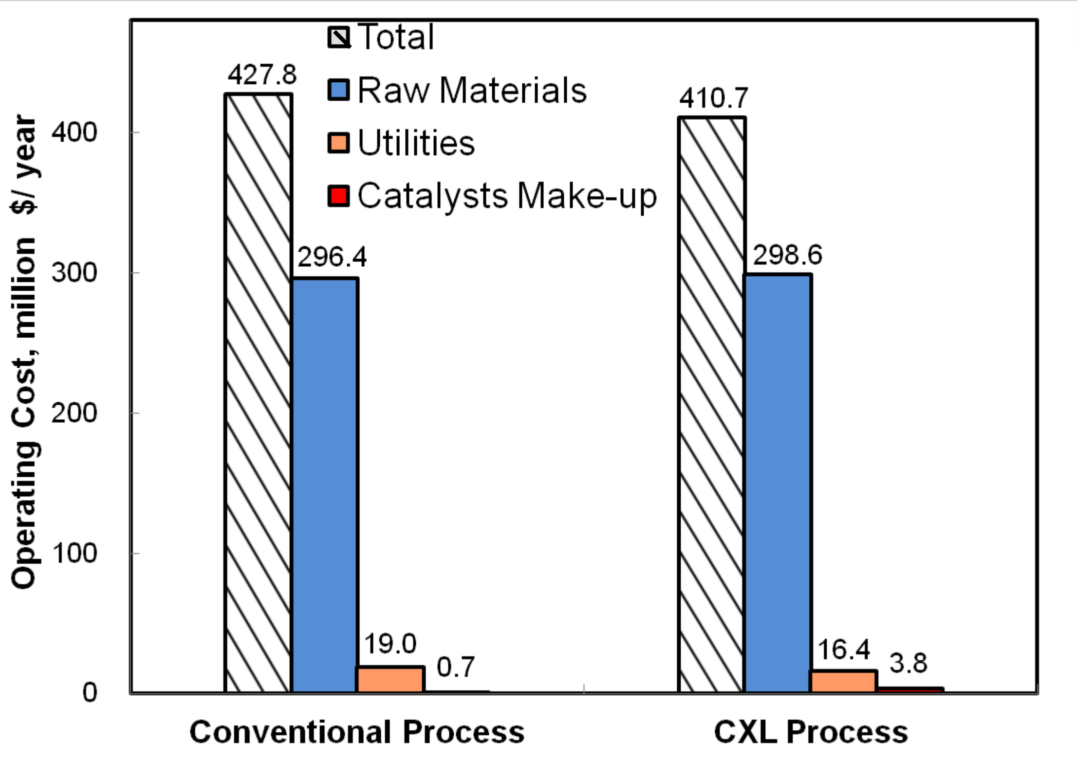
Capital Investment Comparison



Process	Reactor	Heat Exchangers	Distillation Columns	Separators	Compressors	Pumps and Filters	**Total**
Conventional	11.3	7.6	8.2	3.5	0.6	0.9	**32**
CXL	4.2	2.7	5.4	0.8	6.3	0.9	**20.3**

* Price in million $ per year

Operating Cost Comparison



Process	Catalyst Make-up
Conventional	2%
CXL	0.2%

Process	Raw Materials	Utilities	Catalysts Make-up	Solvents	Other Variable Production Costs	Fixed Charges	Plant Overhead Cost	General Expenses	**Total**
Conventional	296.4	19.0	0.7	0.0	30.8	8.3	6.0	66.7	**427.8**
CXL	298.6	16.4	3.8	0.3	23.5	2.2	3.0	62.9	**410.7**

* Price in million $ per year

Hydroformylation Summary

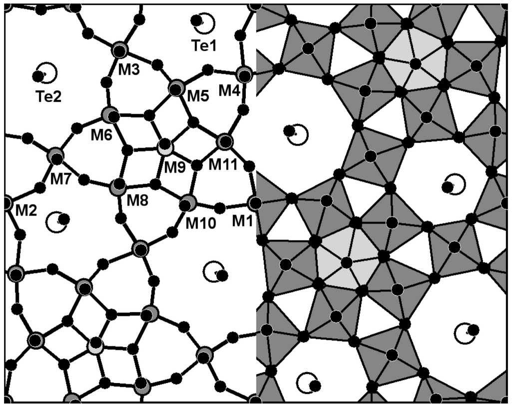
- CXLs provide benefits of **enhancing TOF and regioselectivty** toward linear aldehydes with simple Rh/TPP catalyst complexes
  - **Higher H_2/CO ratio** in the liquid phase at fixed syngas feed composition
  - **Low syngas partial pressure** (i.e. avoiding syngas inhibition)
- Continuous hydroformylation in CXL media demonstrated using nanofiltration membranes with JanaPhos ligand
  - Steady TOF (~ 340 h^{-1}), TON after 52 hours: 17,351; $S_{aldehydes}$ ~ 95%; ***n/i* ~ 8**
- Quantitative economic and environmental assessment shows excellent potential of continuous CXL-based process concept with *in situ* nanofiltration to be commercially viable and environmentally beneficial

Other Opportunities: Higher Olefins

- Linear α-olefins
  - – Ethyl Process (INEOS)
  - – Gulf Process (CP Chem)
  - – Shell Higher Olefins Process
- Selective ethylene oligomerization:
  - – Trimerization (CP Chem)
  - – Tetramerization (Sasol)
- *Selective heterogeneous catalysts?*
  - – Control of branching, carbon # distribution

Other Opportunities: Direct Routes From Propane?

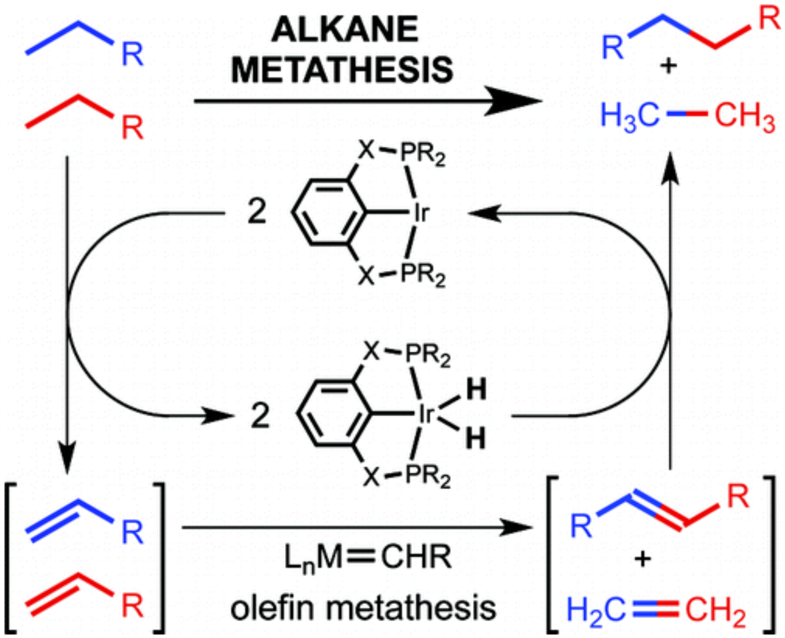
- Direct oxidation of propane to acrylic acid
  - Mixed-metal oxides (e.g. $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$) provide yields up to ~50% [e.g. Ushikubo US 5,380,933A 1995], sensitive to morphology
- Ammoxidation of propane to acrylonitrile
  - Mixed metal oxides (e.g. $Mo_{0.6}V_{0.187}Nb_{0.085}Te_{0.14}O_x$) have achieved yields in excess of 60% [Grasselli, Nanostructured Catalysts: Selective Oxidations, Ch.5, 2011]
- Improved understanding of catalyst phases needed for improved design



[Sanfiz *J. Phys Chem. C* **2010** *114* 1912]

Other Opportunities: Metathesis of Light Alkanes?

- One-pot metathesis of propane or *n*-butane
- Three-step reaction scheme requires tandem or multi-functional catalysts
- Need for improved dehydrogenation catalysts and more robust metathesis



[Haibach *Acct. Chem. Res.* **2012** *45* 1947]

Concluding Remarks

- *Emerging feedstocks* (biomass, shale gas) provide exciting challenges for developing novel technologies with reduced environmental footprints
  - Potential game changers for the US chemicals industry
- Multi-scale approach that benefits from expertise of chemists and engineers to concurrently address all process elements (catalyst, reaction mechanisms, reactors, etc.) expedites discovery of *resource-efficient* technologies
- Quantitative *sustainability assessments* (economic, LCA) are powerful tools in guiding R&D toward practically viable processes
- *University/Industry/Government partnerships* that engage stakeholders across the entire value chain key for timely technology commercialization with emerging feedstocks

"Chemicals from Emerging Feedstocks" Initiative in Kansas

Mission: To *develop economical technologies for chemicals/fuels that prevent waste, conserve resources.*

ADM
EVONIK INDUSTRIES
DUPONT
P&G
Chevron Phillips
ExxonMobil
ConocoPhillips
UOP
EASTMAN

- *Chemicals from Biomass*: USDA/ADM Grant ~$7 M/4 years; Awarded in 2011
- *Chemicals from Natural Gas*: NSF Grant ~$4.4 M/4 yrs; Awarded in 2013.

Graduate Students

- Meng Li
- Shirley Xie
- Grace Pan
- Xin Jin
- Madhav Ghanta
- Dupeng Li
- Wenjuan Yan

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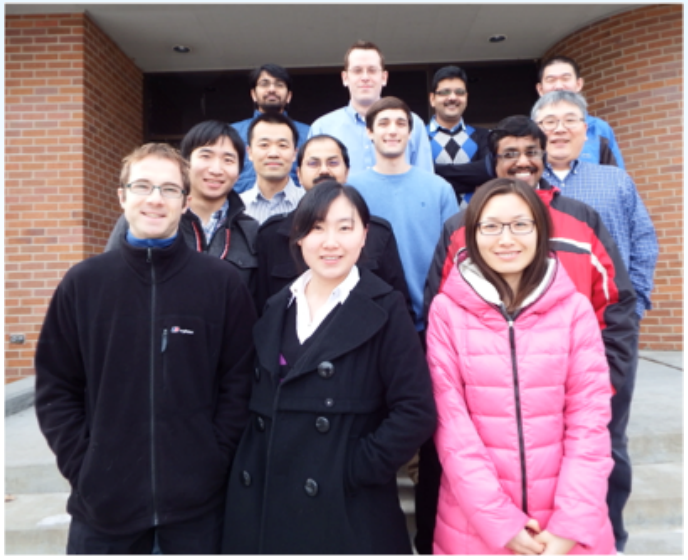
- Xiaobin Zuo
- Geoffrey Akien
- Amit Chaudhari
- Bibhas Sarkar
- Andrew Danby
- Michael Lundin



Faculty Collaborators

- Daryle Busch
- Raghunath V. Chaudhari
- Jon Tunge
- Shenqiang Ren

Funding Agencies

- National Science Foundation
- U.S. Department of Agriculture
- State of Kansas

CEBC Industry Partners

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