Redefining Feedstocks for the Chemical Industry: Opportunities and Challenges for Catalysis

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PIRE-ECCI/ICMR Summer Program on Techniques of Surface Science and Catalysis

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Overview

- Overview of Feedstock Challenges for the Chemical Industry
- Developing Technologies/Challenges Based on Alternate Feedstocks
  - Methane
  - Coal
  - Biomass
- Examples of Ongoing Dow Research in
  - Autothermal oxidation of ethane to ethylene
  - Ethane to vinyl chloride
  - Seed oil-based polyols
- Closing Remarks

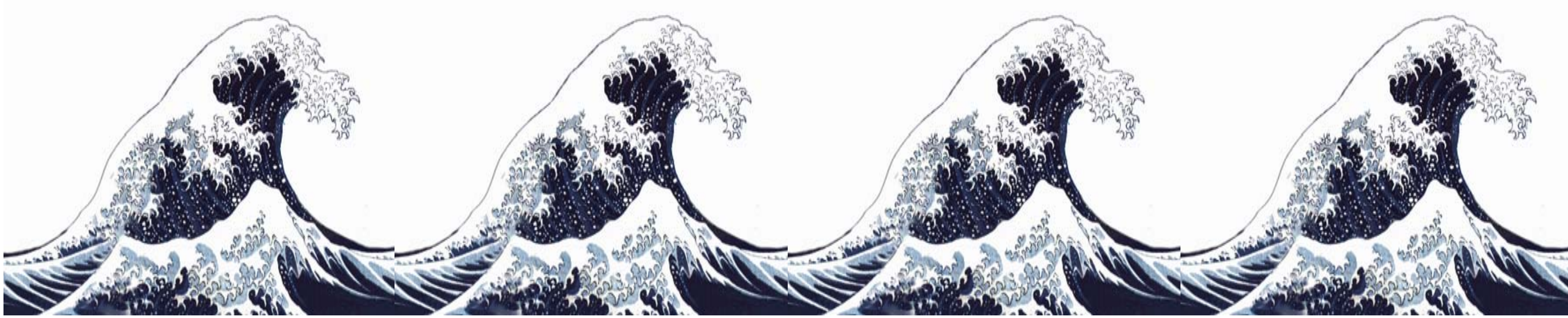
The Chemical Industry - Technology Waves

Inorganic
- mined materials
- electrochemical
- active reagents allow transformations

Functionalization
- use inorganics to transform organic substrates
- make dyes, solvents and drugs

Cellulosics
- use inorganics to transform natural materials
- partially synthetic polymers

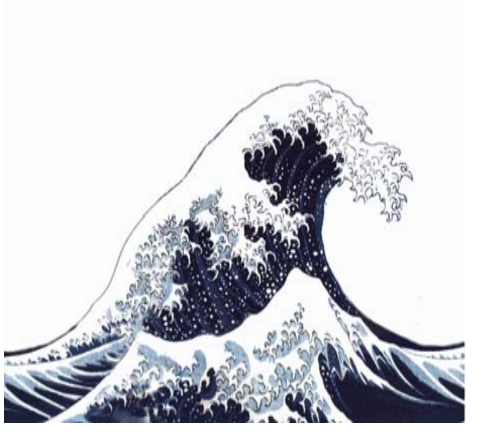
Polymers
- took off with synthetic rubber
- continues today



1760-1910	1870-1930	1895-1935	1925-present
rocks ⇨	coal ⇨	biomass ⇨	petroleum NGL

The Chemical Industry - Technology Waves

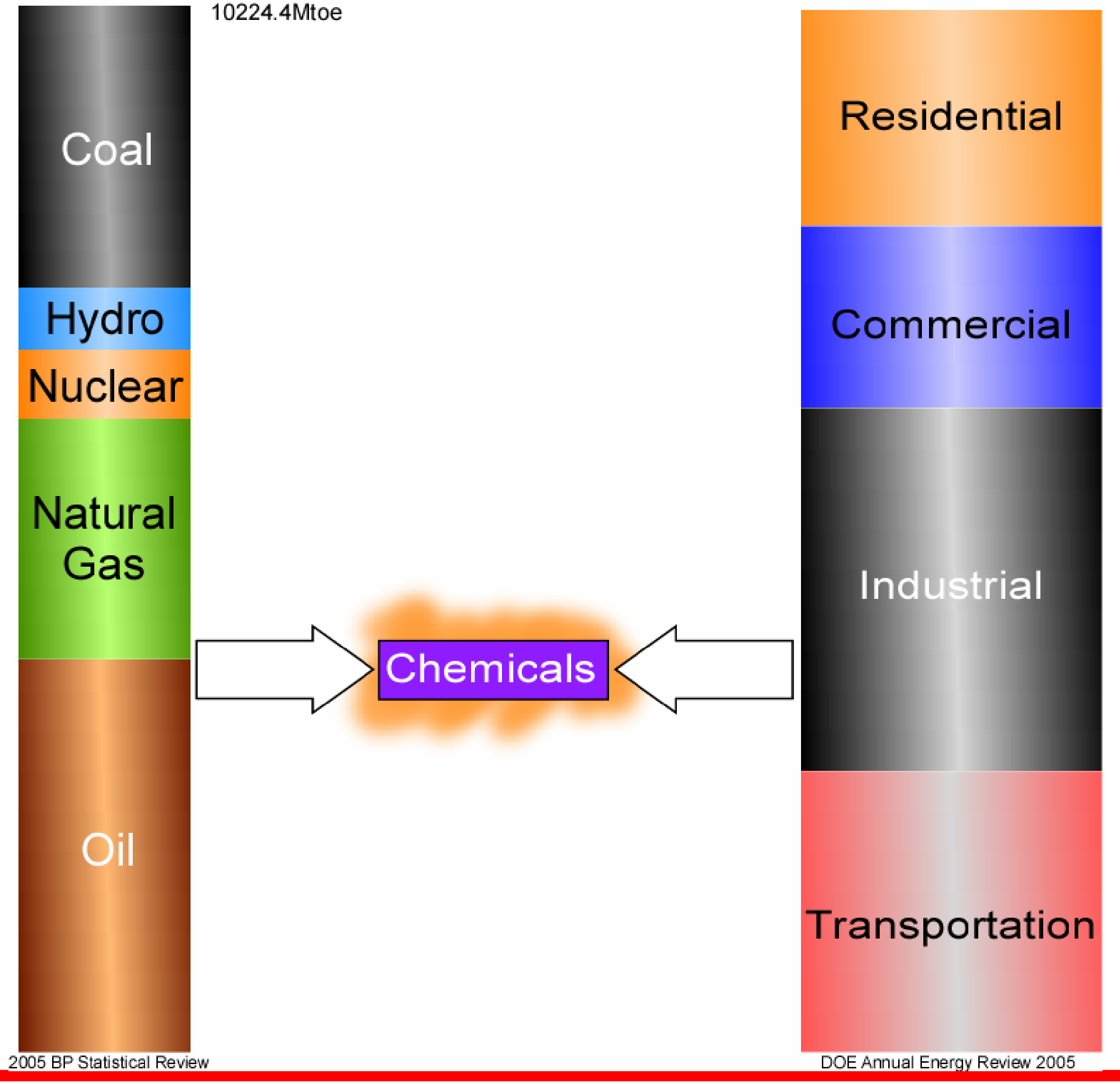
Next?
- raw material competition
- new materials
- energy



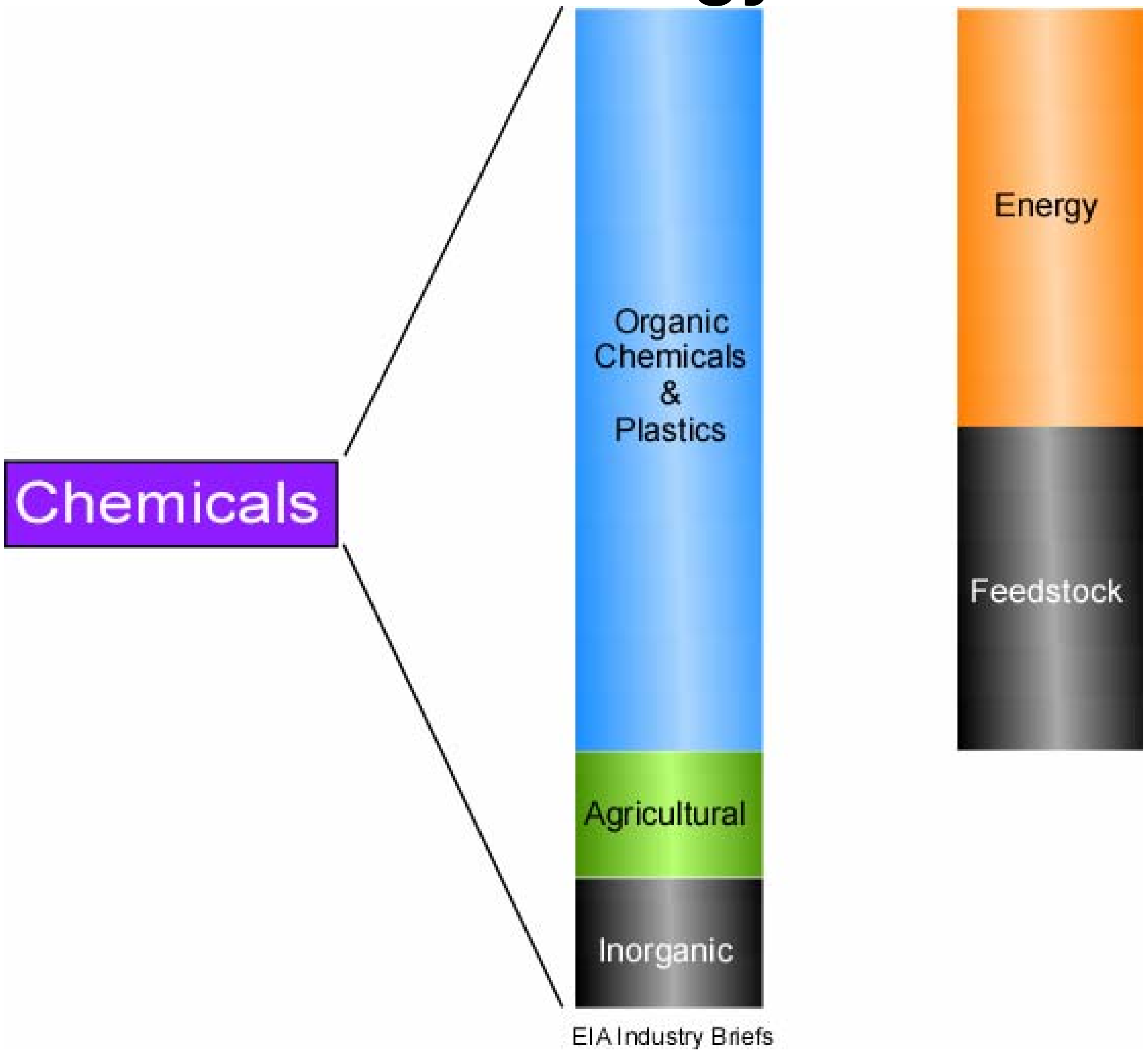
200?- ?

methane
coal
biomass

Energy


10224.4Mtoe
Coal
Hydro
Nuclear
Natural Gas
Oil
2005 BP Statistical Review
Chemicals
Residential
Commercial
Industrial
Transportation
DOE Annual Energy Review 2005

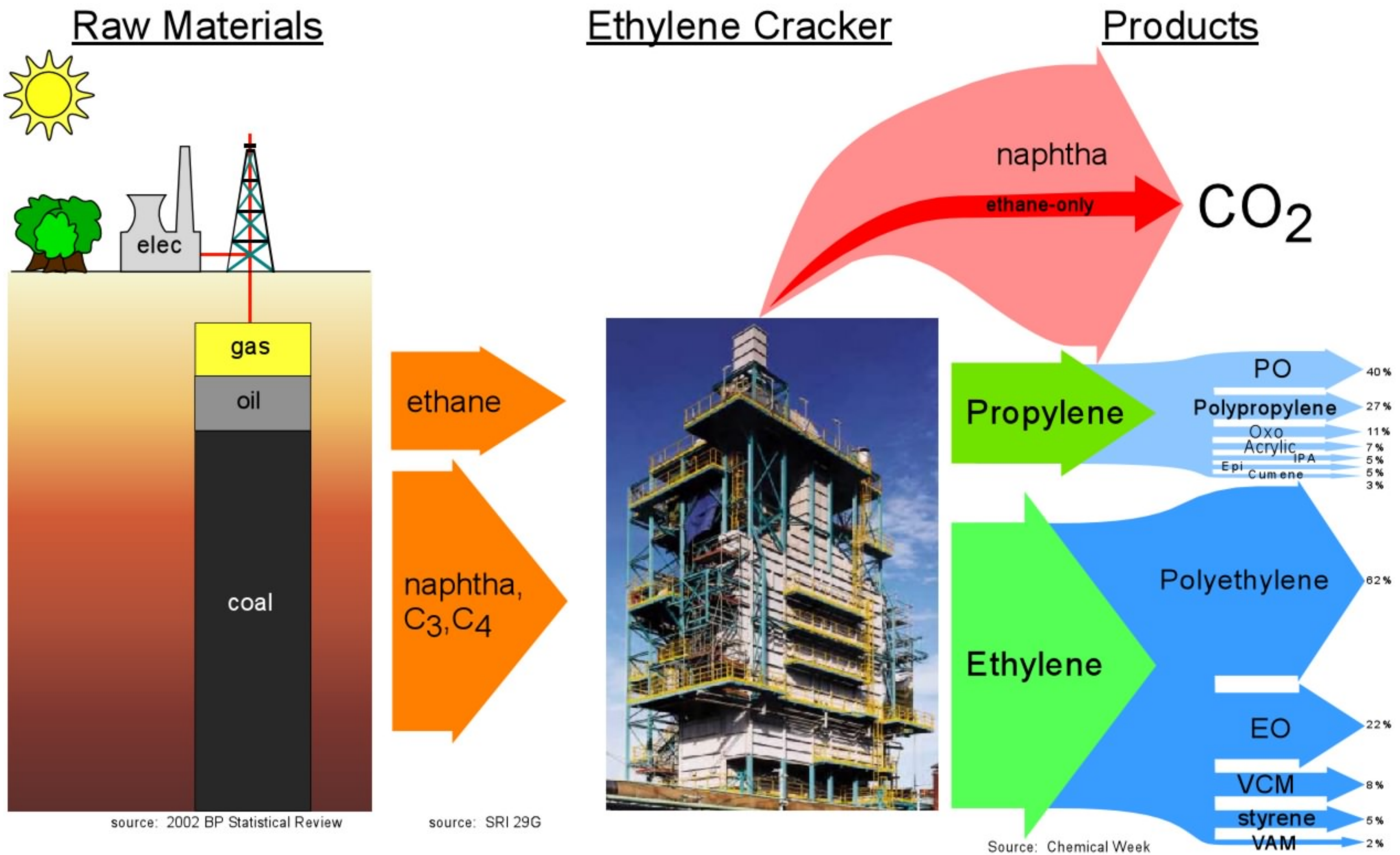
Energy


Chemicals
Organic Chemicals & Plastics
Agricultural
Inorganic
EIA Industry Briefs
Energy
Feedstock

Foundation of the Chemical Industry

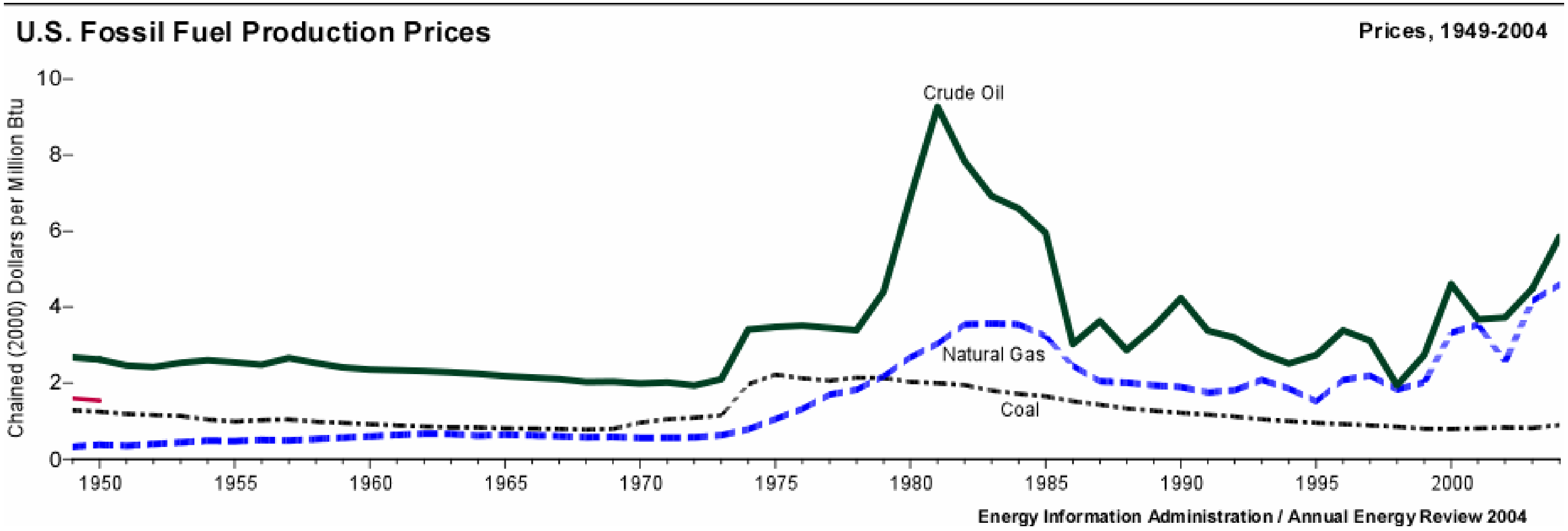
- **Ethylene is the largest volume organic chemical intermediate**
- **Ethylene and propylene derived chemicals and plastics dominate the industry**

Industry Today



Dow Today

Energy and the Chemical Industry



BTU parity


ALL NEW!
SHOCKING!
BIZARRE!
INCREDIBLE!
and it's ALL TRUE!
WEEKLY WORLD NEWS
THE WORLD'S ONLY RELIABLE NEWSPAPER
WHAT THE GOVERNMENT DOESN'T WANT YOU TO KNOW . . .
NO MORE OIL!
WORLD SUPPLY WILL BE GONE IN 6 MONTHS
• ECONOMY WILL COLLAPSE!
• MILLIONS WILL STARVE!
DRY!
DRY!
DRY!

WEEKLY WORLD NEWS

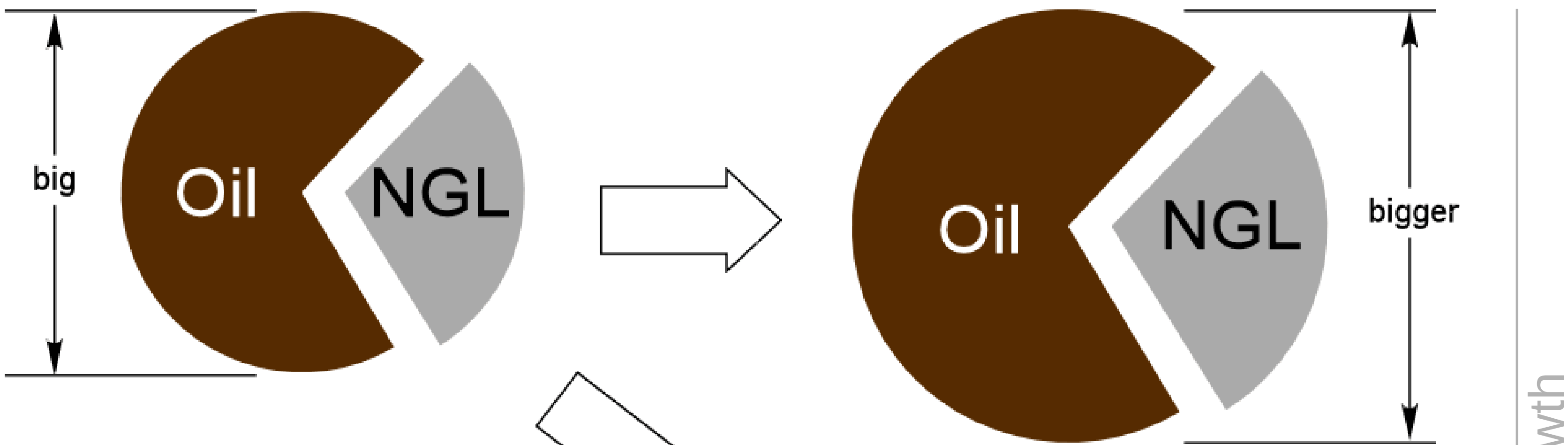
April 15, 2003

DOUBLE ISSUE!

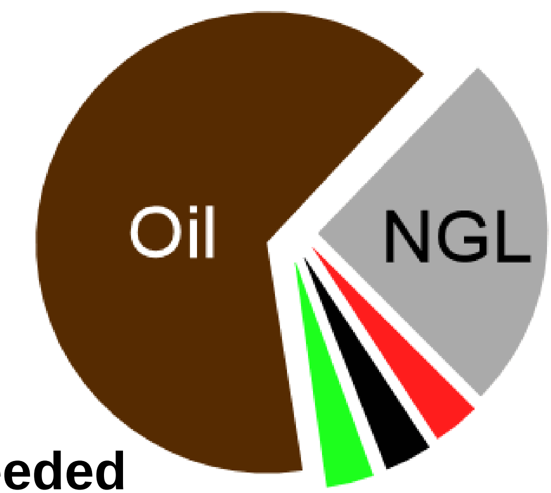
OIL FOUND ON MOON!

Gas prices will fall to 10¢ a gallon as Arab oil becomes obsolete!

Growth and Feedstock Flexibility



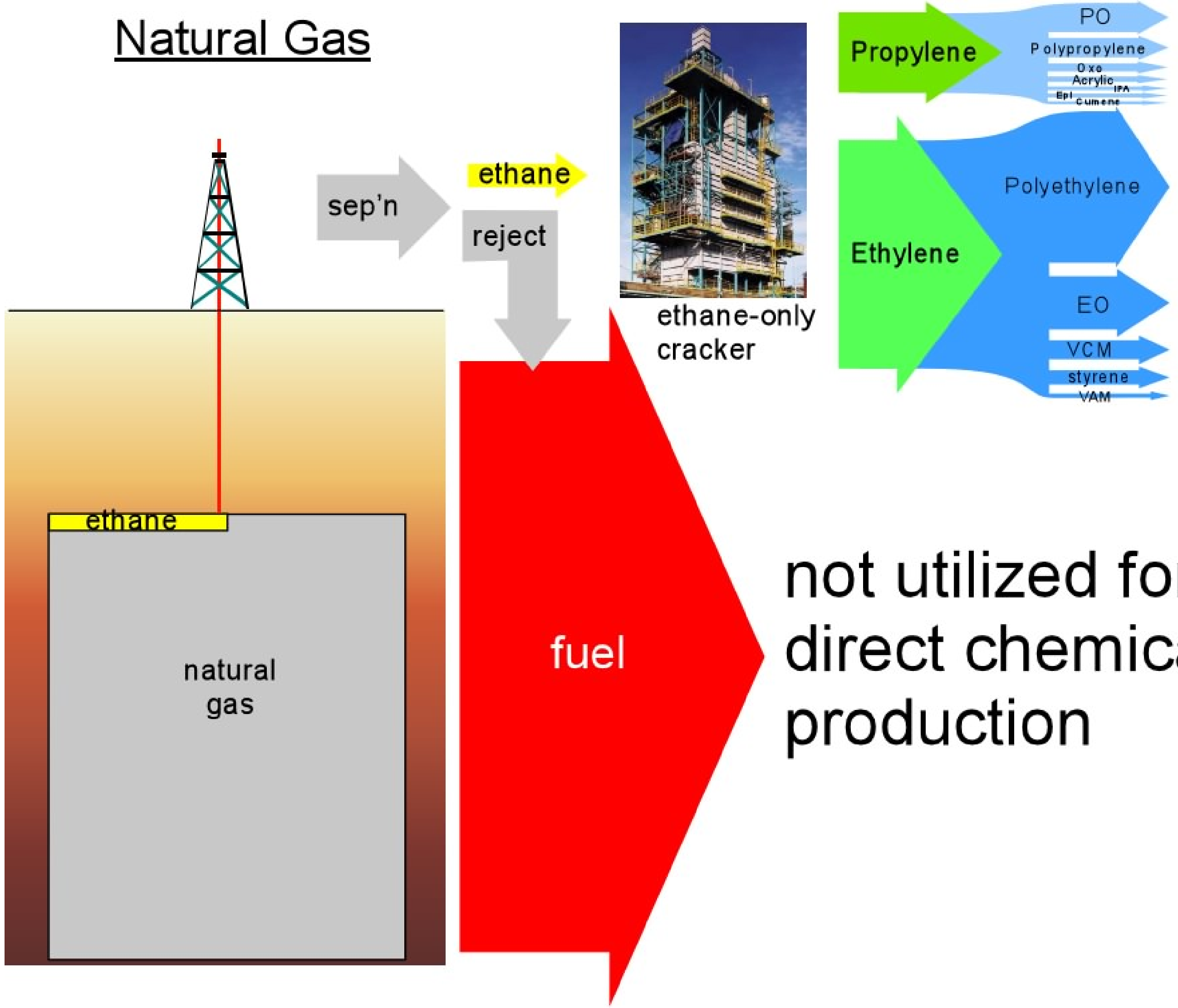
- **Feedstock portfolio must be expanded for the Chemical Industry to maintain competitiveness**
  - **Coal**
  - **Methane**
  - **Biomass, …**
- **Innovative technologies/processes needed**



Current Trends/Challenges for the Chemical Industry

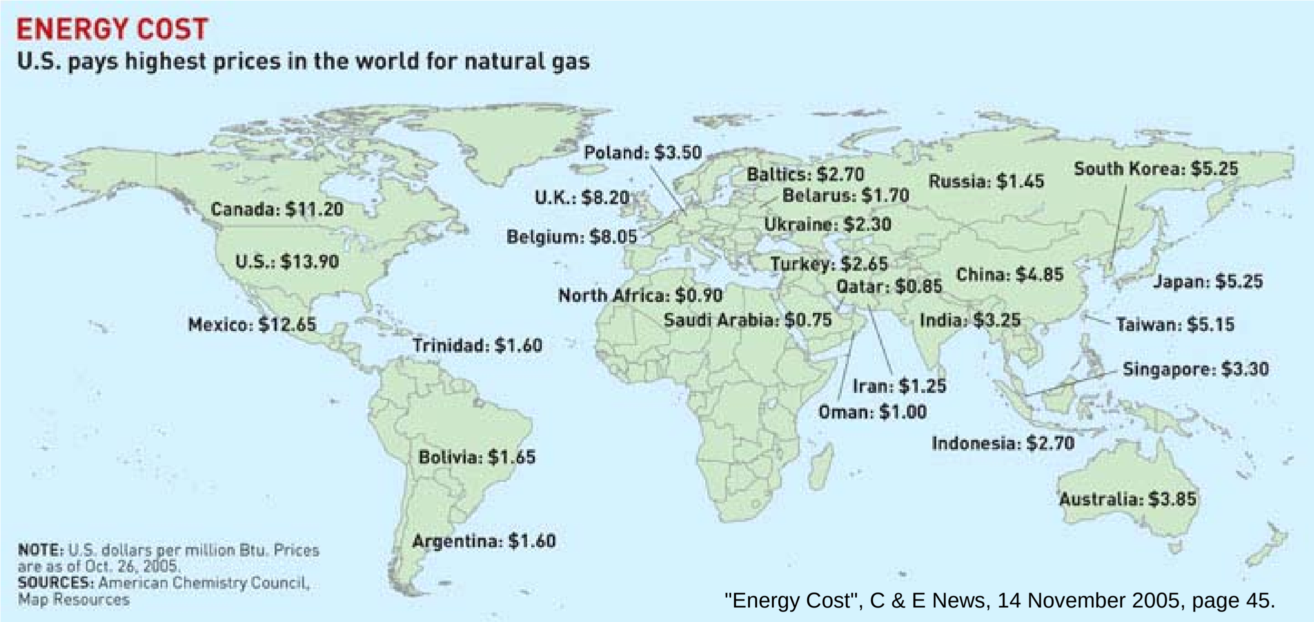
- **Feedstock portfolio must be expanded to remain competitive.**
  - **Coal, methane, biomass, …**
- **New feedstocks will lead to new products/intermediates which will need to be integrated.**
- **The development of new/improved processes for existing products will be needed to stay competitive.**
  - **Energy efficiency, carbon-management, capital costs**
- **Energy is really the issue**
  - **Our feedstocks are fuels to others**
  - **Atom efficiency is important, but so is energy efficiency**

Natural Gas

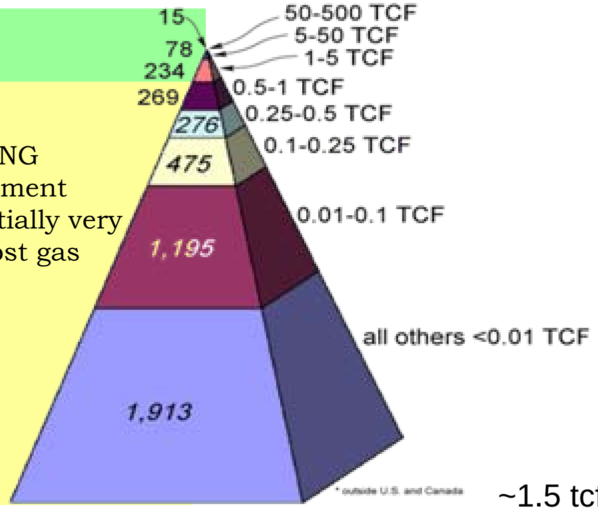


not utilized for direct chemical production

Stranded Gas



"Energy Cost", C & E News, 14 November 2005, page 45.



- sub-LNG investment
- potentially very low cost gas

- Competition for reserves includes
  - ammonia and methanol
  - Gas-to-Liquids (GTL)
  - LNG
- R&D challenges
  - alkane activation to useful products
  - formation of intermediates that can be shipped
- Options include FPSO

~1.5 tcf = 20 years at 2 B lb/yr with MTO

Methane Conversion Technologies

Syngas Methods

- cost of syngas generation is very high
- commercially practiced technology

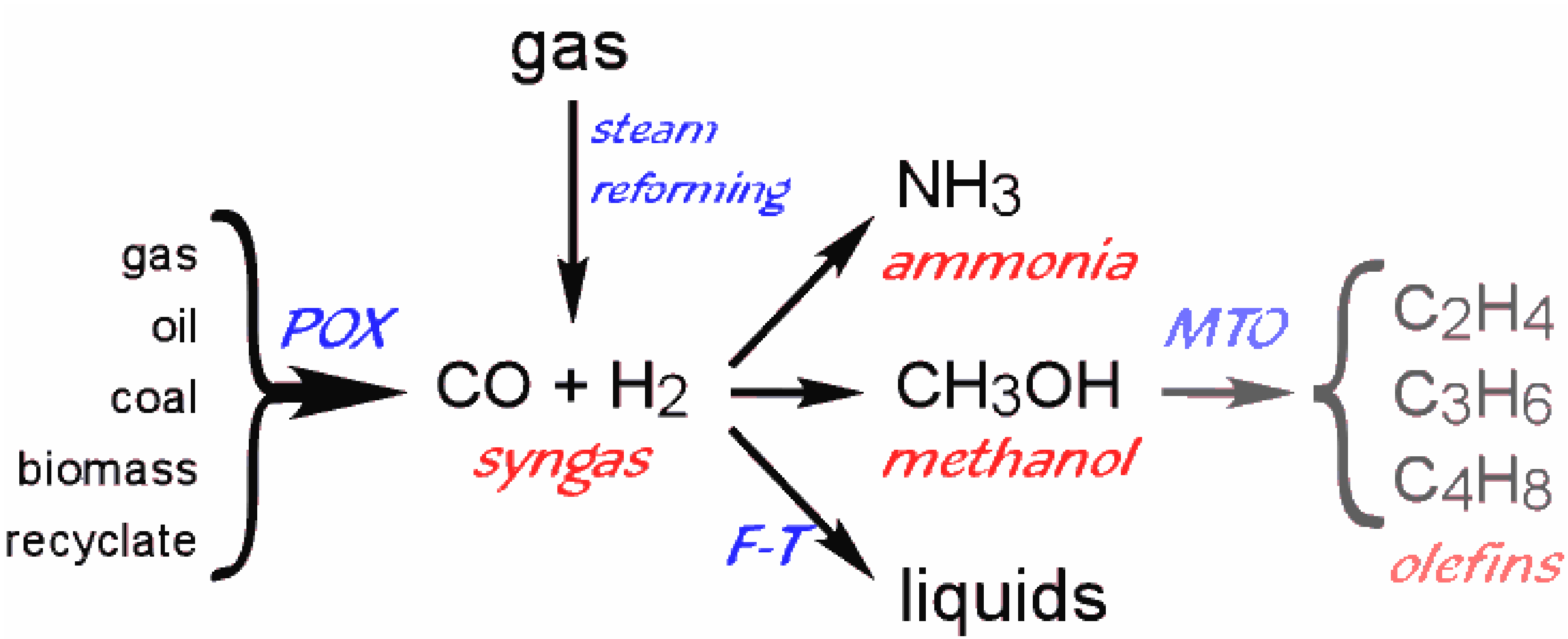
Direct Methods

- selectivity problems lead to separation problems
- in need of a performance leap
- often high temperature required to initiate
- flammability limits operation

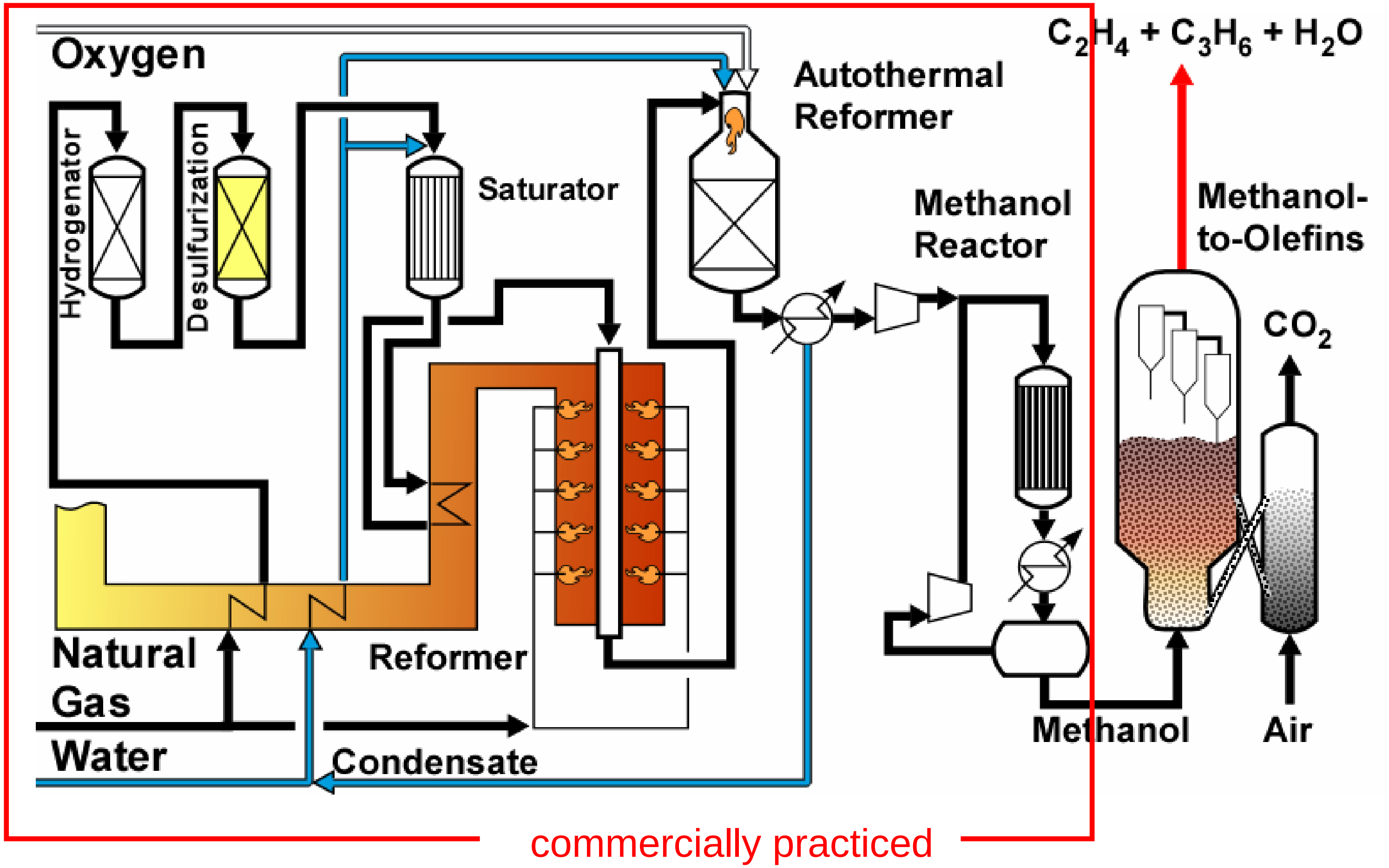
Heteroatom

- heteroatom allows separation
- heteroatoms can lower temperature of activation
- viability requires recycle for e.g. halides and sulfur

Syngas-based Options



Natural Gas-to-Olefins



- shown using MTO
- World-scale cracker equivalent 2X current largest methanol scale

Natural Gas-to-Olefins

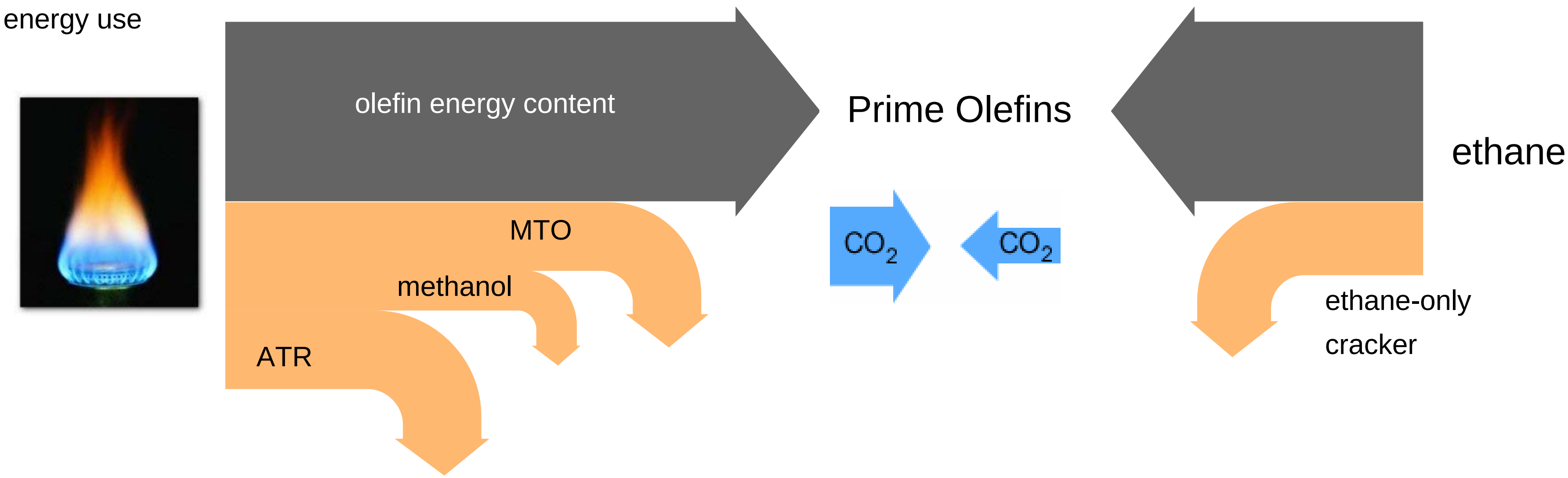
$$34\ CH_4 + 17\ O_2 \xrightarrow{POX} 34\ CO + 68\ H_2$$

1.2 mt/mt olefin

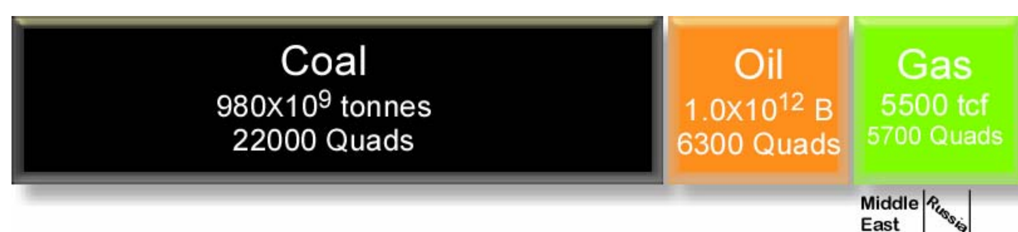
$$34\ CO + 68\ H_2 \xrightarrow{\text{methanol synthesis}} 34\ CH_3OH$$

$$34\ CH_3OH \xrightarrow{MTO} 16\ CH_2CH_2 + 32\ H_2O$$

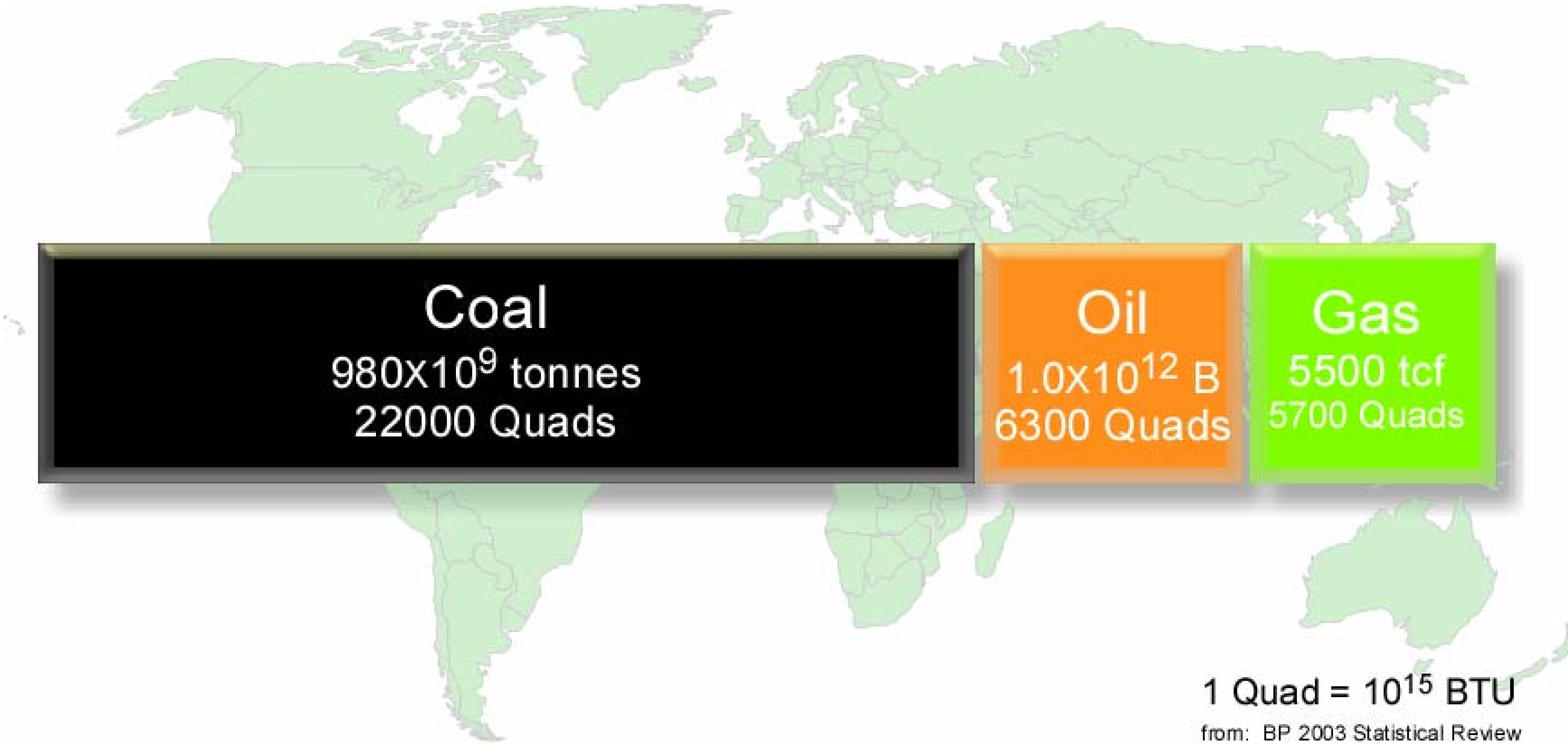
Natural Gas-to-Olefins



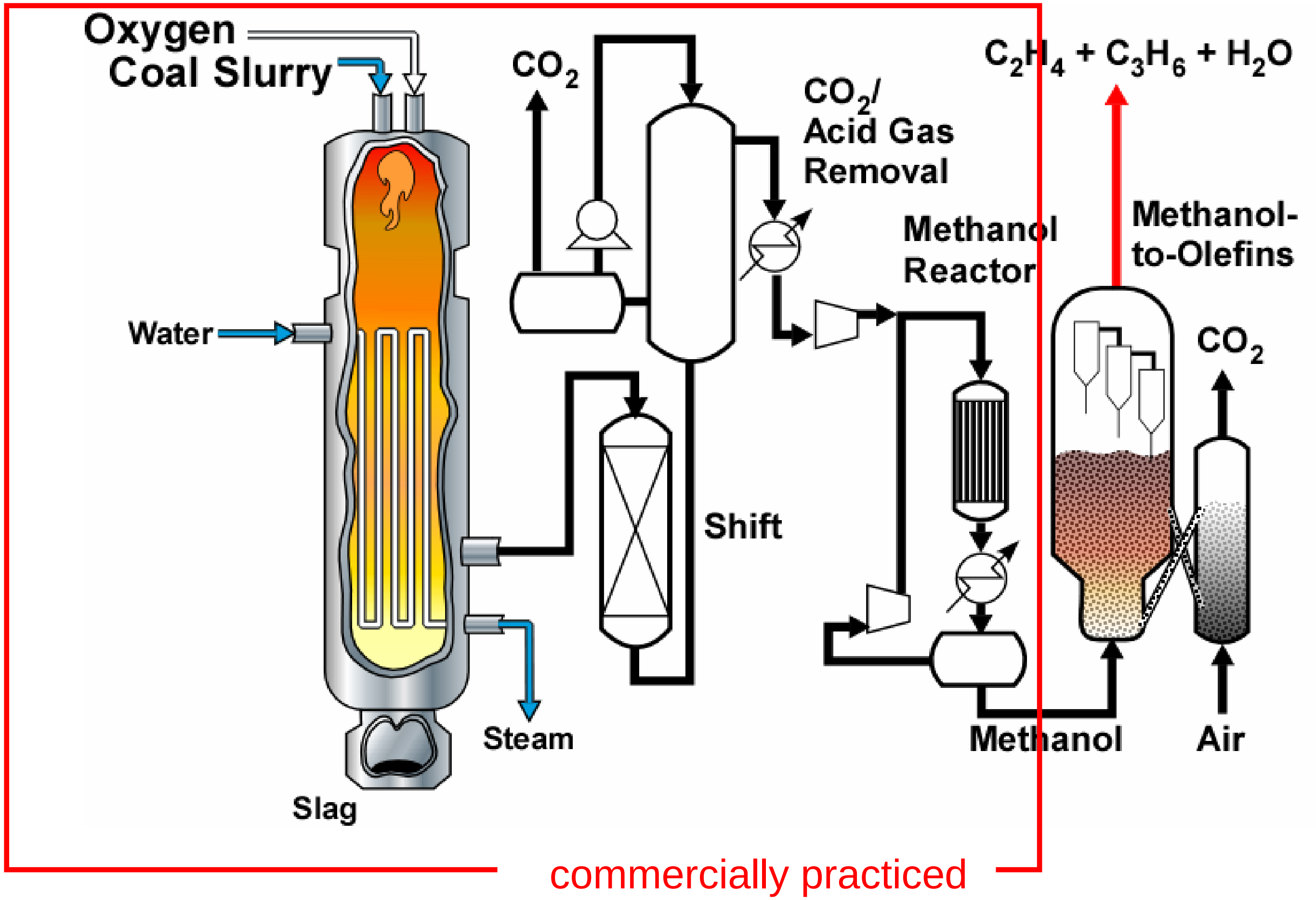
- No current olefin production from methane
- Methane serves as base for chemicals
  - death of U.S. ammonia and methanol
- Significant capital investment



Fossil Reserves

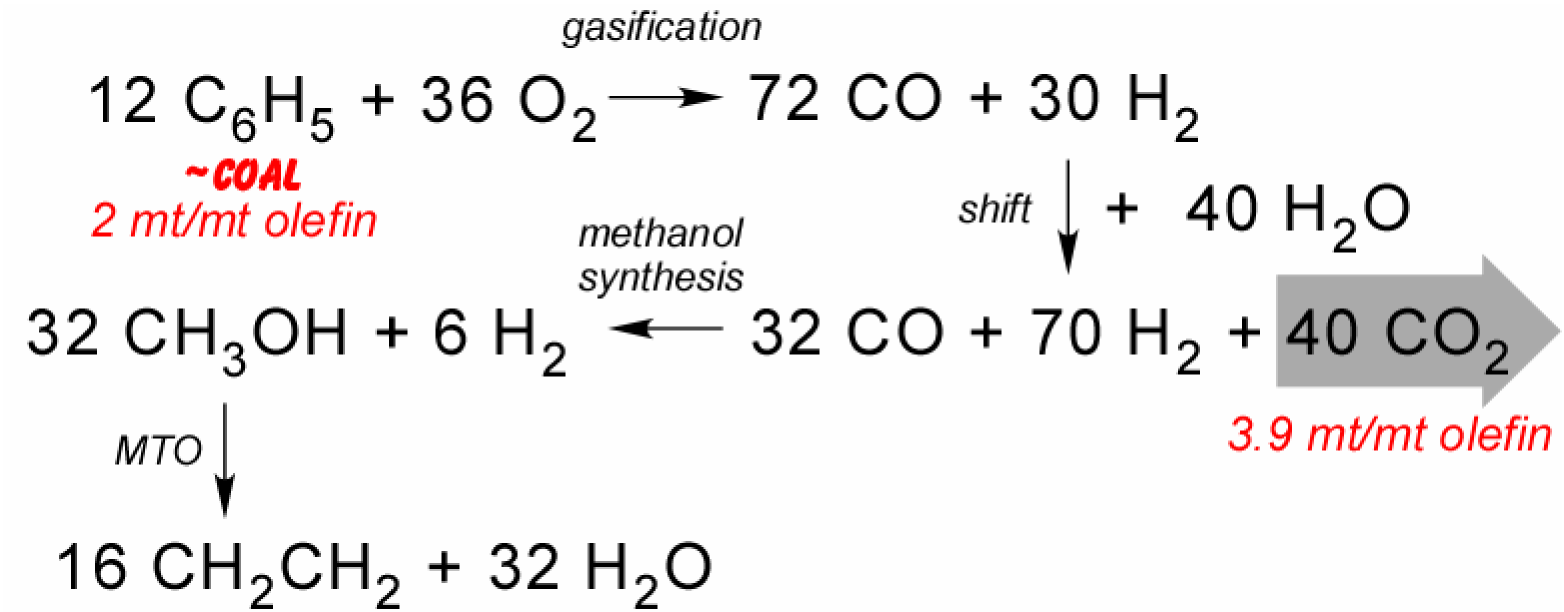


Coal-to-Olefins



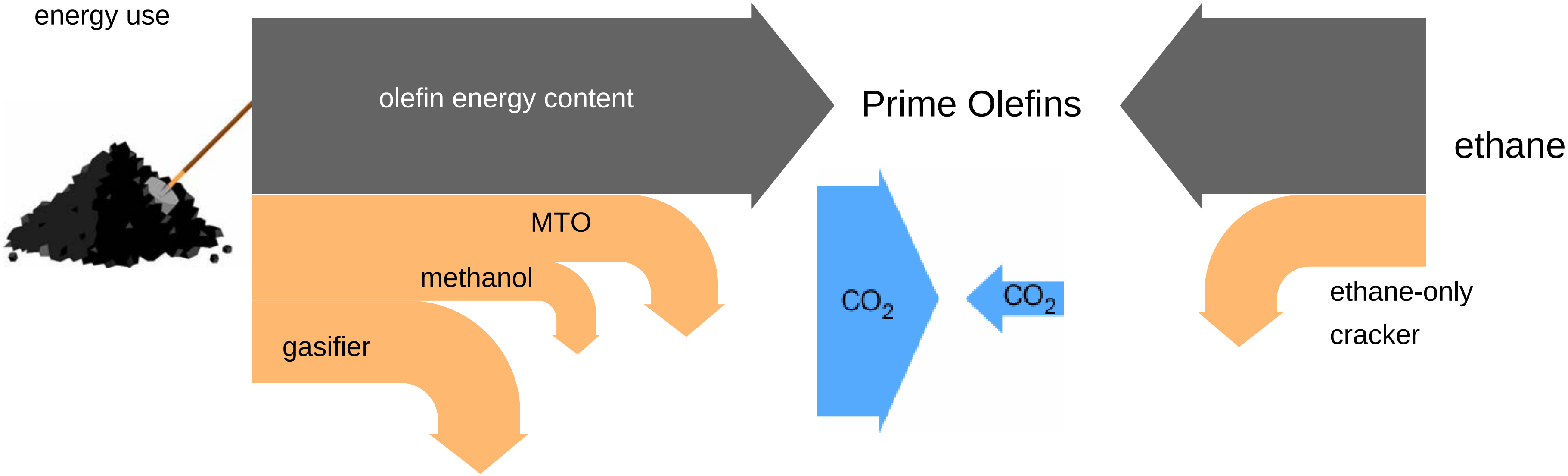
- **Shown using MTO**
- **Single world-scale olefins complex greatly exceeds current coal-based methanol**

Coal-to-Olefins



- **Idealized and simplified**
- **No energy balance, only mass balance**

Coal-to-Olefins

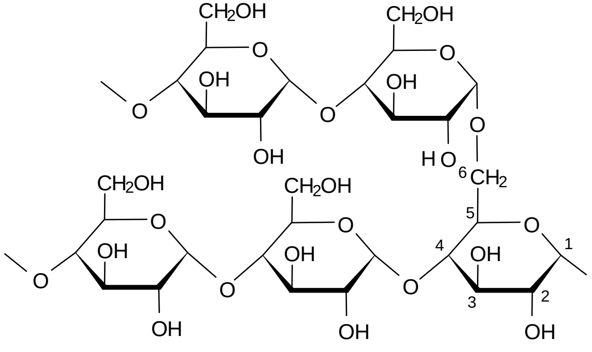


- **No current olefin production from coal**
- **Chemical production from coal is commercial**
- **Significant capital investment**
- **CO_2 issues**

Biomass Feedstock Options

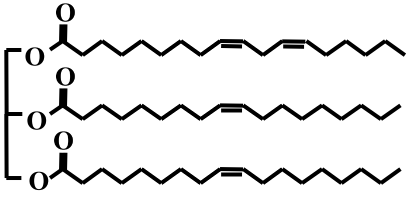
Sugar & Starch

- Refined global commodity
- 150 MMT
- 12-25 ¢/lb
- Carbohydrates



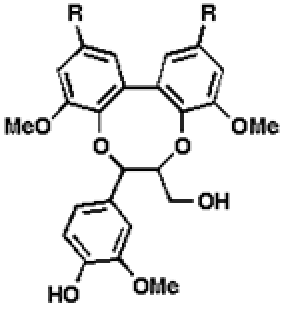
Fats & Oils

- Refined global commodity
- 150 MMT
- 15-40 ¢/lb
- Functionalized Hydrocarbon

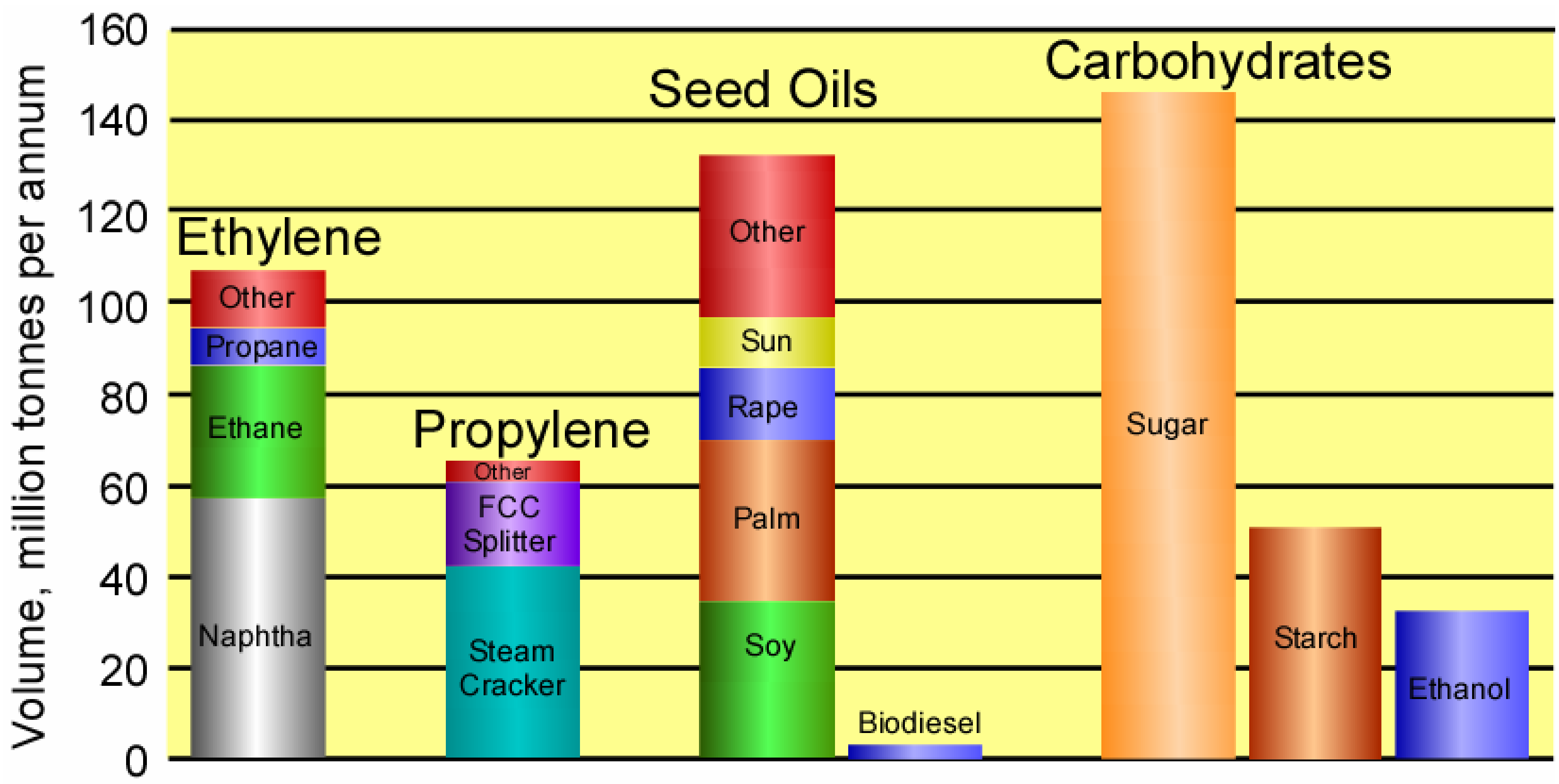


Lignocellulosics

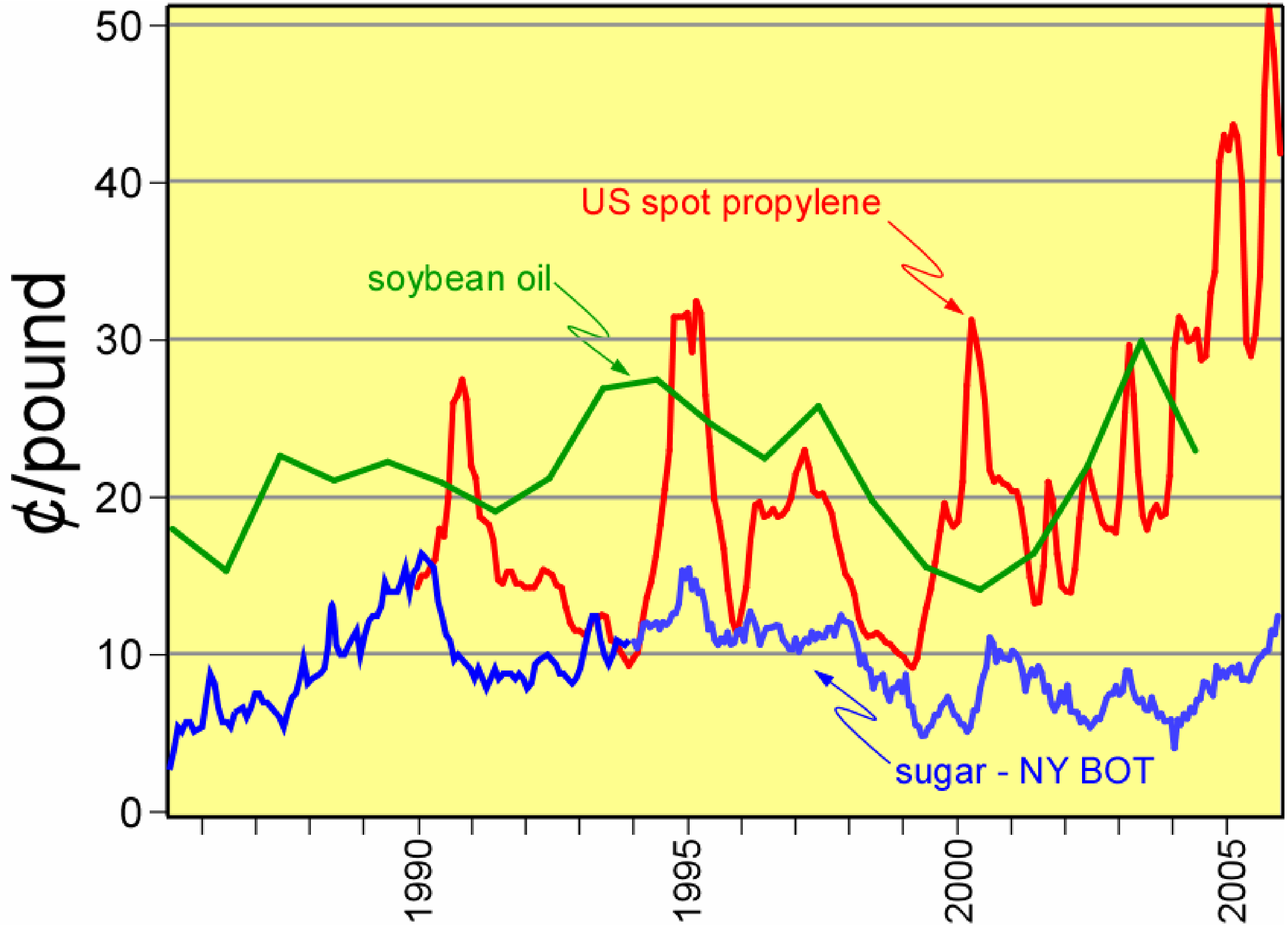
- Crude Product
- Limited supply chain
- 100 Giga T
- Fuel value +
- Aromatic Hydrocarbons & carbohydrates



Biomass Feedstocks



Biomass Feedstock Price



Biomass Conversion Technologies

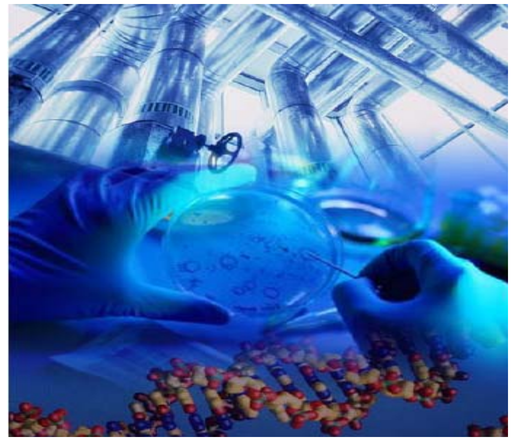
Thermochemical

Dow Core Competencies

- Hydroformylation
- Hydrocholorination
- Hydrogenation
- Epoxidation
- Polymerization

Fats & Oils
Sugar

Biorefinery



Complicated Process Mix

- Gasification
- Pyrolysis
- Fermentation
- Thermochemical
- Power generation

LignoCellulosics

Fermentation

Newer Technology in Dow

- Bioseparation
- Commercial Experience

Sugar & Starch
Cellulose (future)

Market Acceptance

Exact Replacements

- Cost saving is driver
- Defend against new competitors

Equivalent in Application

- Expanded Offering
- Customer Validation

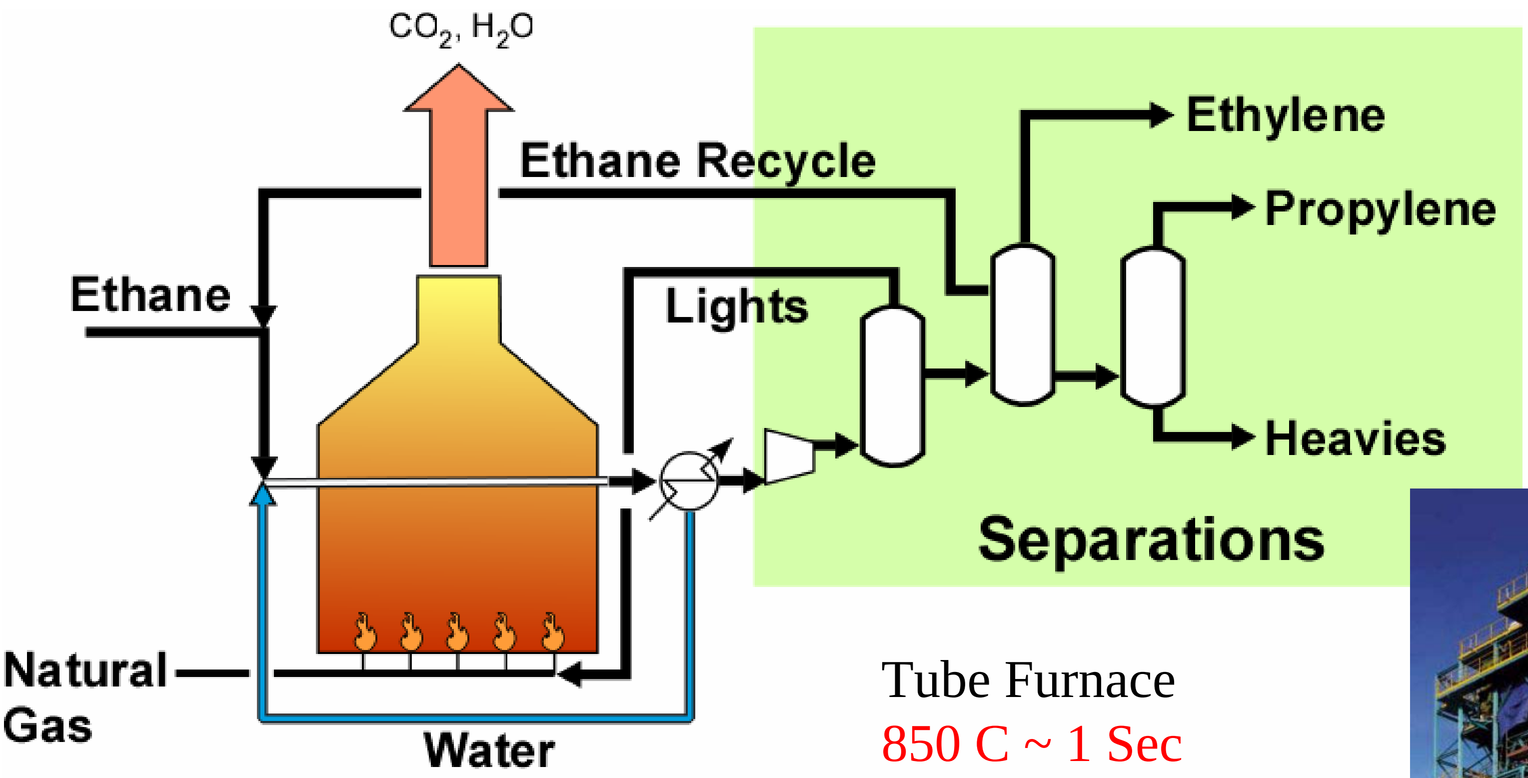
New Products

- Significant Improvement in cost/performance required
- Customer Driven

Increasing Risk

Example of Research Activities in Alkane Activation

Ethylene from Ethane by Steam Cracking



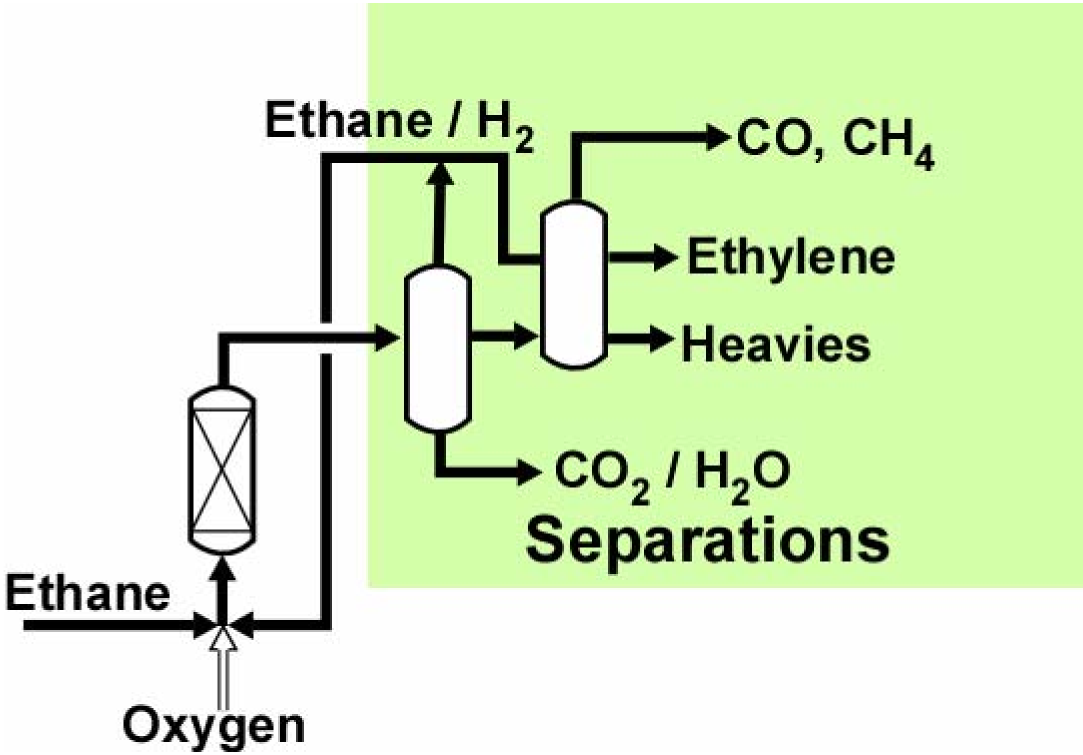
Tube Furnace
850 C ~ 1 Sec

Feed: $C_2H_6 + O_2$ (Air)

Products: $C_2H_4 + C_3H_6$ + Heavies + $H_2O + CO_2$

Economic Drivers: Capital Intensity, Yield, Energy Integration

Ethylene from Ethane by Partial Oxidation



Feed: $C_2H_6 + O_2$ (Pure)

Products: C_2H_4 + Heavies + H_2O + CO + CO_2 + CH_4

Economic Drivers: Capital Reduction, Yield, Byproduct value vs. O_2 Cost

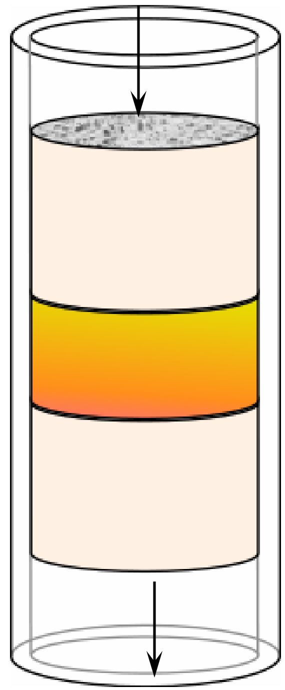
Autothermal Catalytic Partial Oxidation

Feed

C_2H_6
O_2
H_2

Equilibrium is Coke and COx

Catalyst



Temperature: 900-1100 °C
Residence Time : 2-20 mSec

Product

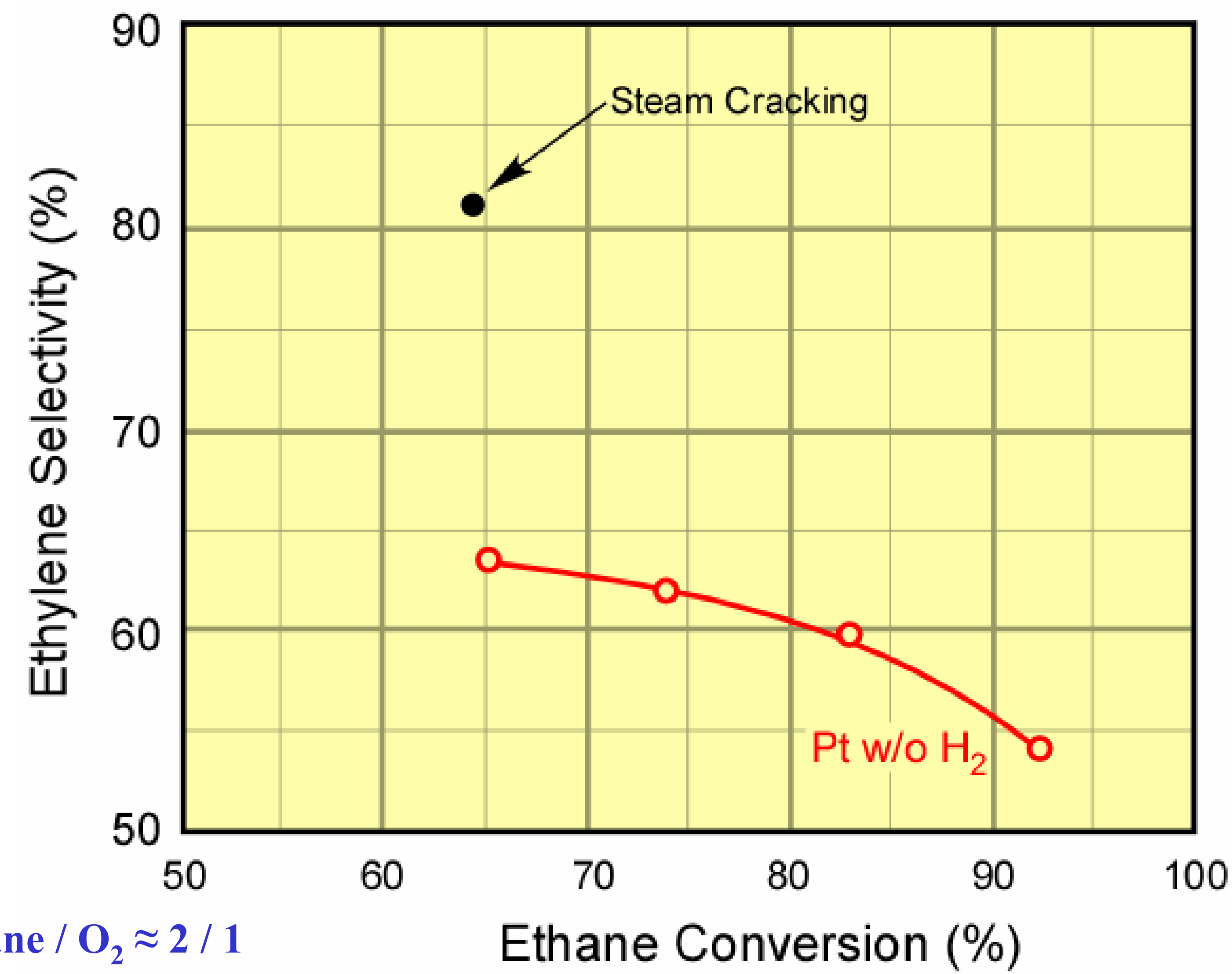
C_2H_4, C_3H_6, C_2H_2
CO, CO_2, CH_4,
H_2, H_2O ...

~ 80% C_2H_4 selectivity
~70% C_2H_6 conversion

Autothermal Catalytic Partial Oxidation

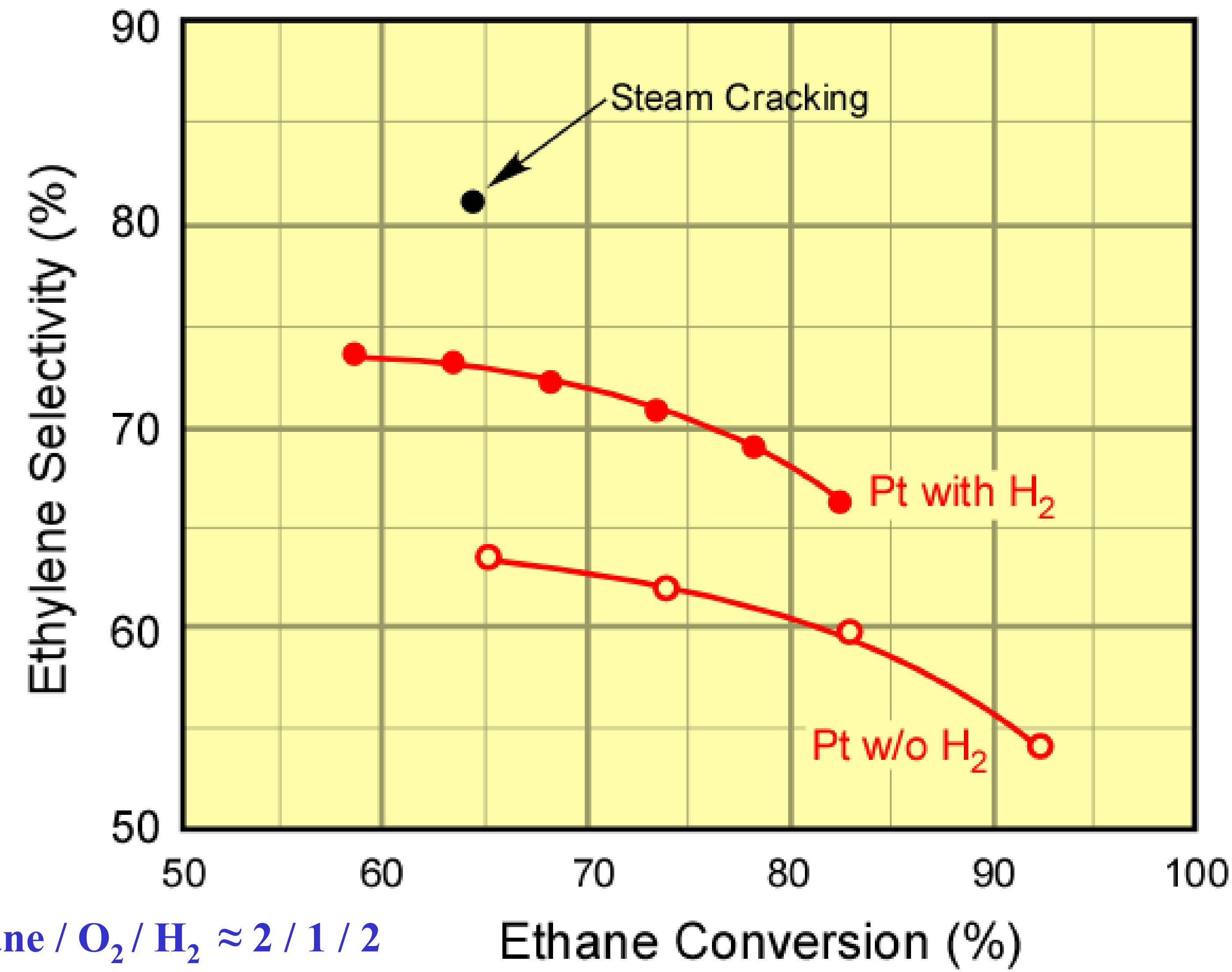
- Alkane/hydrogen/oxygen mixtures with incandescent catalyst
- Similar to HCN or HNO_3
- Very fast chemistry - small reactor
- Adiabatic – no external heat transfer
- Self controlled - less Instrumentation
- Well outside flammability range
- Selectivity to olefins vs. CO_x is the main challenge
- Differs from conventional oxydehydrogenation (selectivity & conversion balance)

Partial Oxidation Performance



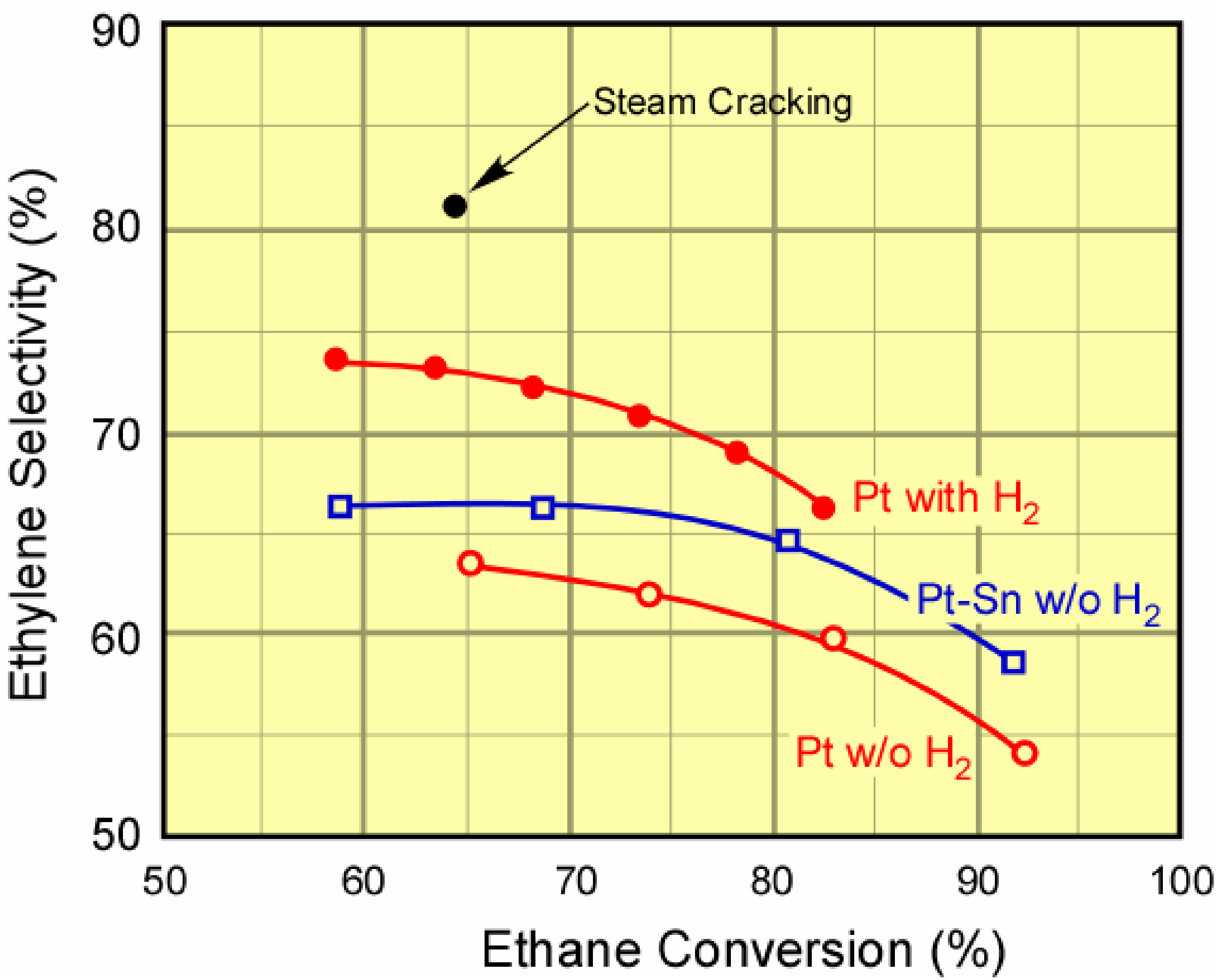
ethane / $O_2 \approx 2 / 1$

Partial Oxidation Performance

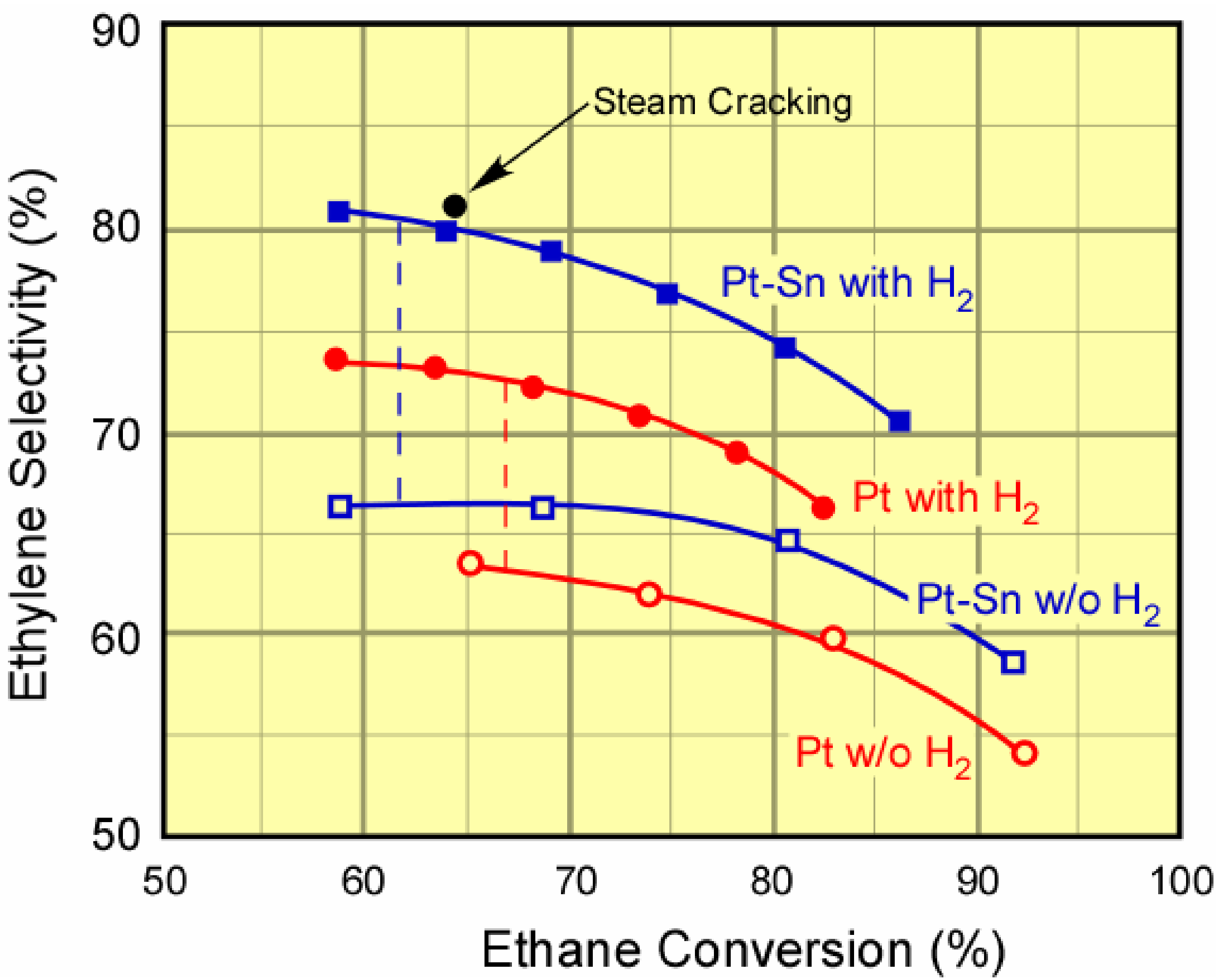


ethane / O_2 / H_2 ≈ 2 / 1 / 2

Partial Oxidation Performance



Partial Oxidation Performance



Autothermal Catalytic Partial Oxidation

Parameters

Strong Effects

- Fuel / O_2 ratio - Similar to Cracker Severity (Temperature not an independent variable!)
- Catalyst formulation
  - Metals (e.g. promotion effects)
  - Refractory Support and Structure
- Hydrogen in Feed

Weak Effects

- Throughput
- Feed Diluent

Current Activities

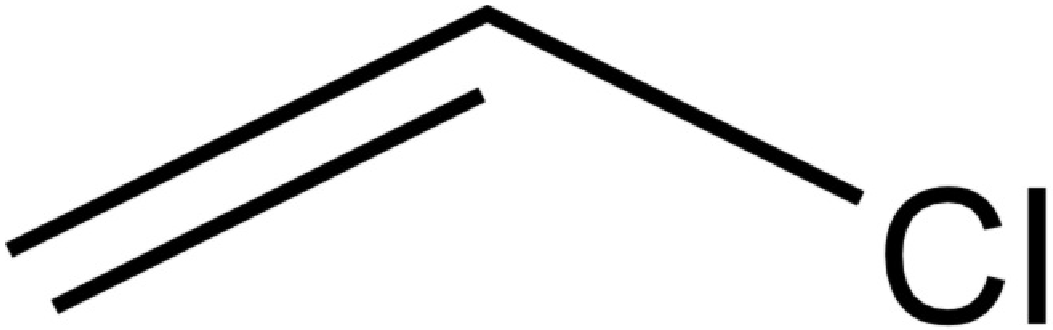
U.S. Department of Energy Grant in 2004 ($ 3.2 million – 3 yrs)
Project includes reactor design, catalyst development and process economic analyses

Partners:

Velocys - Microchannel Process Technology
Pacific Northwest National Laboratory - Catalyst optimization
Dow– Process knowledge / Assessment of economic and energy advantages

First phase - designing, building and operating a bench-scale reactor with channel dimensions identical to those of a commercial-scale unit.

Second phase - groundwork for increasing the process volume to commercial levels by demonstrating reactors containing numerous channels.

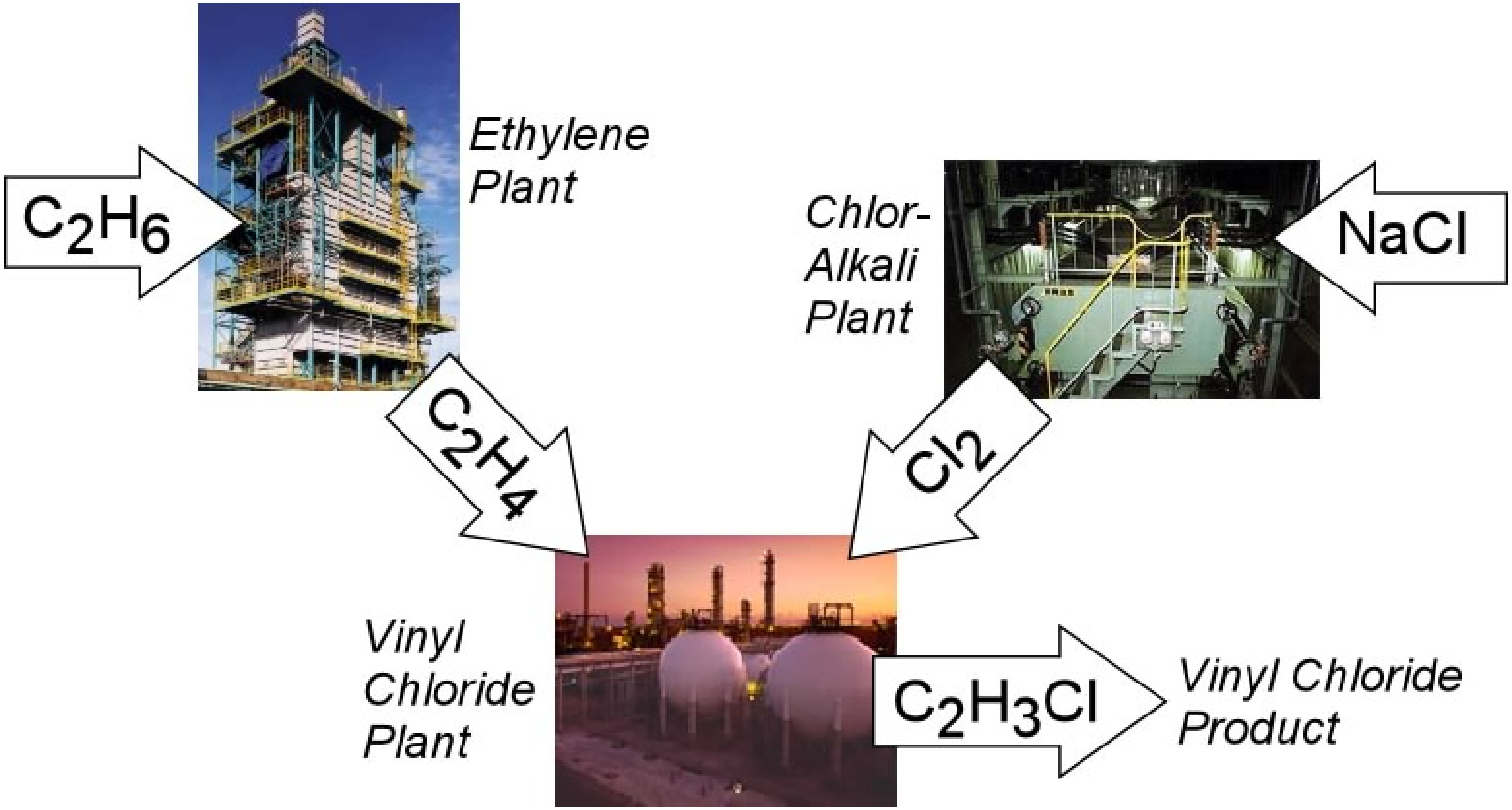


Vinyl Chloride Monomer(VCM)

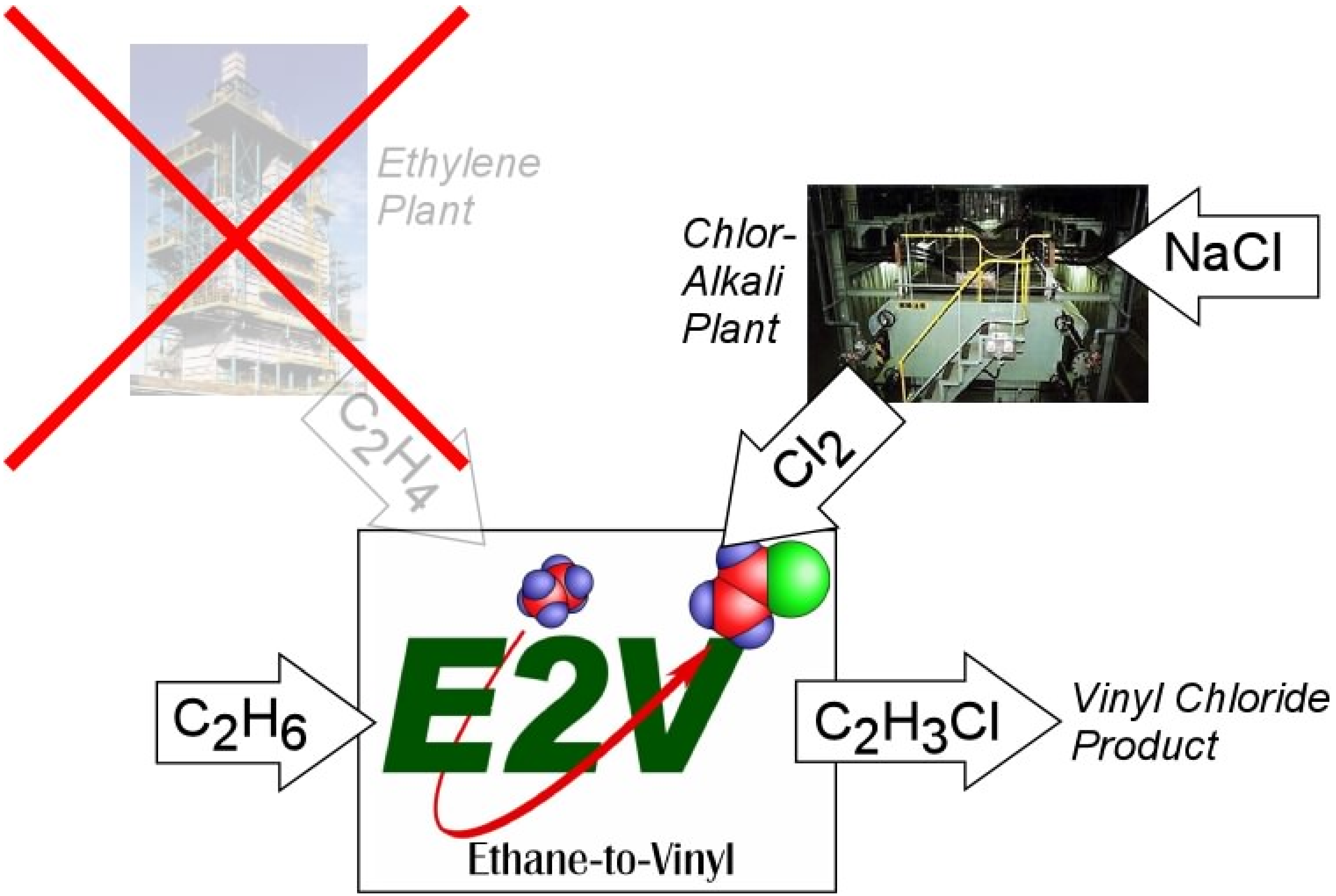
Dow produces ~5 billion pounds/year
World demand is 49 billion pounds
Growth averages 4-5%

Source: Chemical Week product focus

Conventional VCM

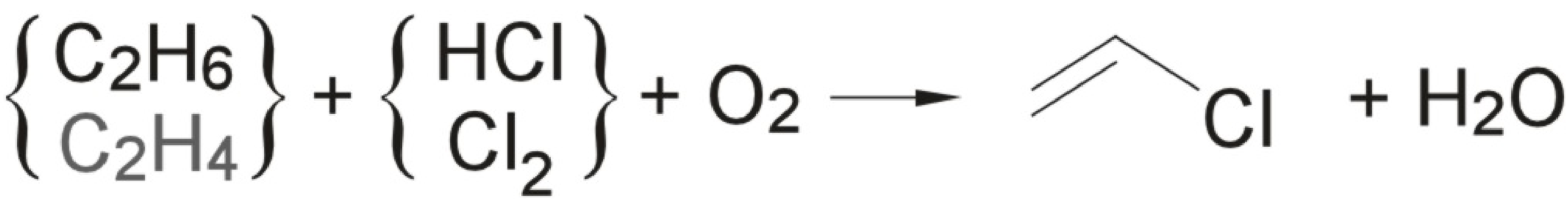


E2V

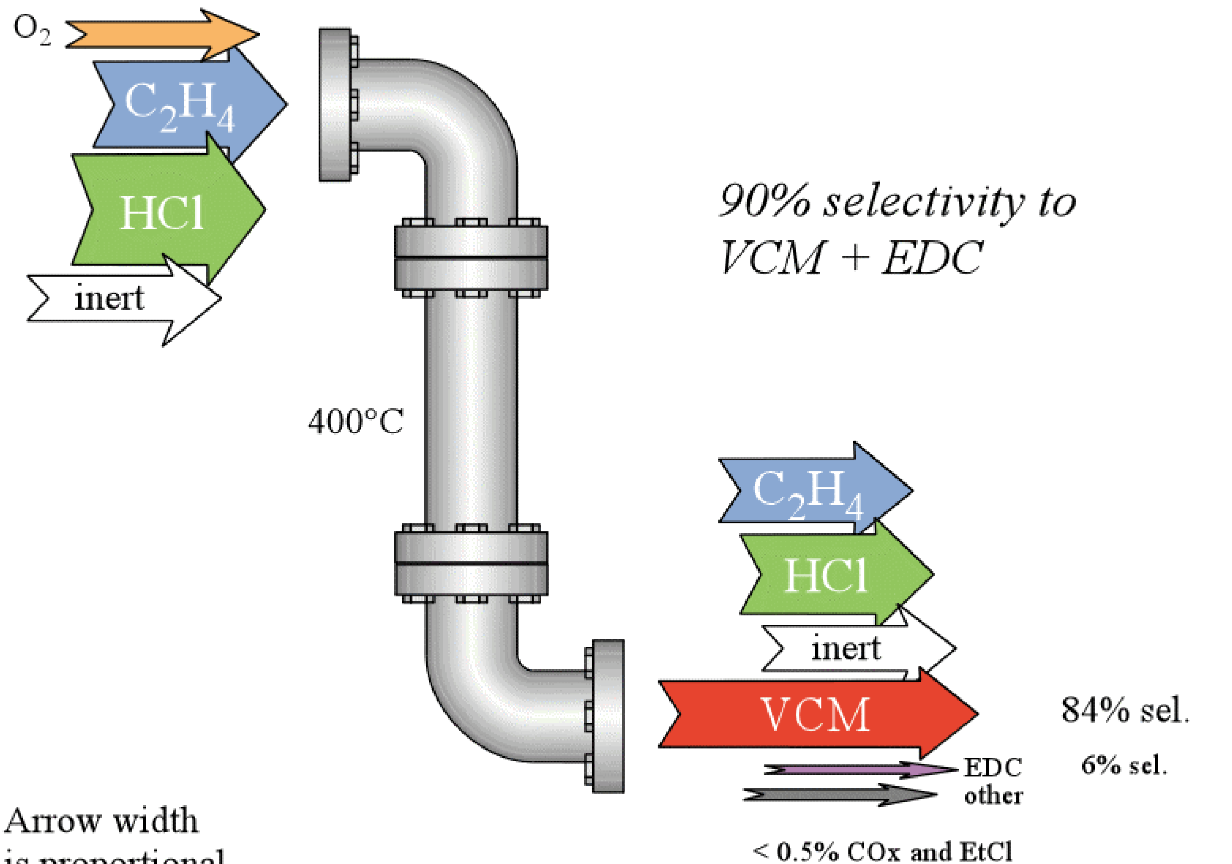


Ethylene
Plant
C_2H_4
Chlor-
Alkali
Plant
NaCl
Cl_2
C_2H_6
E2V
Ethane-to-Vinyl
C_2H_3Cl
Vinyl Chloride
Product

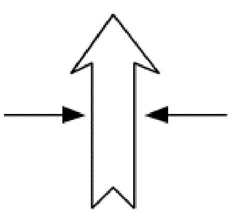
Vision



Lab Results



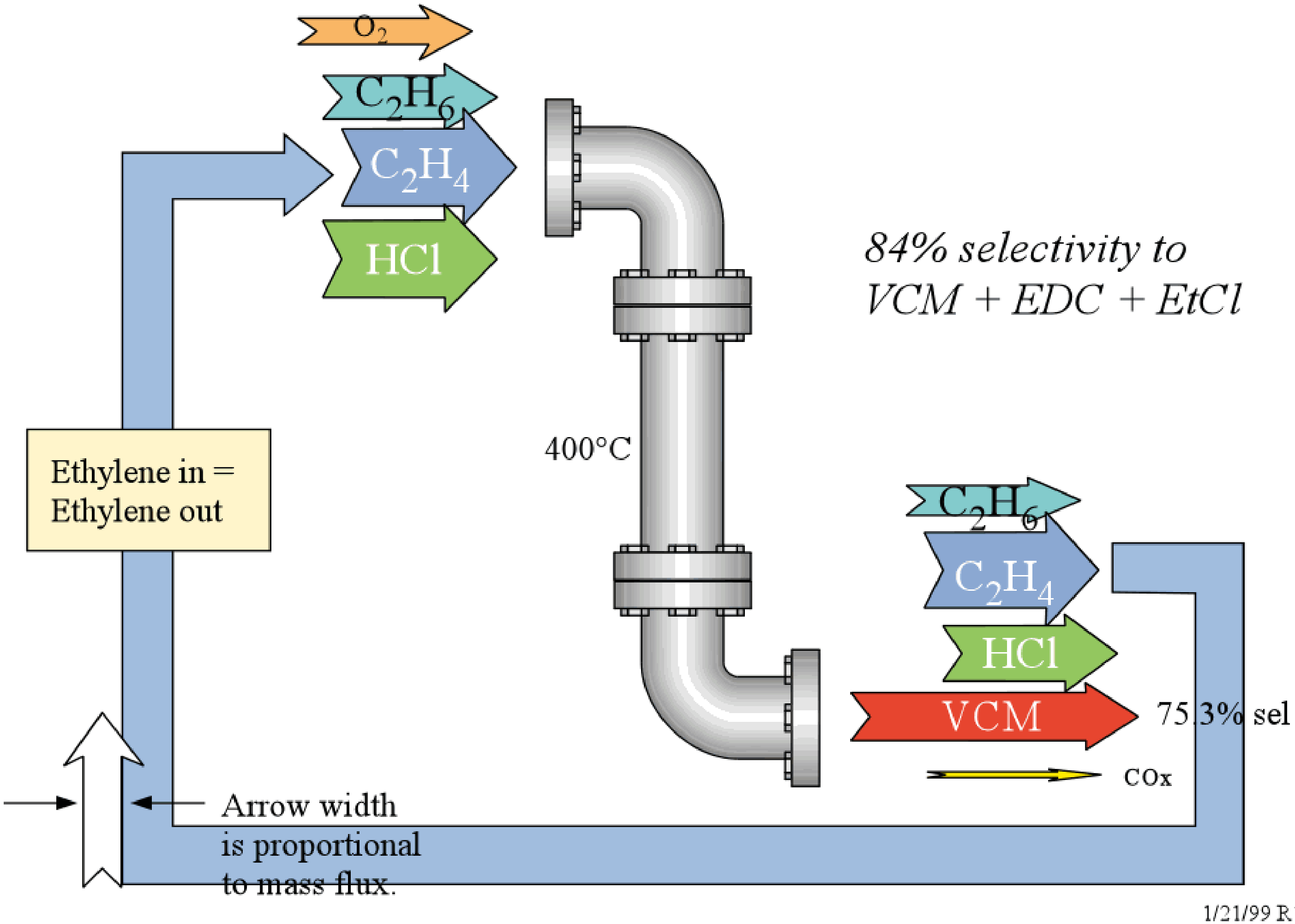
90% selectivity to VCM + EDC



Arrow width is proportional to mass flux.

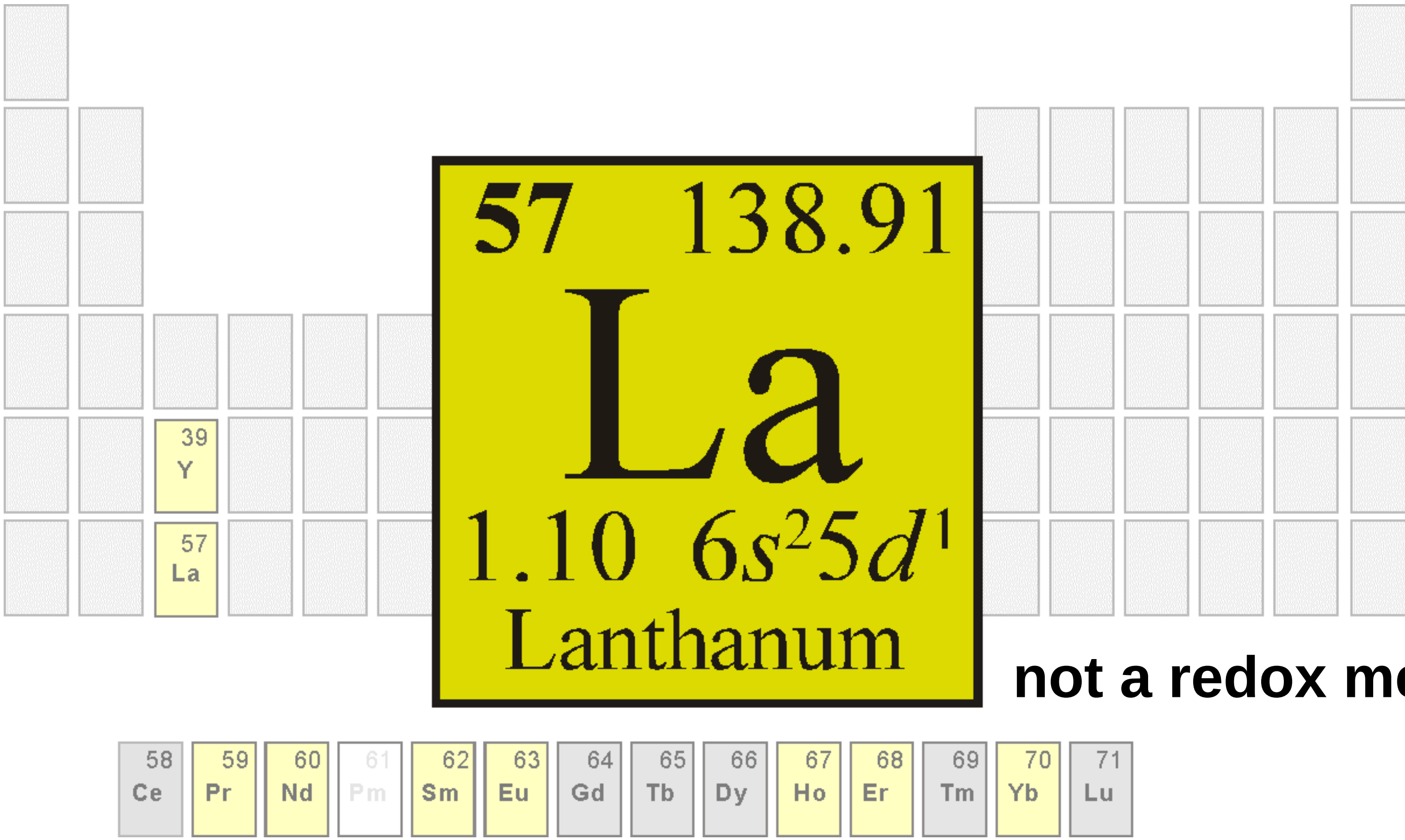
12-23-98 data

Lab Results



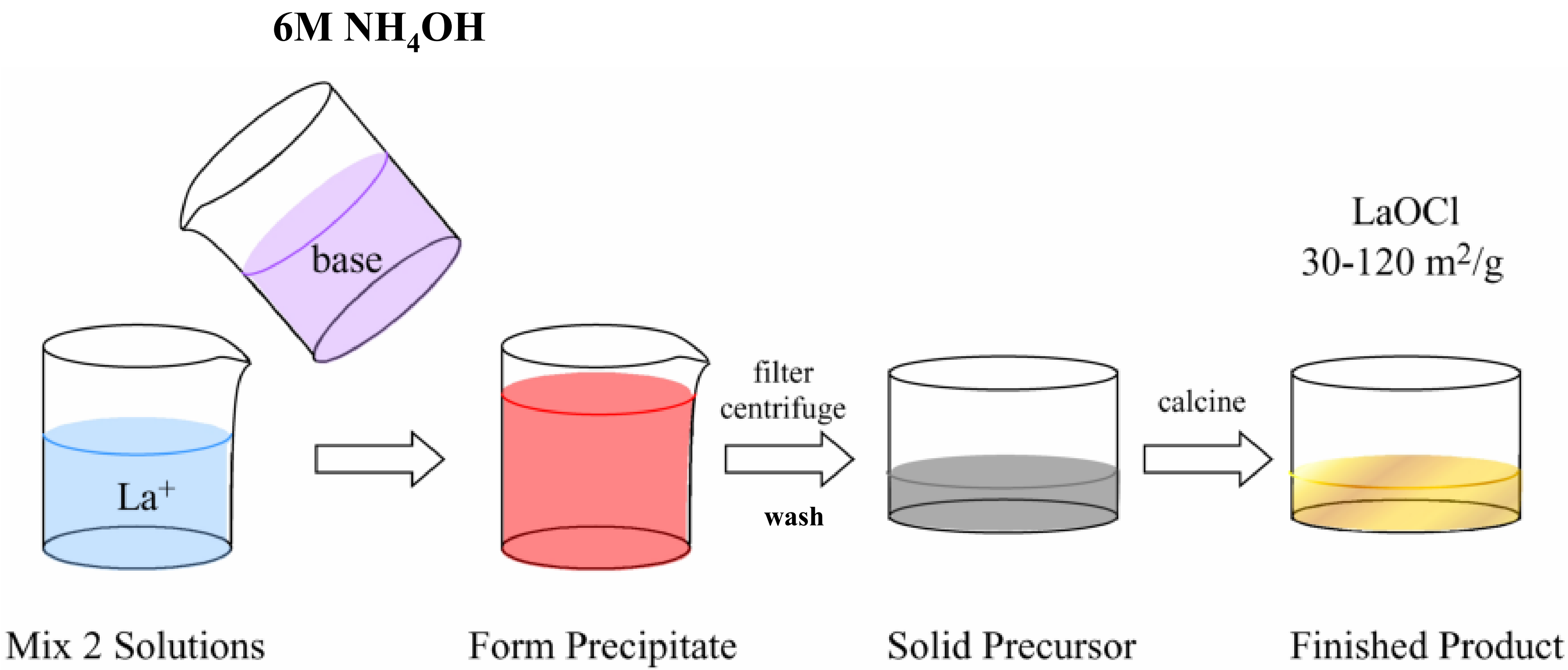
O_2
C_2H_6
C_2H_4
HCl
400°C
84% selectivity to
VCM + EDC + EtCl
Ethylene in =
Ethylene out
C_2H_6
C_2H_4
HCl
VCM
75.3% sel
COx
Arrow width
is proportional
to mass flux.
1/21/99 R1

Lanthanide Catalyst

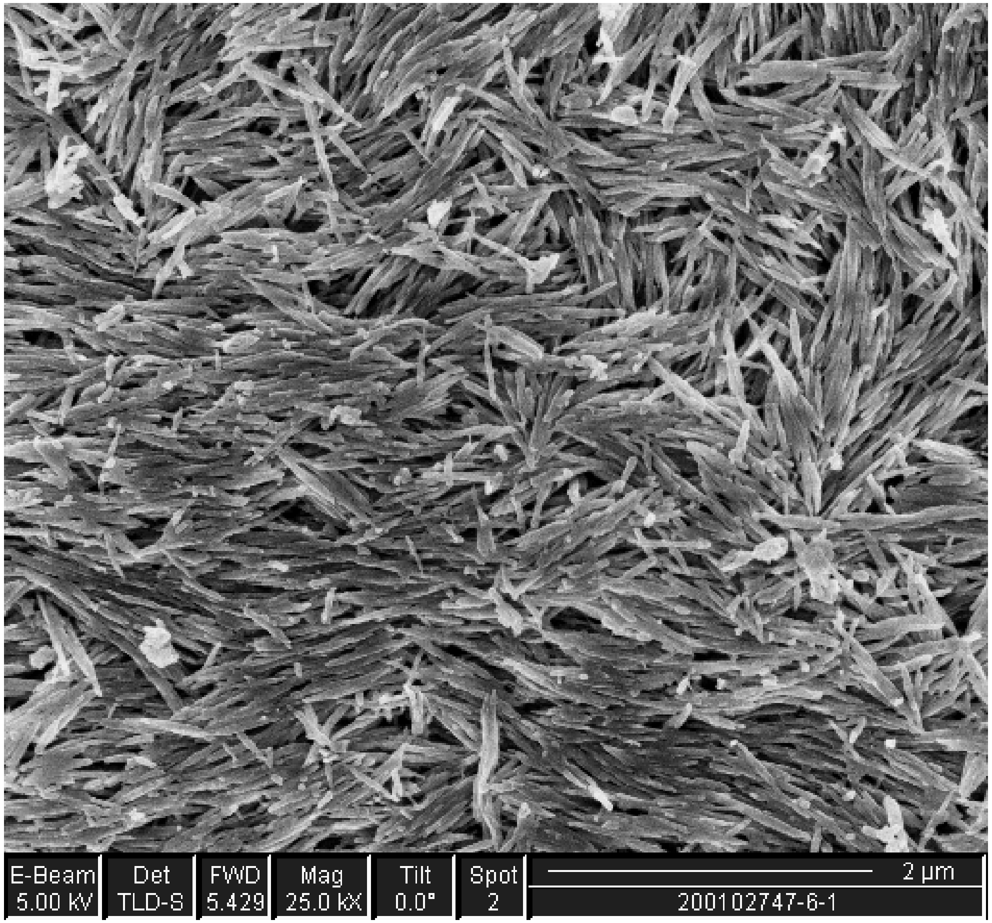


not a redox metal!

Catalyst Preparation



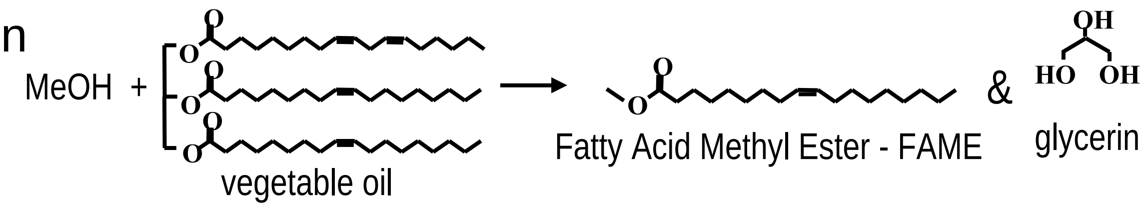
LaOCl


E-Beam
5.00 kV
Det
TLD-S
FWD
5.429
Mag
25.0 kX
Tilt
0.0°
Spot
2
2 µm
200102747-6-1

Example of Research Activities in Renewable Feedstocks

Dow Efforts in Biomass-based Feedstocks

- **Oils & Fats – Oleochemical Program**
  - Leverage capacity & supply chain developed for Biodiesel
  - Focus on thermochemical transformations
    - ➔ Hydroformylation
    - ➔ Ethenolysis
    - ➔ Epoxidation



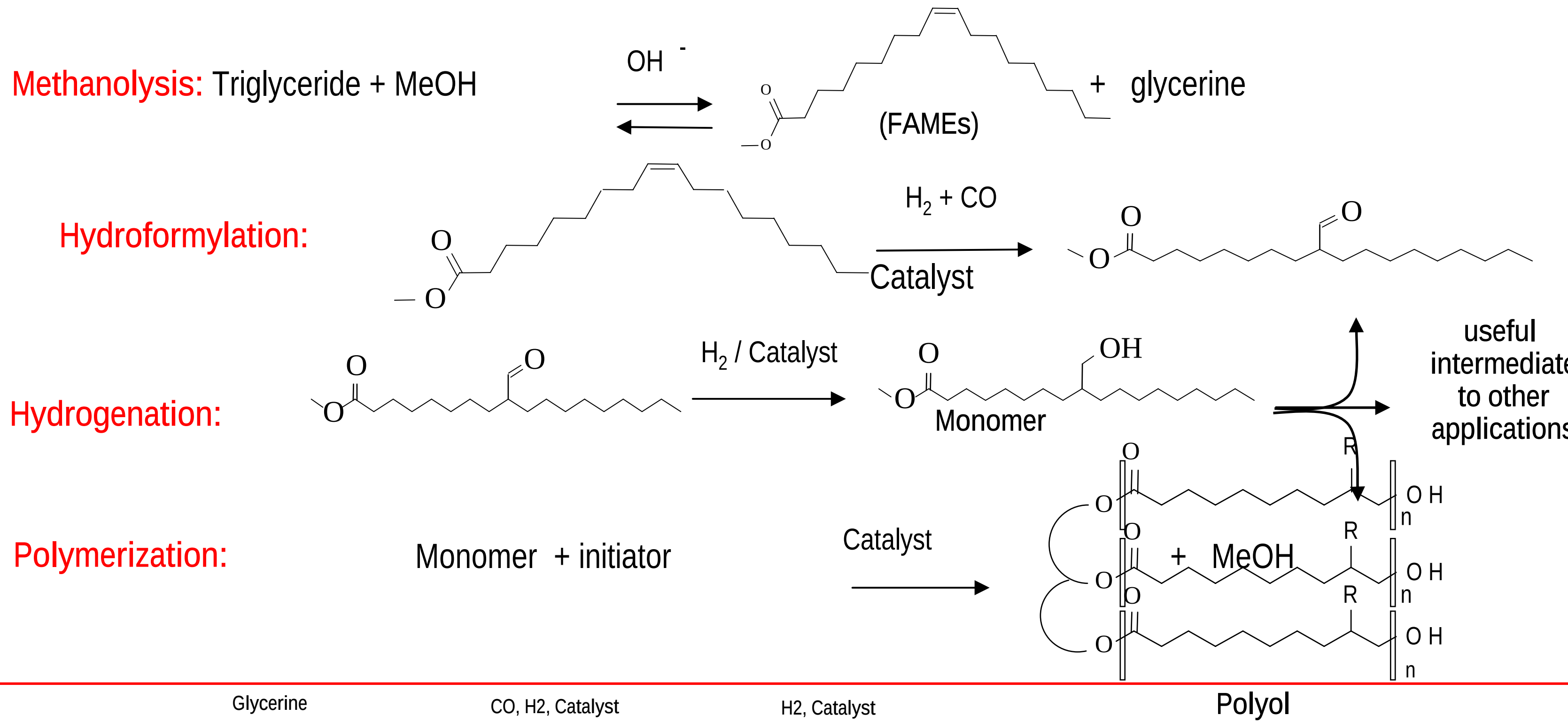
  - Platform of molecules for replacement or extension of Dow products
  - Glycerin as feedstock for Dow intermediates & products
- **Sugar & Starch**
  - Follow bioethanol growth and identify opportunities
  - Identify right technology/market matches
    - ➔ thermochemical & fermentation
- **Lignocellulosics**
  - Supply chain development will be driven by biofuel development
    - ➔ Leverage our gasification expertise

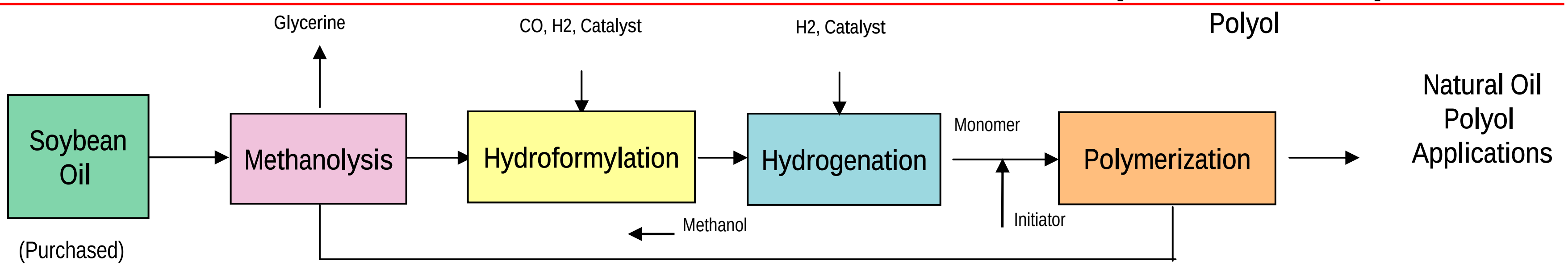
Natural Oil Polyol

Soybean oil based polyol

- Flexible foam applications
- Product with substitution of PO based polyol
- Market minimum: Match current product(s) performance
- Potential for performance enhancements

Process


Methanolysis: Triglyceride + MeOH
OH -
+ glycerine
(FAMEs)
Hydroformylation:
H2 + CO
Catalyst
Hydrogenation:
H2 / Catalyst
Monomer
useful intermediate to other applications
Polymerization:
Monomer + initiator
Catalyst
+ MeOH
Polyol


Glycerine
CO, H2, Catalyst
H2, Catalyst
Soybean Oil
(Purchased)
Methanolysis
Hydroformylation
Hydrogenation
Monomer
Polymerization
Natural Oil Polyol Applications
Methanol
Initiator

Closing Remarks

- **Alternative feedstocks for chemical industry increasingly important**
- **Breakthrough / step change processes required**
- **Novel catalysts and reactor concepts**
- **Fundamental understanding of catalytic mechanisms**
- **Consistent (long-term) focus**
- **Industry & academic (& government) partnerships necessary to tackle long-term research issues**