Integration: Critical at the Start of the Chemical Industry, *Not So Much Now….*

Mark Jones

Executive External Strategy and Communications Fellow
The Dow Chemical Company

3 March 2015

What I hope to leave you with

- Integration was crucial in the development of the chemical industry but has decreased in importance
- Inorganic chemistry created the chemical industry and remains important, but not particularly valued
- Scale remains the major source of competitive advantage in commodity chemicals

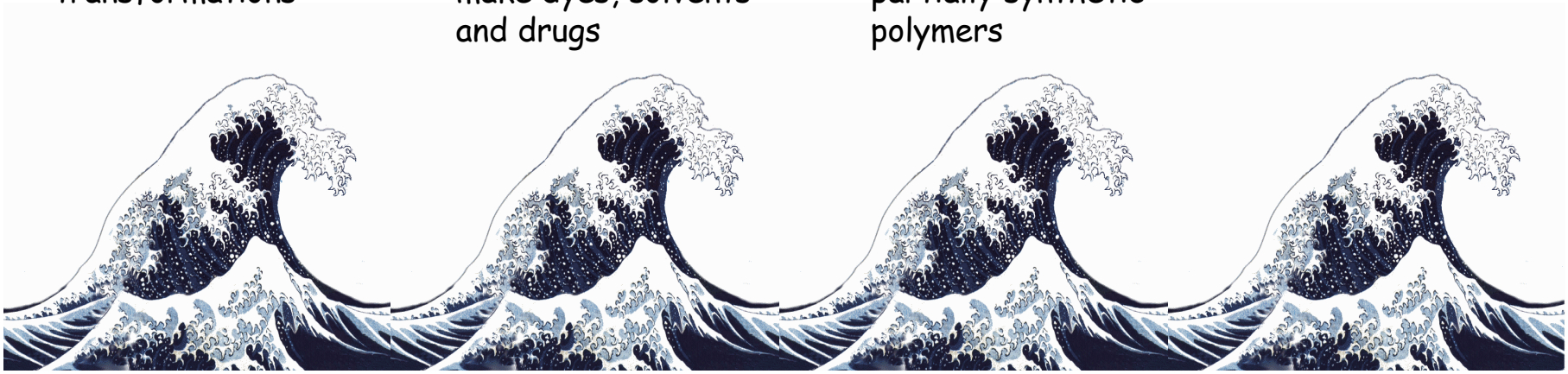
Chemical Industry Technology Waves

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

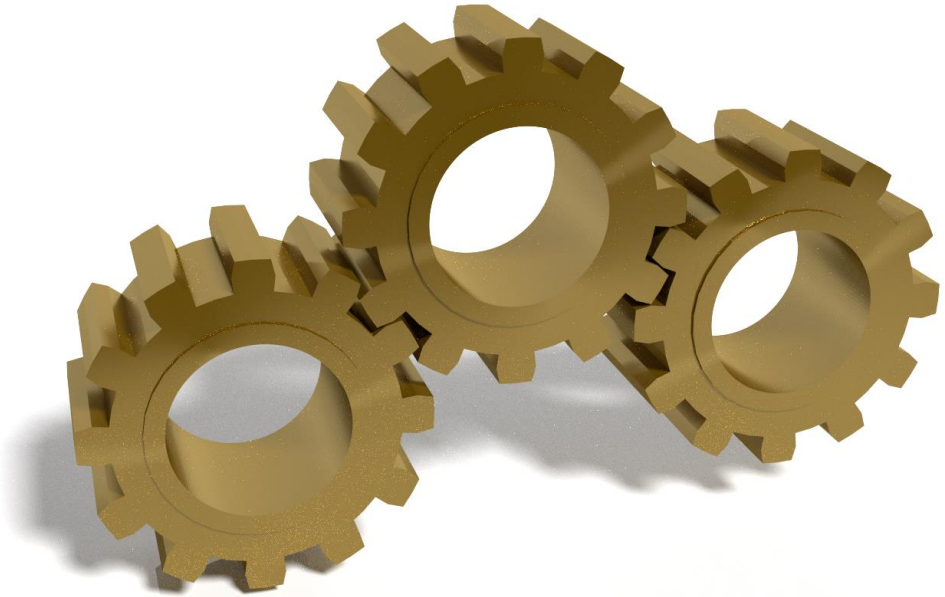
Polymers
- took off with synthetic rubber
- continues today



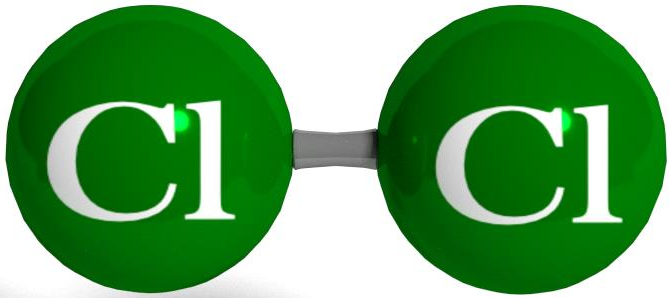
1760-1910	1870-1930	1895-1935	1925-present
rocks ⇨	coal ⇨	biomass ⇨	petroleum NGL

What is Integration?

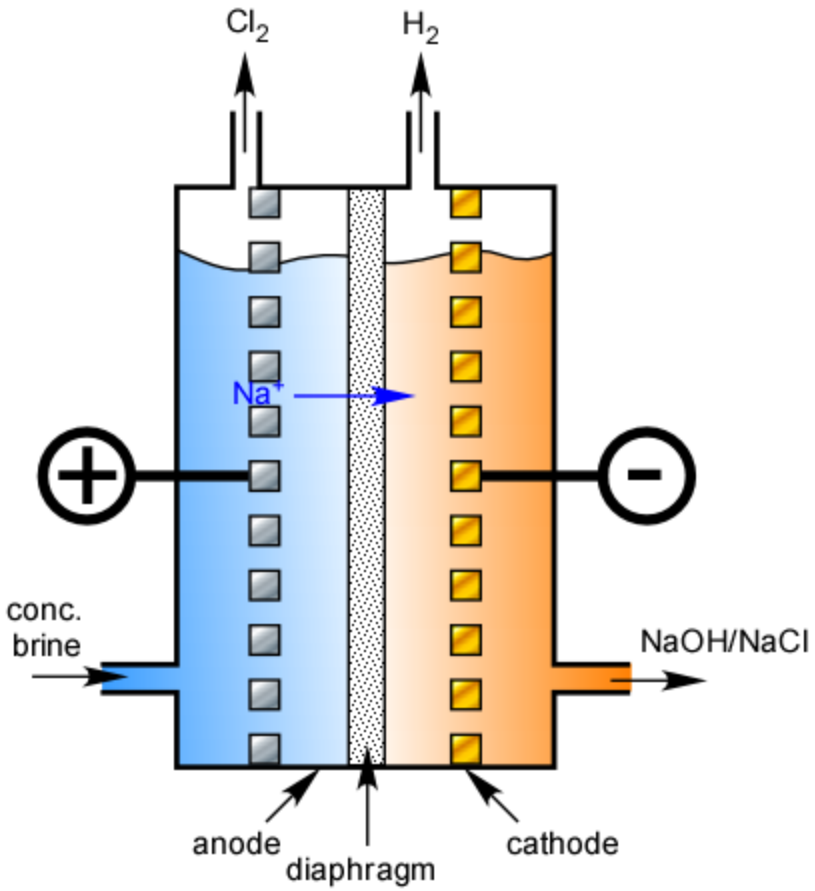
Integration



Linkage of mass and energy flows that create a significant advantage.


Cl
Cl

Chlor-Alkali



$$2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$$

$$2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$$

$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + Cl_2 + H_2$$

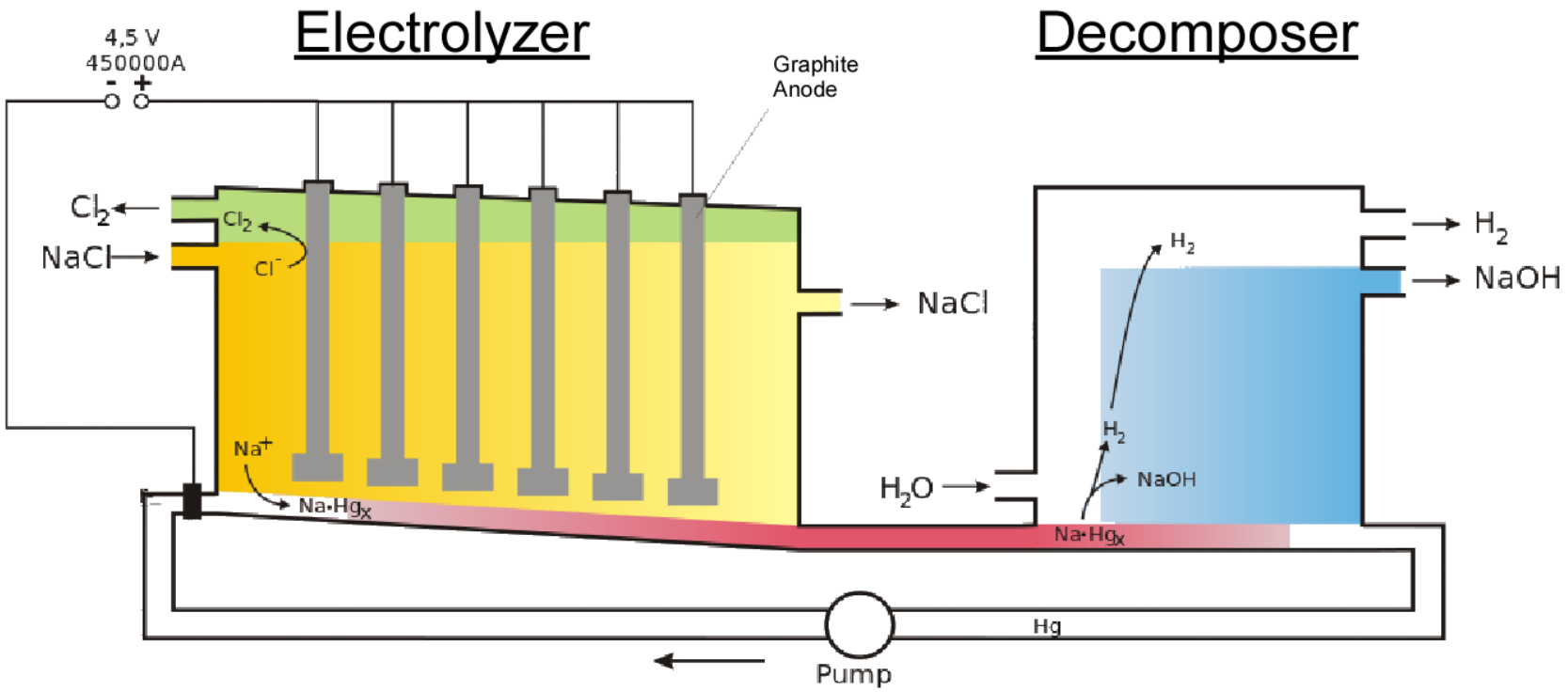
Bleach was the Product

$$Cl_2 + 2\ NaOH \longrightarrow NaOCl + NaCl + H_2O$$

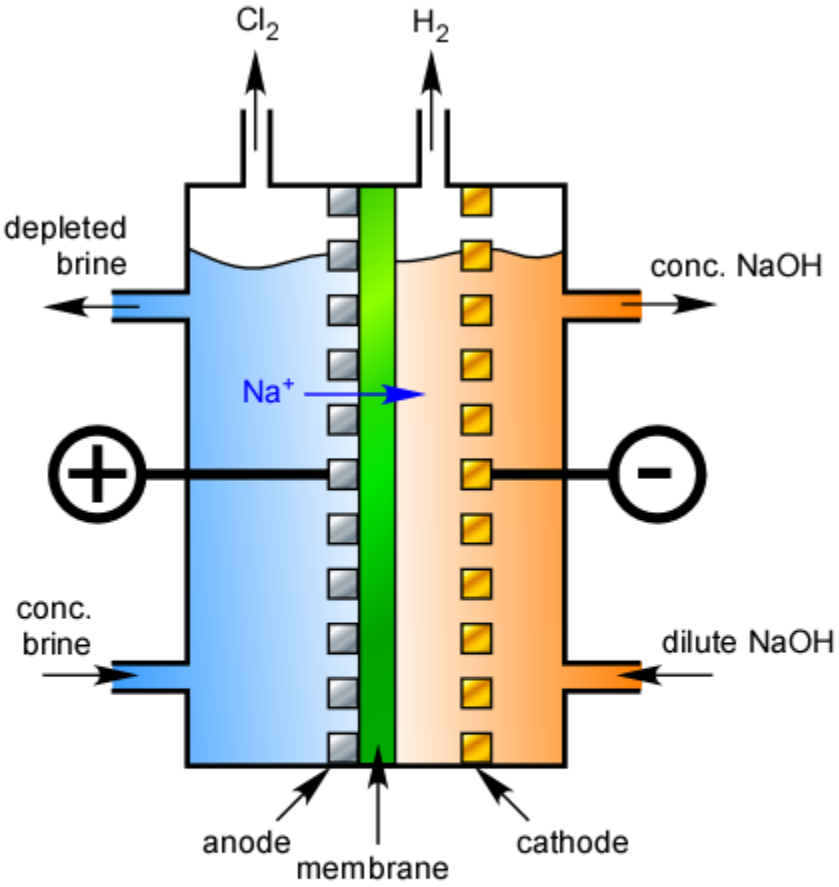
The oxidizing power of chlorine was what was desired.

No net production of alkali

Mercury Cells



Membrane Cells

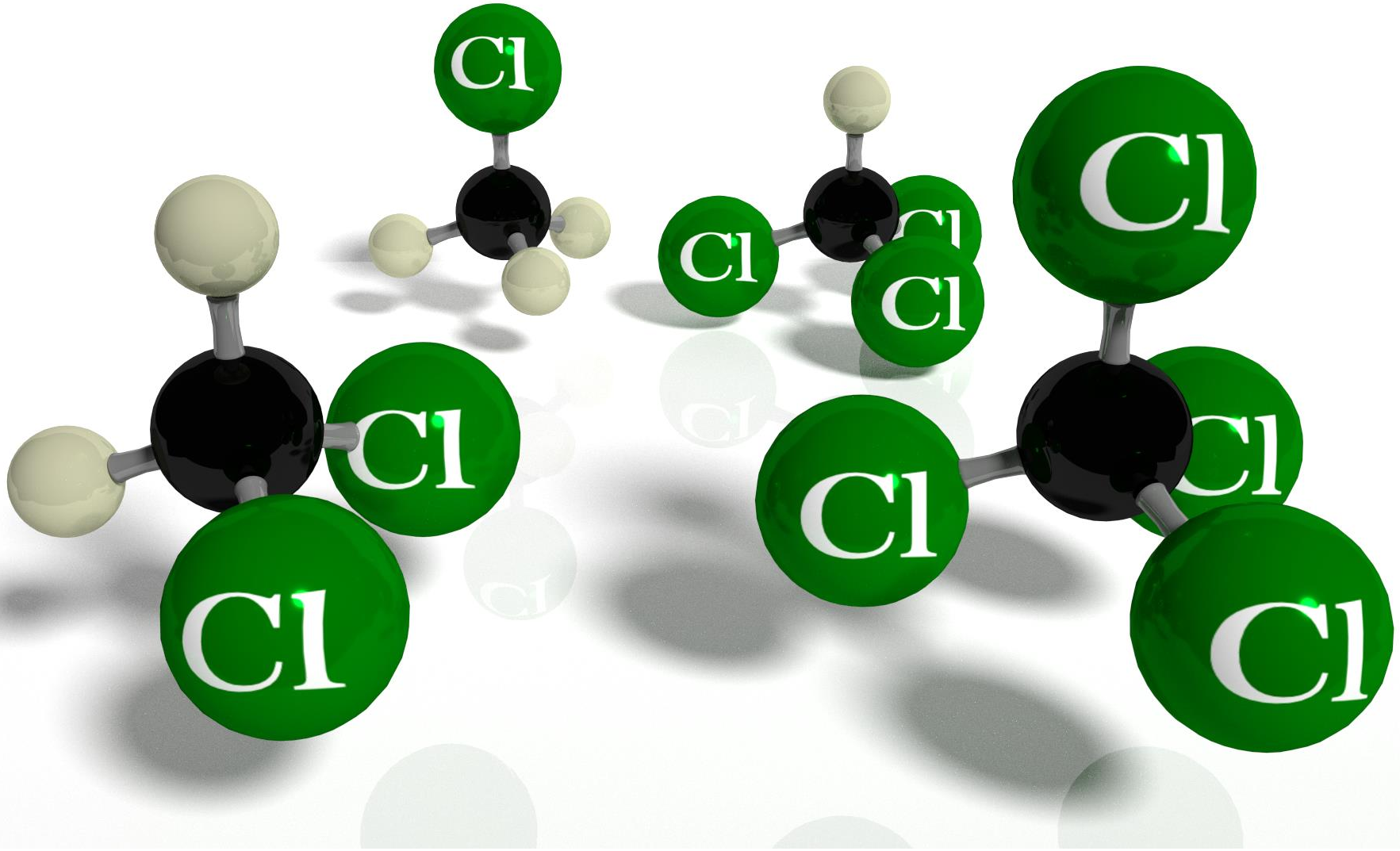


$$2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$$

$$2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$$

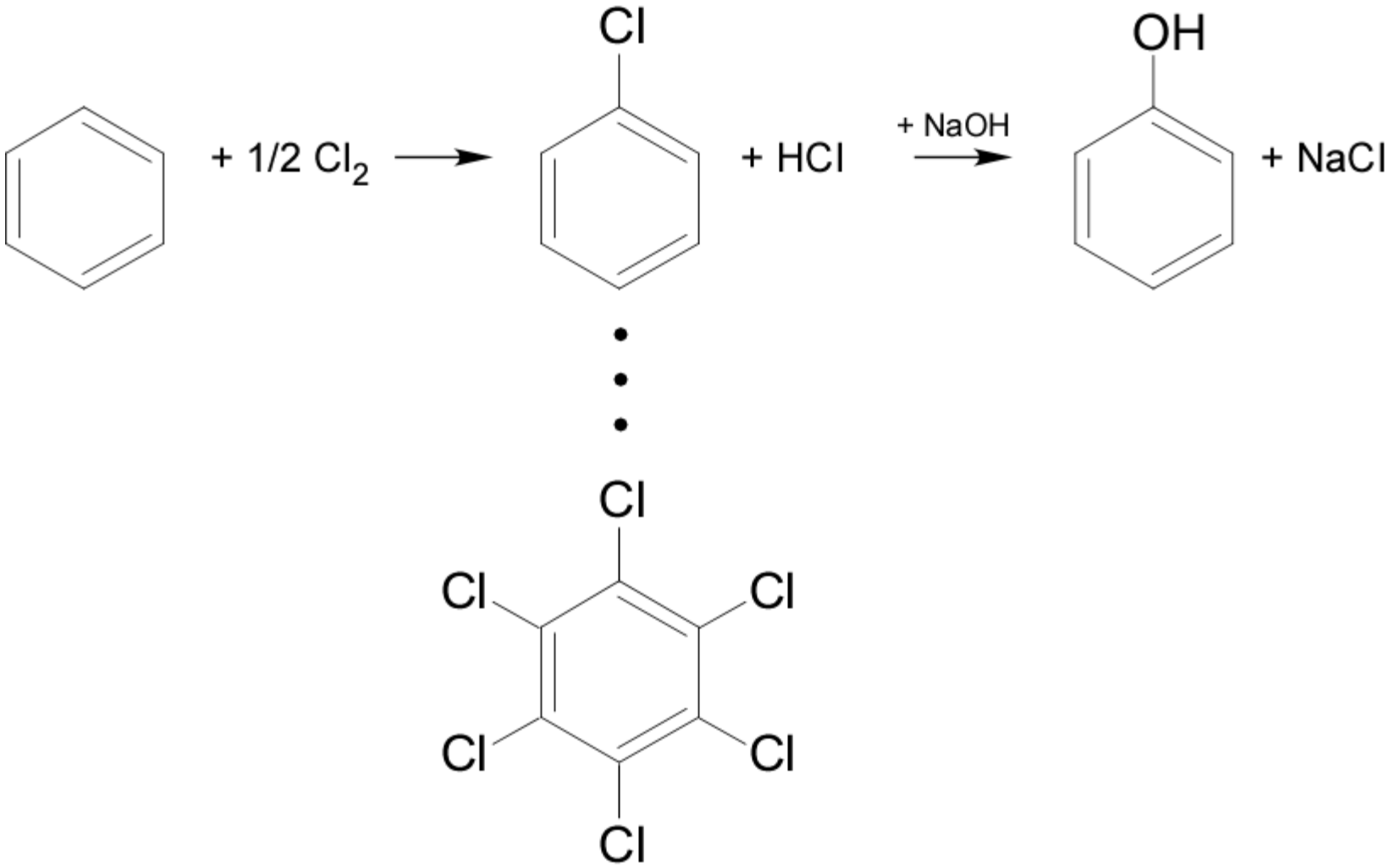
$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + Cl_2 + H_2$$

Organochlorides

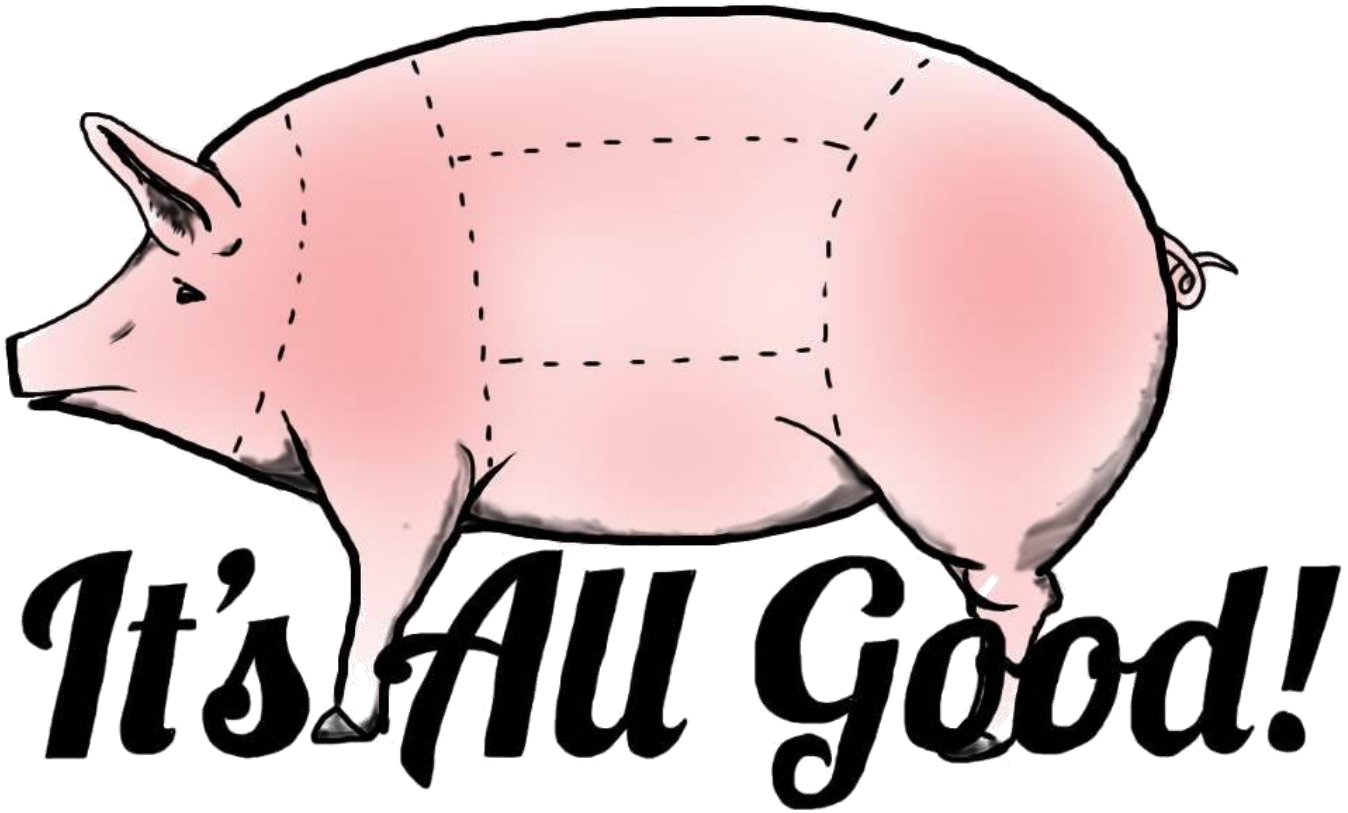



Pyrene
FIRE EXTINGUISHER
Pyrene
CARBON TETRACHLORIDE
TO OPERATE
TURN HANDLE TO LET
WORK LIKE A PUM
Pyrene Manufacturing Company
NEWARK NEW JERSEY

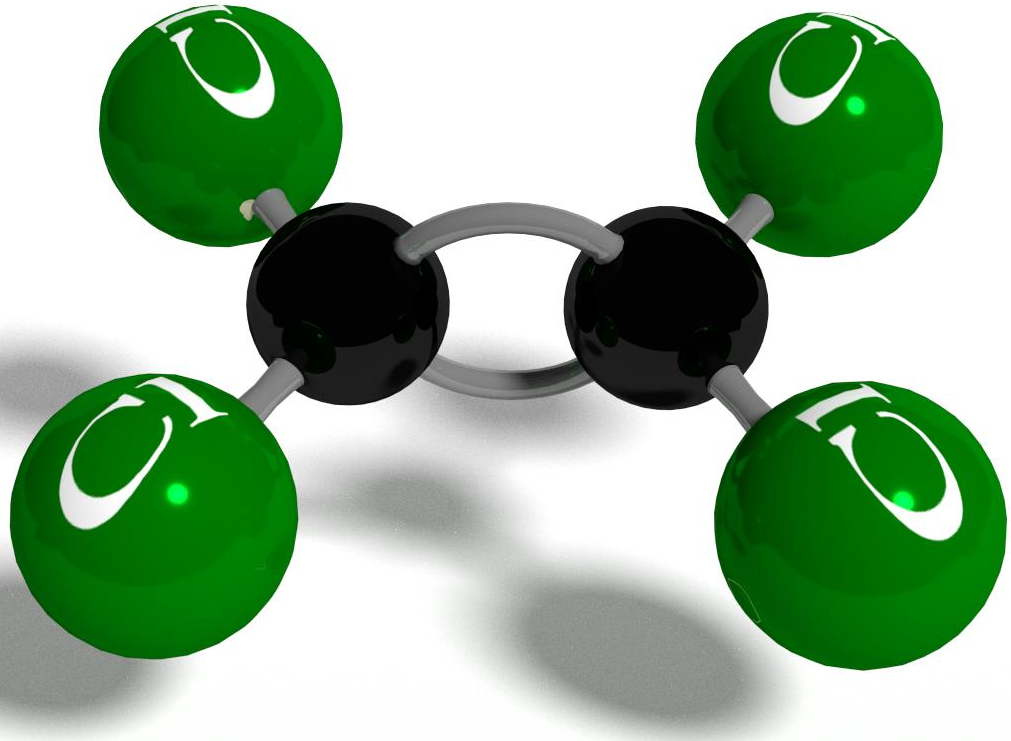
Chlorine as an Oxidant



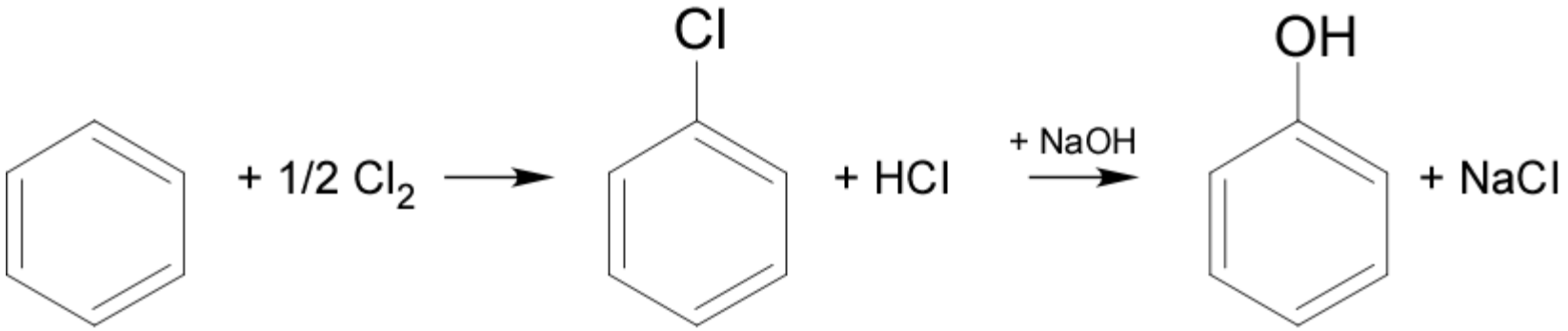
All Reaction Products Find Uses



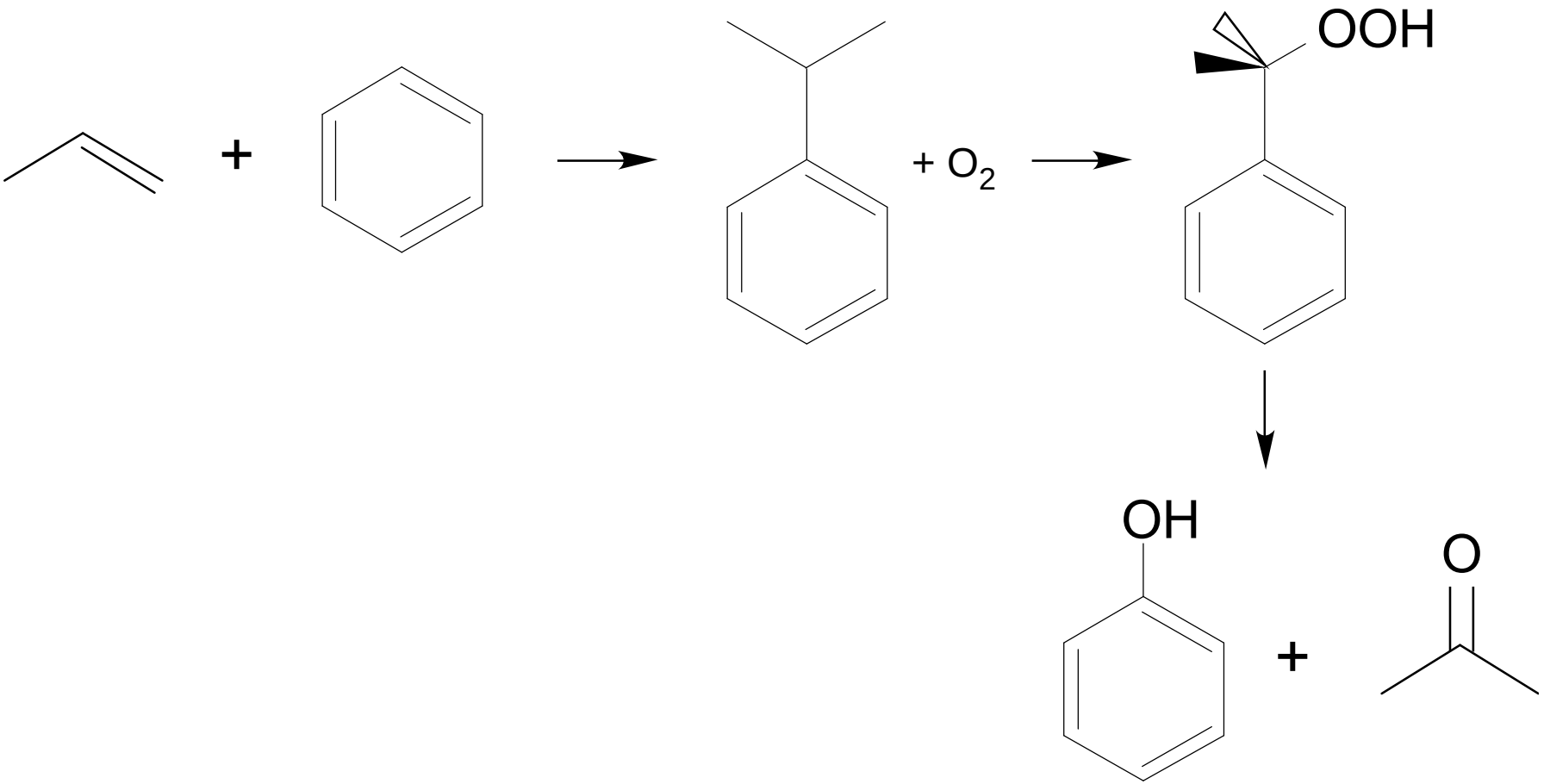
Perchloroethylene



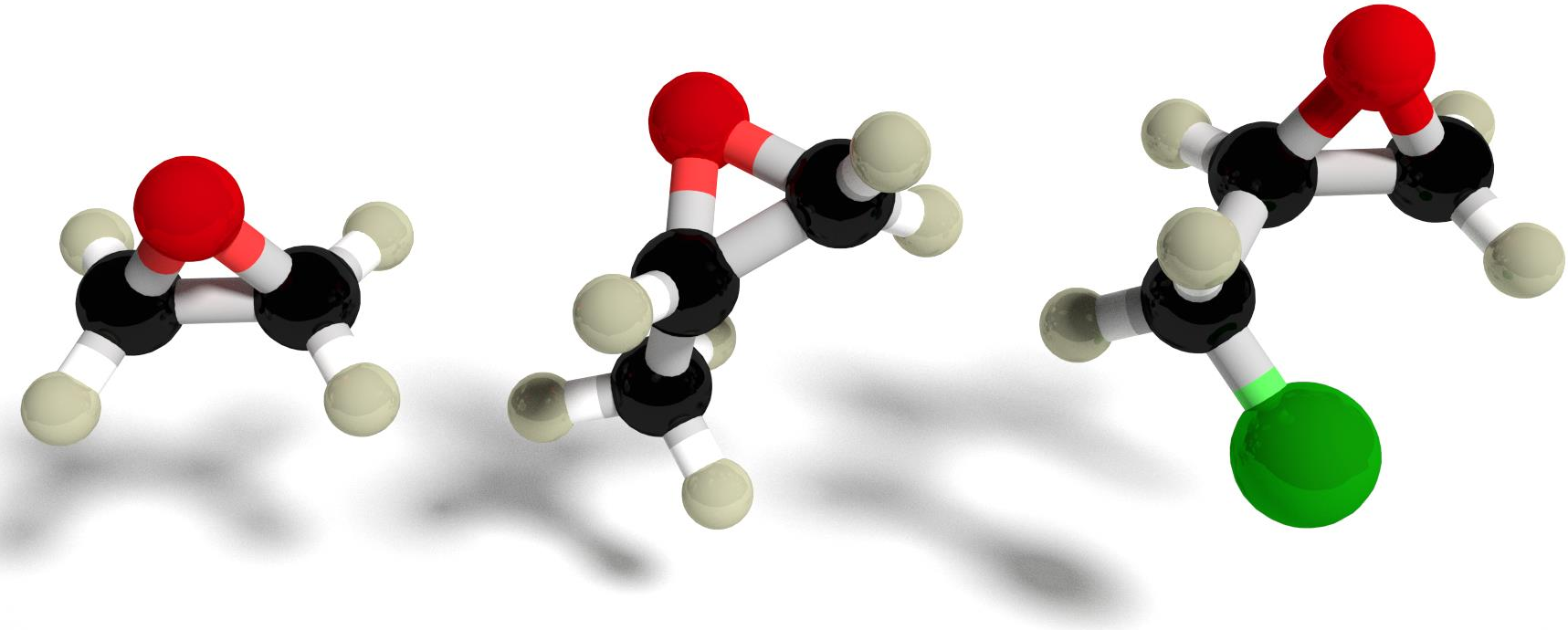
Chlorine as an Oxidant



Phenol Today

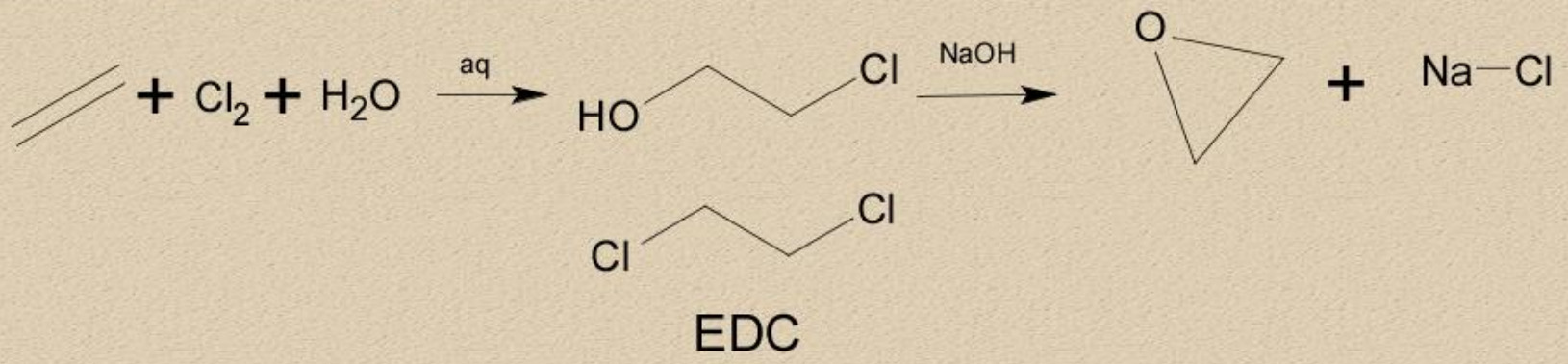


Epoxides



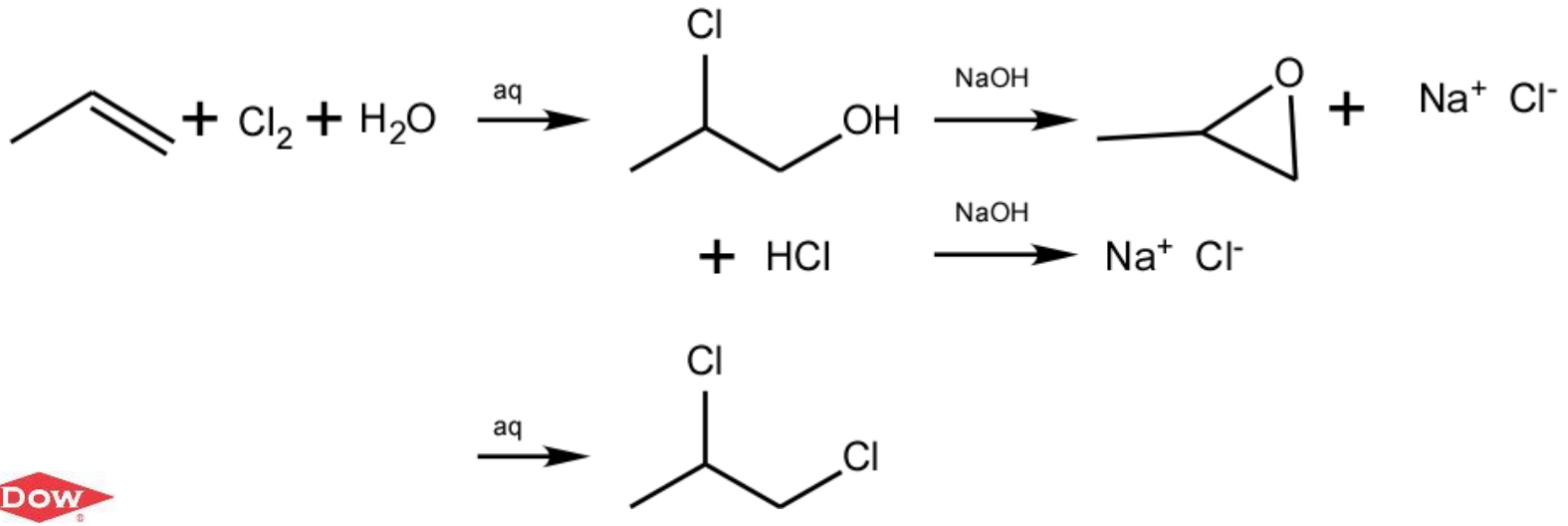
Chlorohydrin Chemistry

Clorohydrin Ethylene Oxide



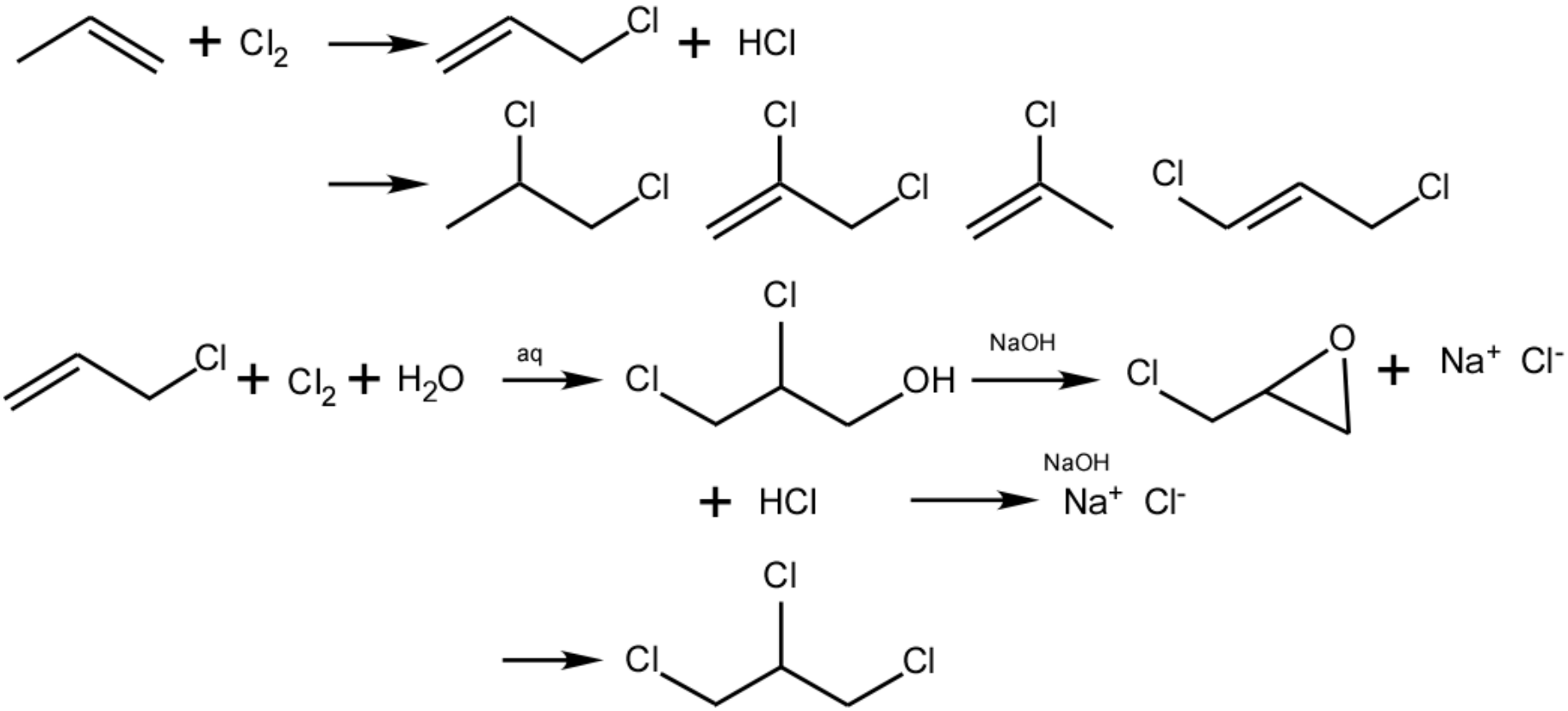
1915-1975

Chlorohydrin Propylene Oxide

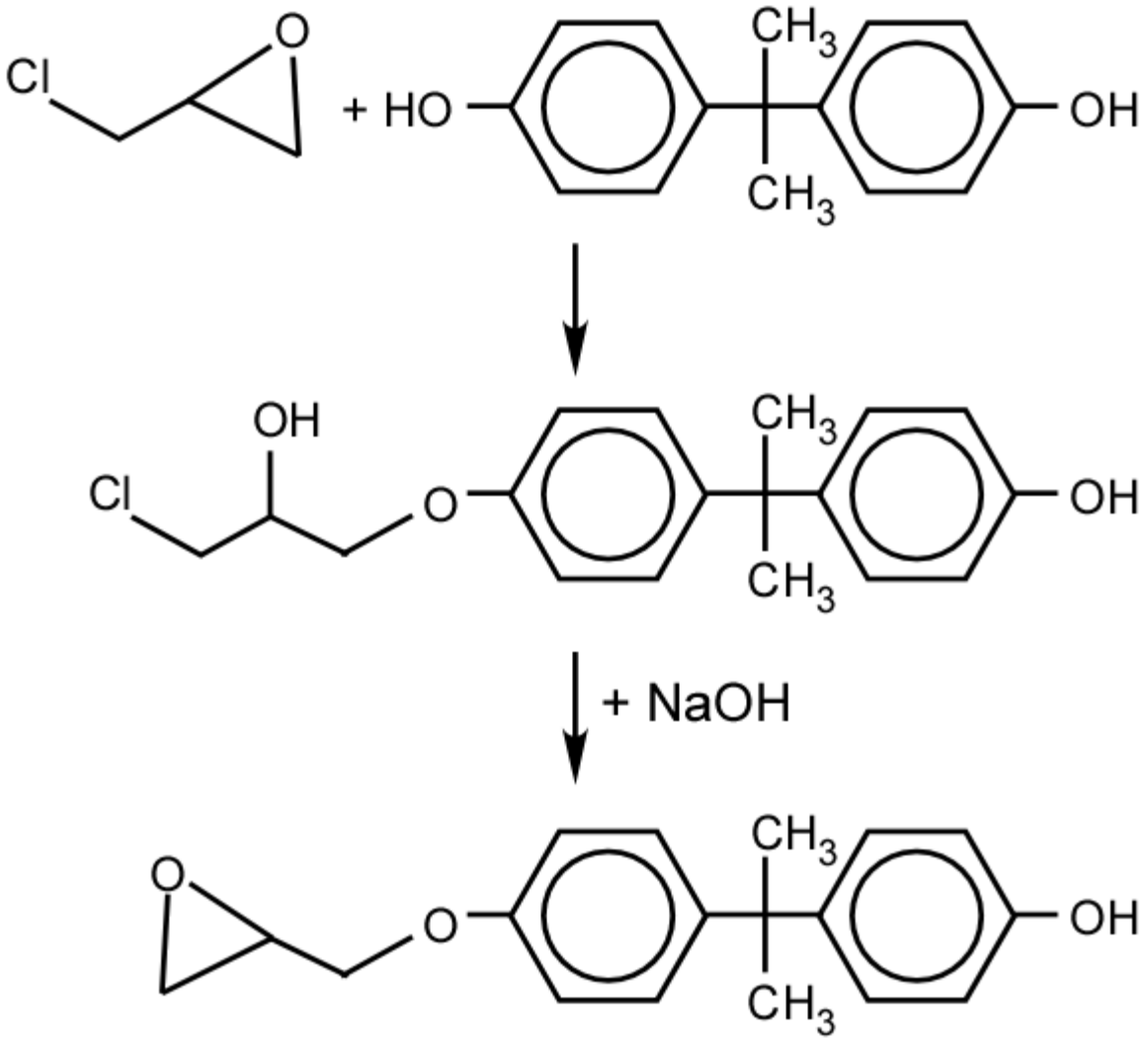


More Chlorohydrin Chemistry

Chlorohydrin Epichlorohydrin

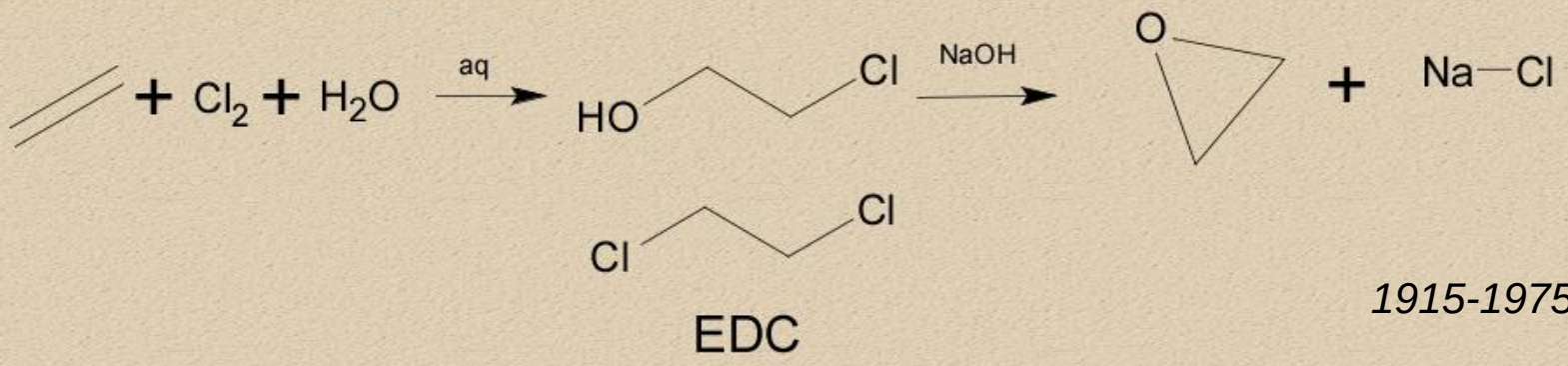


Epoxy Resins



Direct Oxidation

Clorohydrin Ethylene Oxide

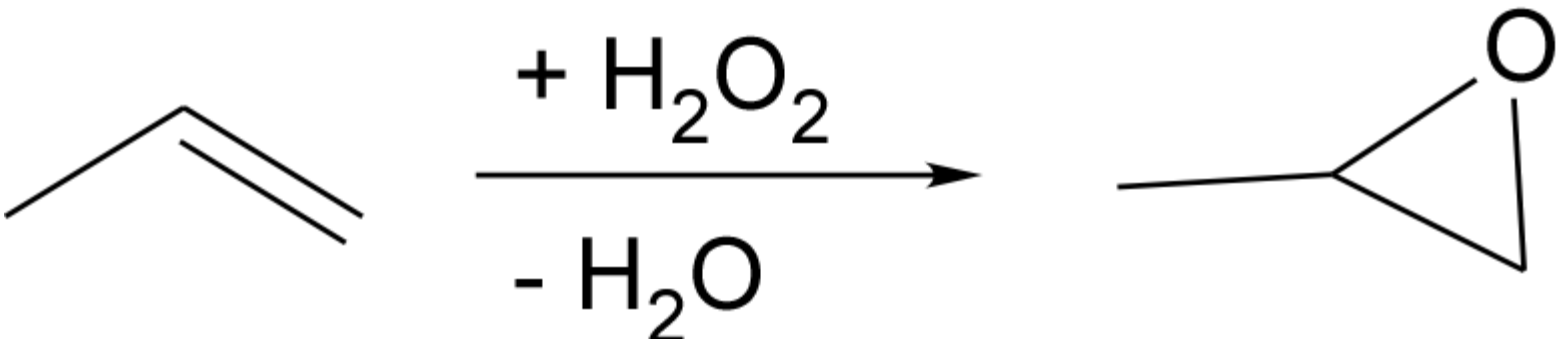


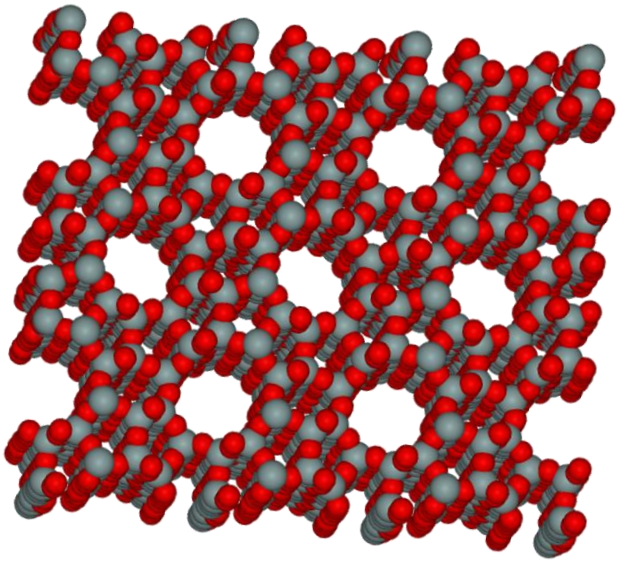
1915-1975

Direct Oxidation Ethylene Oxide

1937

Hydroperoxidation



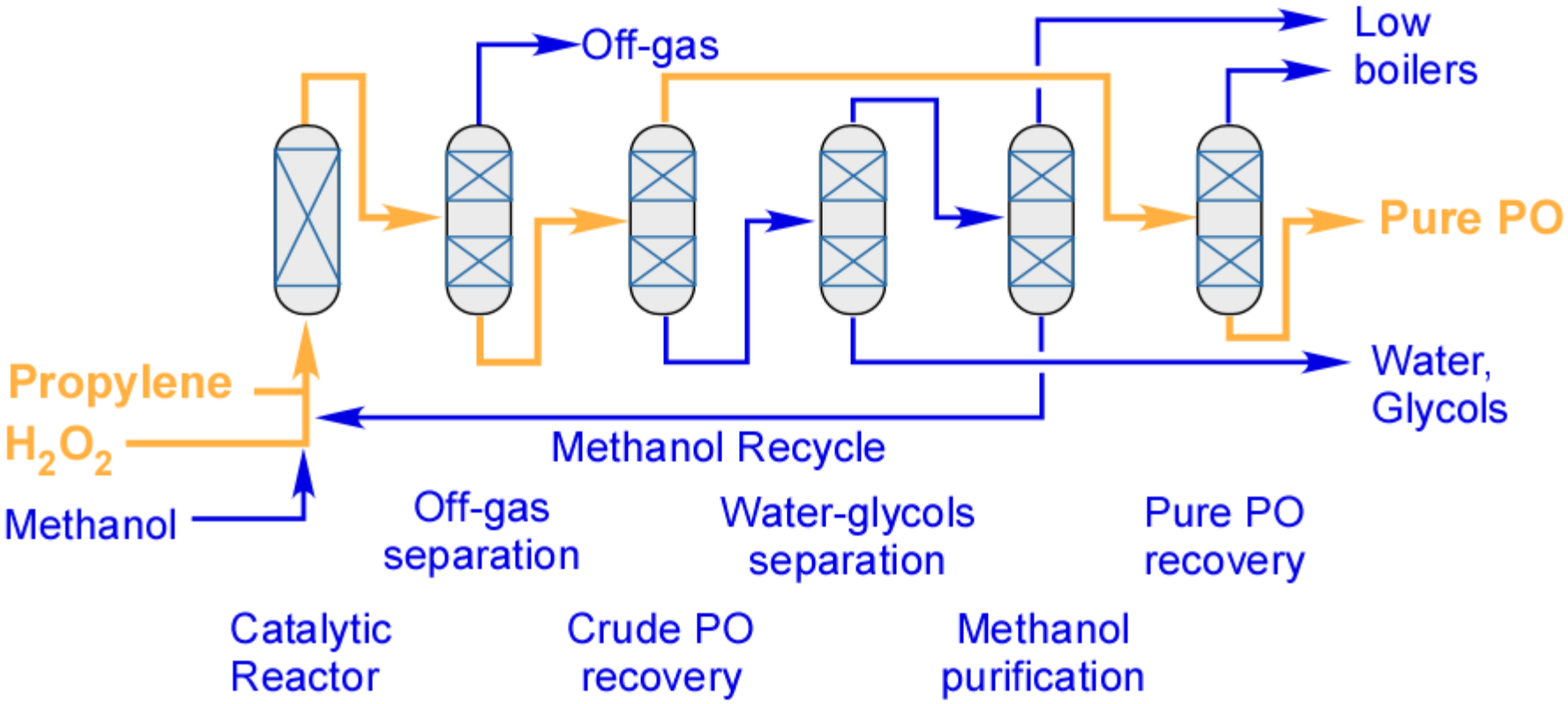


titanium silicate catalyst

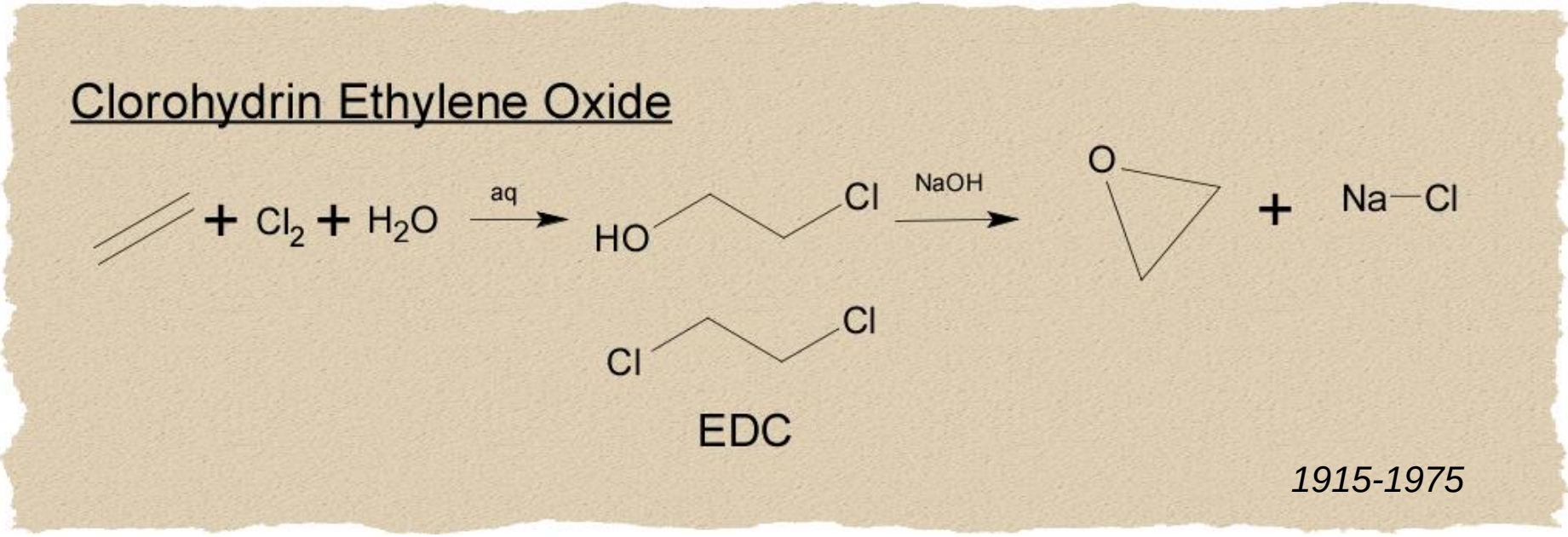
0.5 nm pores

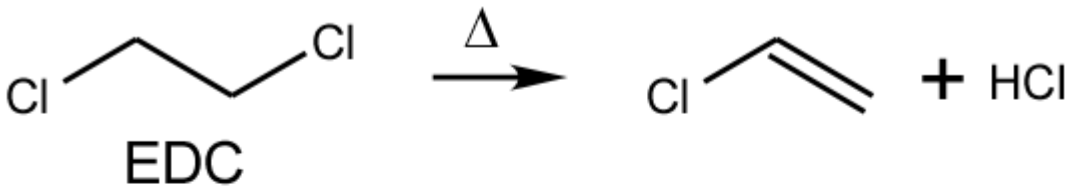
suitable for packed bed reactor

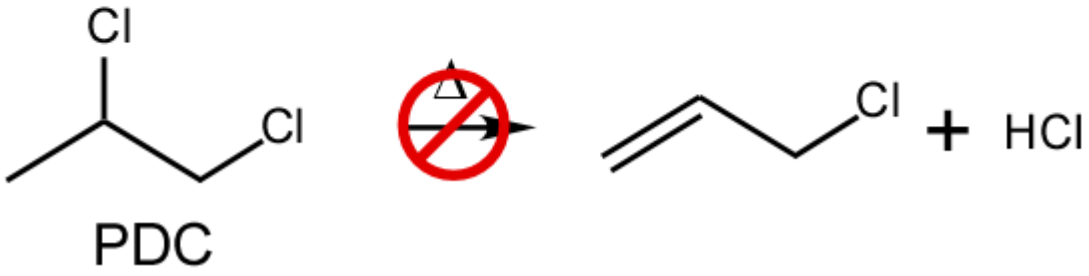
Simplified Process Flowsheet



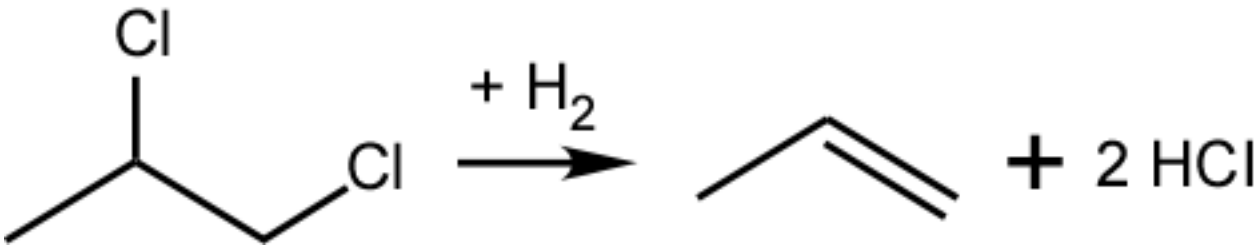
Chlorohydrin Chemistry







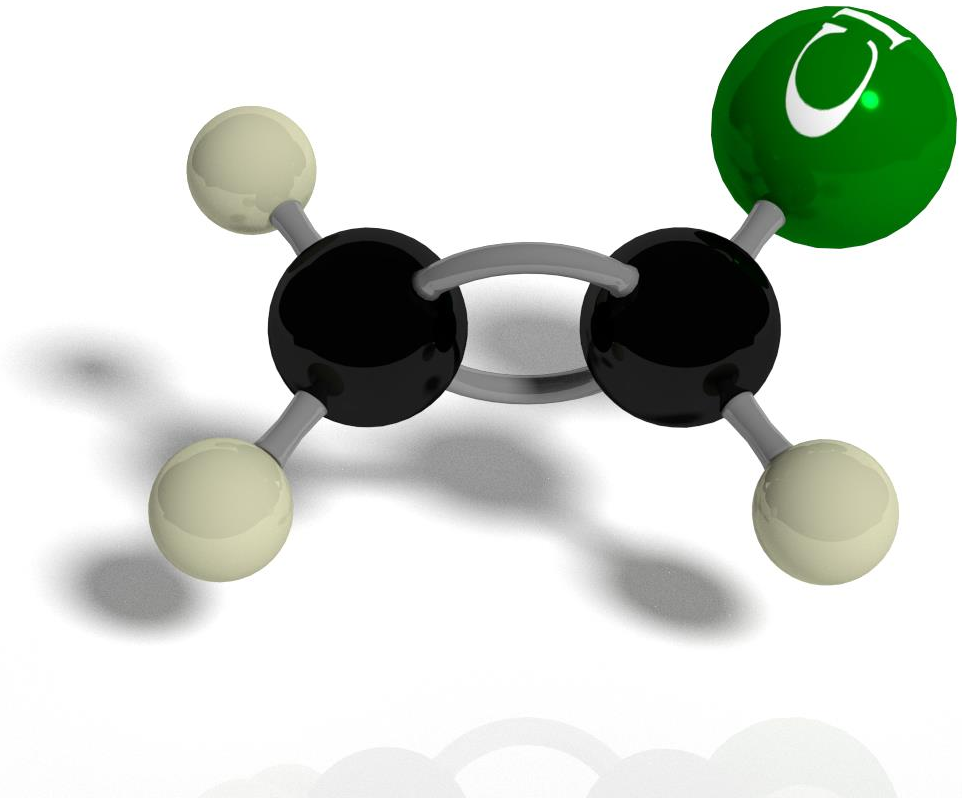
PDC Hydro



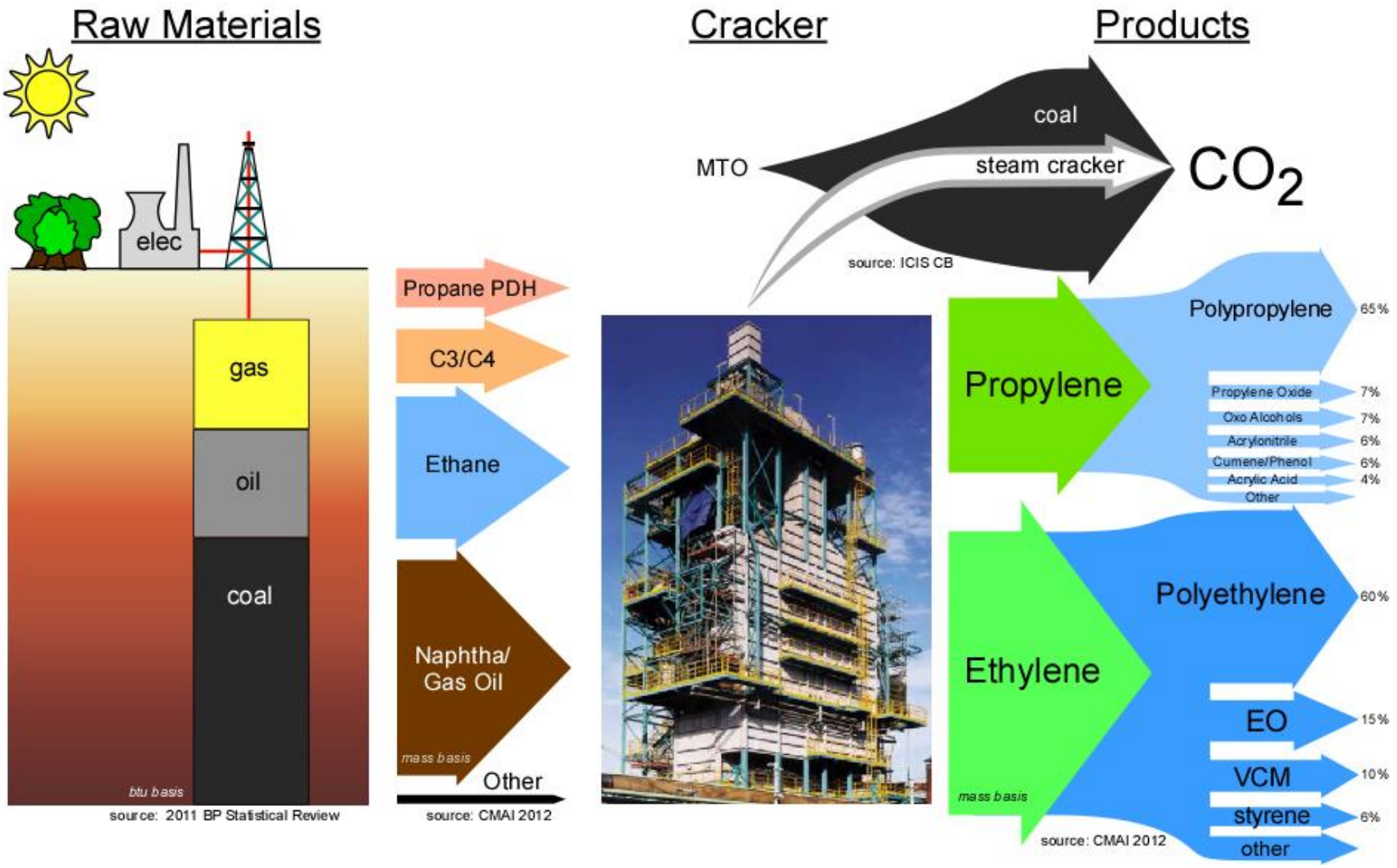
PtCu catalyst developed by Larry Ito

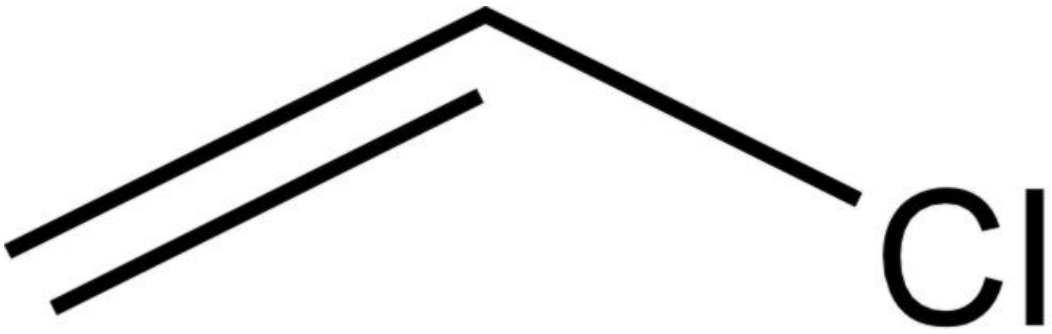
Carbon supported

Vinyl Chloride



Chemical Industry Snapshot



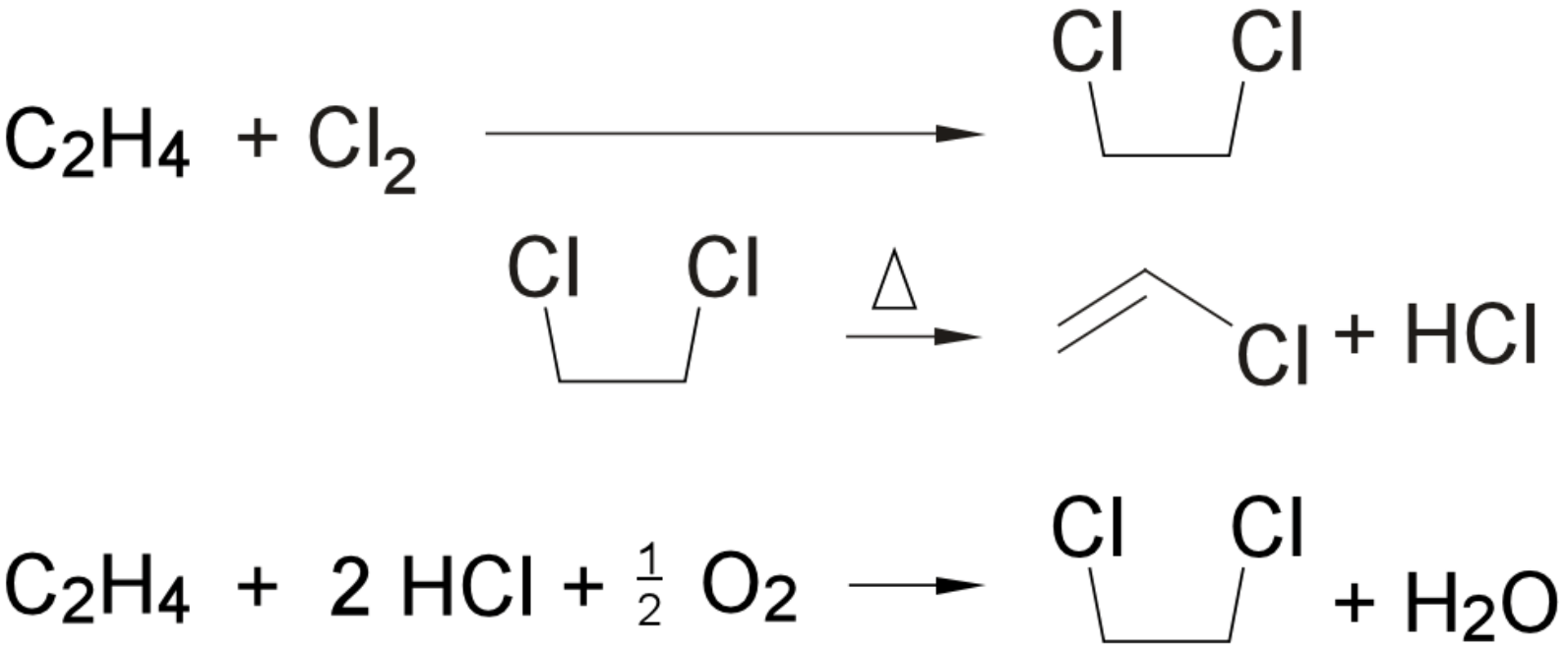


Vinyl Chloride Monomer(VCM)

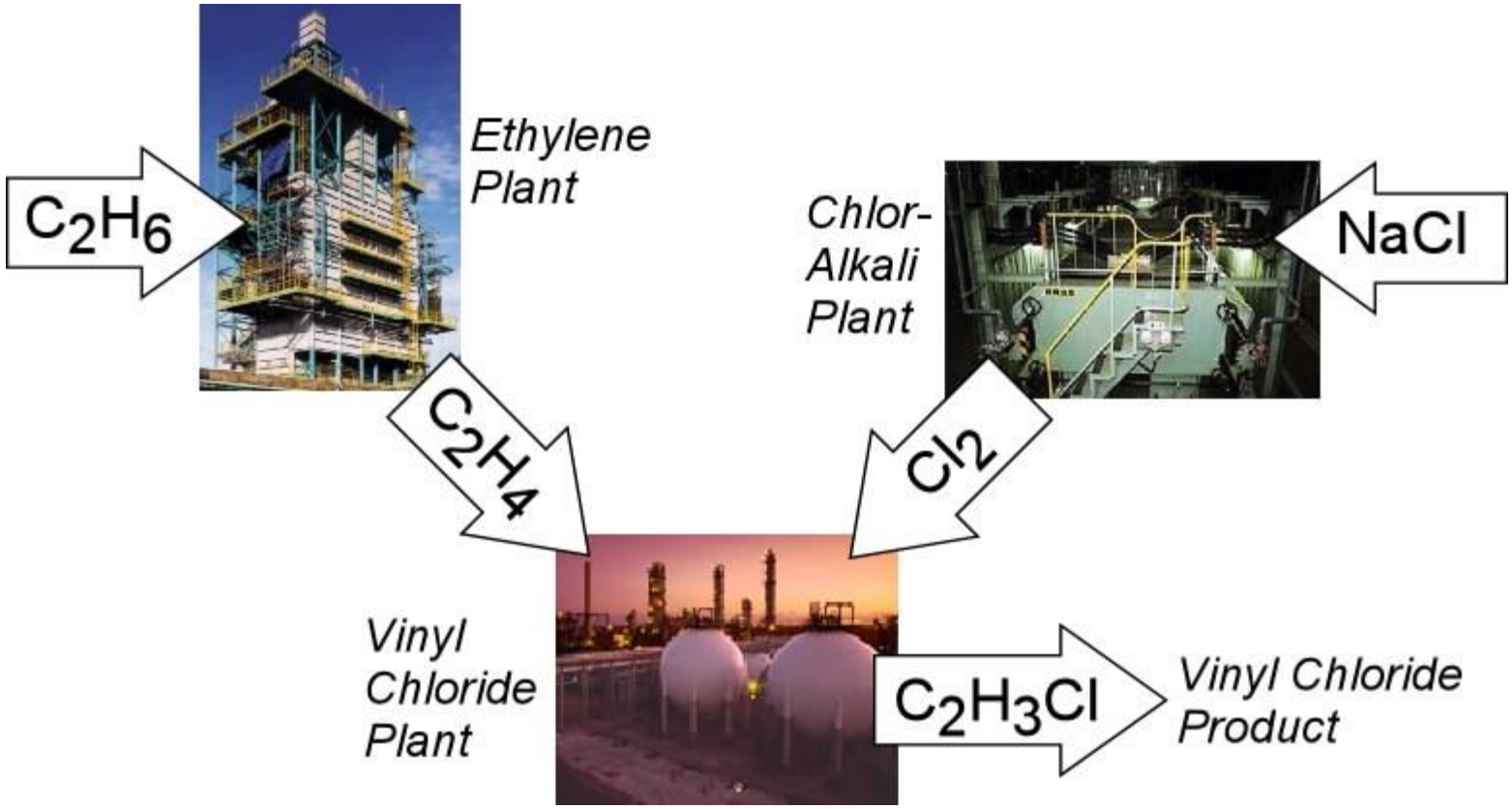
Dow produced ~5 billion pounds/year
World demand is 49 billion pounds
Growth averages 4-5%

Source: Chemical Week product focus

Conventional Production



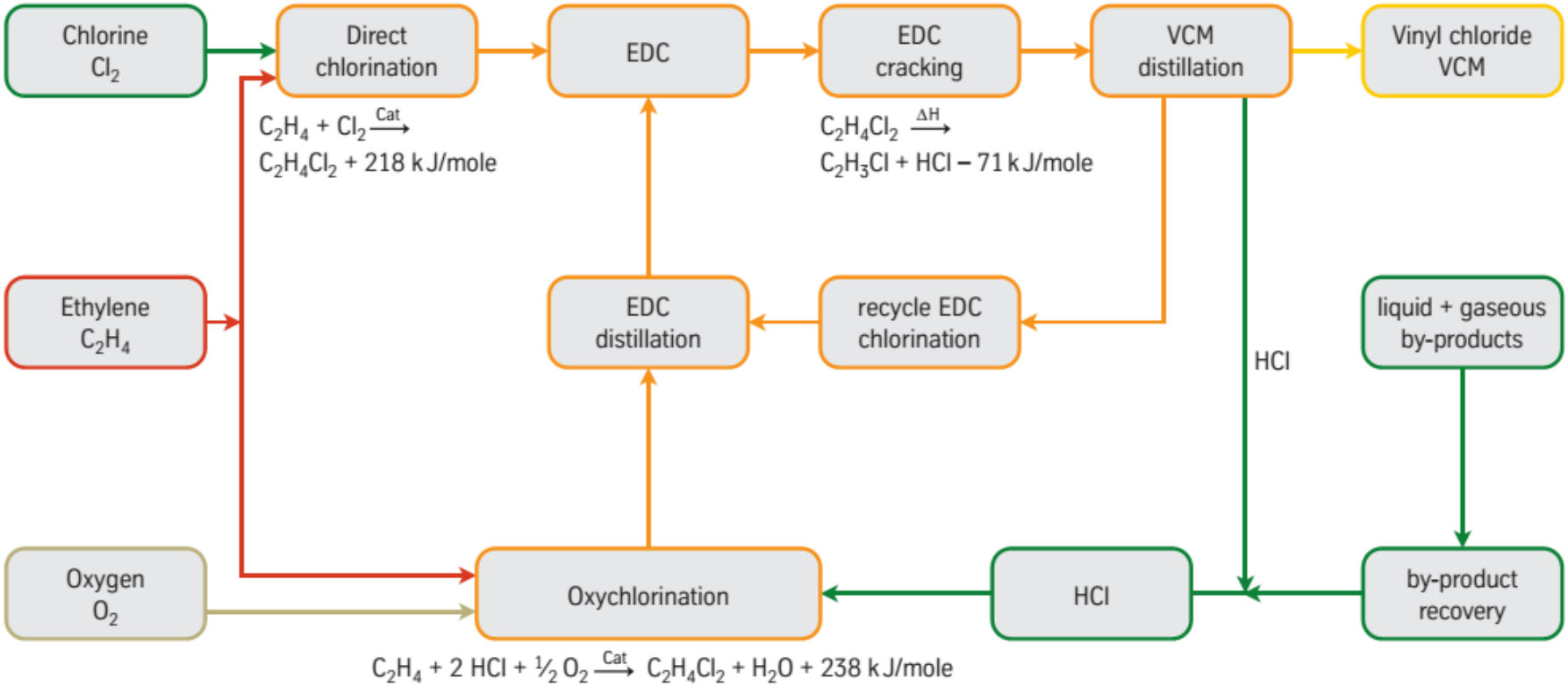
Conventional VCM



More Detail

VCM synthesis: $2\ C_2H_4 + Cl_2 + \frac{1}{2}\ O_2 \longrightarrow 2\ C_2H_3Cl + H_2O$

Schematic diagram of a VCM plant

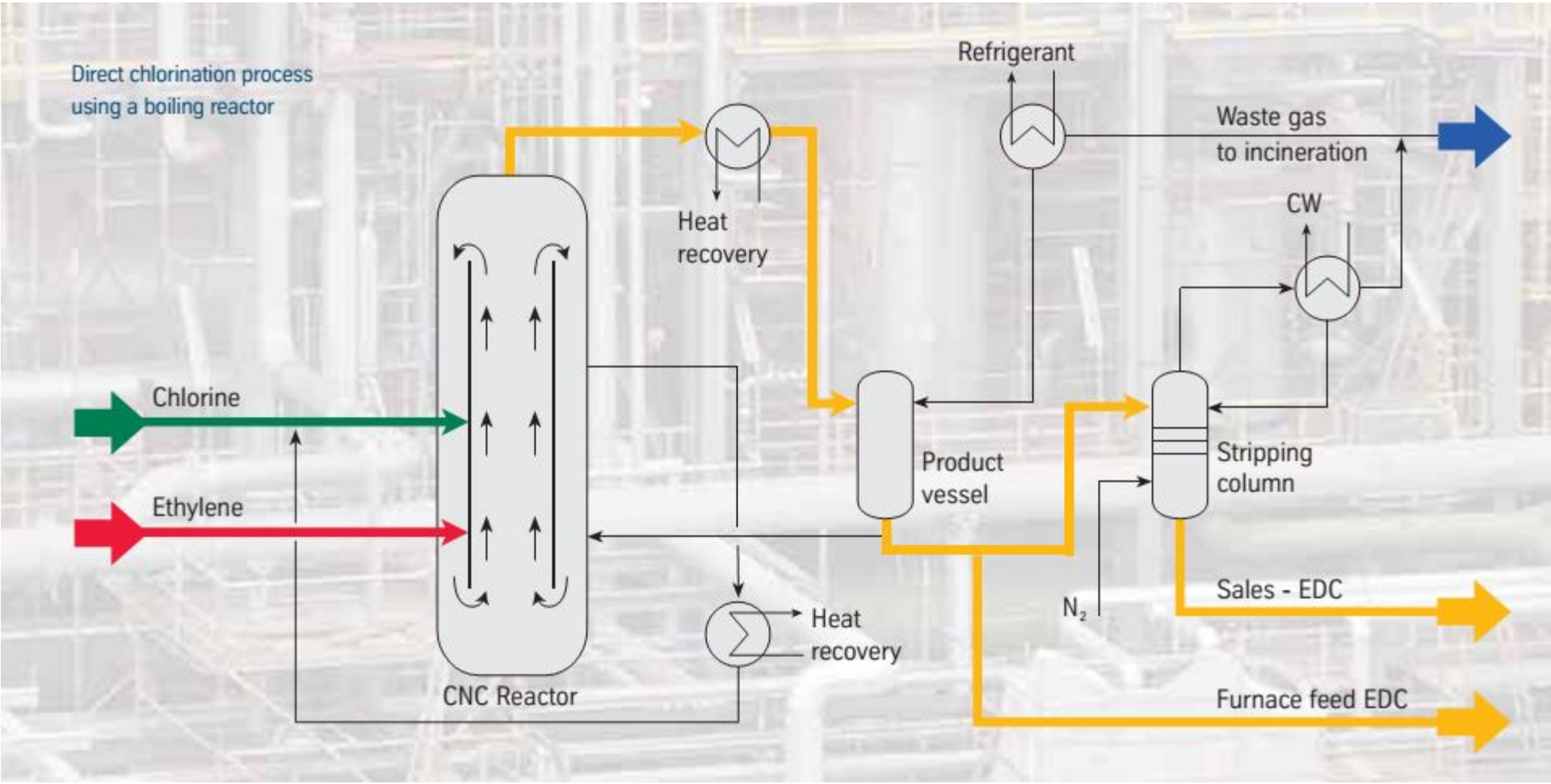


Vinnolit

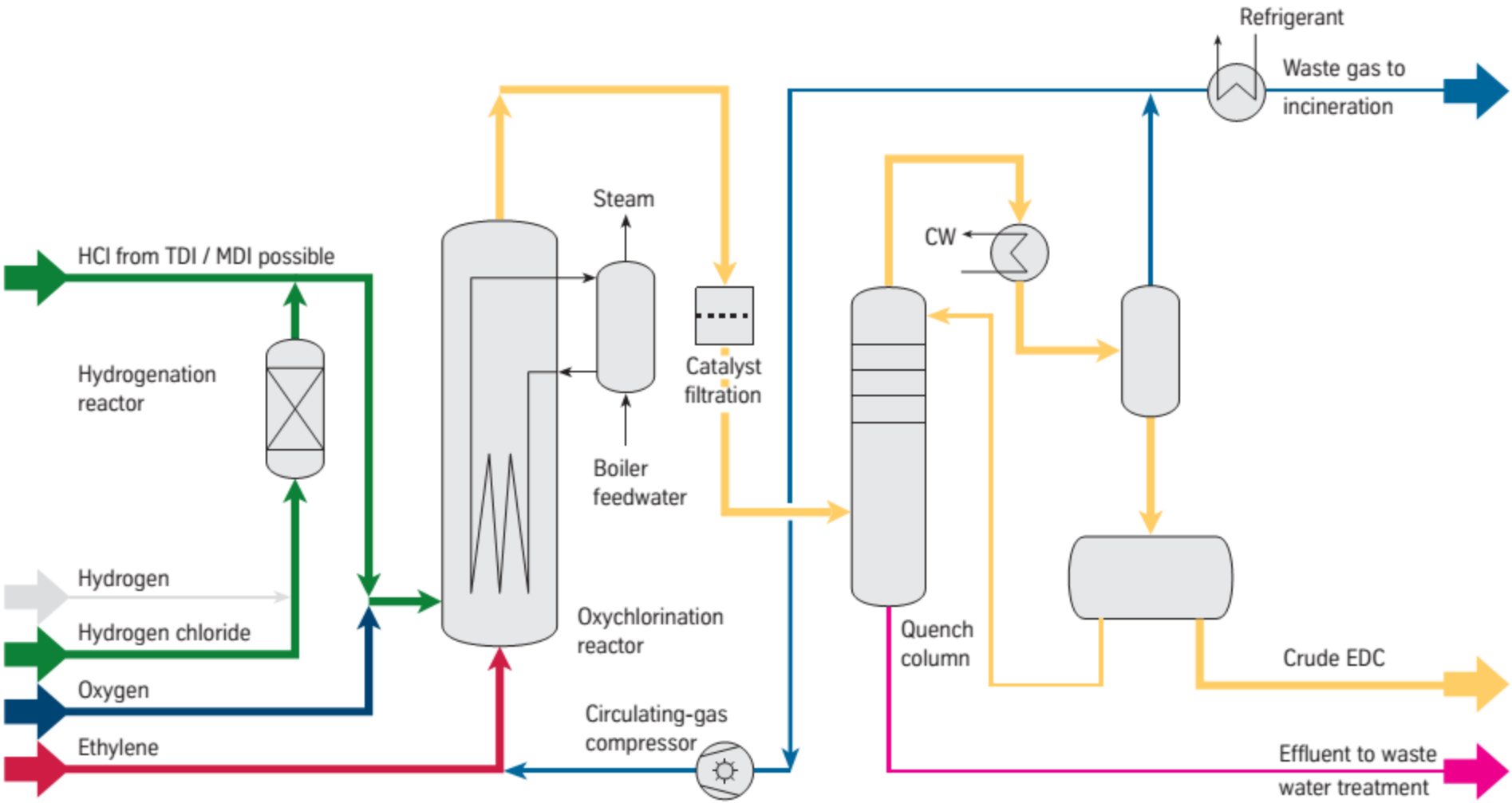
Uhde ThyssenKrupp

DOW

Direct Chlorination



Oxychlorination

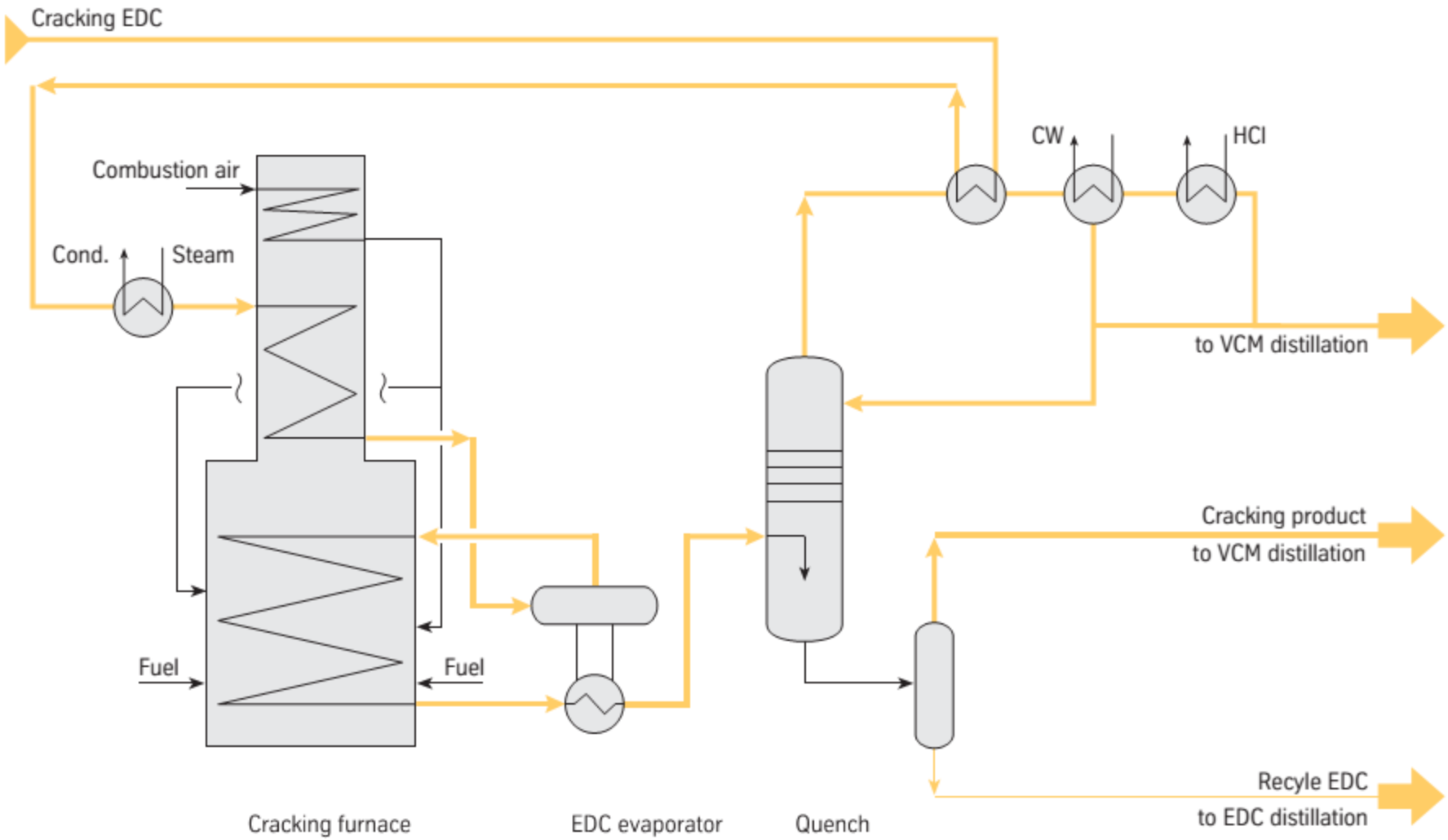


Vinnolit

Uhde ThyssenKrupp

DOW

Cracking

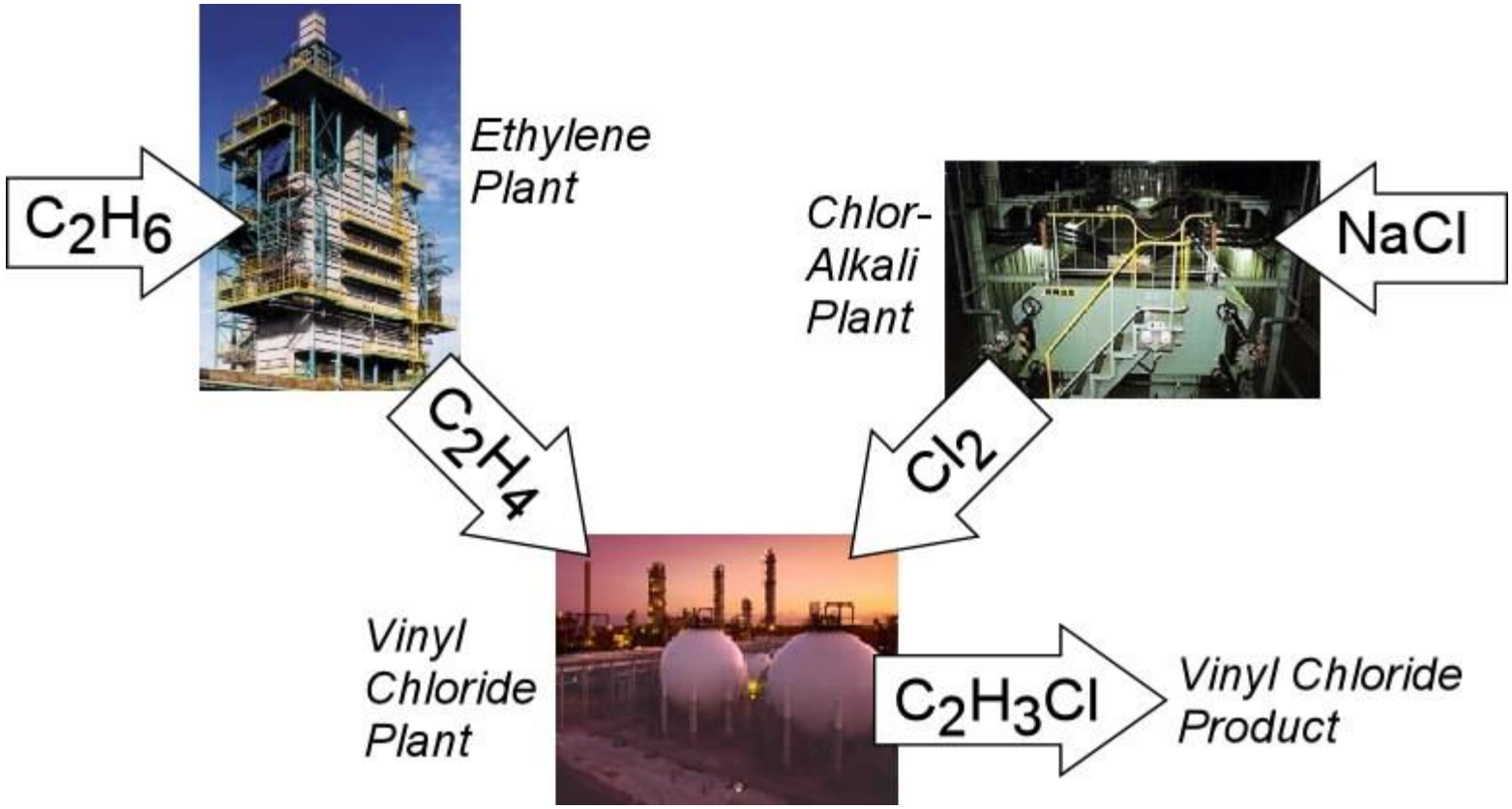


Vinnolit

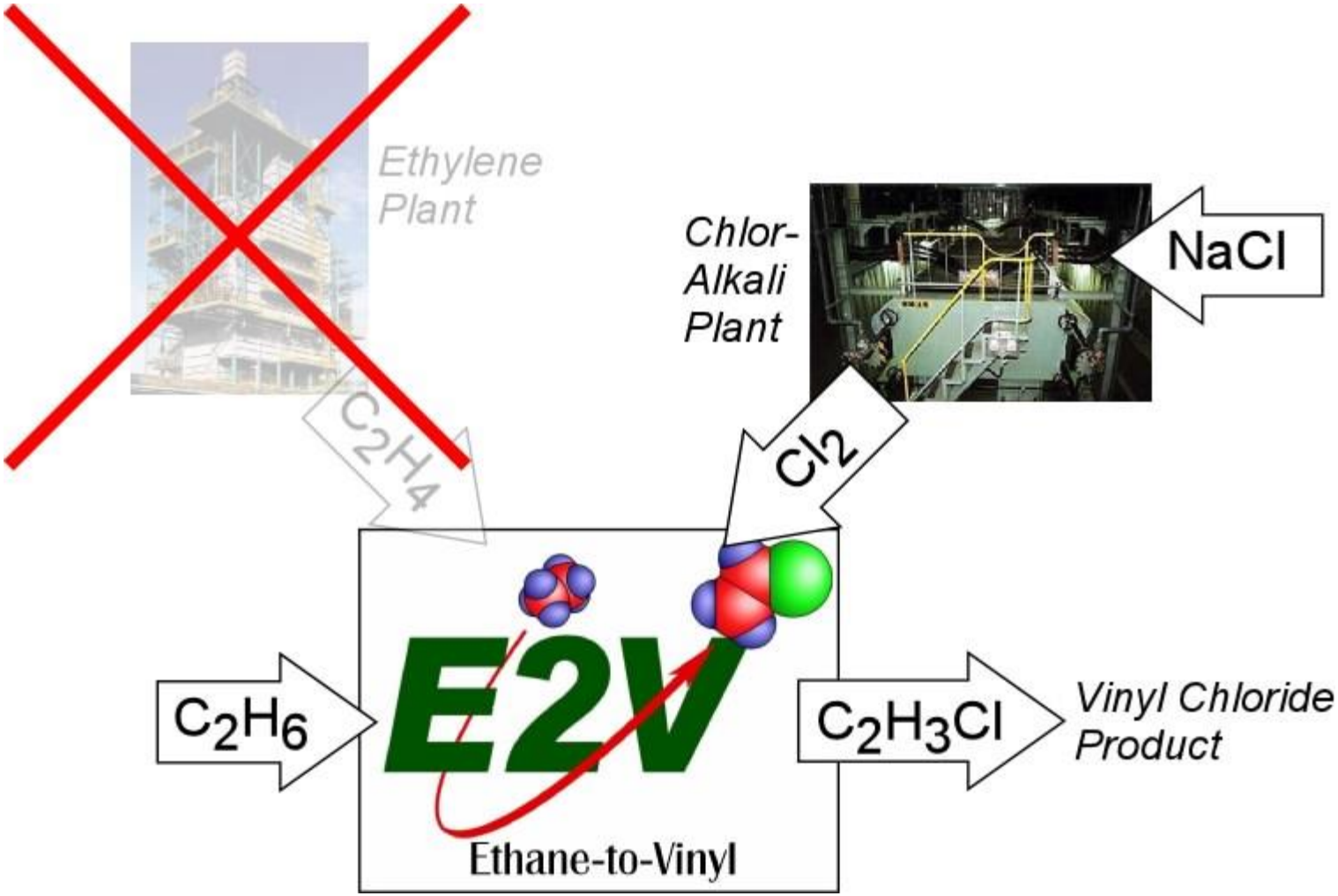
Uhde ThyssenKrupp

DOW

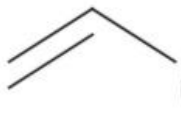
Conventional VCM



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

$$\left\{\begin{matrix} C_2H_6 \\ C_2H_4 \end{matrix}\right\} + \left\{\begin{matrix} HCl \\ Cl_2 \end{matrix}\right\} + O_2 \longrightarrow \text{  } + H_2O$$

Technical Lead

United States Patent [19]

Li

[11] **4,300,005**

[45] **Nov. 10, 1981**

[54] PREPARATION OF VINYL CHLORIDE

[75] Inventor: **Tao P. Li**, Chesterfield, Mo.

[73] Assignee: **Monsanto Co.**, St. Louis, Mo.

[21] Appl. No.: **856,889**

[22] Filed: **Dec. 2, 1977**

[51] **Int. Cl.**[3] **C07C 17/10**

[52] **U.S. Cl.** **570/224**

[58] **Field of Search** ..... 260/656 R, 654 A; 570/224

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,217,064	11/1965	McGreevy et al.	260/656 R
3,308,184	3/1967	Bajars	260/680 D
3,308,198	3/1967	Bajars	260/680 D
3,359,343	12/1967	Bajars	260/680 D
3,427,359	2/1969	Rectenwald et al.	260/656 R
4,042,639	8/1977	Gordon et al.	260/656 R

FOREIGN PATENT DOCUMENTS

1039369	8/1966	United Kingdom	260/656 R

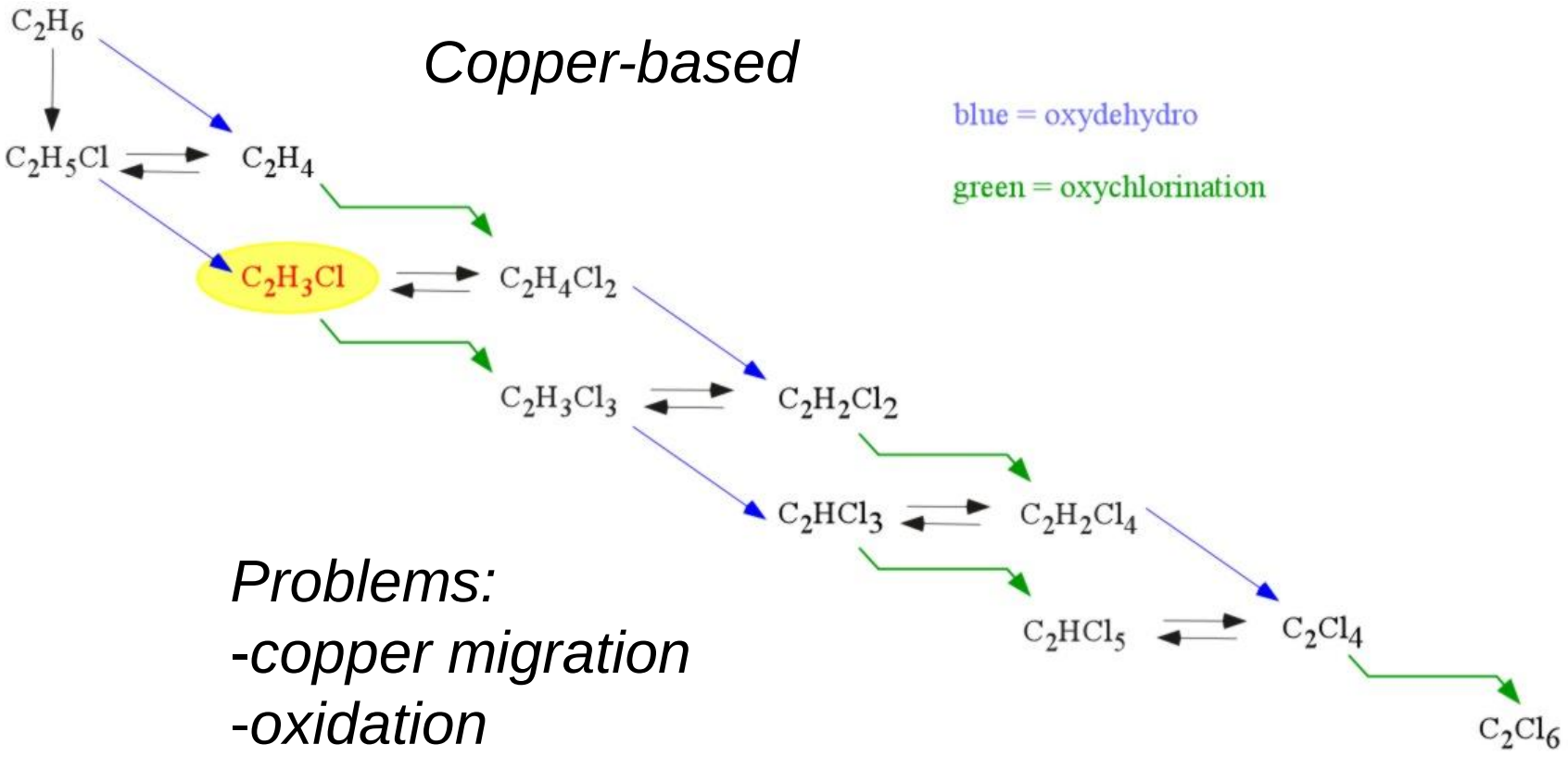
Primary Examiner—Delbert E. Gantz
Assistant Examiner—Joseph A. Boska

[57] **ABSTRACT**

Monohalogenated olefins are selectively prepared in high yields from alkanes having 2 to 4 carbon atoms by the reaction of such hydrocarbons with a hydrogen halide and a source of oxygen at a temperature from about 400° to about 650° C. in contact with a catalyst comprising a copper halide and an alkali metal phosphate, particularly potassium phosphate, deposited on an inorganic support. Typically, vinyl chloride is prepared in one step from ethane.

10 Claims, No Drawings

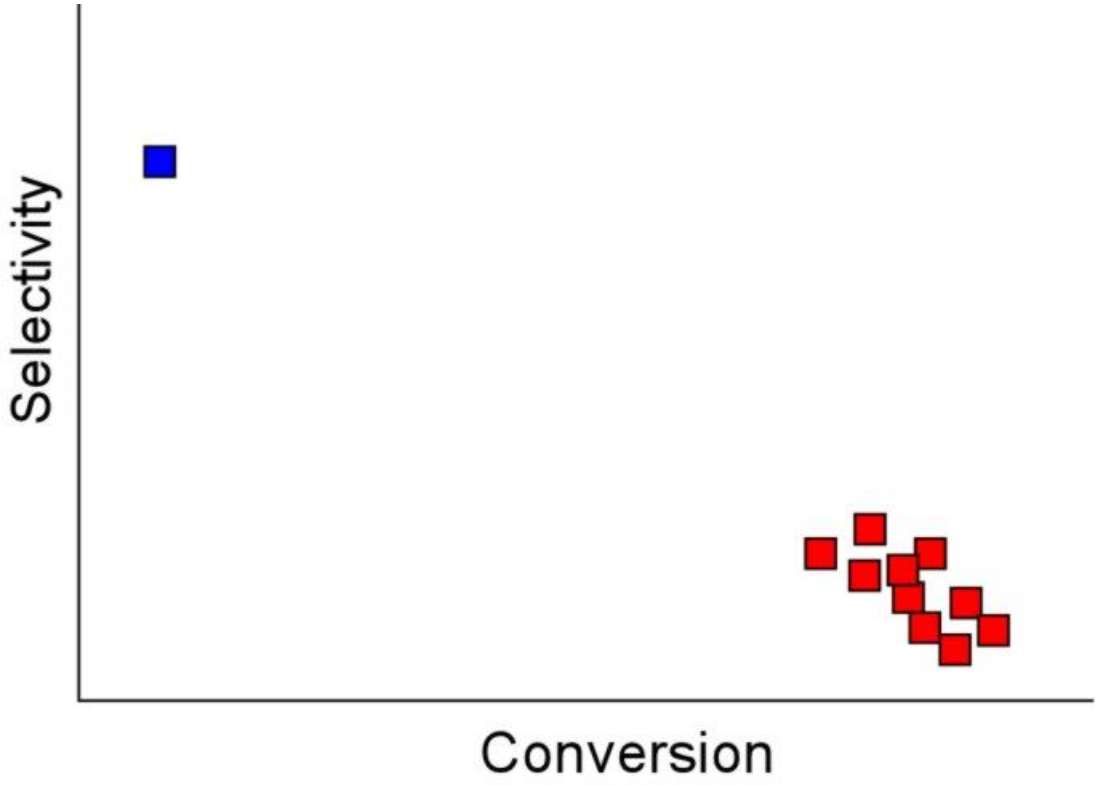
Mechanism



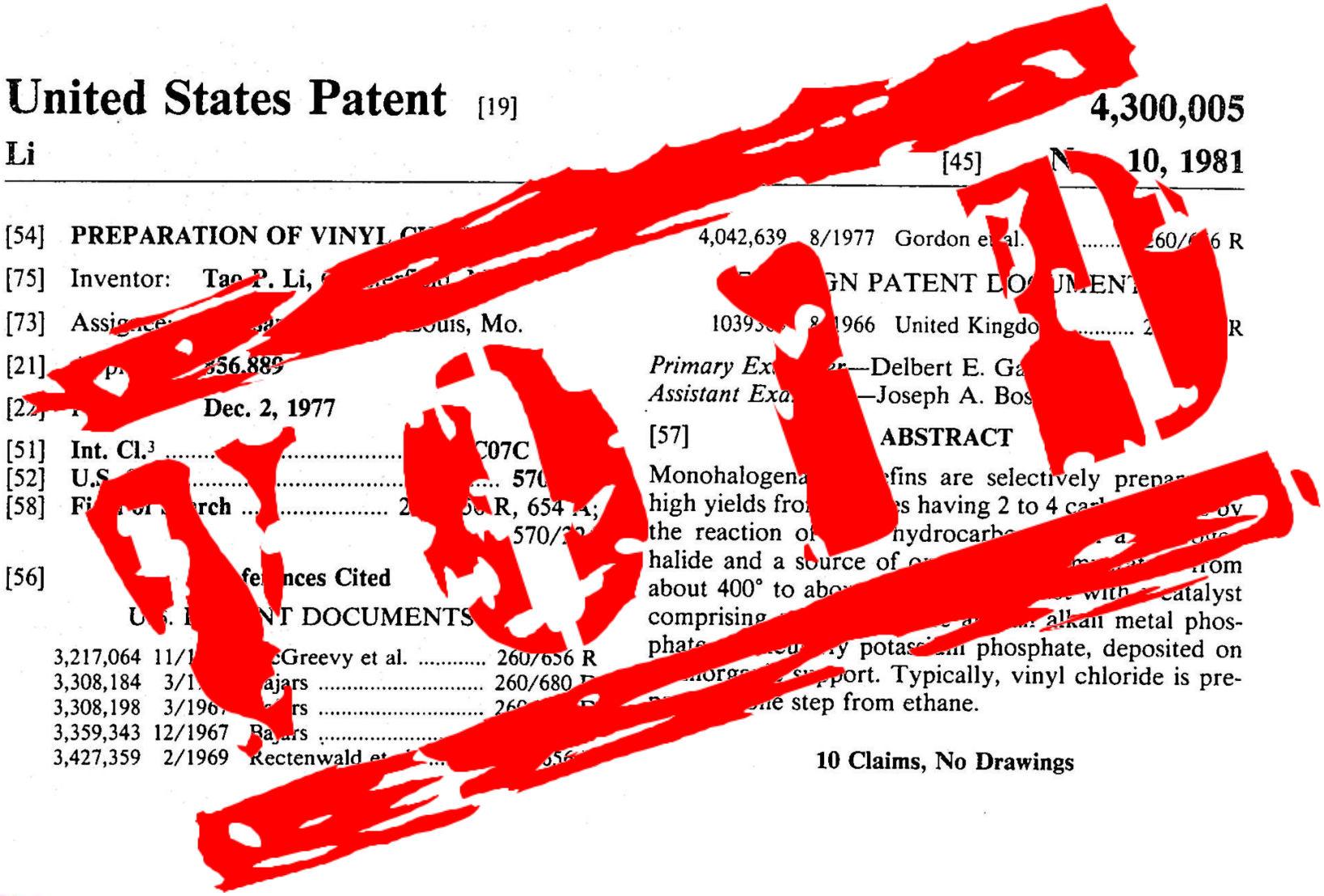
Copper-based

Problems:
-copper migration
-oxidation
-side-products

Literature Review



Technical Lead



United States Patent [19]

Li

[45] N 10, 1981

[54] PREPARATION OF VINYL C

[75] Inventor: Tao P. Li, [illegible]

[73] Assig[illegible] Louis, Mo.

[21] [illegible] 856.889

[22] [illegible] Dec. 2, 1977

[51] Int. Cl.[3] C07C

[52] U.S. 570

[58] Fi[illegible] rch ..... 2[illegible] R, 654 A; 570/2[illegible]

[56] [illegible]nces Cited

U.S. [illegible]NT DOCUMENTS

3,217,064 11/1[illegible] McGreevy et al. ..... 260/656 R
3,308,184 3/1[illegible] Bajars ..... 260/680 [illegible]
3,308,198 3/196[illegible] [illegible]rs ..... 260[illegible]
3,359,343 12/1967 Bajars .....
3,427,359 2/1969 Rectenwald et [illegible] ..... 56[illegible]
4,042,639 8/1977 Gordon et al. ..... 260/[illegible]6 R

[illegible]GN PATENT DO[illegible]UMENT

1039[illegible] 8/1966 United Kingdo[illegible] ..... 2[illegible] R

Primary Ex[illegible]r—Delbert E. Ga[illegible]
Assistant Exa[illegible]—Joseph A. Bos[illegible]

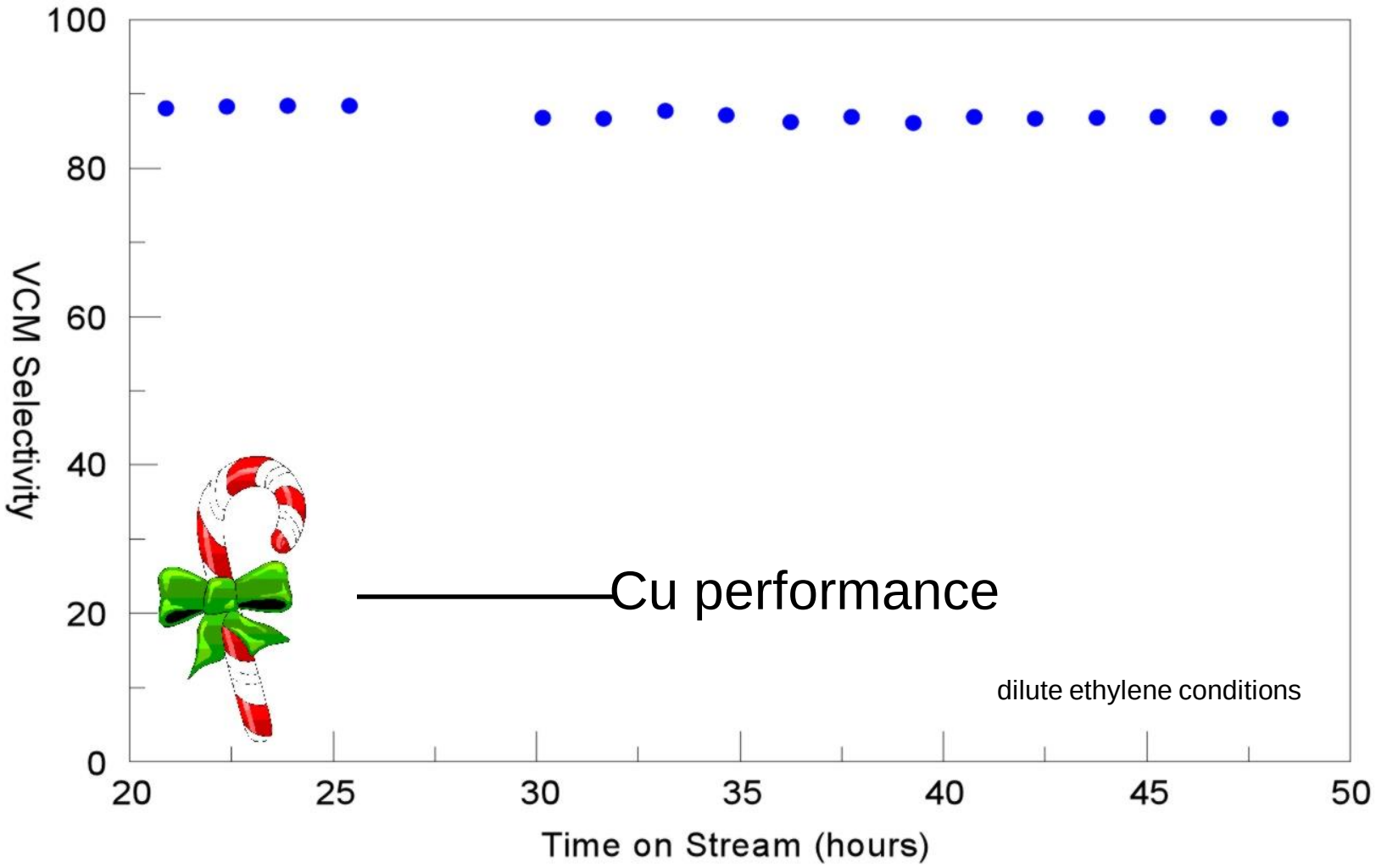
[57] ABSTRACT

Monohalogena[illegible]efins are selectively prepar[illegible] high yields fro[illegible]s having 2 to 4 car[illegible] by the reaction o[illegible] hydrocarb[illegible] a [illegible] halide and a source of o[illegible] from about 400° to abo[illegible] with [illegible] catalyst comprising [illegible] alkali metal phosphate[illegible] potassium phosphate, deposited on [illegible] support. Typically, vinyl chloride is pre[illegible] step from ethane.

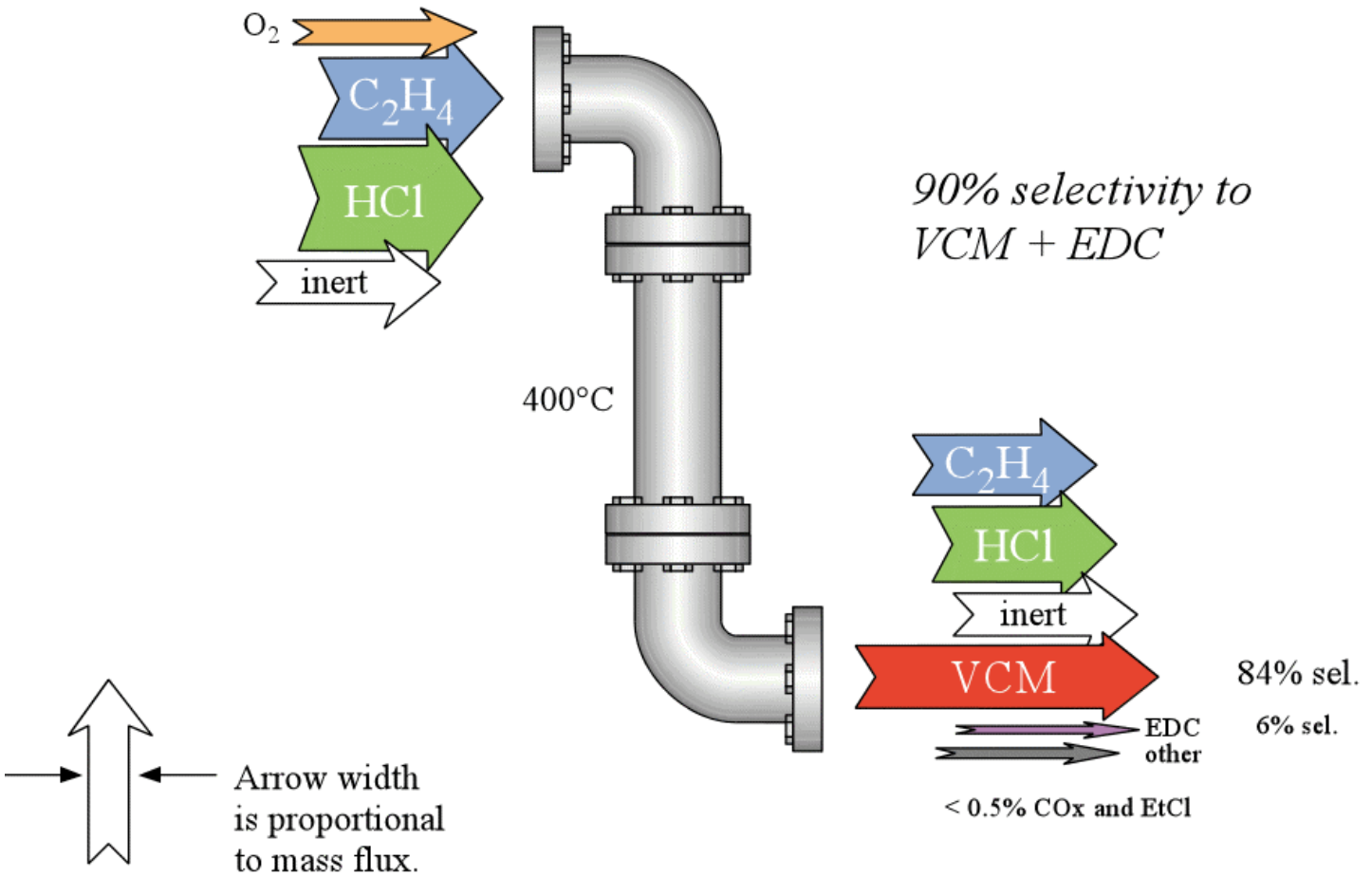
10 Claims, No Drawings

DOW

Breakthrough



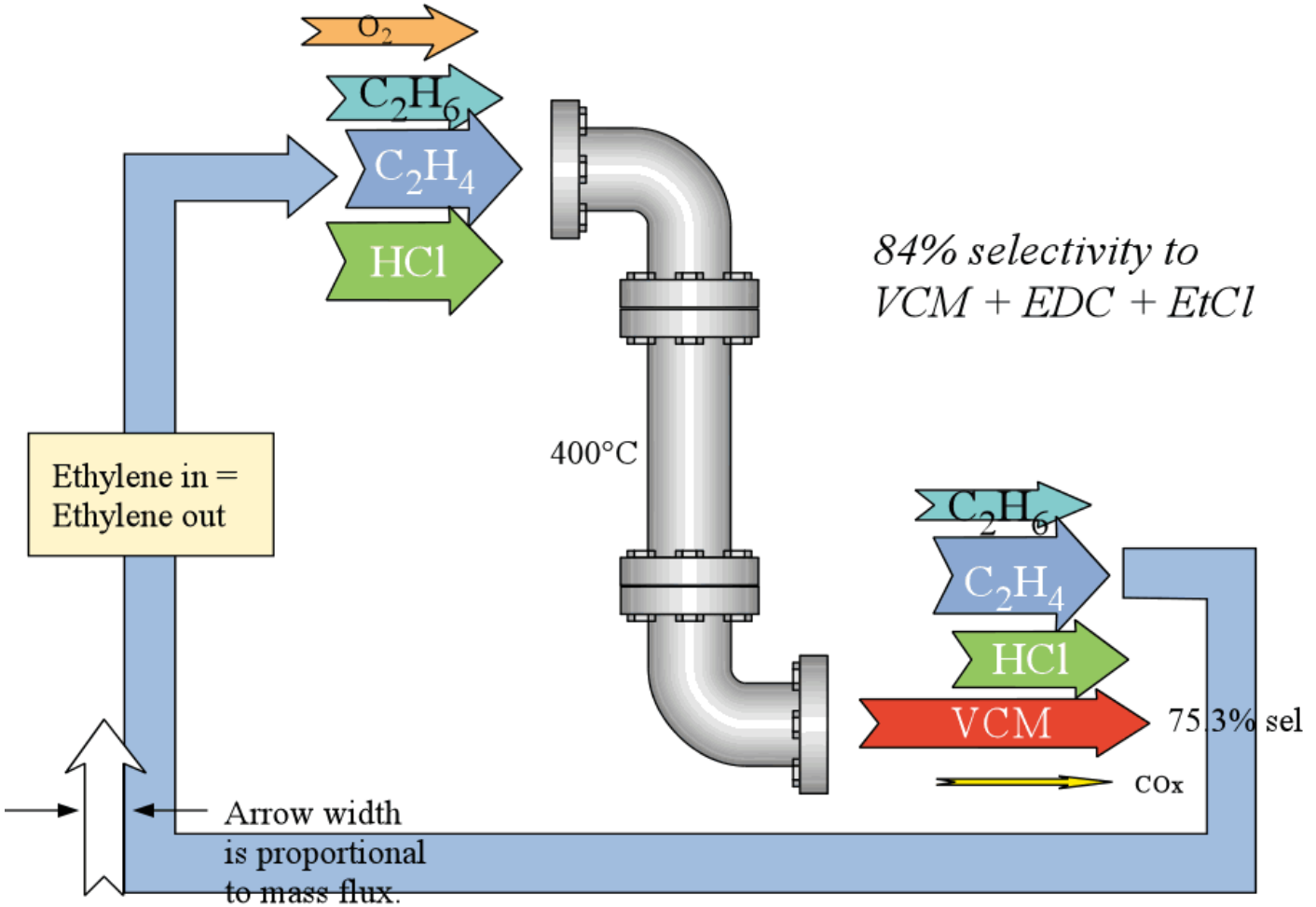
Lab Results



90% selectivity to VCM + EDC

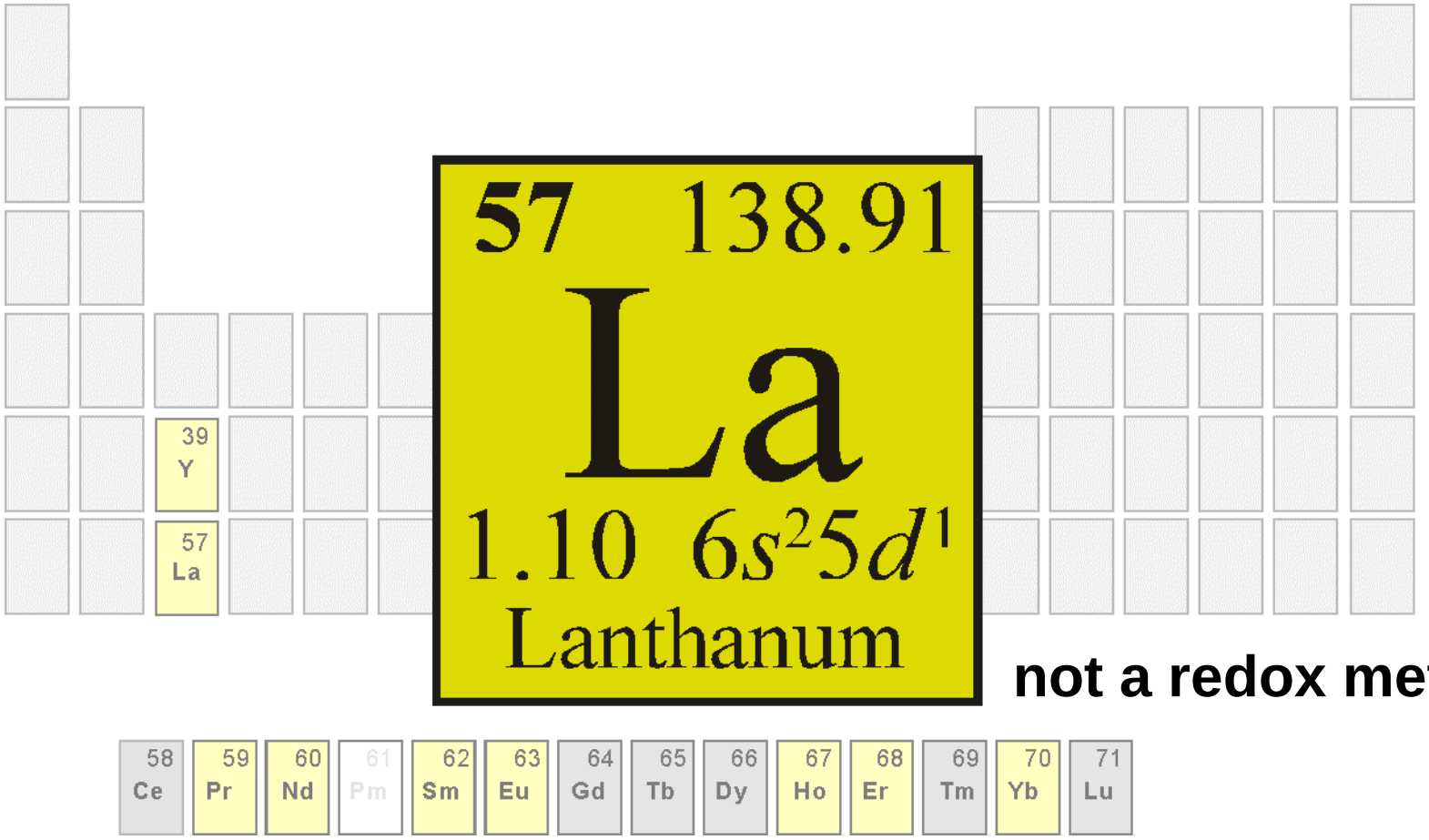
12-23-98 data

Lab Results



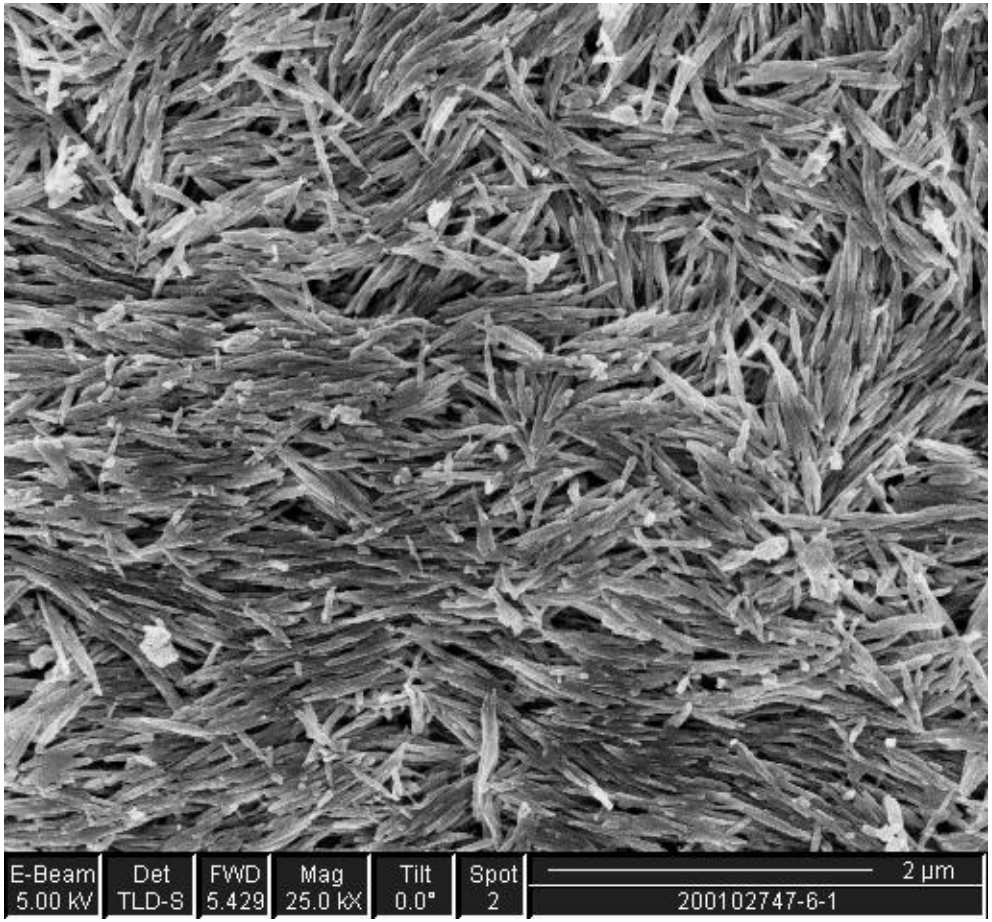
1/21/99 R1

Lanthanide Catalyst

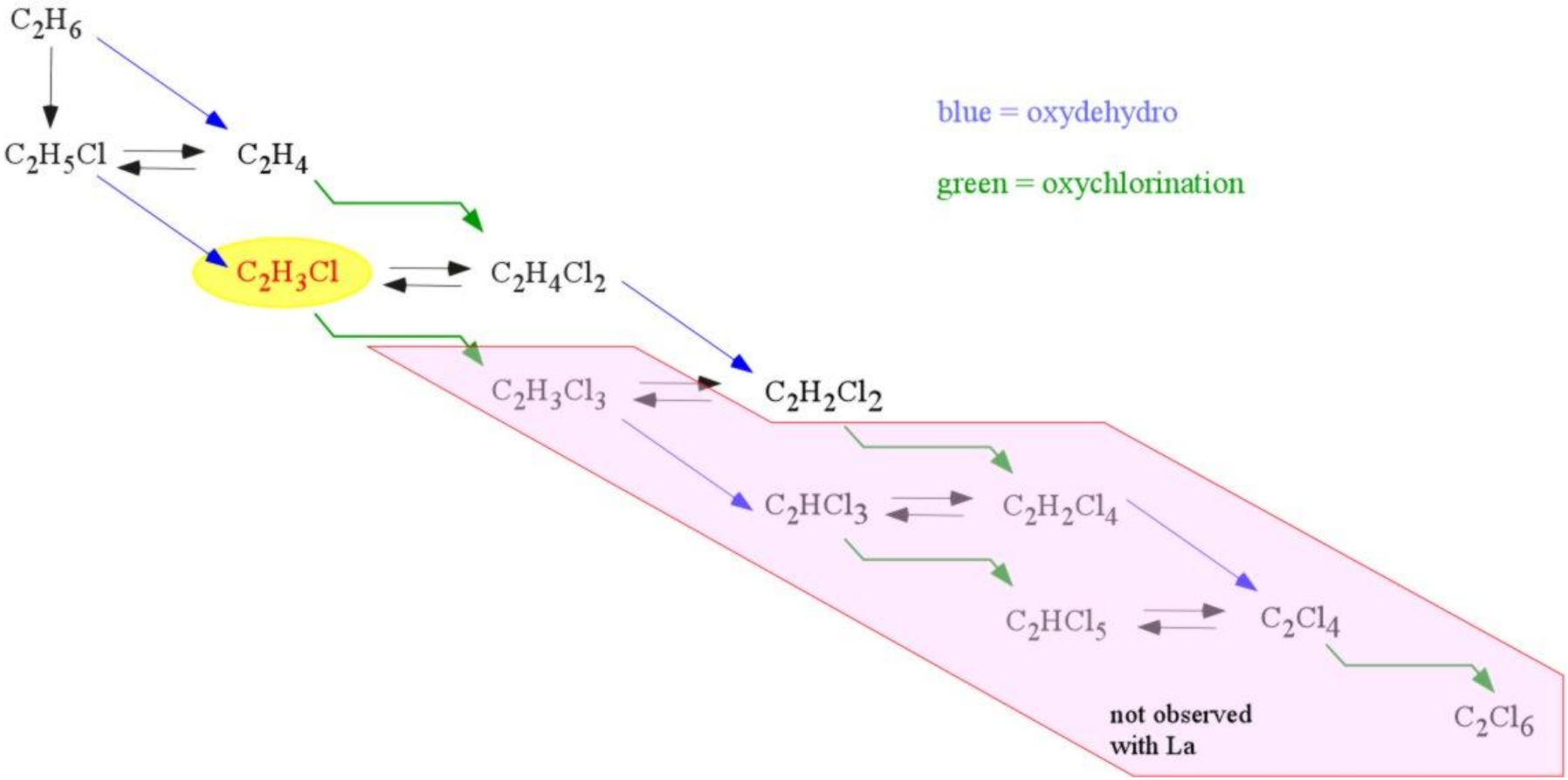


not a redox metal!

LaOCl

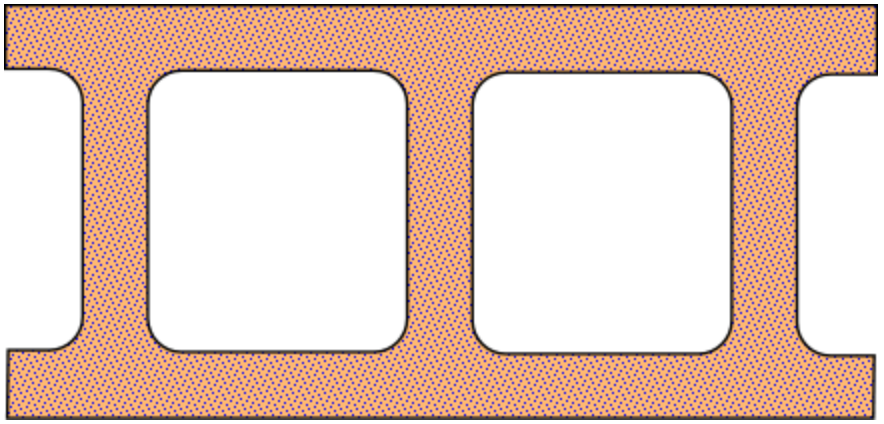

E-Beam
5.00 kV
Det
TLD-S
FWD
5.429
Mag
25.0 kX
Tilt
0.0°
Spot
2
2 µm
200102747-6-1

LaOCl Results

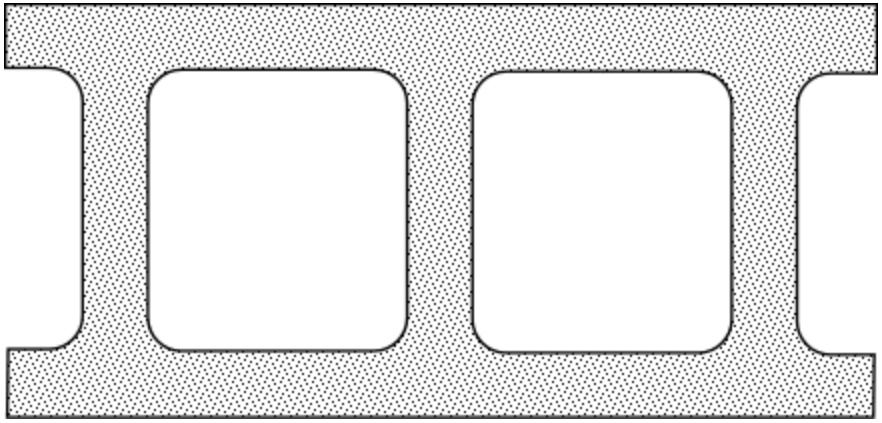


Particle Transformation

$LaOCl_3$



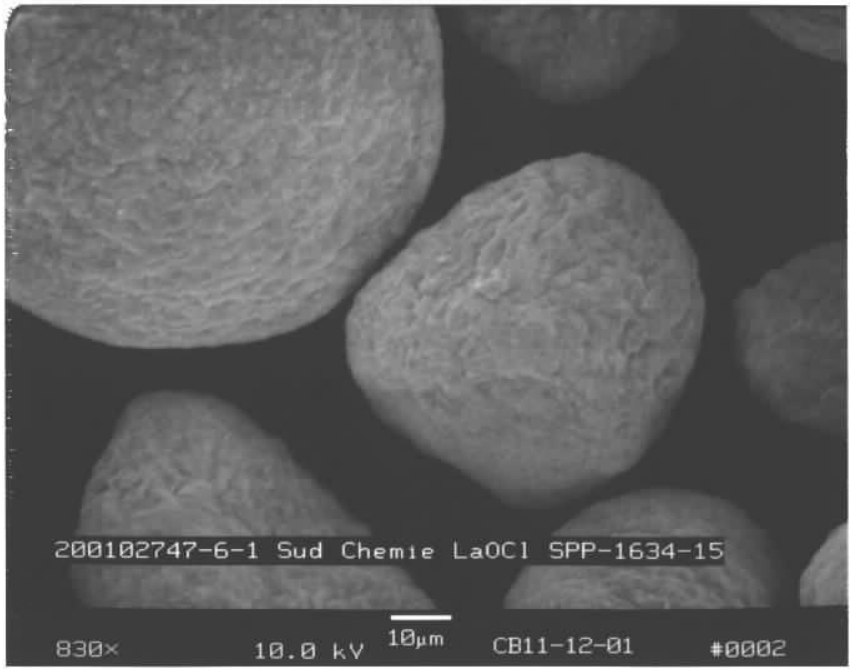
LaOCl



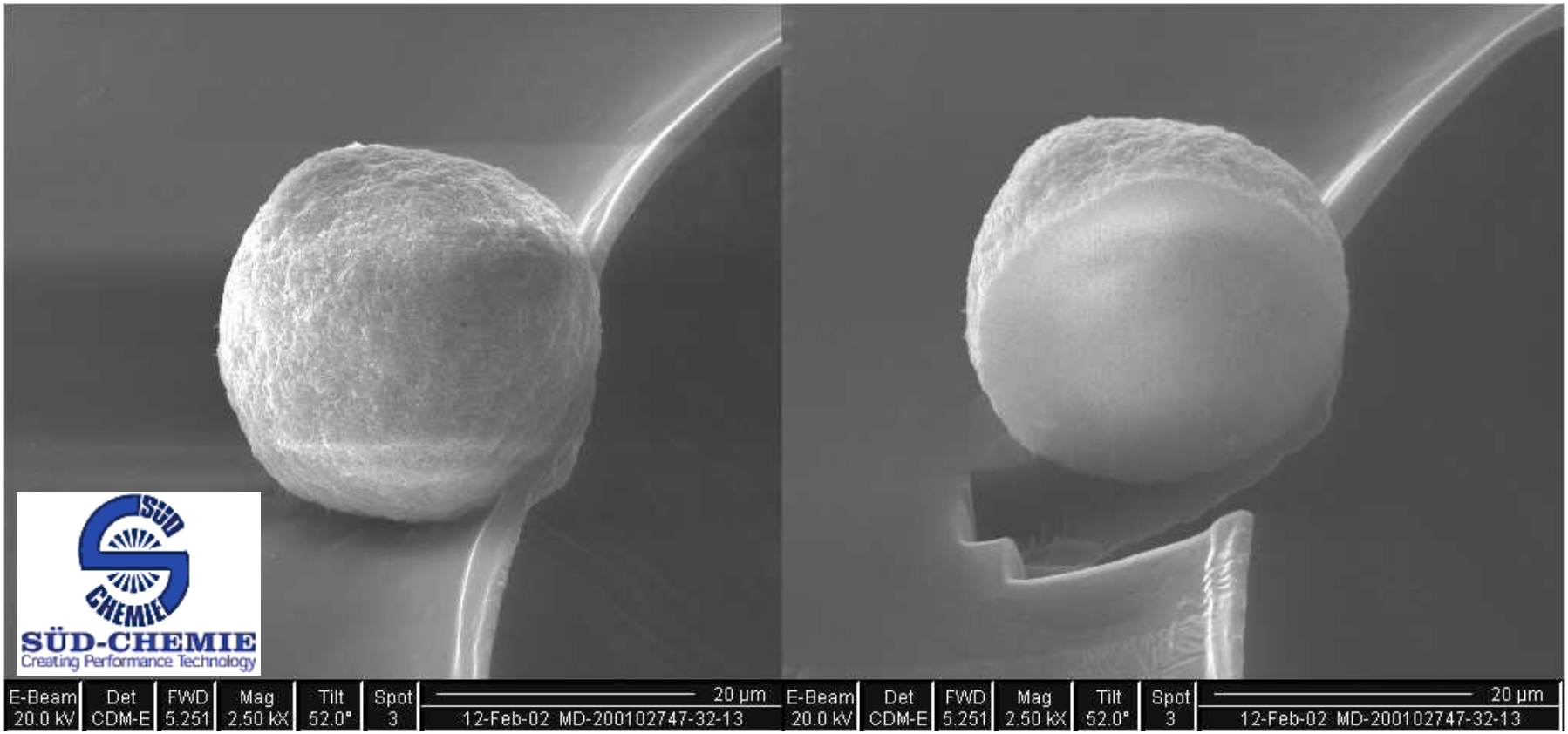
chemical transformation
preserved gross structure

Vendor

SÜD-CHEMIE
Creating Performance Technology

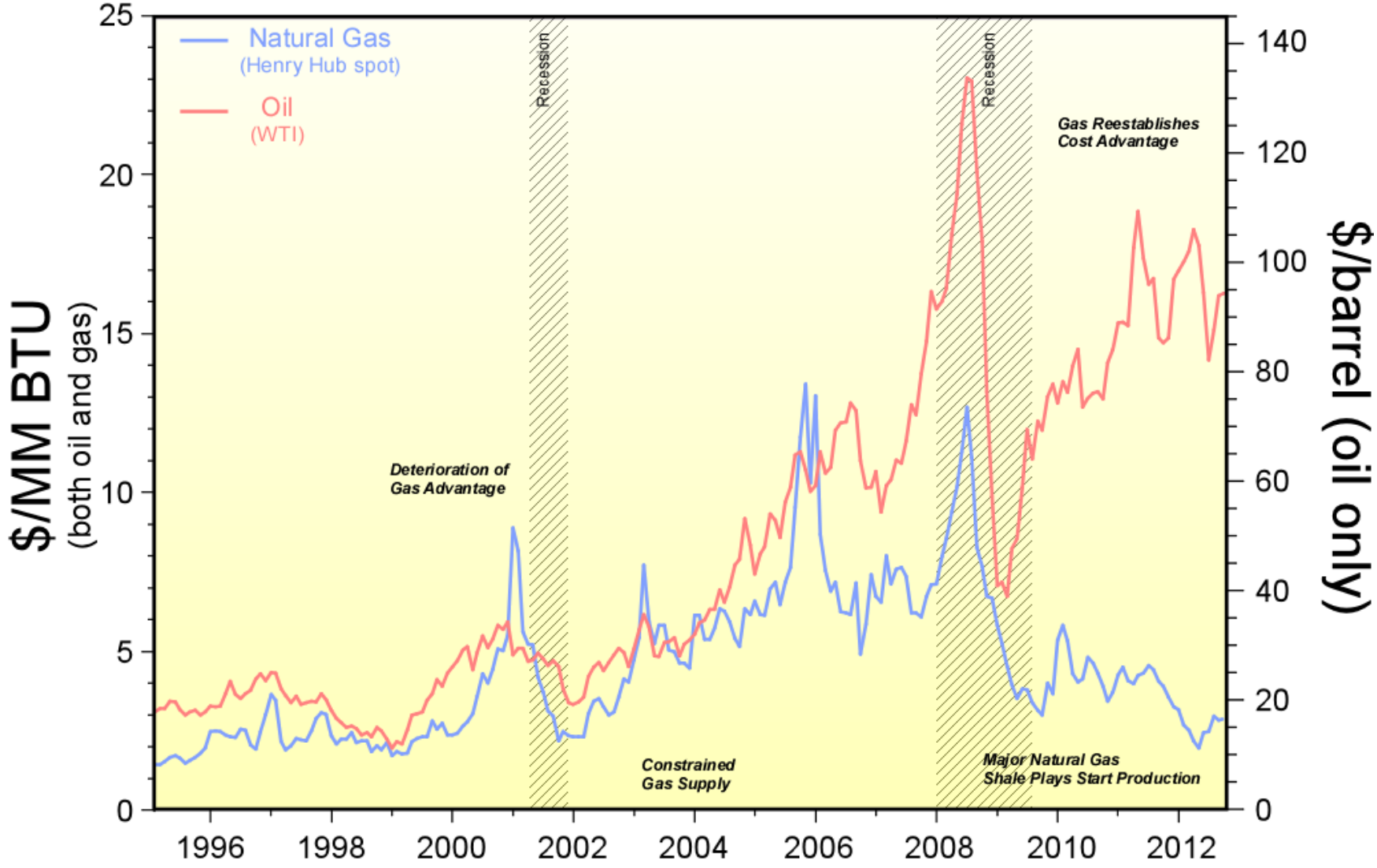


Catalyst Particle

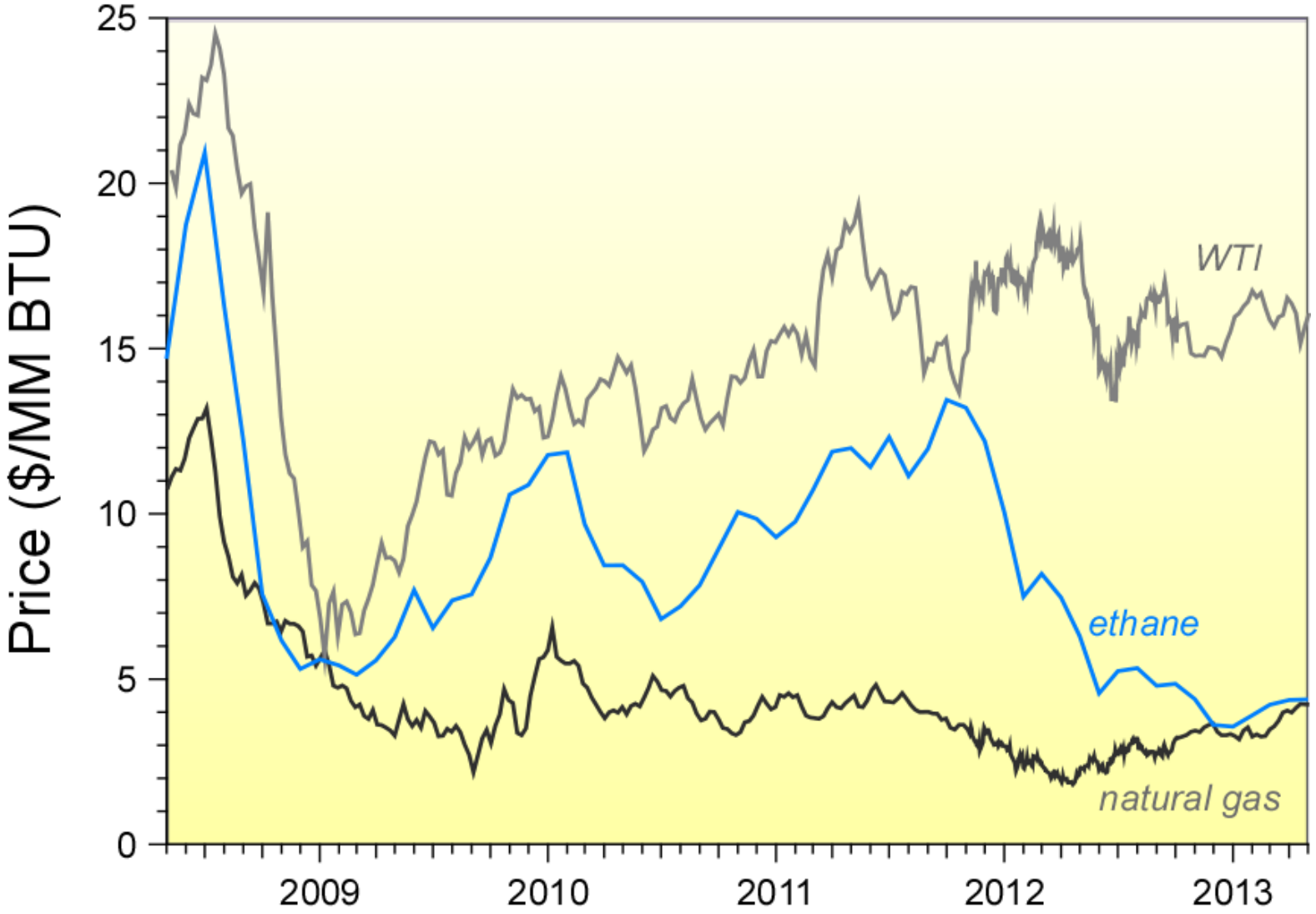


Fluidized Bed

Recent Industry History

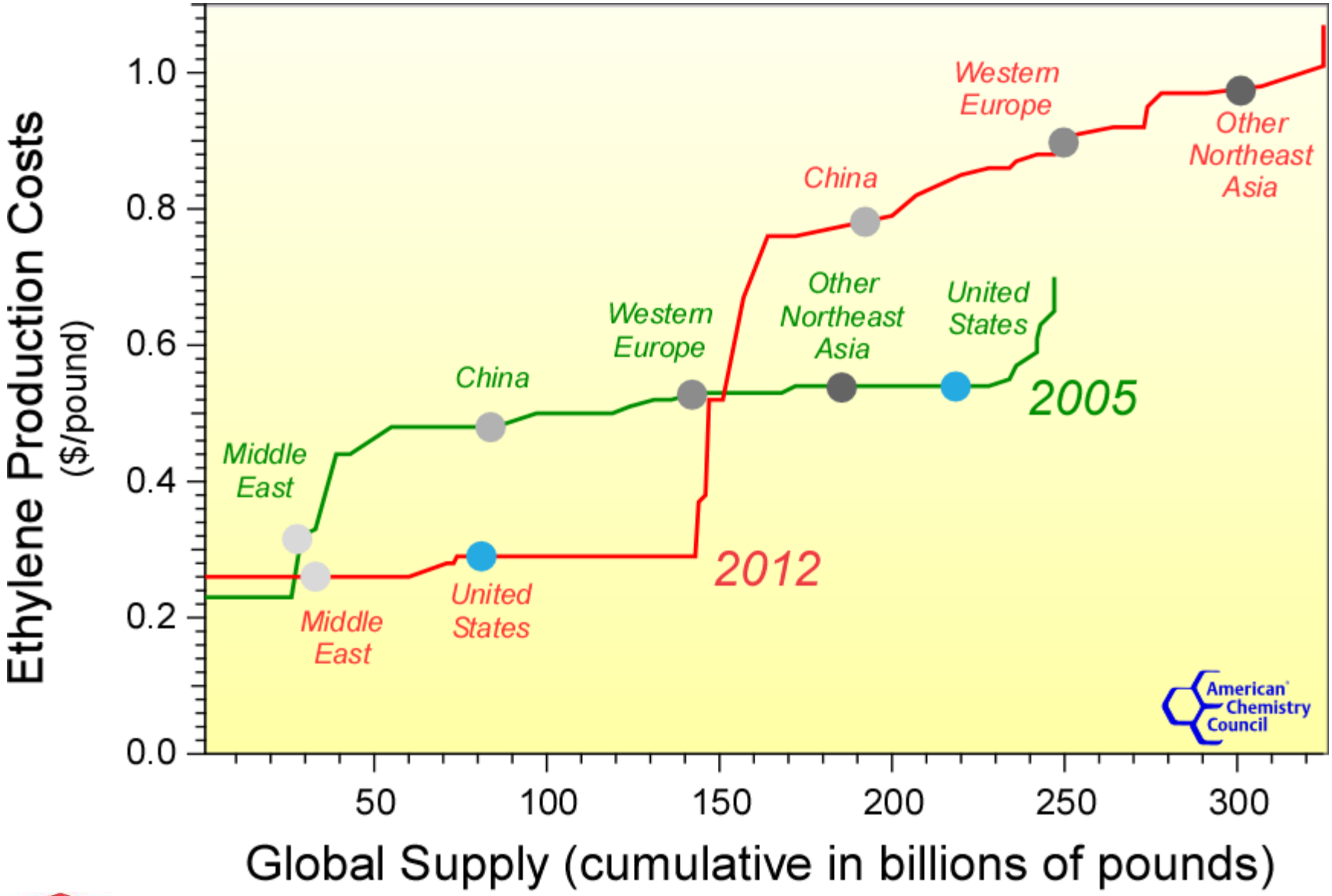


Ethane Price Now Tracks Gas

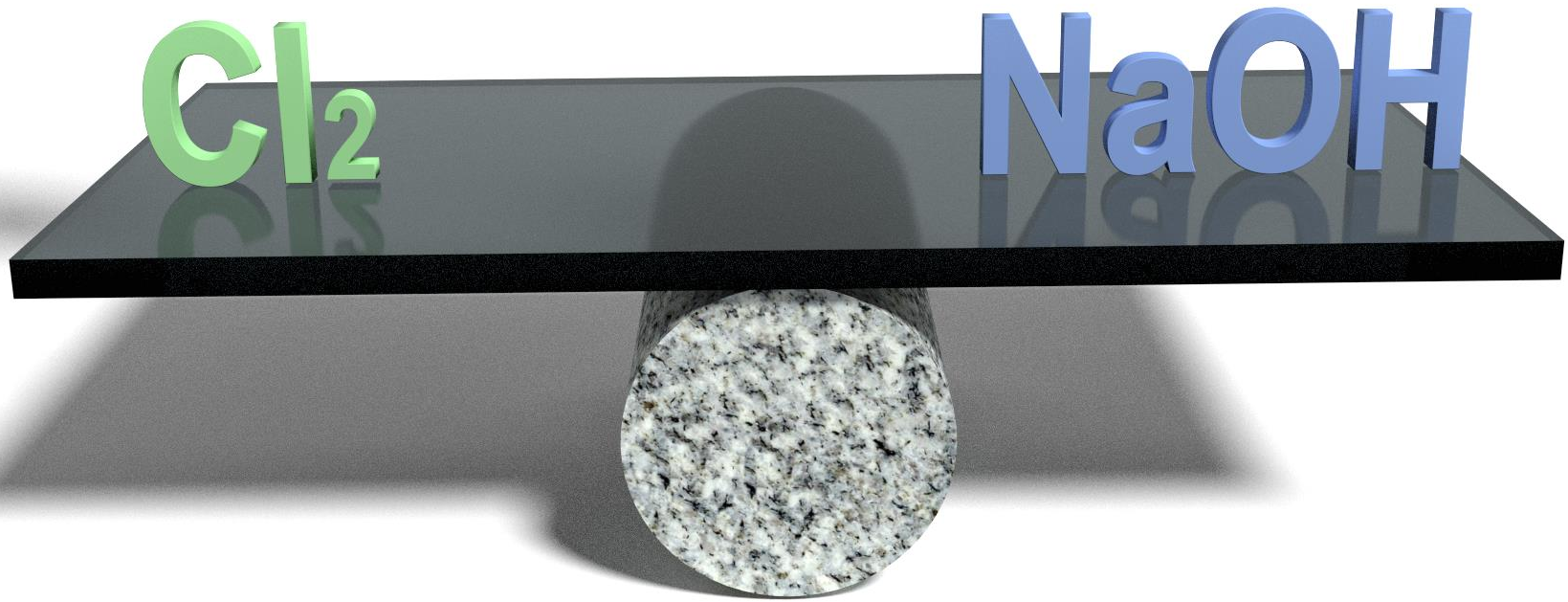


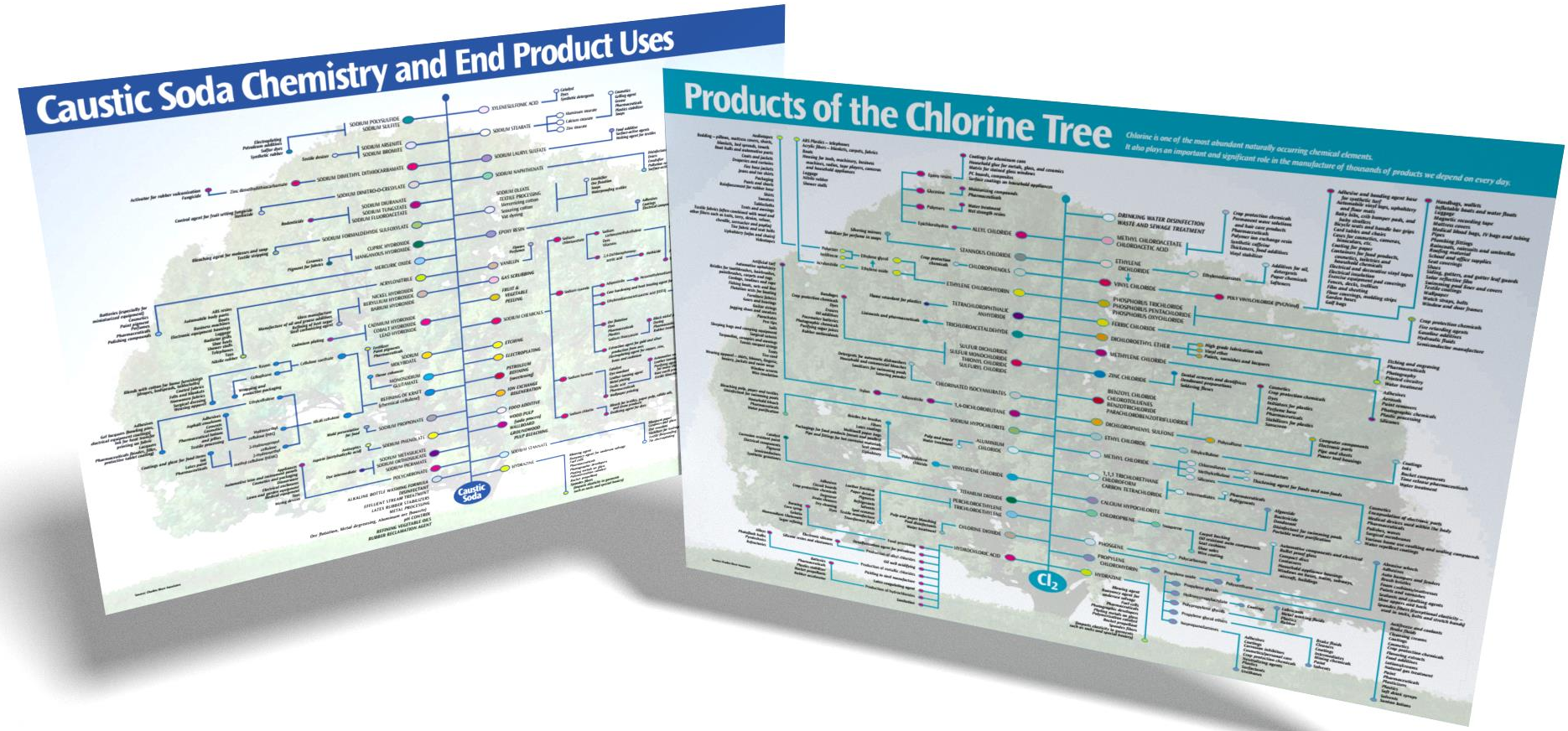
Live Long and Prosper

Impact of Low Gas Prices

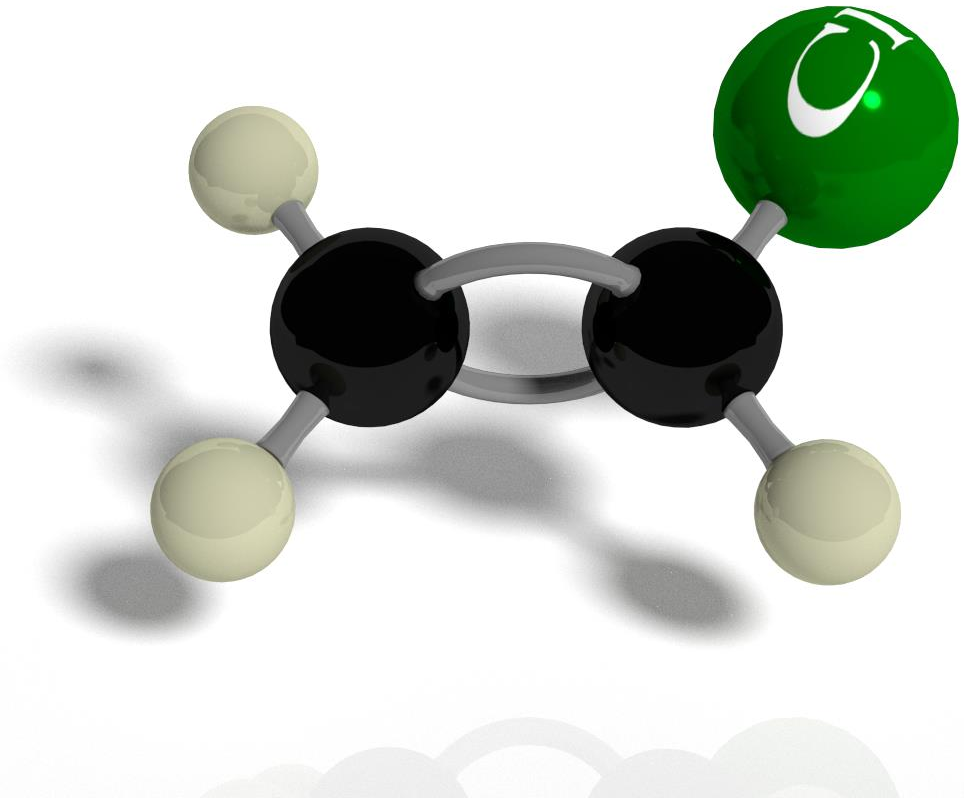


Balancing the ECU

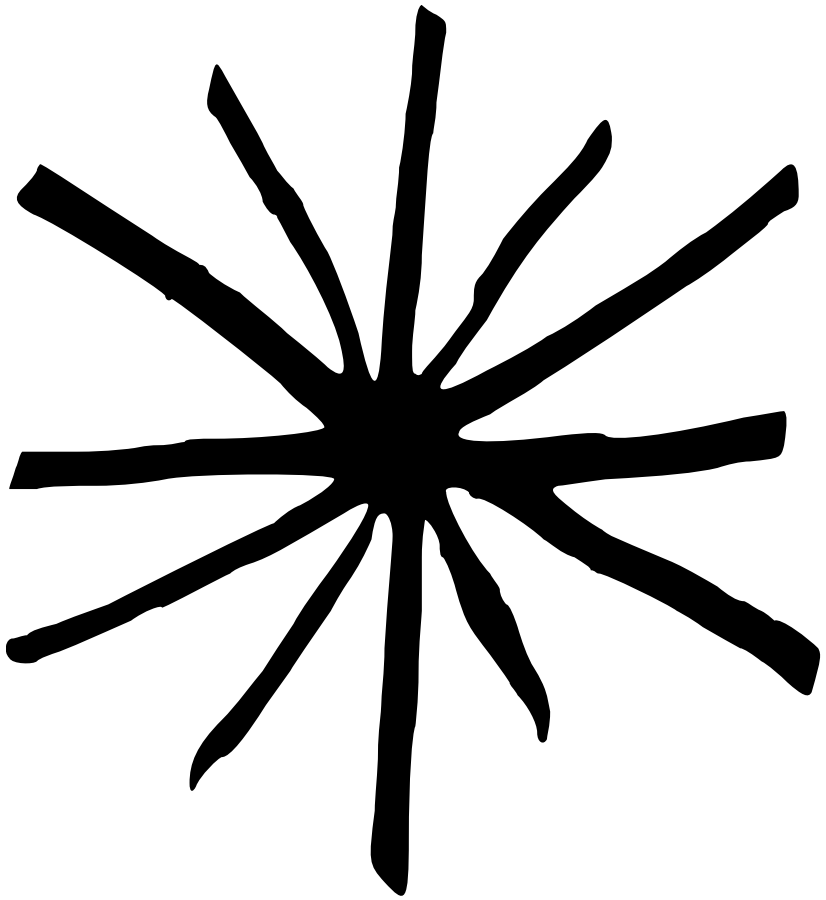



Caustic Soda Chemistry and End Product Uses
Caustic Soda
Products of the Chlorine Tree
Chlorine is one of the most abundant naturally occurring chemical elements.
It also plays an important and significant role in the manufacture of thousands of products we depend on every day.
Cl2

Vinyl Chloride



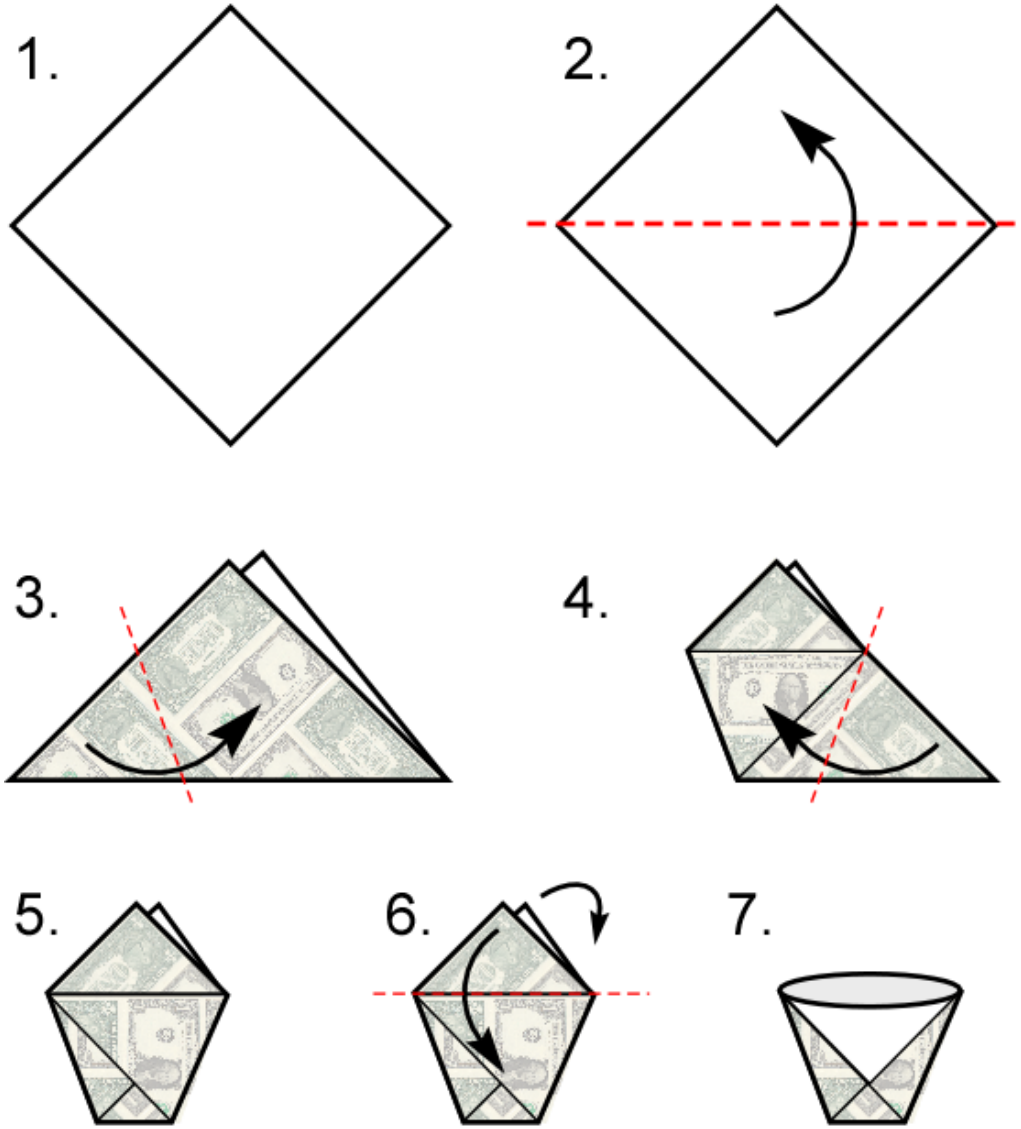
Breakfast of Champions



Scale Always Wins

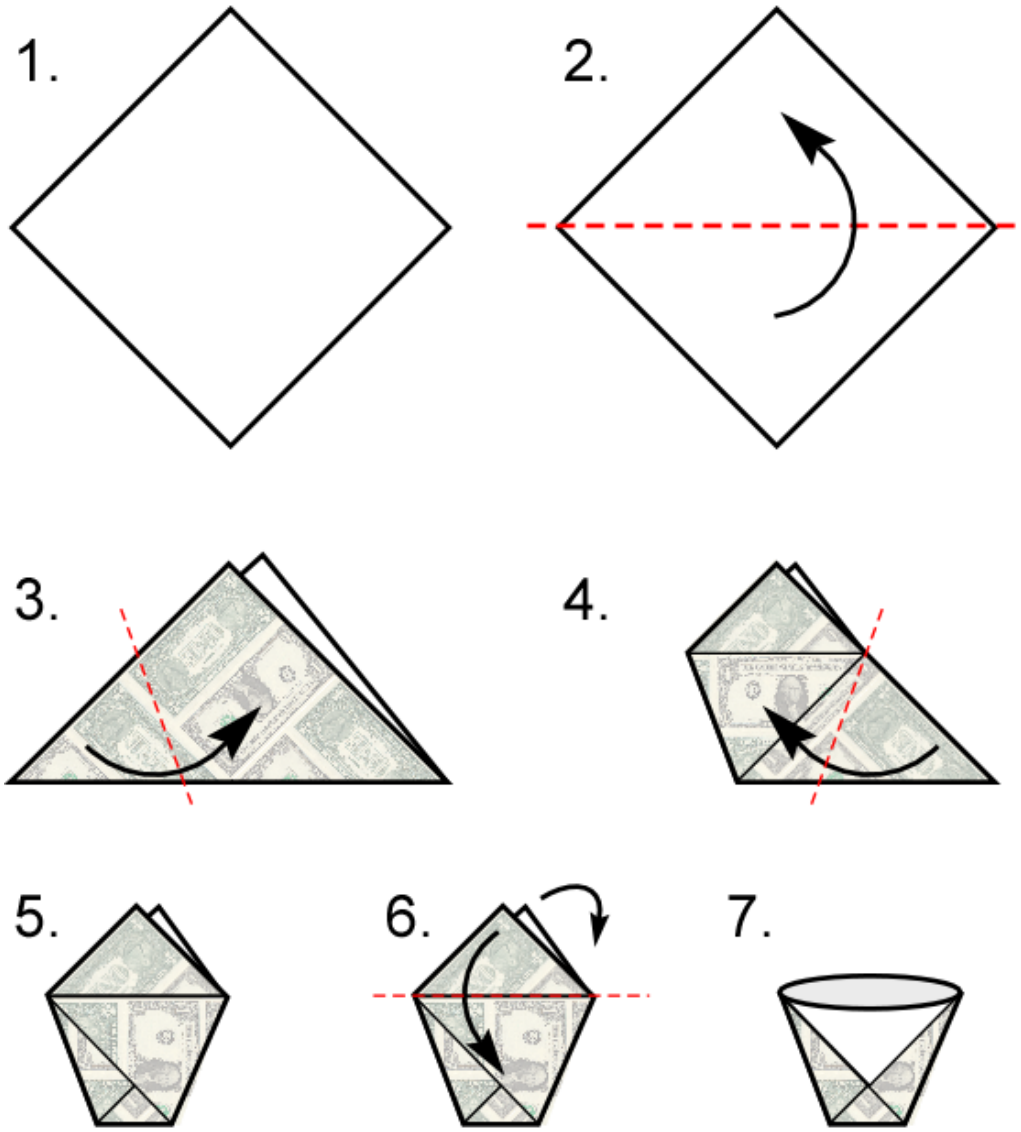
If you are moving mass around, scale reduces cost faster than experience.

Scale is Important – *An Example*



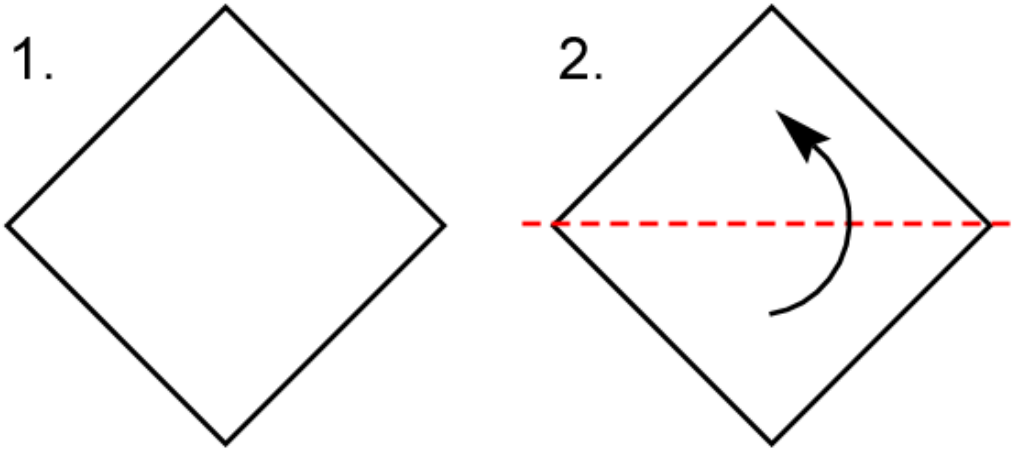
Make a cup with an 8½" square and another with a 4¼" square

Scale is Important – *An Example*

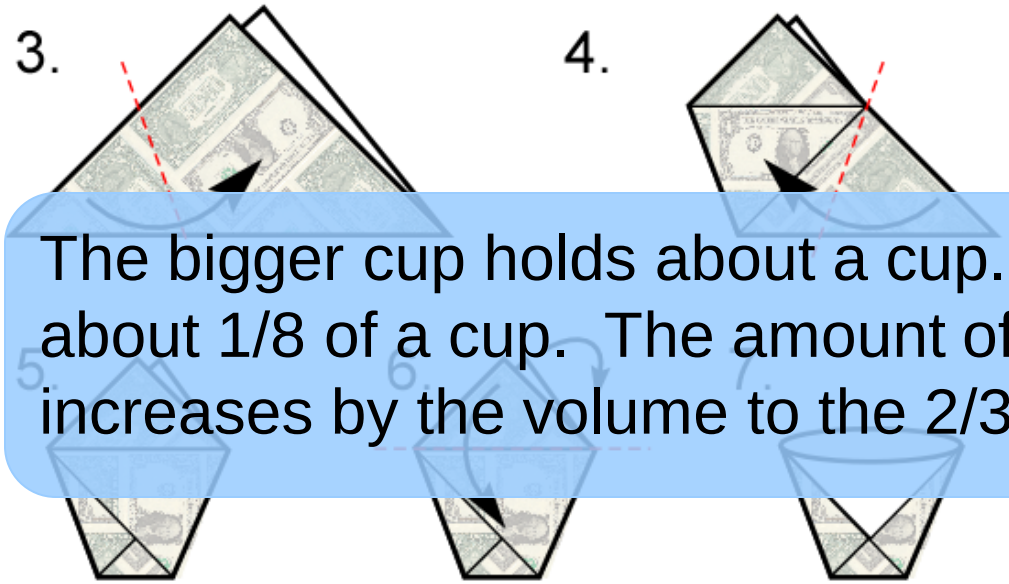


Make a cup with an 8½” square and another with a 4¼” square

Scale is Important – *An Example*

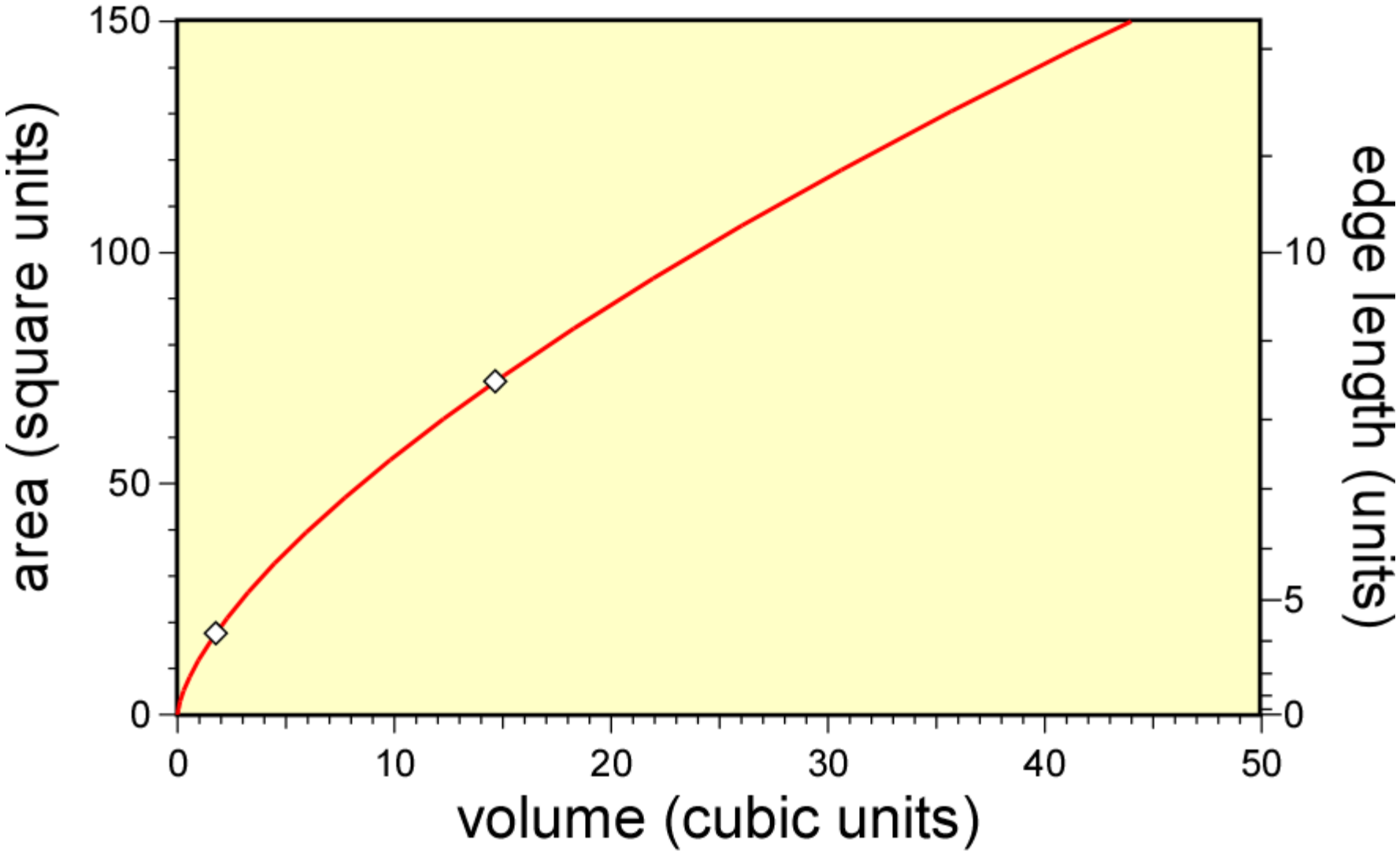


Make a cup with an 8½" square and another with a 4¼" square

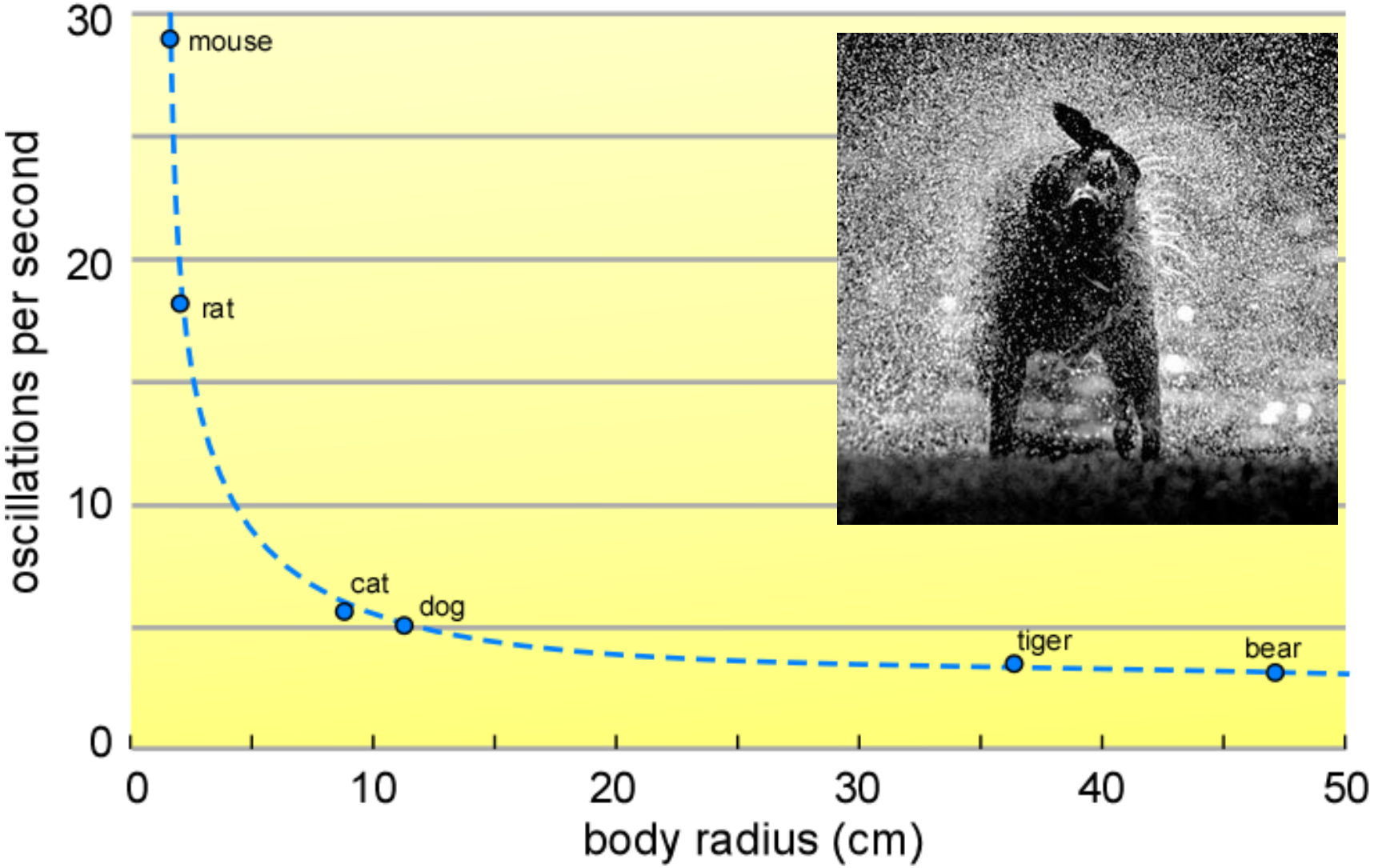


The bigger cup holds about a cup. The smaller only about 1/8 of a cup. The amount of paper required increases by the volume to the 2/3 power.

Power Law

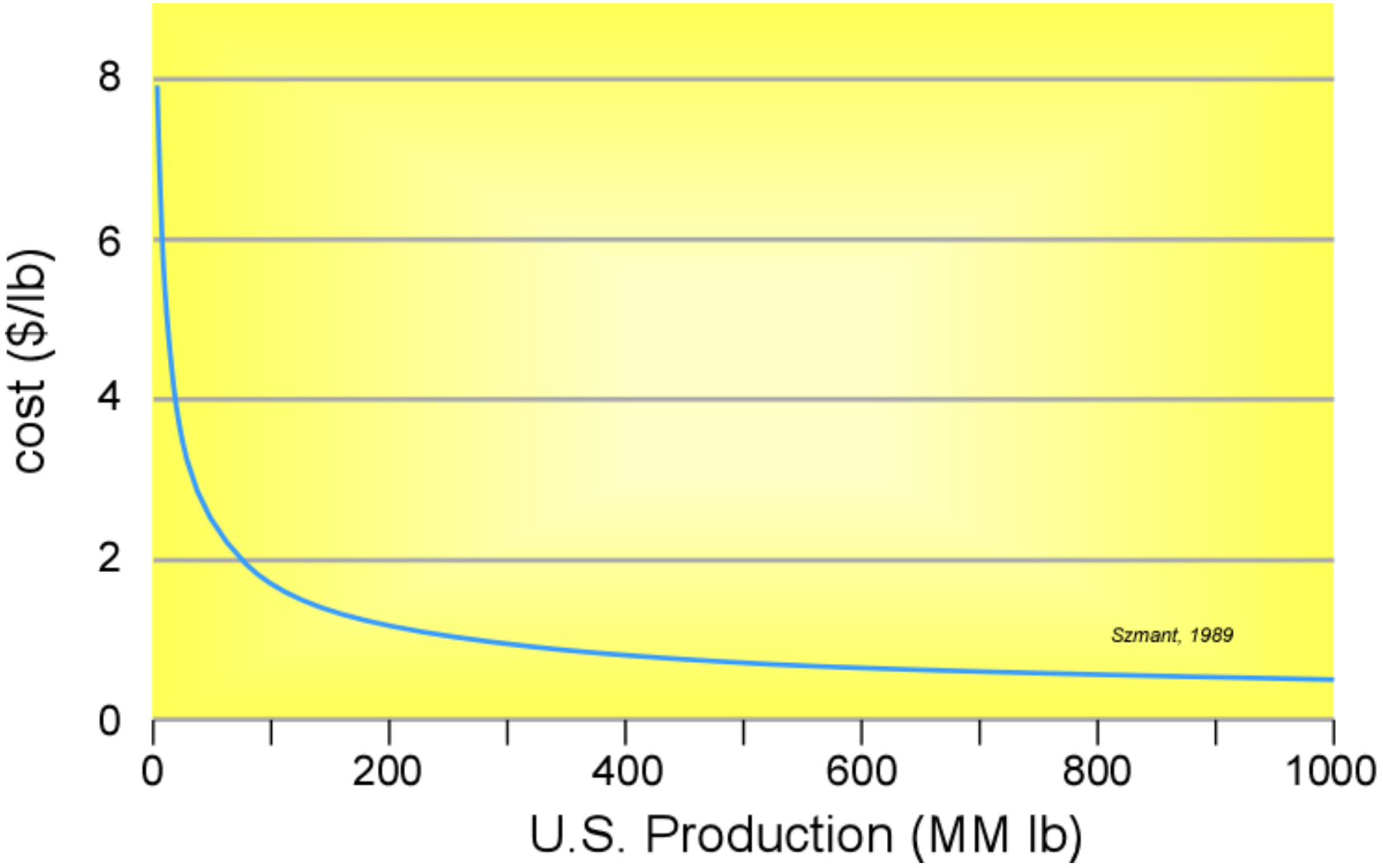

150
100
50
0
area (square units)
0
10
20
30
40
50
volume (cubic units)
10
5
0
edge length (units)

Interesting Correlation

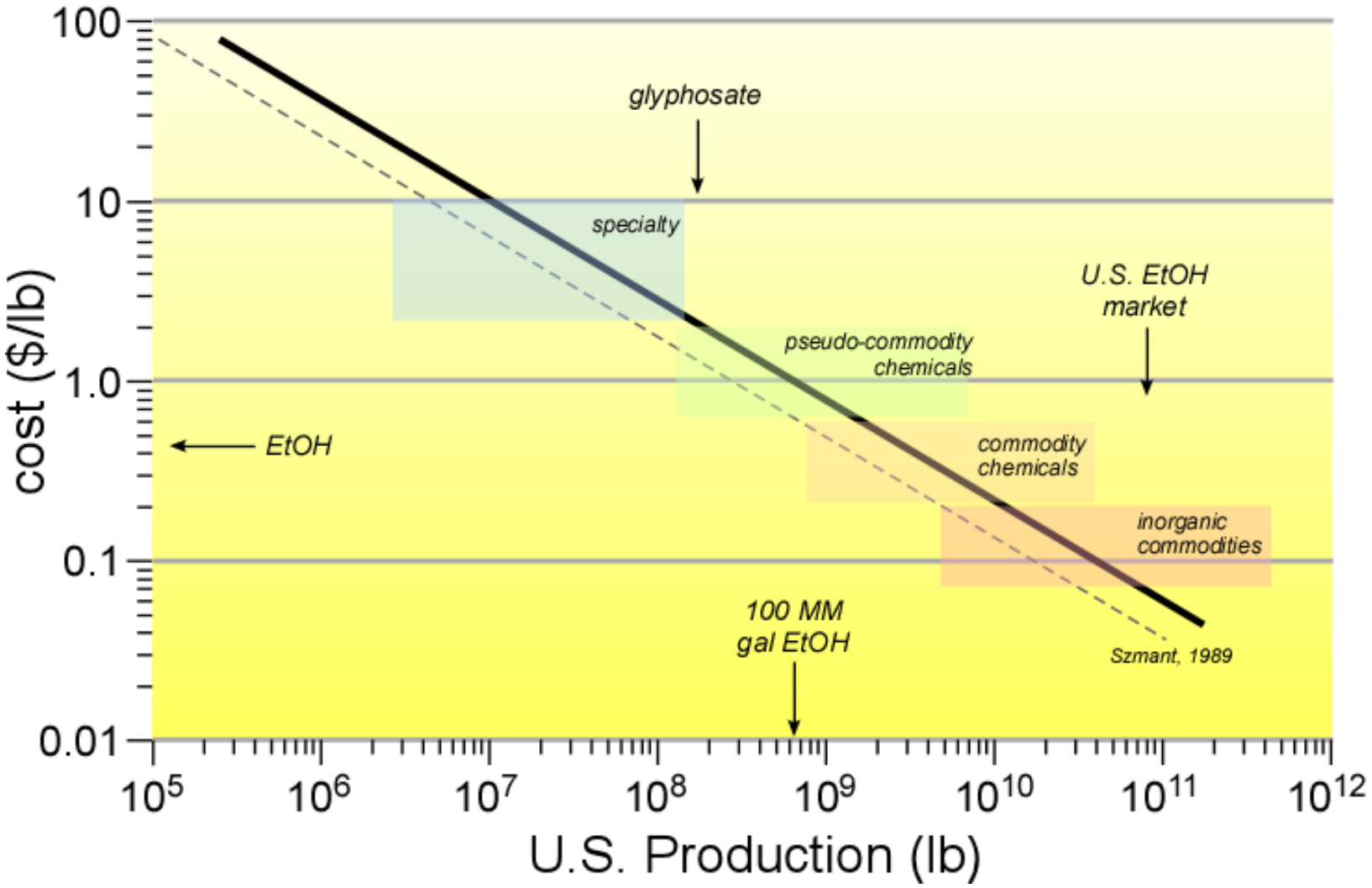


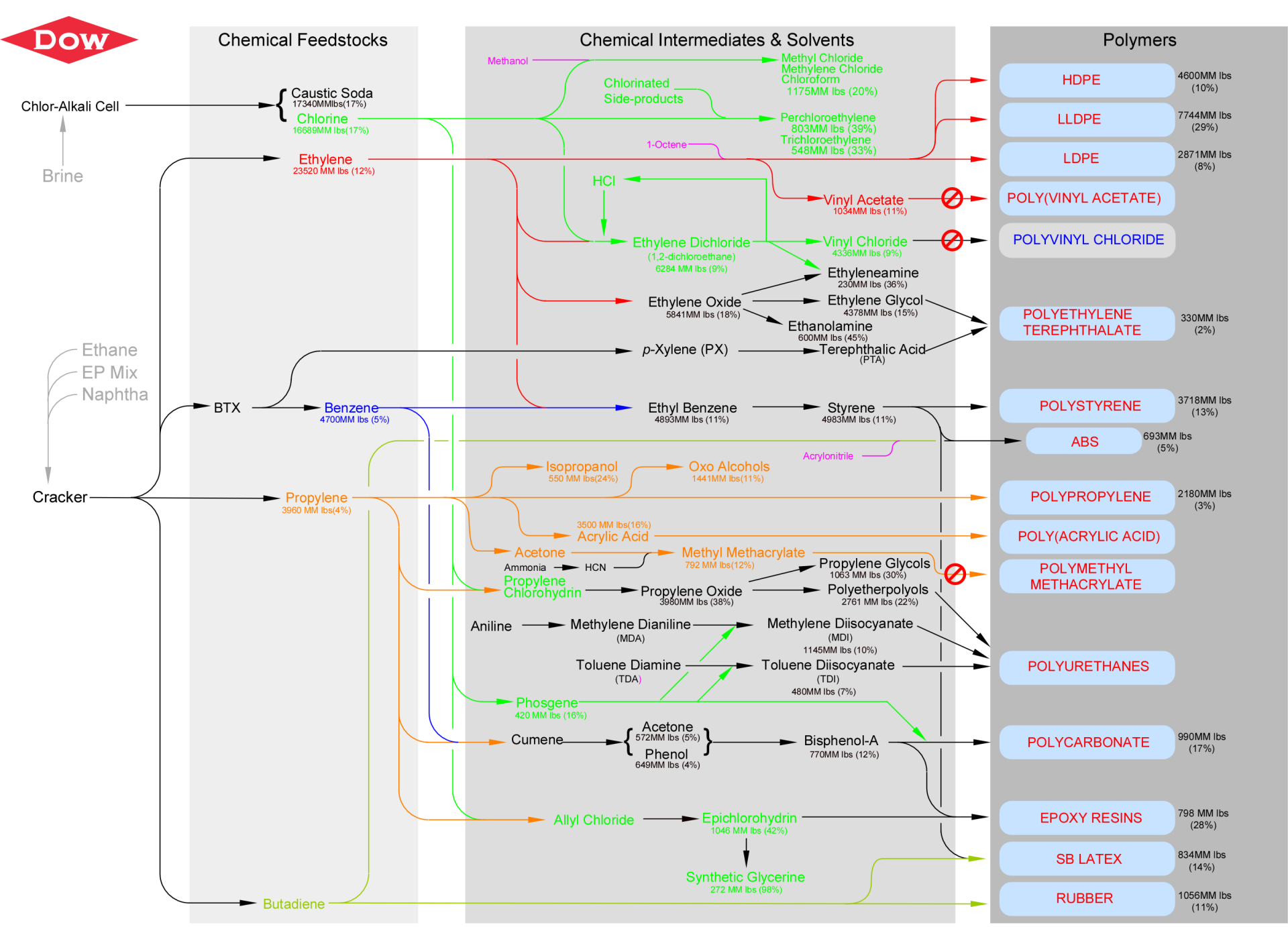
Andrew Dickerson, Grant Mills, Jay Bauman, Young-Hui Chang, David Hu, The Wet-Dog Shake, Fluid Dynamics, 15 October 2010.

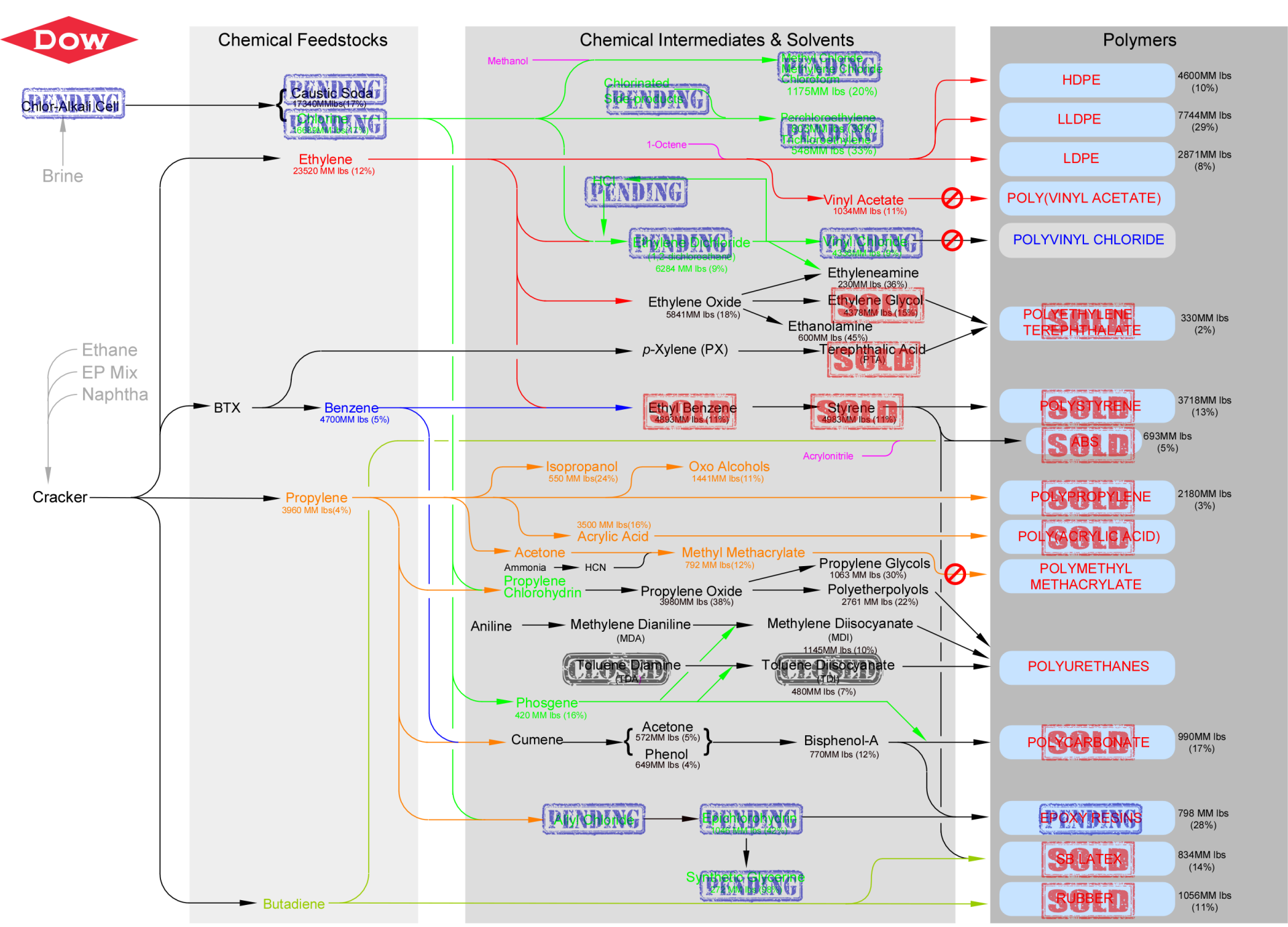
Scale Matters!



Most Common Version



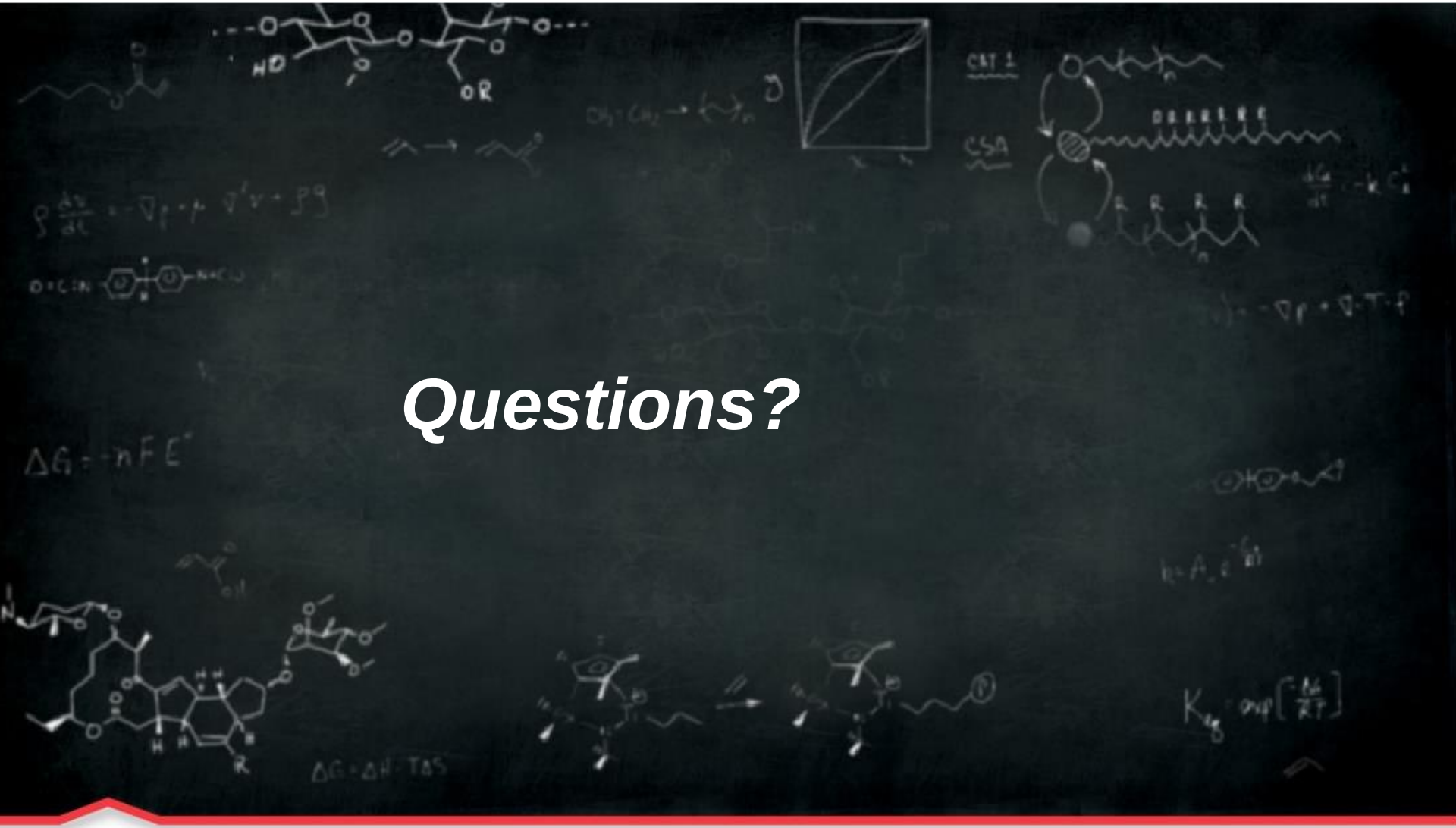

DOW
Chemical Feedstocks
Chemical Intermediates & Solvents
Polymers
Chlor-Alkali Cell
Brine
Caustic Soda
17340MMlbs(17%)
Chlorine
16689MM lbs(17%)
Ethylene
23520 MM lbs (12%)
Ethane
EP Mix
Naphtha
Cracker
BTX
Benzene
4700MM lbs (5%)
Propylene
3960 MM lbs(4%)
Butadiene
Methanol
Methyl Chloride
Methylene Chloride
Chloroform
1175MM lbs (20%)
Chlorinated
Side-products
Perchloroethylene
803MM lbs (39%)
Trichloroethylene
548MM lbs (33%)
1-Octene
HCl
Vinyl Acetate
1034MM lbs (11%)
Ethylene Dichloride
(1,2-dichloroethane)
6284 MM lbs (9%)
Vinyl Chloride
4336MM lbs (9%)
Ethyleneamine
230MM lbs (36%)
Ethylene Oxide
5841MM lbs (18%)
Ethylene Glycol
4378MM lbs (15%)
Ethanolamine
600MM lbs (45%)
p-Xylene (PX)
Terephthalic Acid
(PTA)
Ethyl Benzene
4893MM lbs (11%)
Styrene
4983MM lbs (11%)
Acrylonitrile
Isopropanol
550 MM lbs(24%)
Oxo Alcohols
1441MM lbs(11%)
3500 MM lbs(16%)
Acrylic Acid
Acetone
Ammonia
HCN
Methyl Methacrylate
792 MM lbs(12%)
Propylene
Chlorohydrin
Propylene Oxide
3980MM lbs (38%)
Propylene Glycols
1063 MM lbs (30%)
Polyetherpolyols
2761 MM lbs (22%)
Aniline
Methylene Dianiline
(MDA)
Methylene Diisocyanate
(MDI)
1145MM lbs (10%)
Toluene Diamine
(TDA)
Toluene Diisocyanate
(TDI)
480MM lbs (7%)
Phosgene
420 MM lbs (16%)
Cumene
Acetone
572MM lbs (5%)
Phenol
649MM lbs (4%)
Bisphenol-A
770MM lbs (12%)
Allyl Chloride
Epichlorohydrin
1046 MM lbs (42%)
Synthetic Glycerine
272 MM lbs (98%)
HDPE
4600MM lbs (10%)
LLDPE
7744MM lbs (29%)
LDPE
2871MM lbs (8%)
POLY(VINYL ACETATE)
POLYVINYL CHLORIDE
POLYETHYLENE TEREPHTHALATE
330MM lbs (2%)
POLYSTYRENE
3718MM lbs (13%)
ABS
693MM lbs (5%)
POLYPROPYLENE
2180MM lbs (3%)
POLY(ACRYLIC ACID)
POLYMETHYL METHACRYLATE
POLYURETHANES
POLYCARBONATE
990MM lbs (17%)
EPOXY RESINS
798 MM lbs (28%)
SB LATEX
834MM lbs (14%)
RUBBER
1056MM lbs (11%)
Volumes are world production unless noted.
Purchased chemicals are in pink.
NON-Confidential - from published sources
MEJ-2/2003



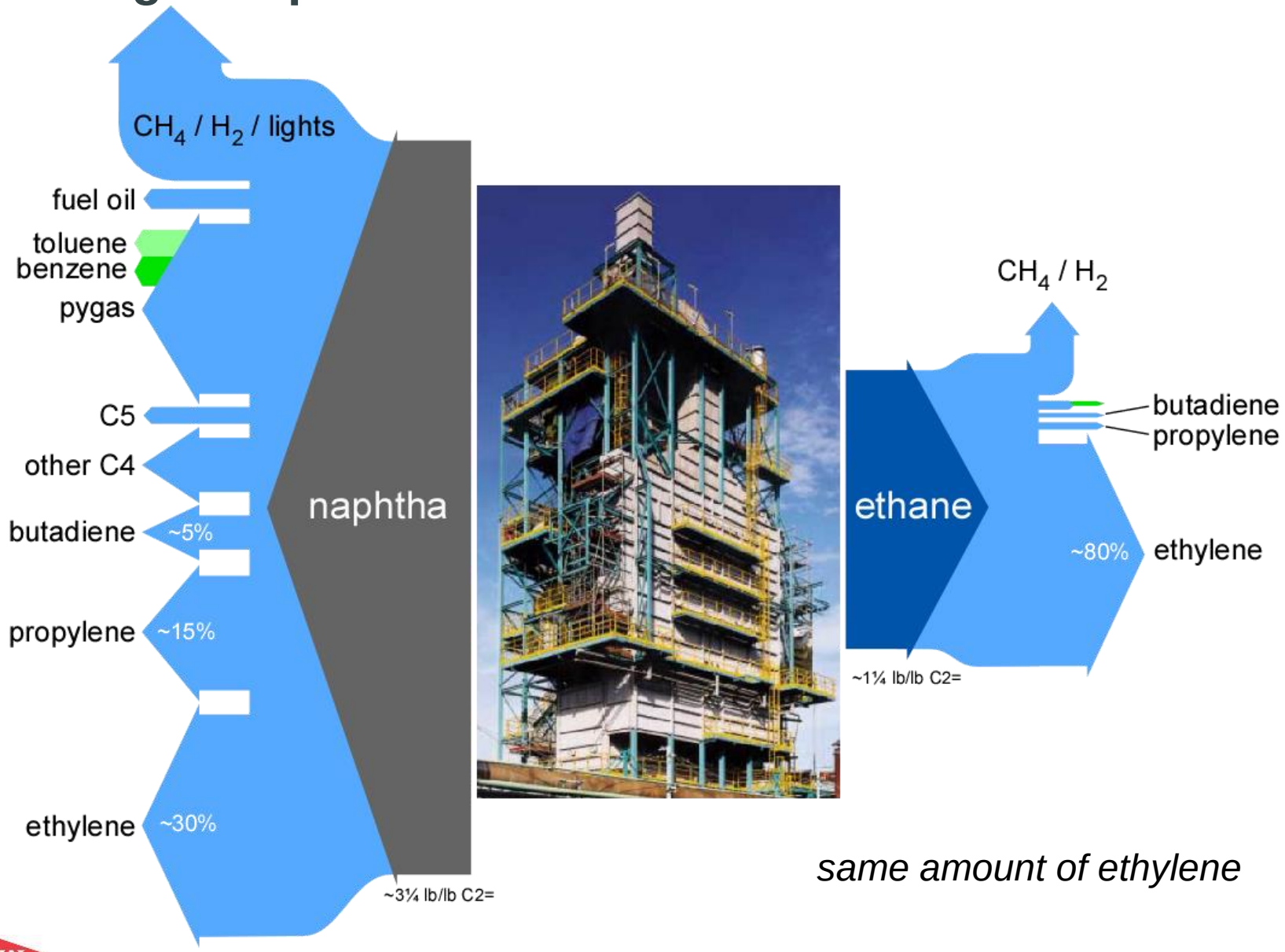
Volumes are world production unless noted. Purchased chemicals are in pink. NON-Confidential - *from published sources* MEJ-2/2003

What I hope to leave you with

- Integration was crucial in the development of the chemical industry but has decreased in importance
  chlorine has largely been replaced as an oxidant
- Inorganic chemistry created the chemical industry and remains important, but not particularly valued
  vinyl and caustic are critical, just not particularly profitable
- Scale remains the major source of competitive advantage in commodity chemicals
  for undifferentiated materials, production cost is king and scale lowers production cost

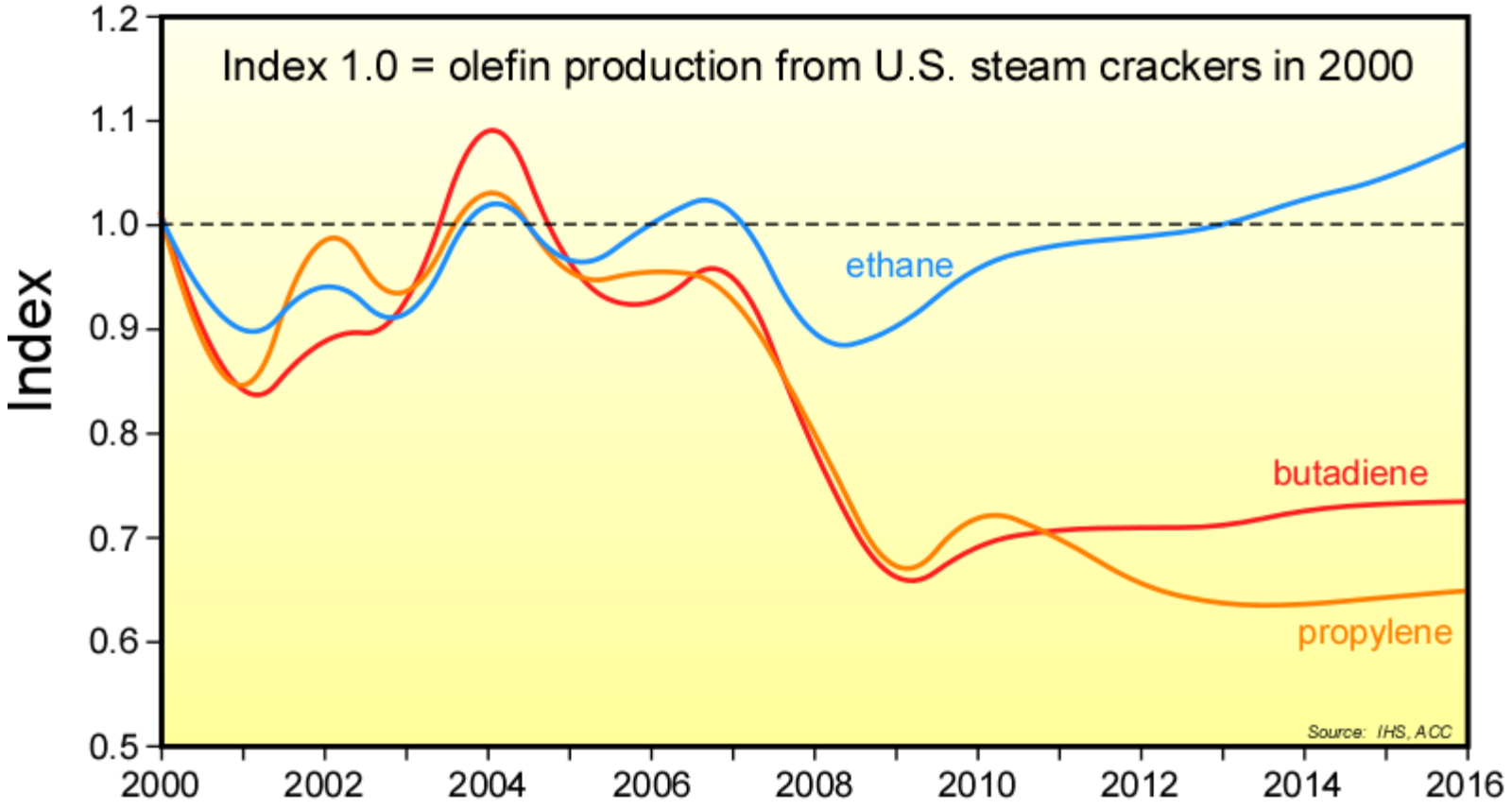

Questions?

Cracking Comparison

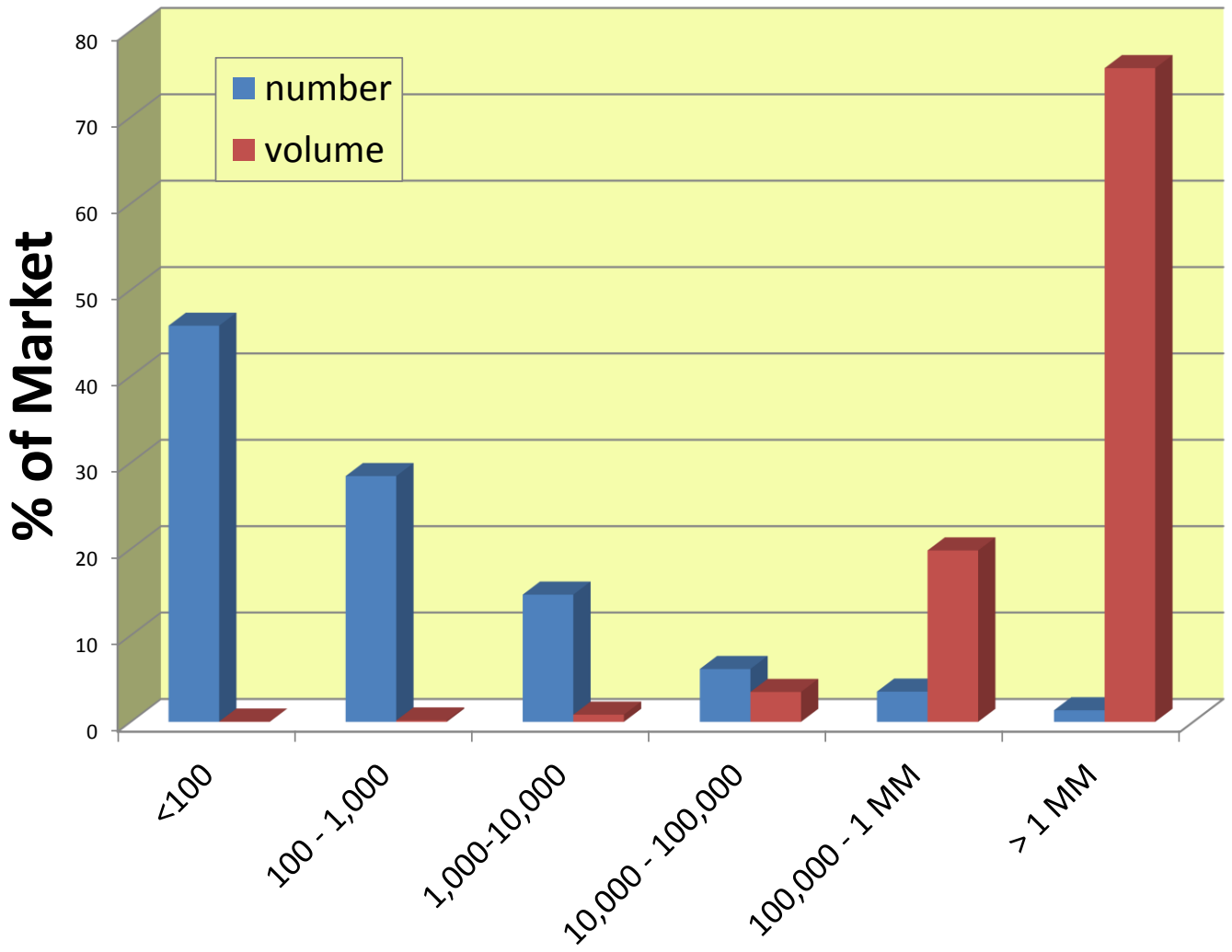


same amount of ethylene

Production of C3/C4 Dropped



Scale Falls Quickly



Brine Mining