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

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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

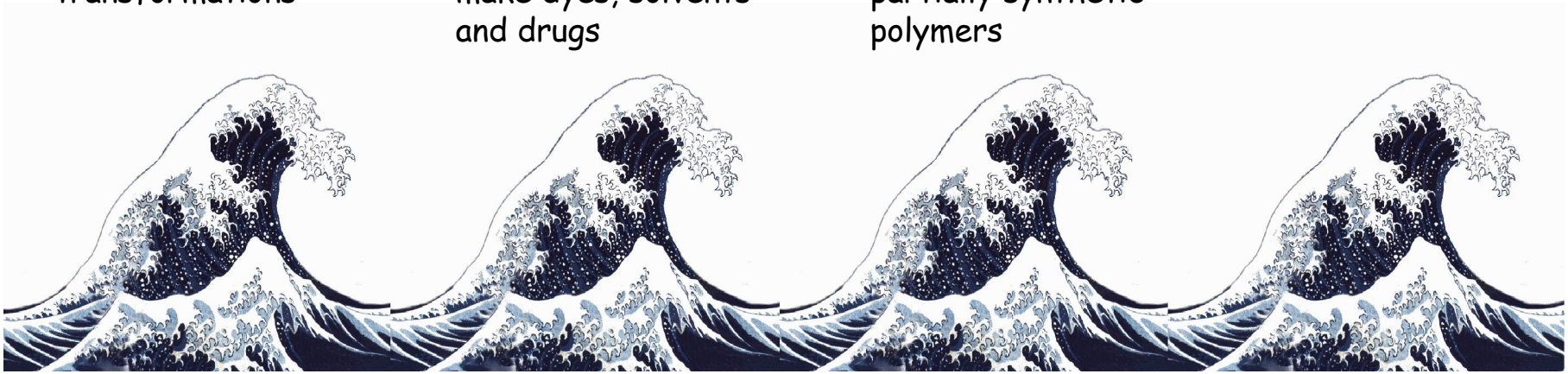
Chemical Industry Technology Waves

Inorganic
- mined materials
- electrochemical
- active reagents allow transformations

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

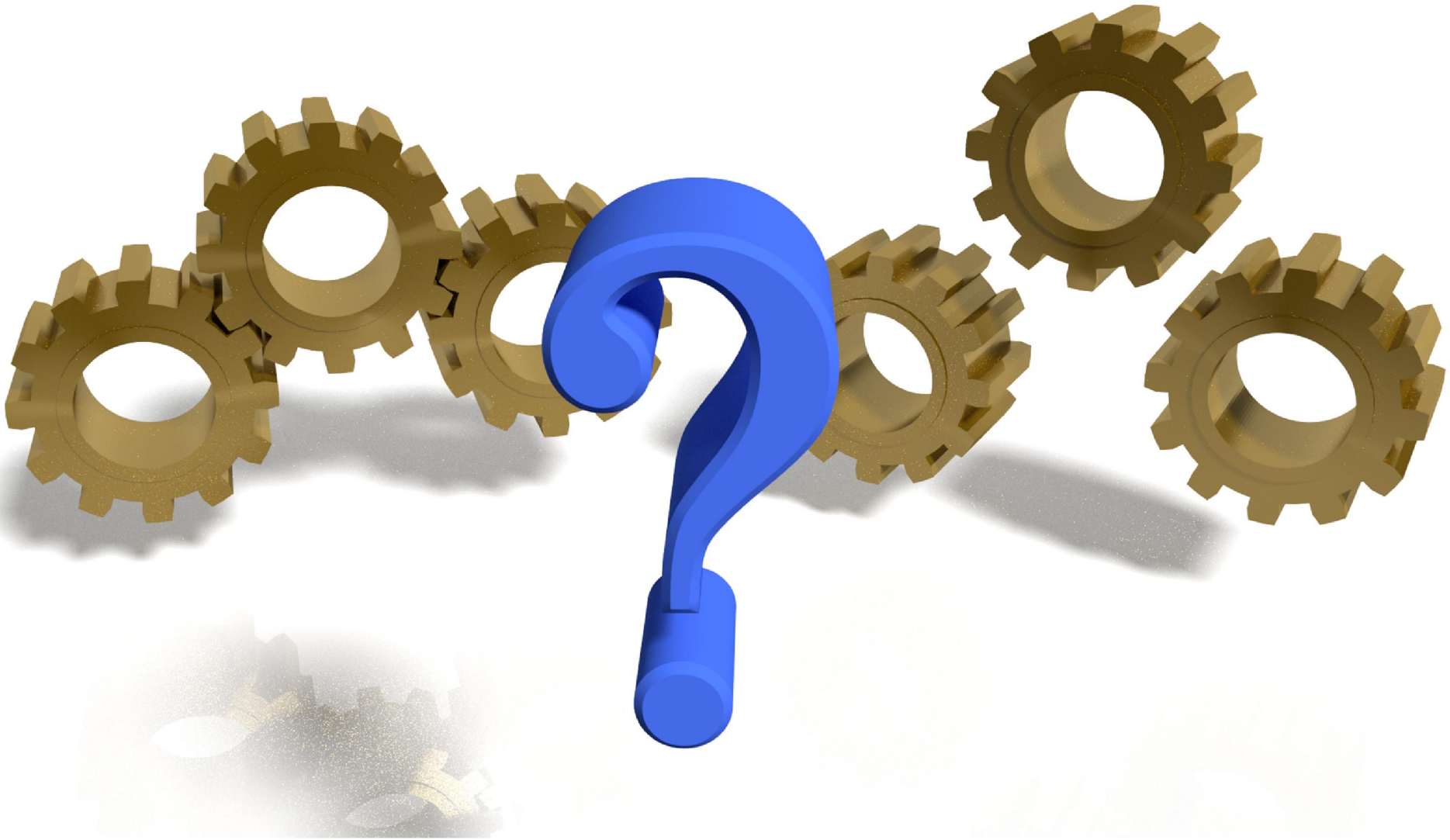
Cellulosics
- use inorganics to transform natural materials
- partially synthetic polymers

Polymers
- took off with synthetic rubber
- continues today

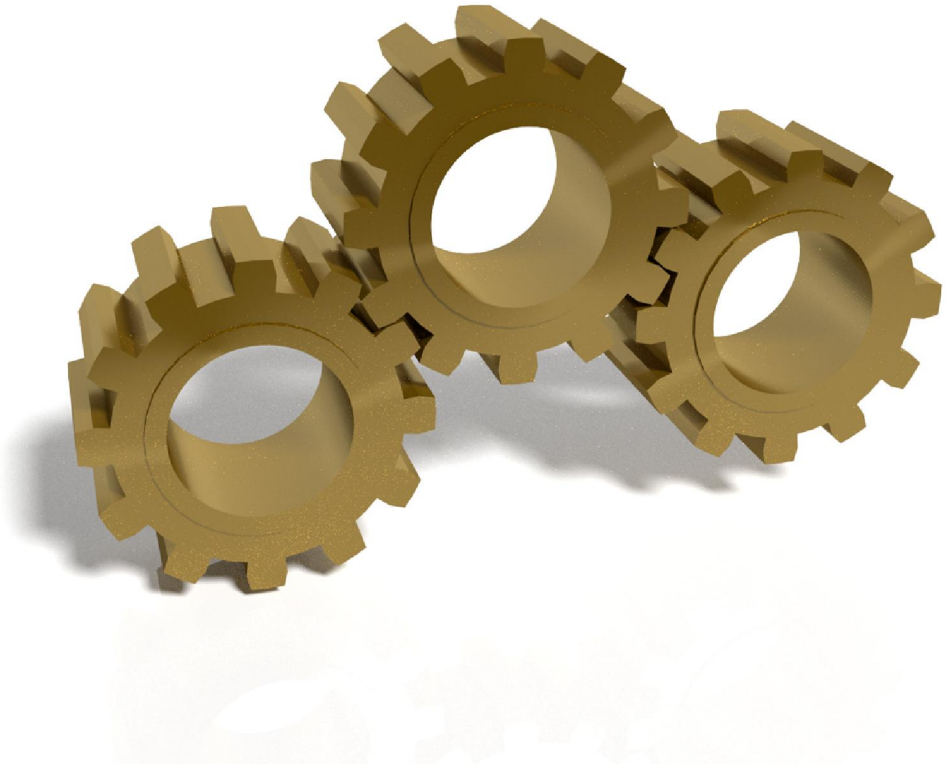


1760-1910	1870-1930	1895-1935	1925-present
rocks ⇨	coal ⇨	biomass ⇨	petroleum NGL

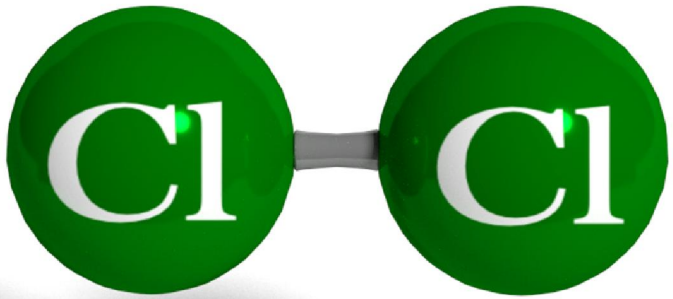
What is Integration?



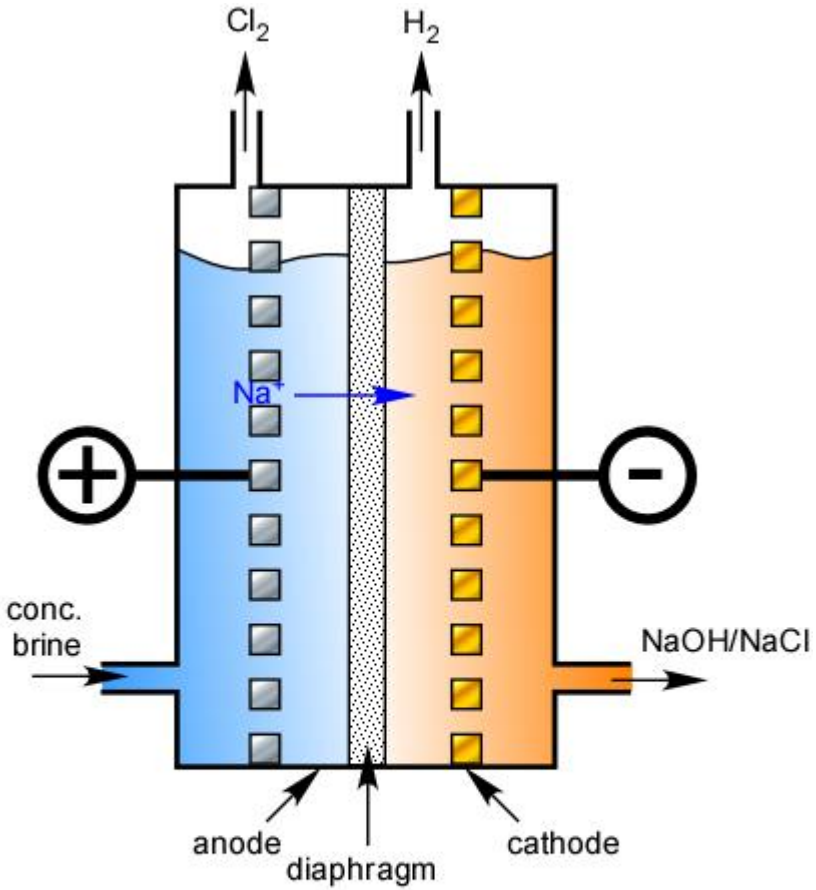
Integration



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


Cl
Cl

Chlor-Alkali



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

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

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

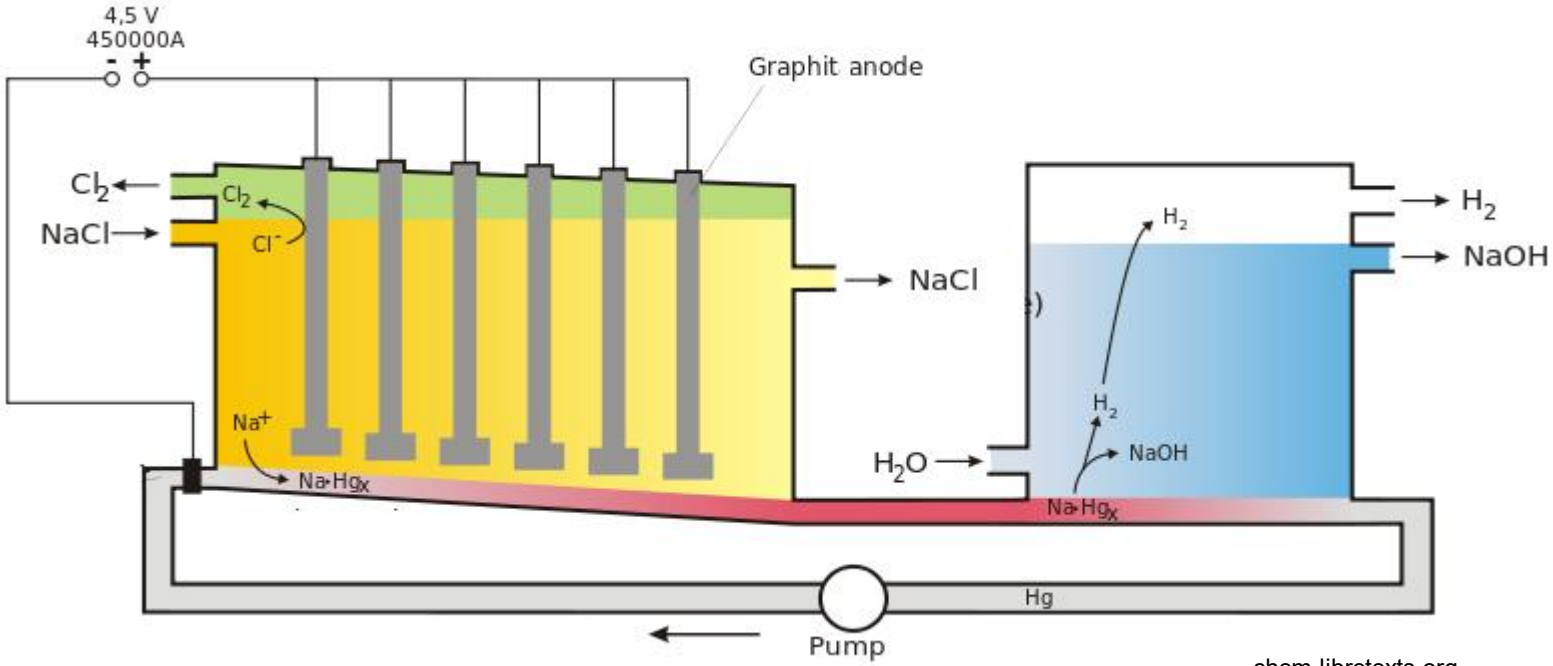
Bleach was the Product

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

The oxidizing power of chlorine was what was desired.

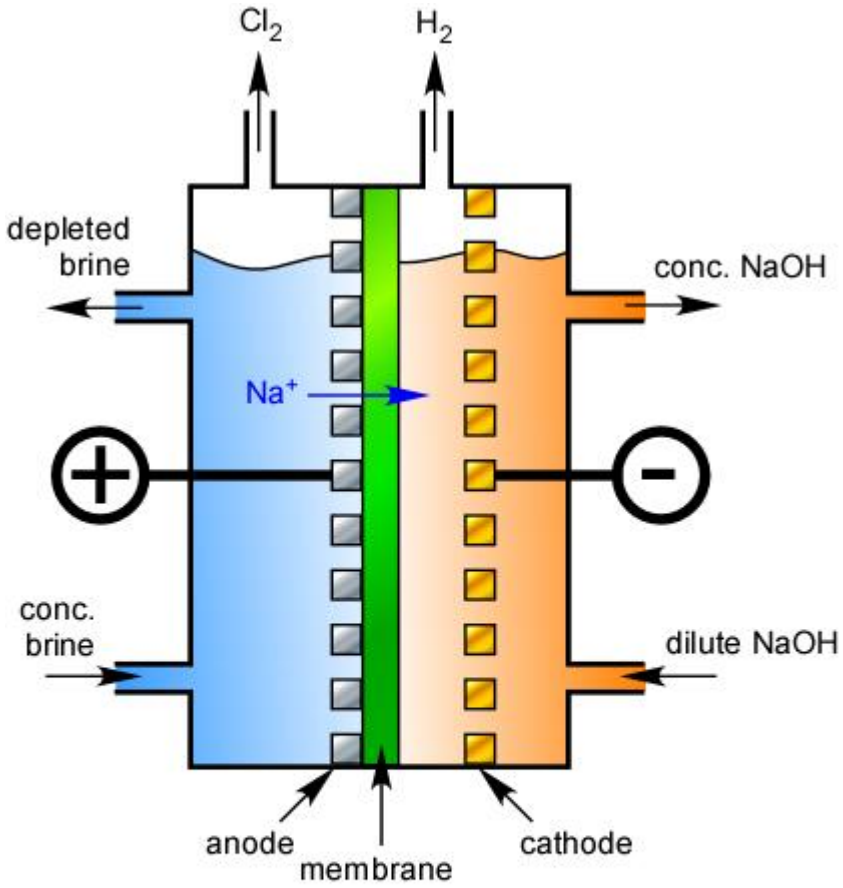
No net production of alkali

Mercury Cells



chem.libretexts.org

Membrane Cells



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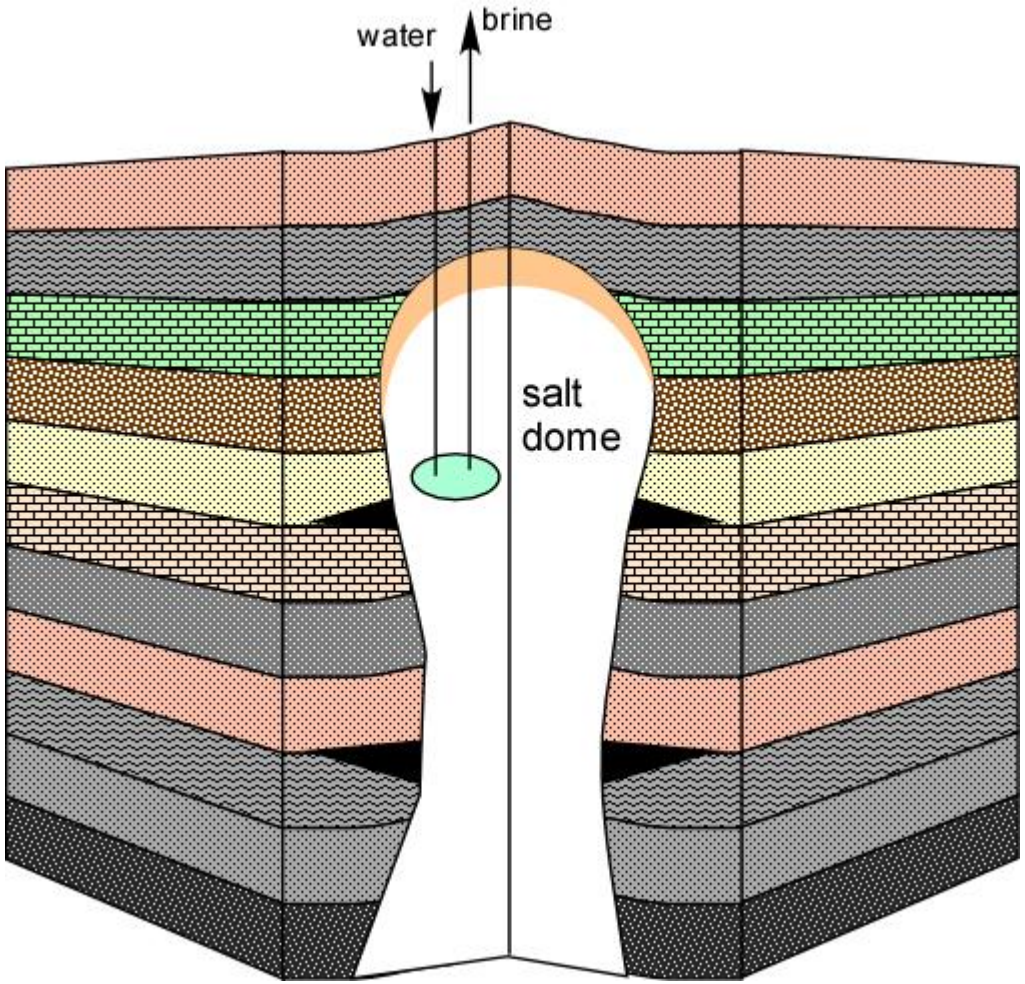
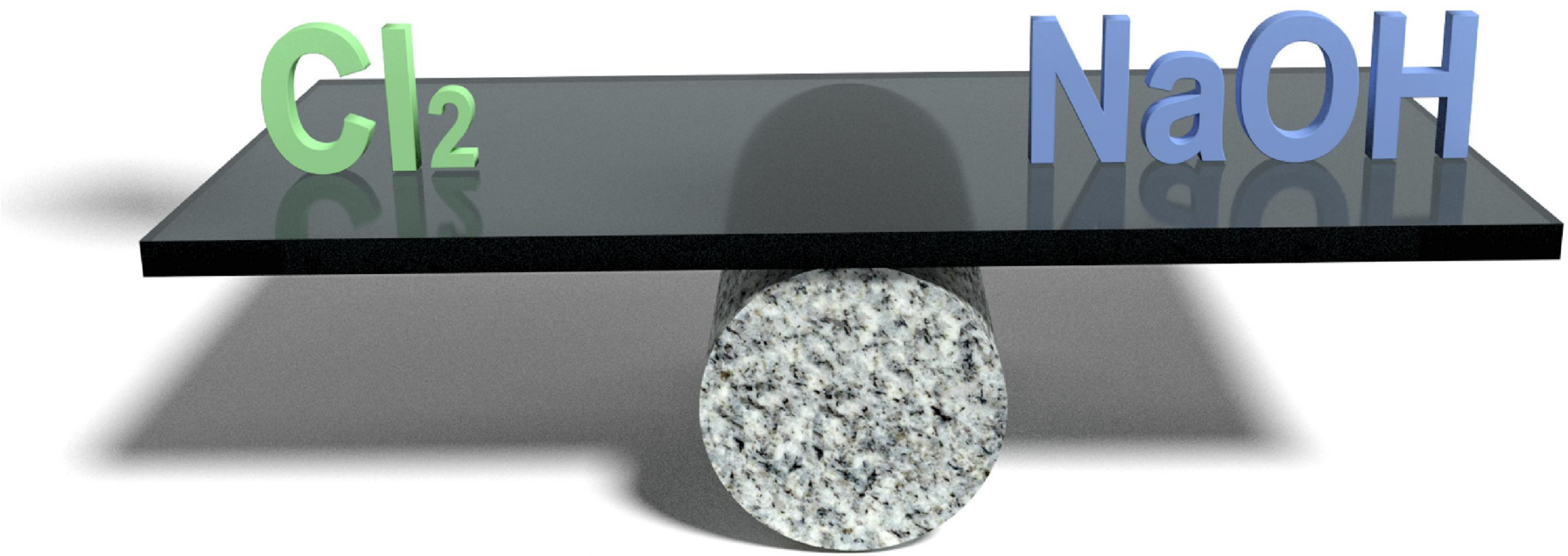
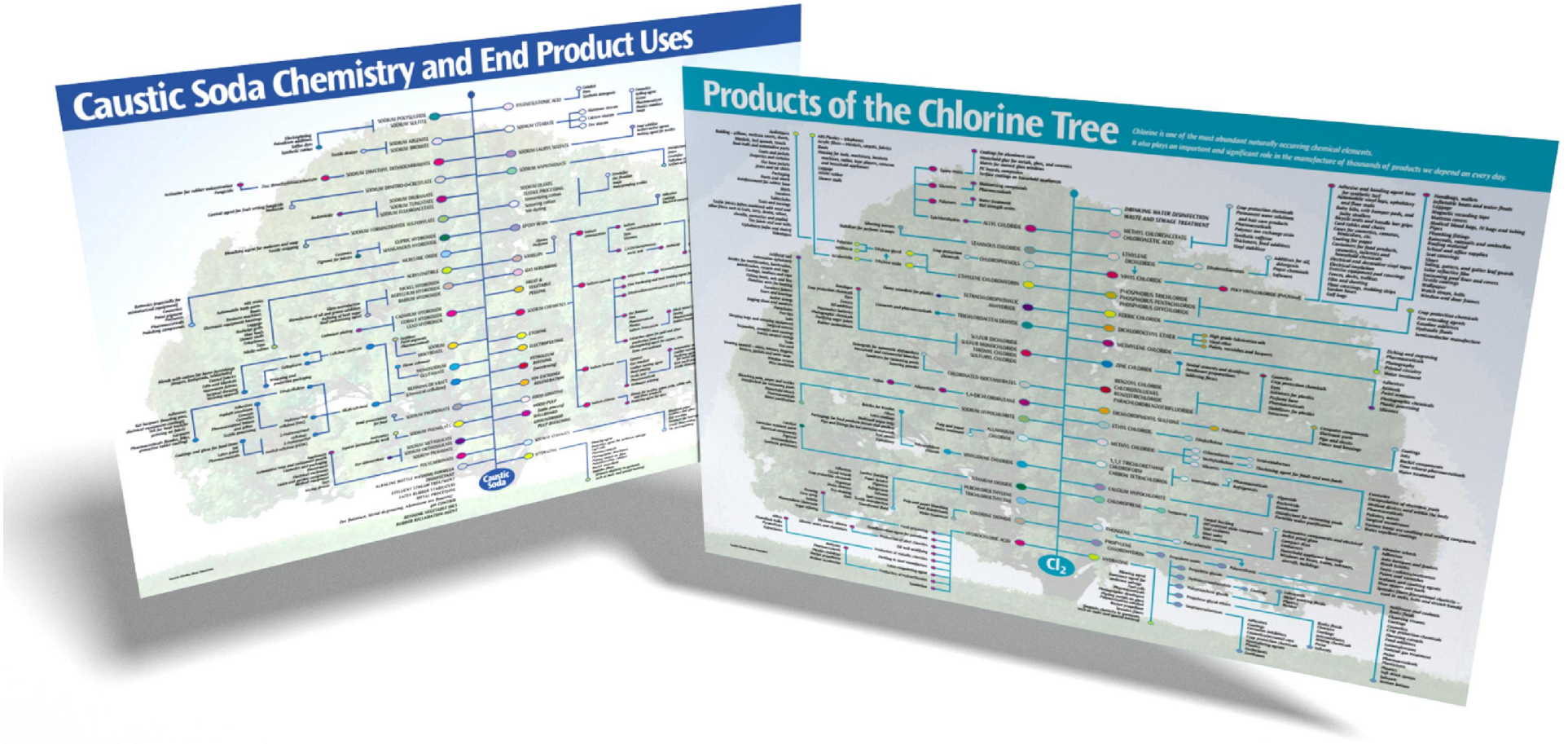
$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + Cl_2 + H_2$$

Brine Mining

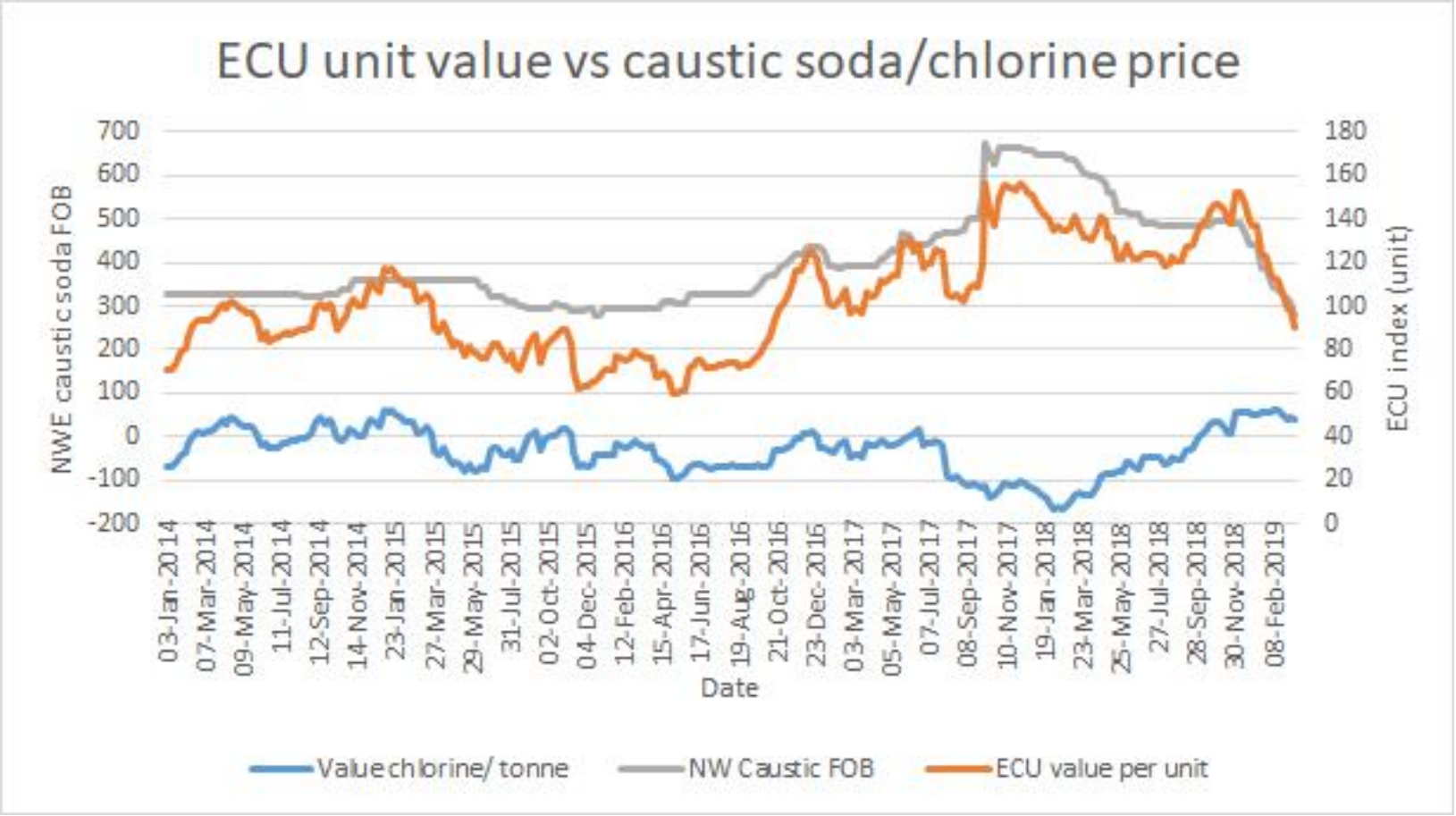


Balancing the ECU



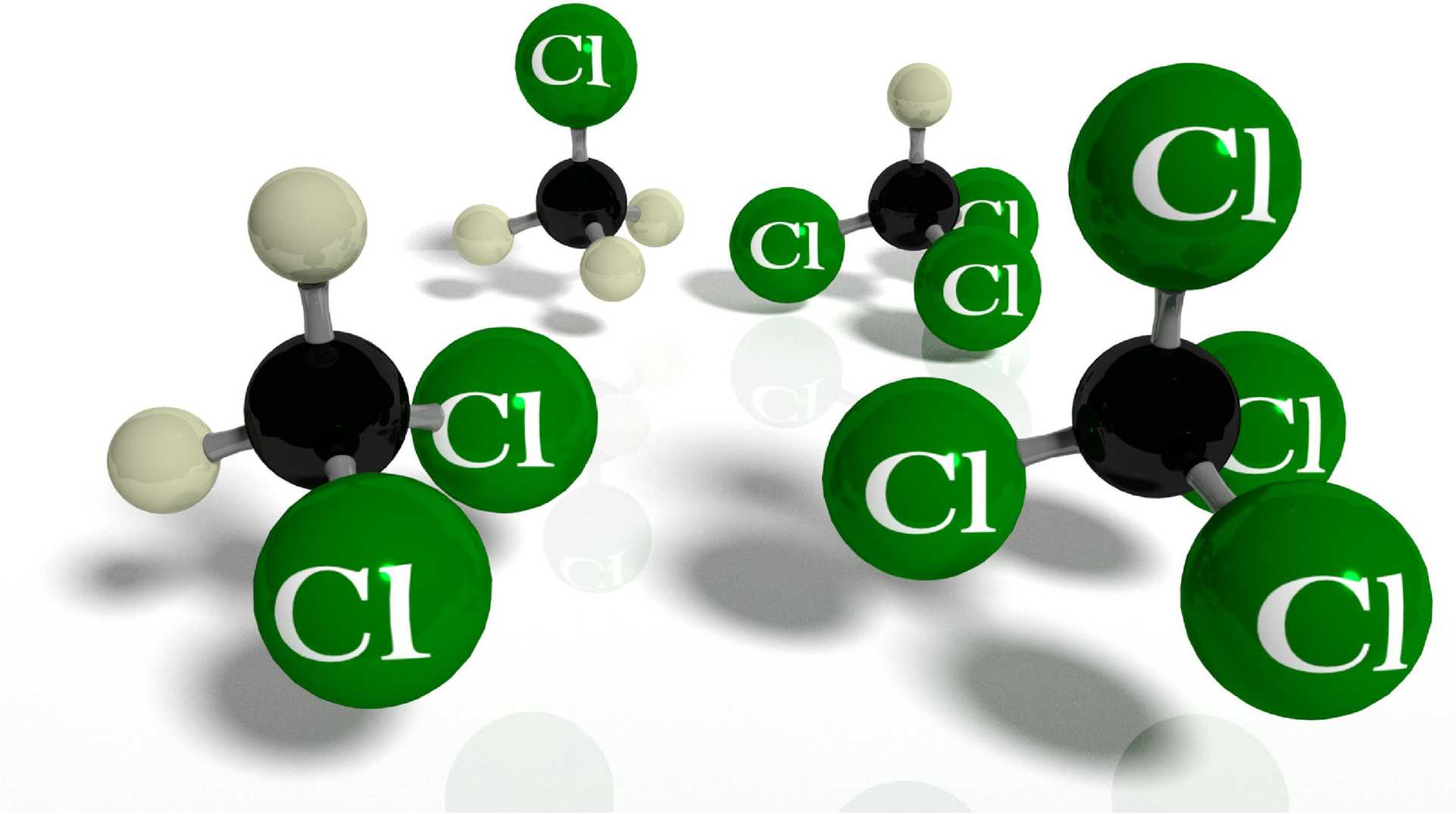

Caustic Soda Chemistry and End Product Uses
Products of the Chlorine Tree
Chlorine is one of the most abundant naturally occurring chemical elements.
It also plays an important and significant role in the manufacture of thousands of products we depend on every day.
Caustic Soda
Cl2

ECU Pricing



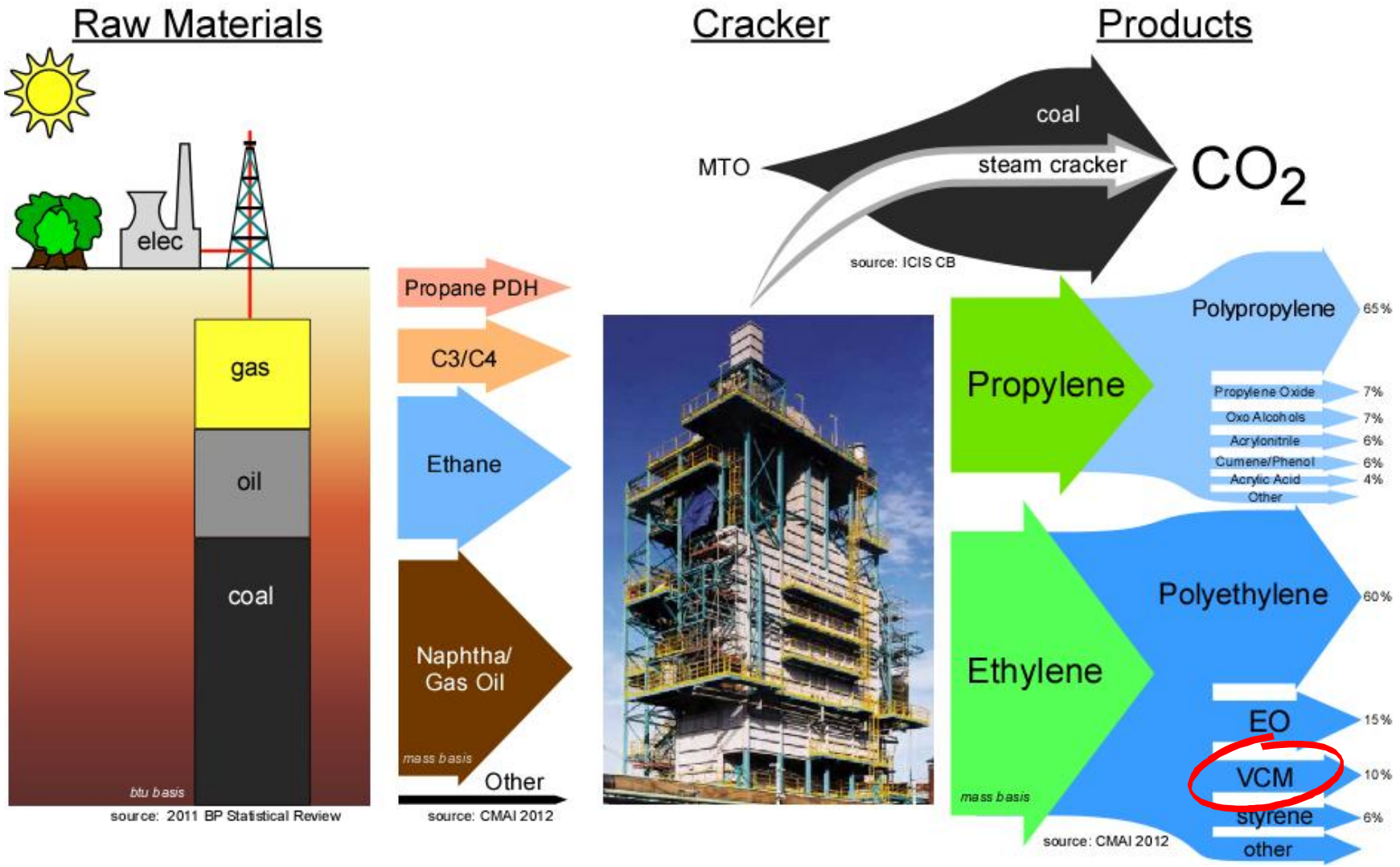
icis.com/explore/resources/news/2019/03/21/10336962/insight-european-ecu-values-fall-to-the-lowest-level-since-2016/

Organochlorides

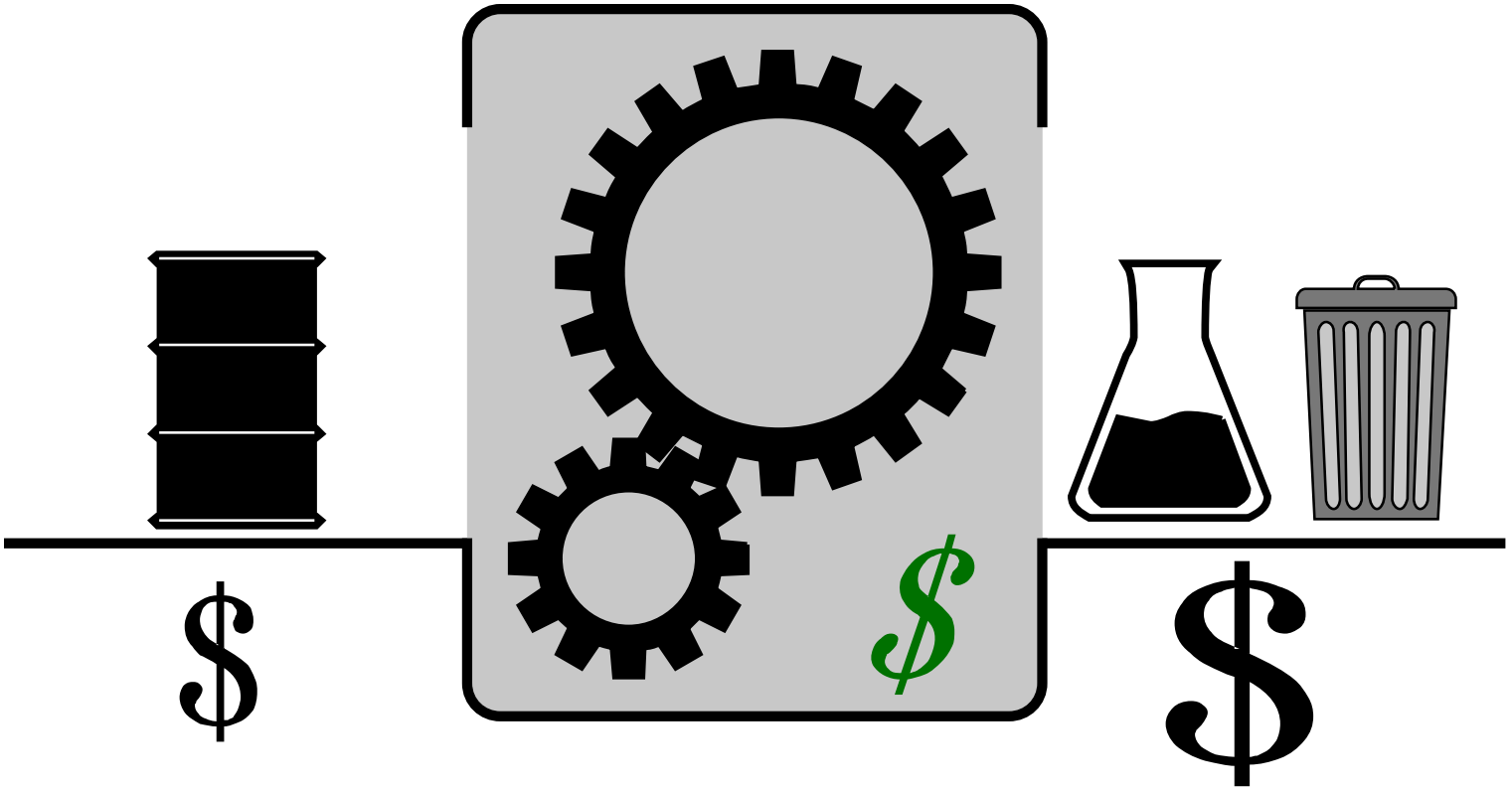



Pyrene
FIRE EXTINGUISHER
Pyrene

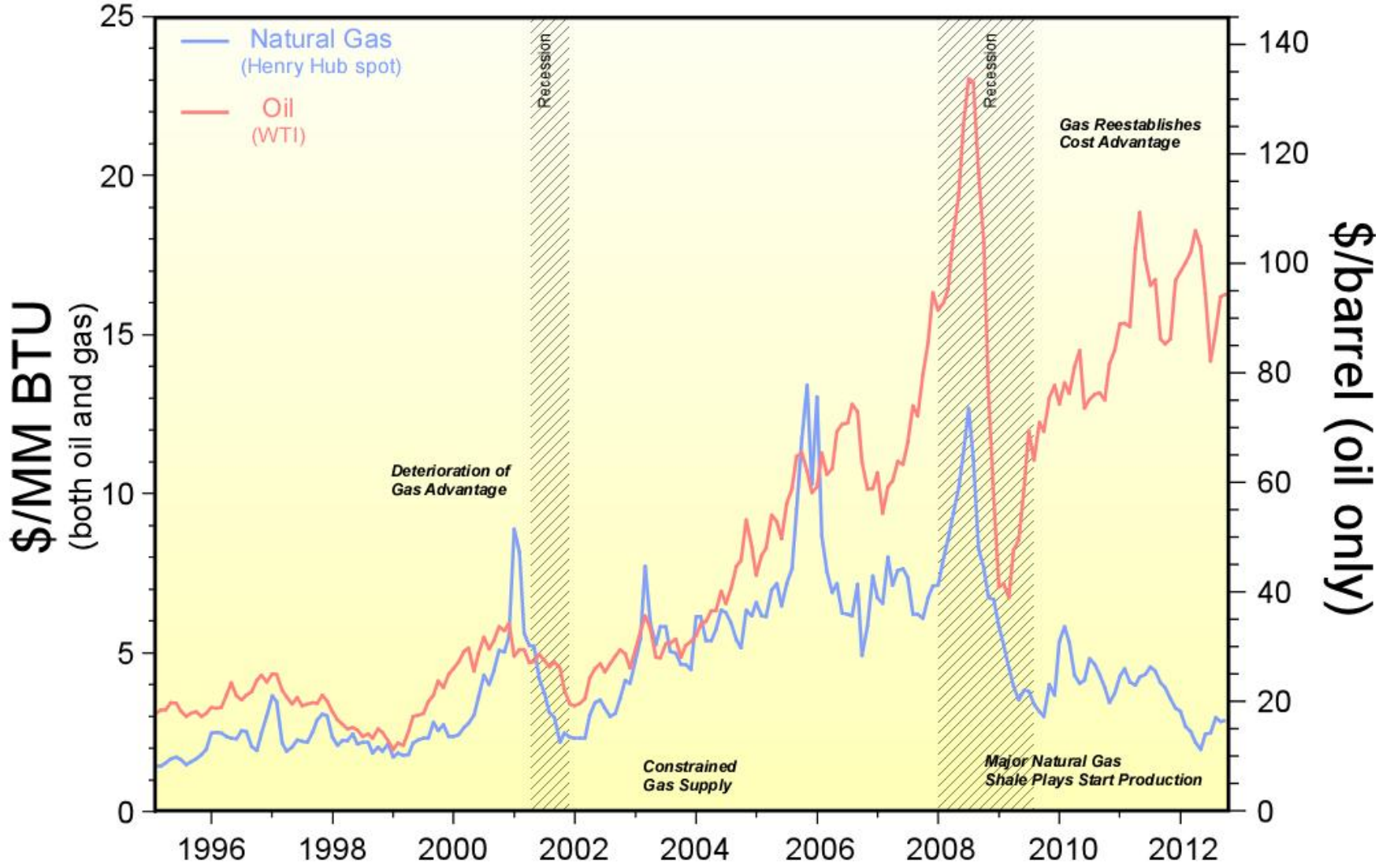
Chemical Industry Snapshot



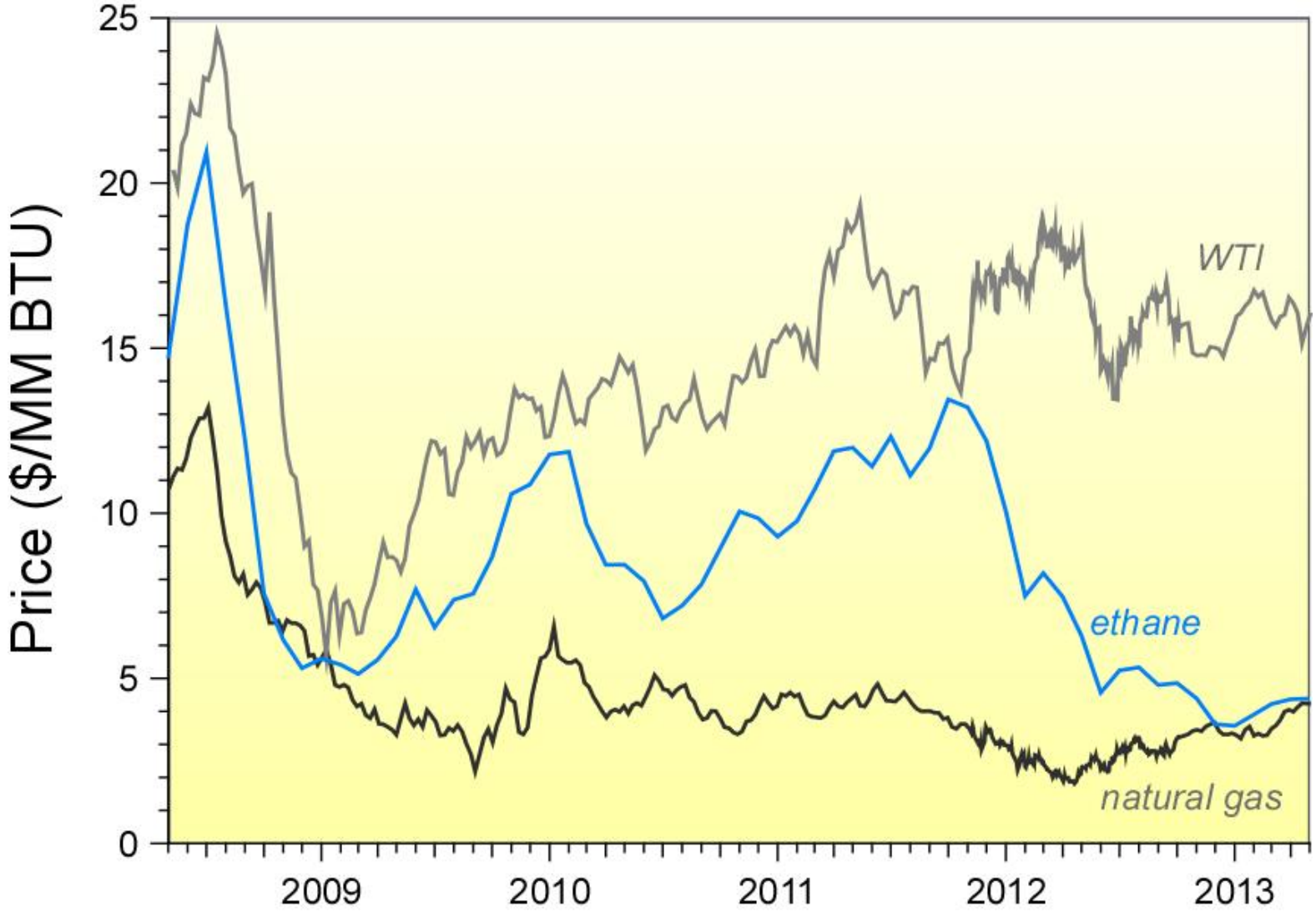
Simplified Chemical Industry



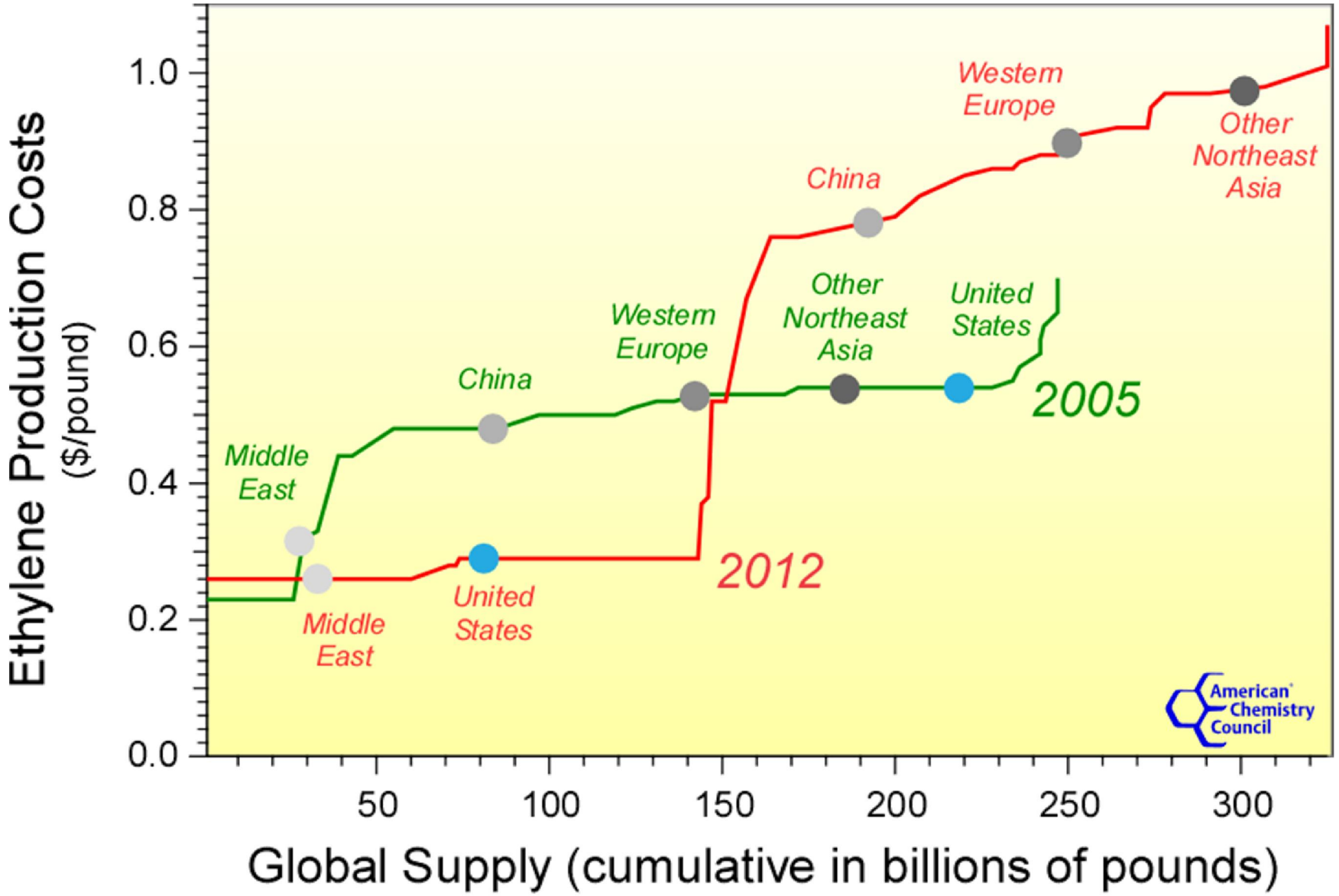
Recent Industry History



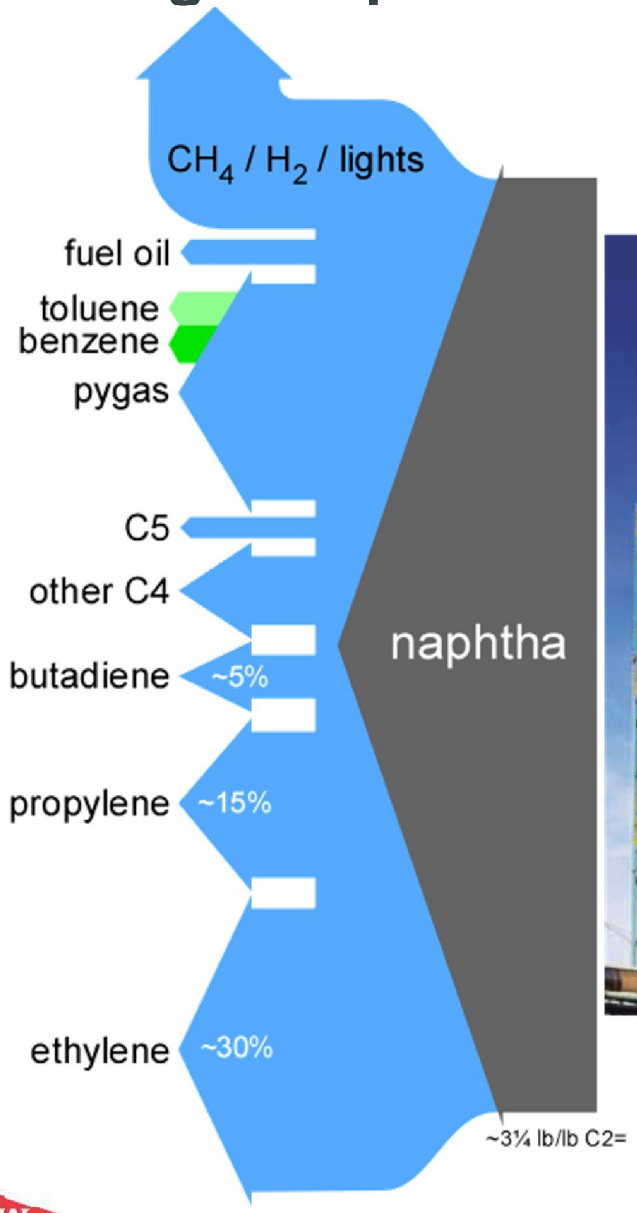
Ethane Price Now Tracks Gas

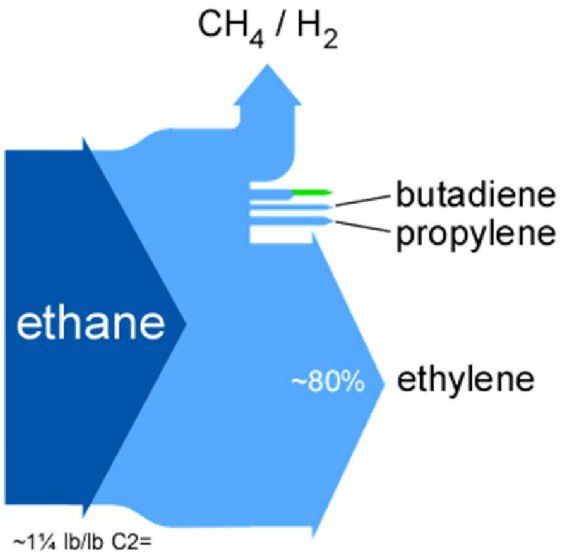


Impact of Low Gas Prices



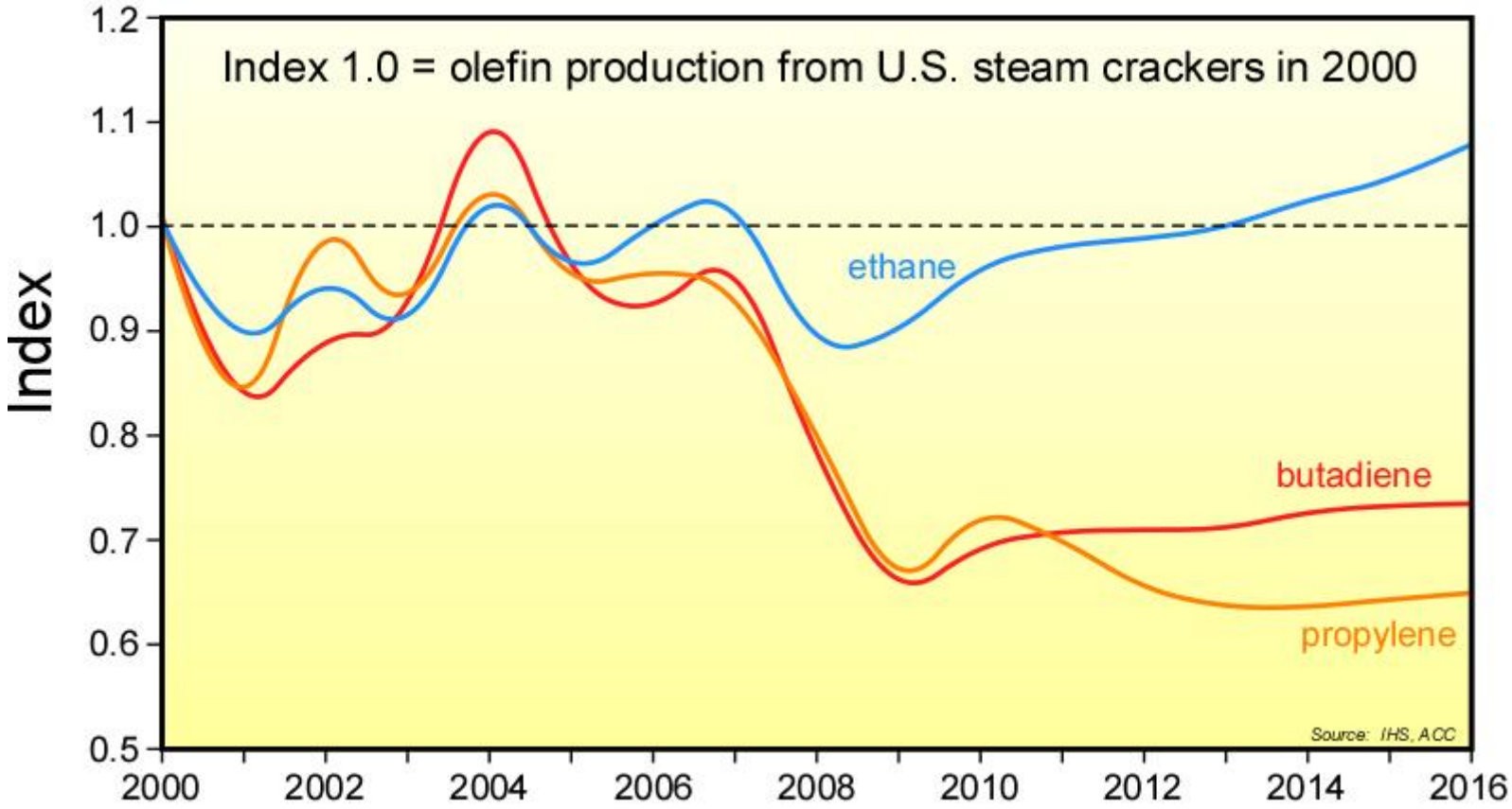
Cracking Comparison



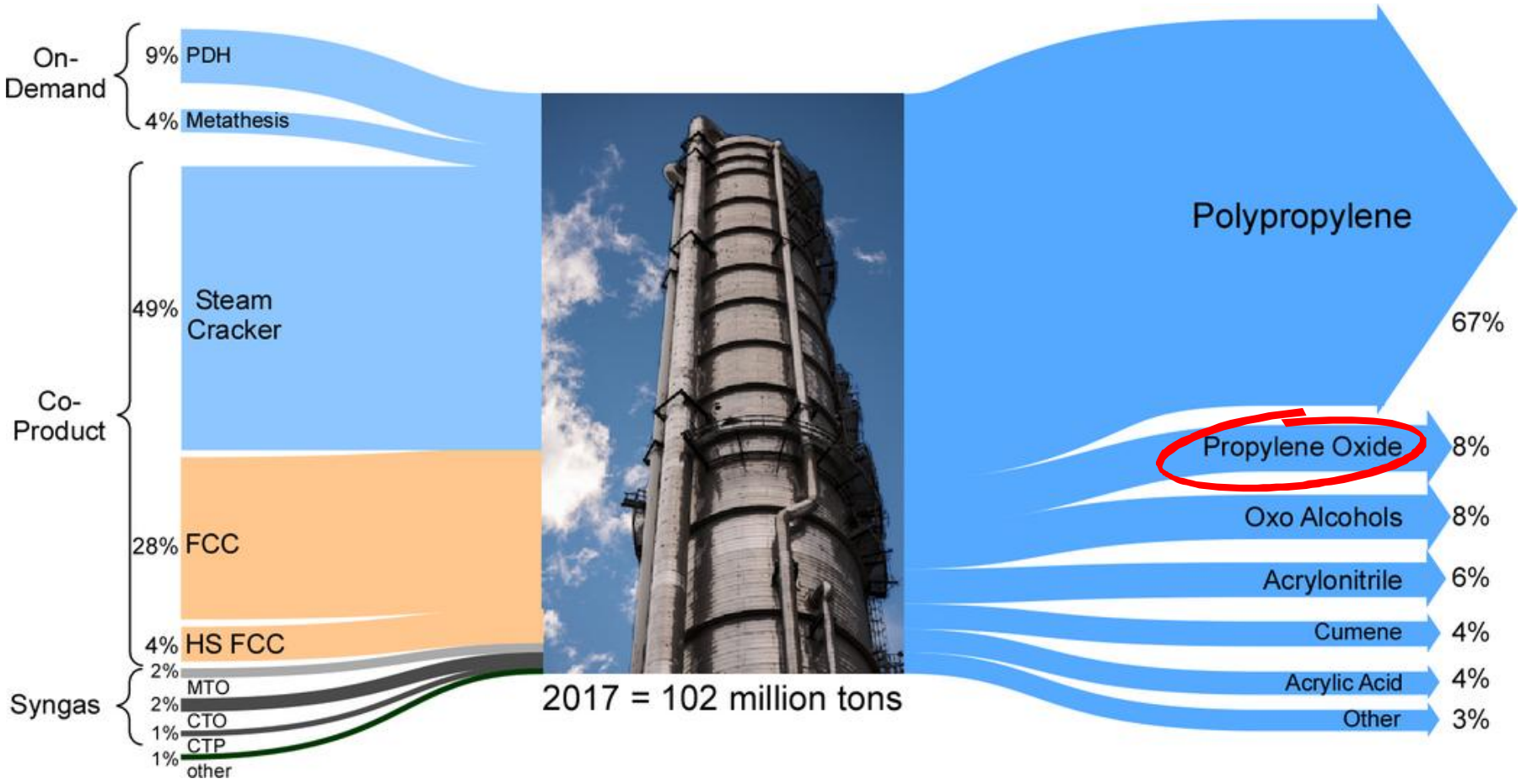


same amount of ethylene

Production of C3/C4 Dropped

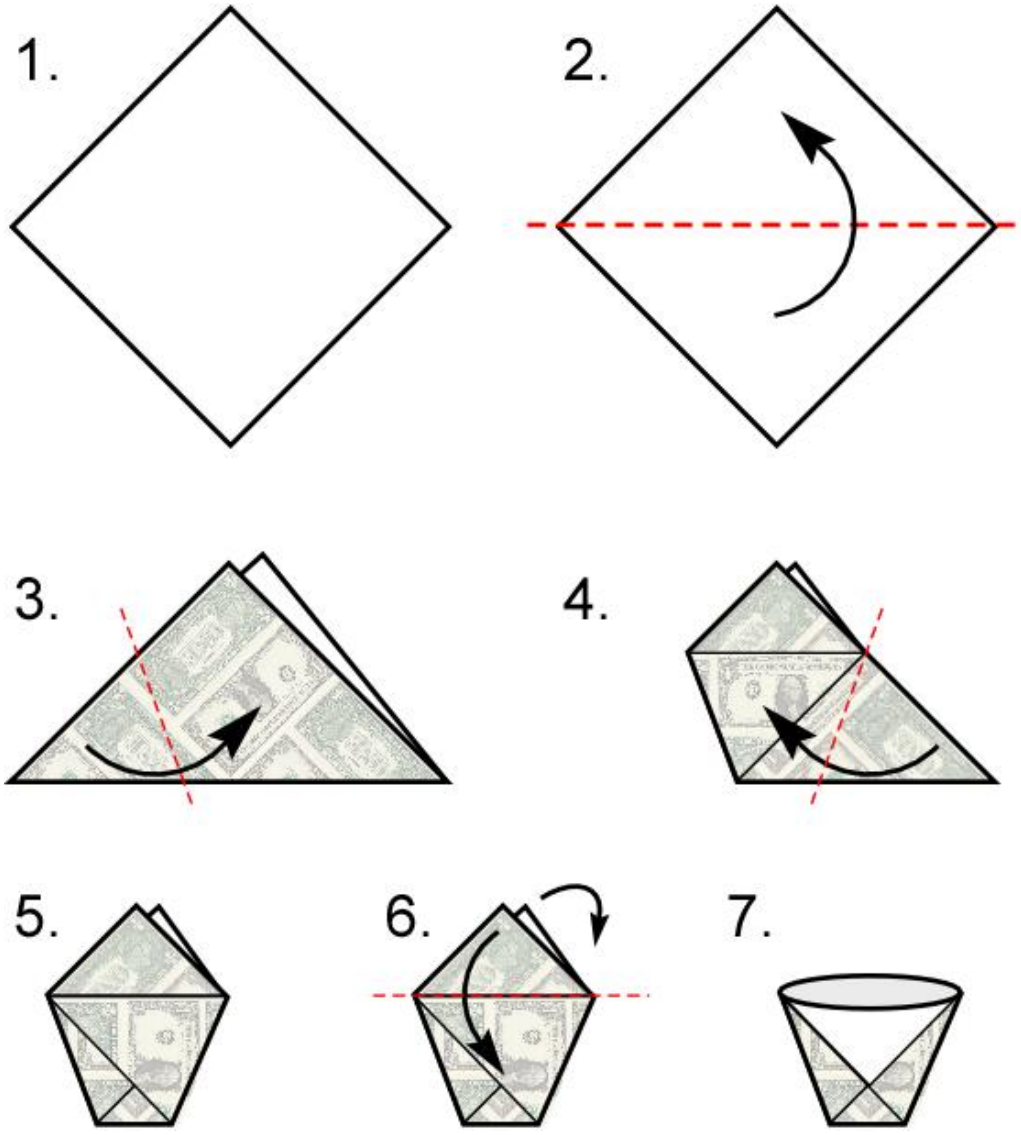


World Propylene



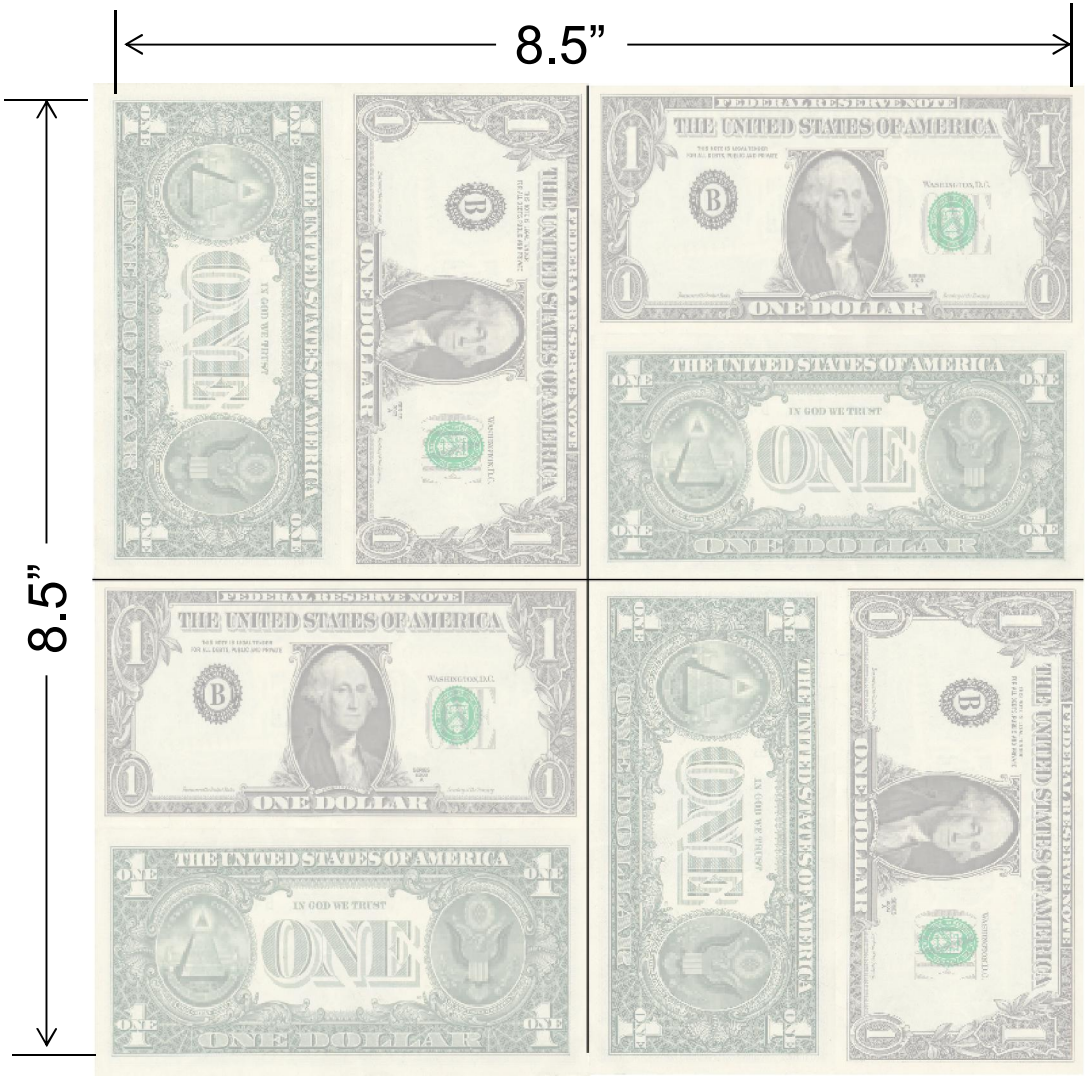
Scale Is Important

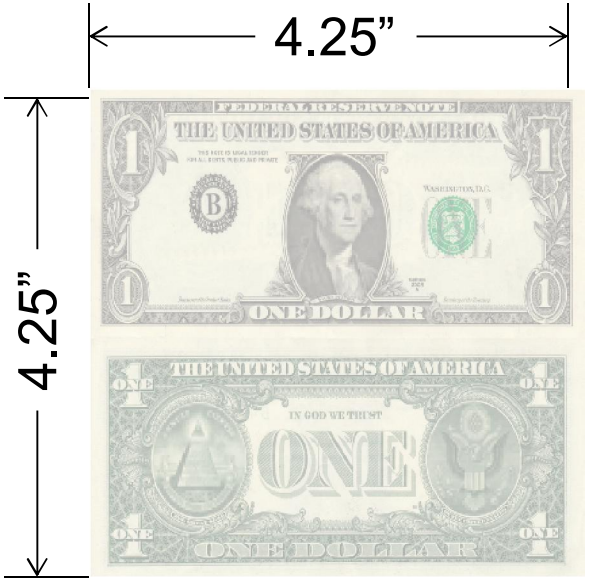
Scale Demo



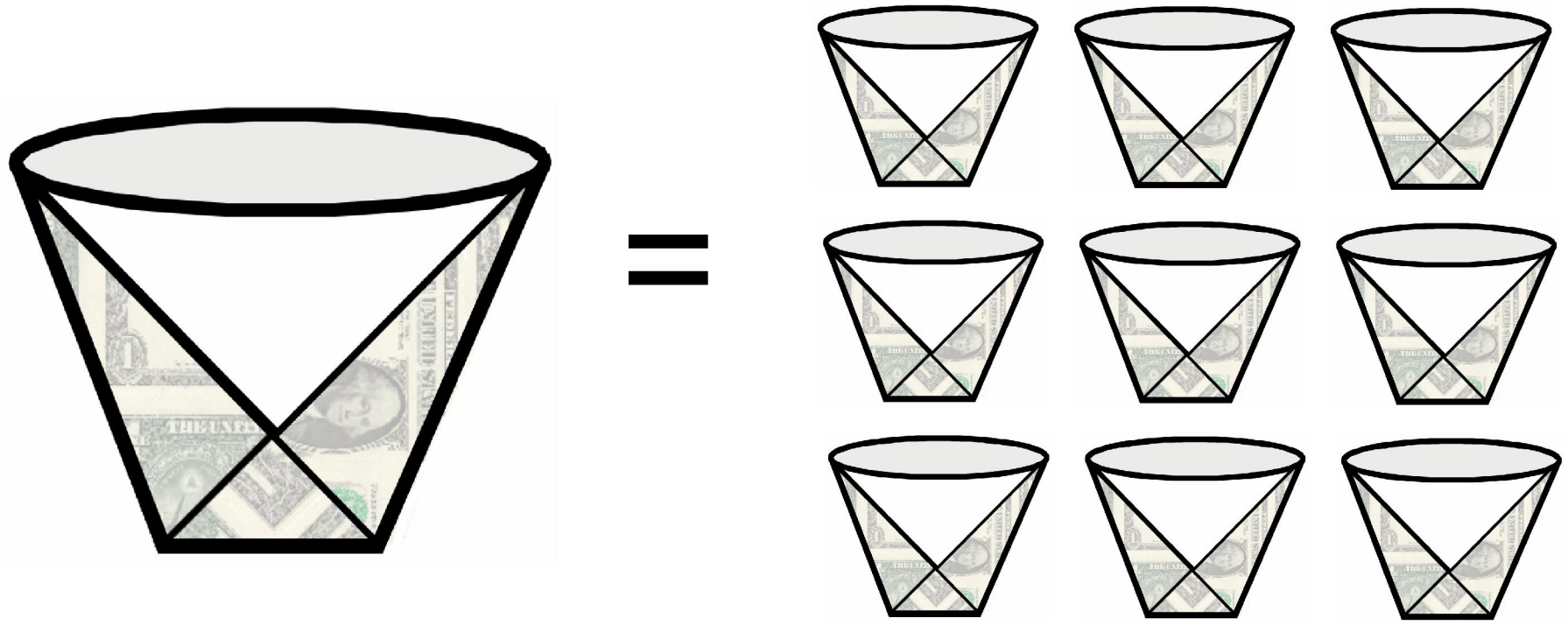
Make a cup with an 8½” square and another with a 4¼” square

Video Demo





Scale Wins



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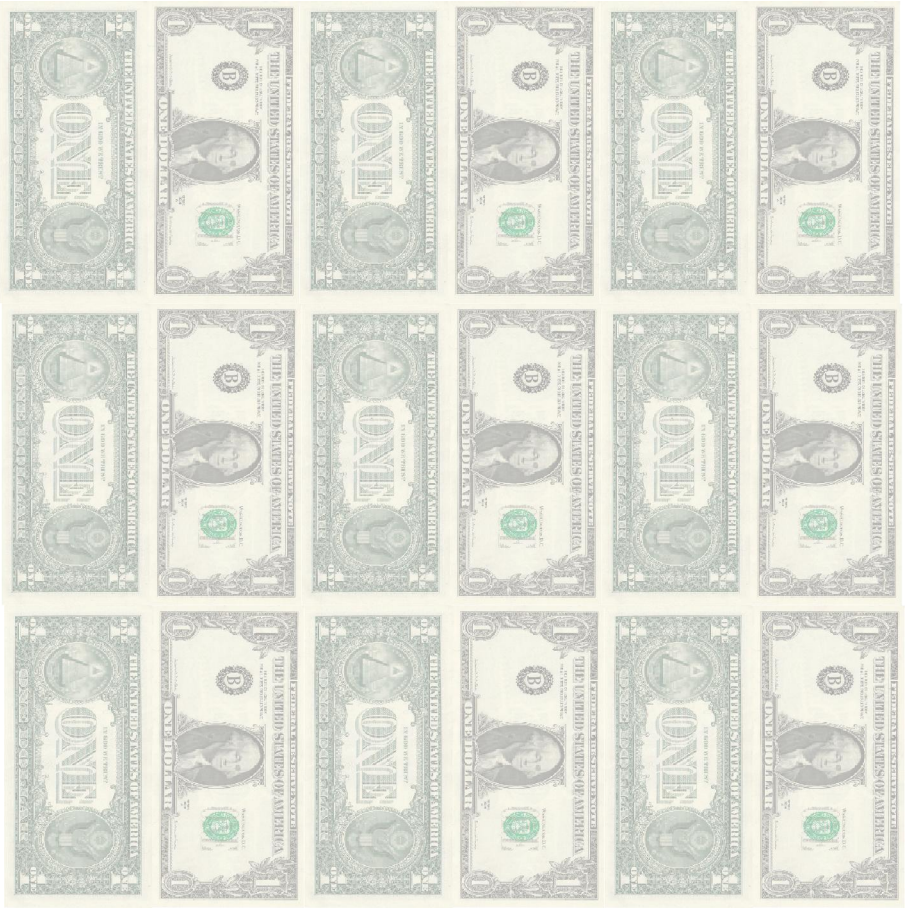
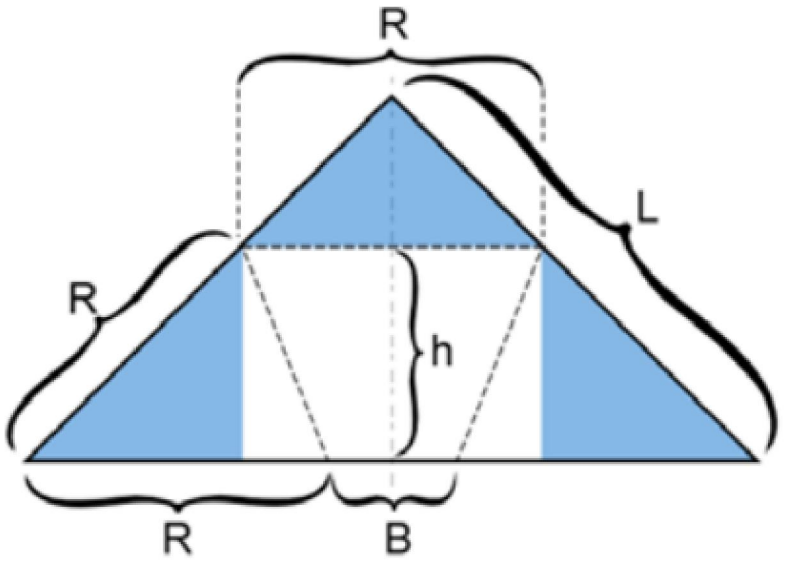


Scale Always Wins

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

Demo Math



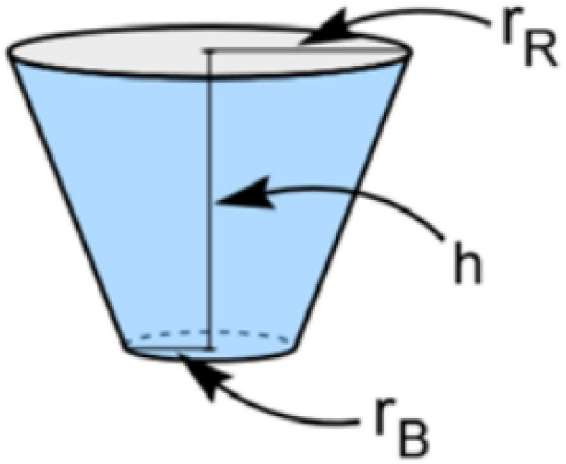
$$A = L^2$$

$$h = \frac{L}{1+\sqrt{2}}$$

$$R = \frac{\sqrt{2}\ L}{1+\sqrt{2}}$$

$$B = \frac{L\,(2-\sqrt{2}\,)}{1+\sqrt{2}}$$

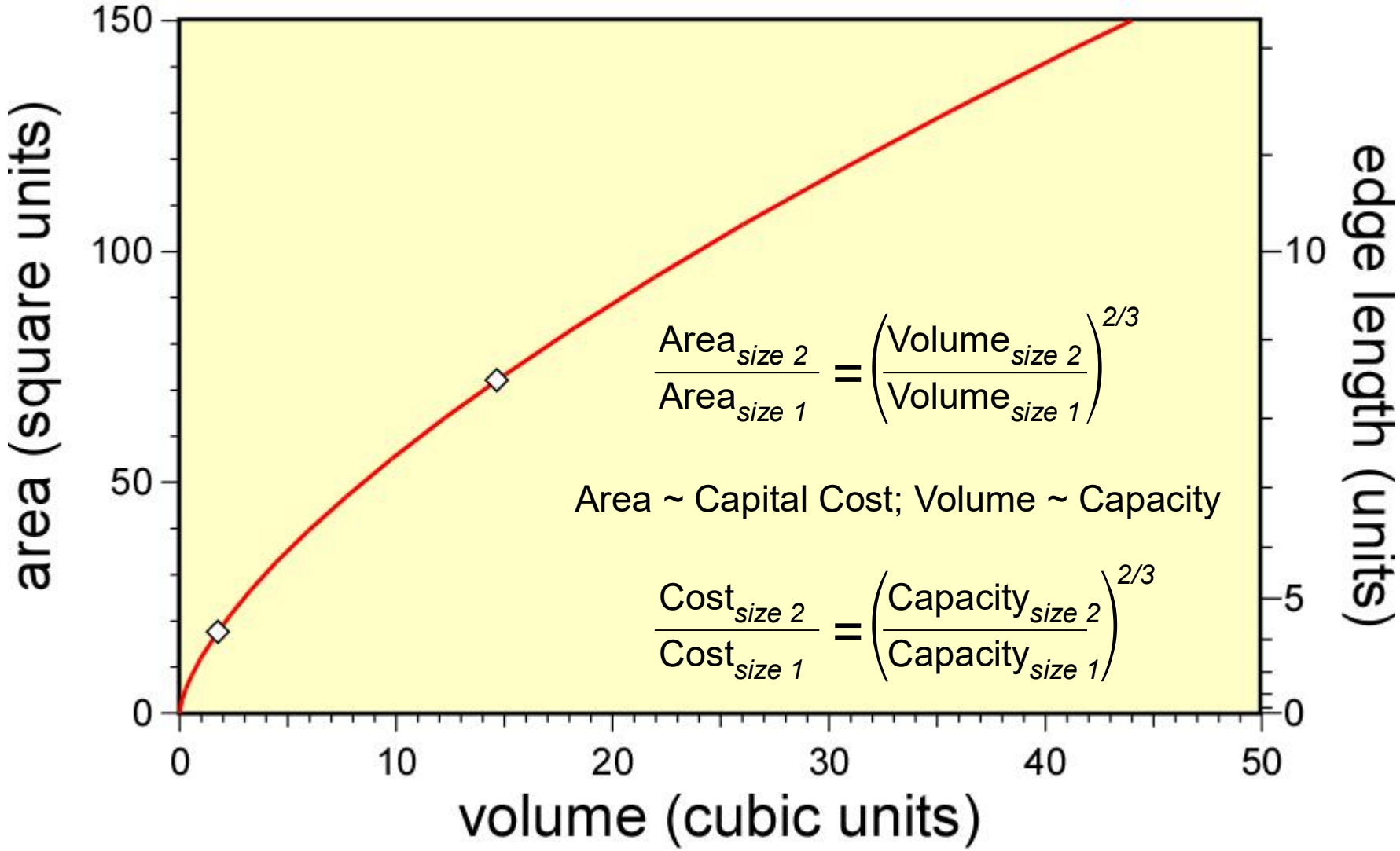
$$\frac{V_L}{V_{L/2}} = 8$$



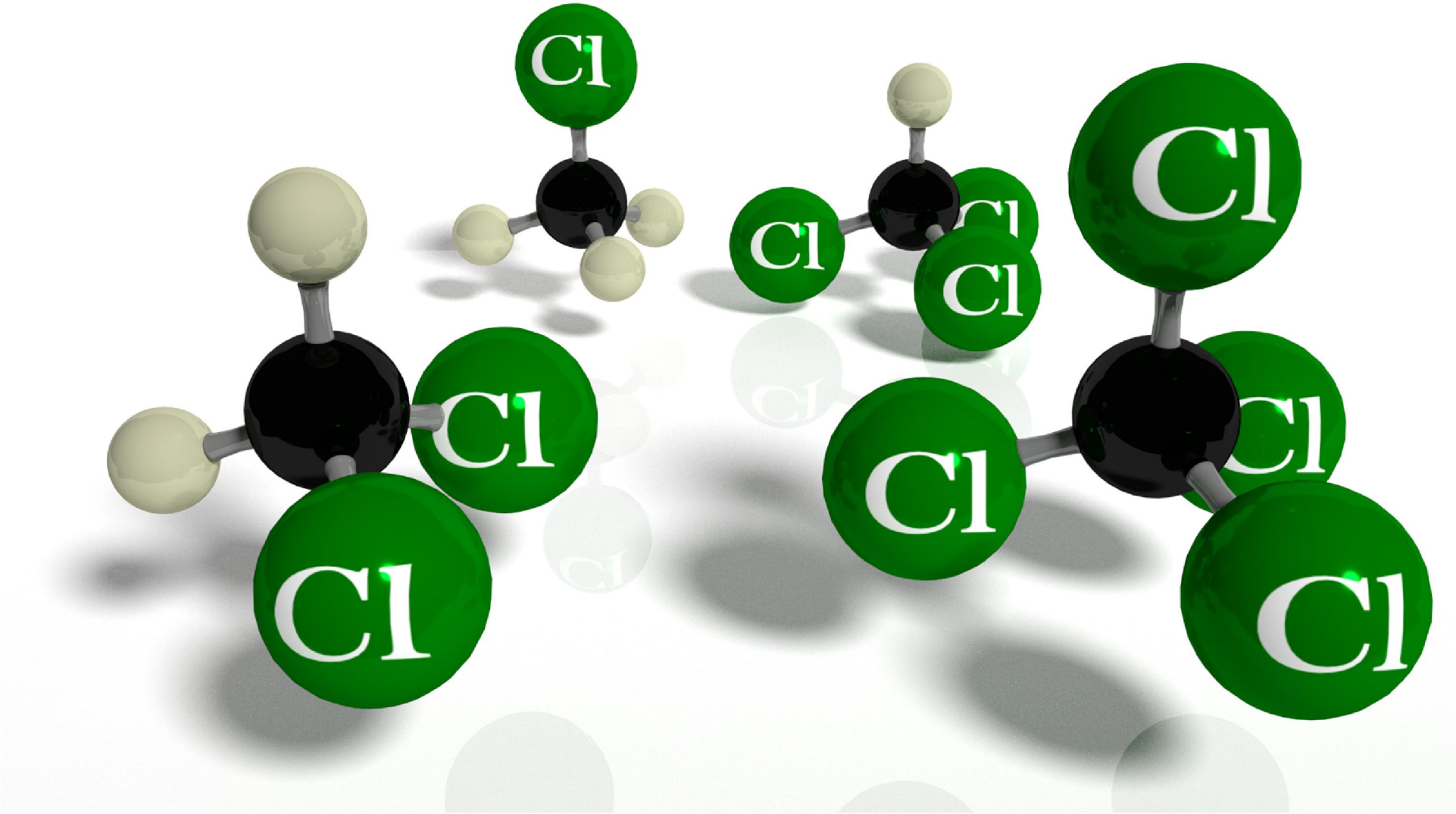
$$r_B = \frac{B}{\pi} = \frac{L\,(2-\sqrt{2}\,)}{\pi\,(1+\sqrt{2}\,)}$$

$$r_R = \frac{R}{\pi} = \frac{\sqrt{2}\ L}{\pi\,(1+\sqrt{2}\,)}$$

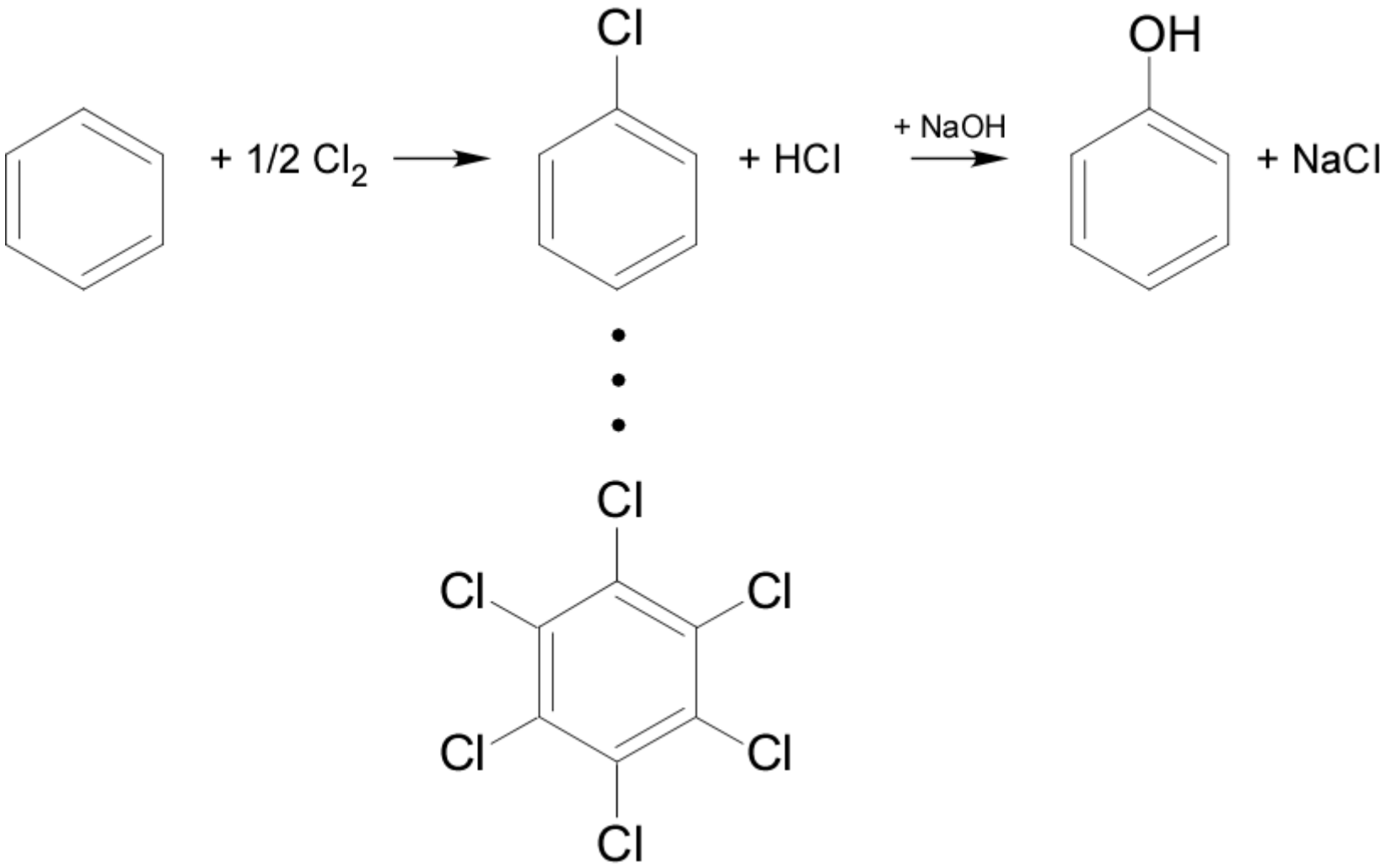
Power Law


150
100
50
0
area (square units)
0
10
20
30
40
50
volume (cubic units)
10
5
0
edge length (units)
$\frac{\text{Area}_{size\ 2}}{\text{Area}_{size\ 1}} = \left(\frac{\text{Volume}_{size\ 2}}{\text{Volume}_{size\ 1}}\right)^{2/3}$
Area ~ Capital Cost; Volume ~ Capacity
$\frac{\text{Cost}_{size\ 2}}{\text{Cost}_{size\ 1}} = \left(\frac{\text{Capacity}_{size\ 2}}{\text{Capacity}_{size\ 1}}\right)^{2/3}$

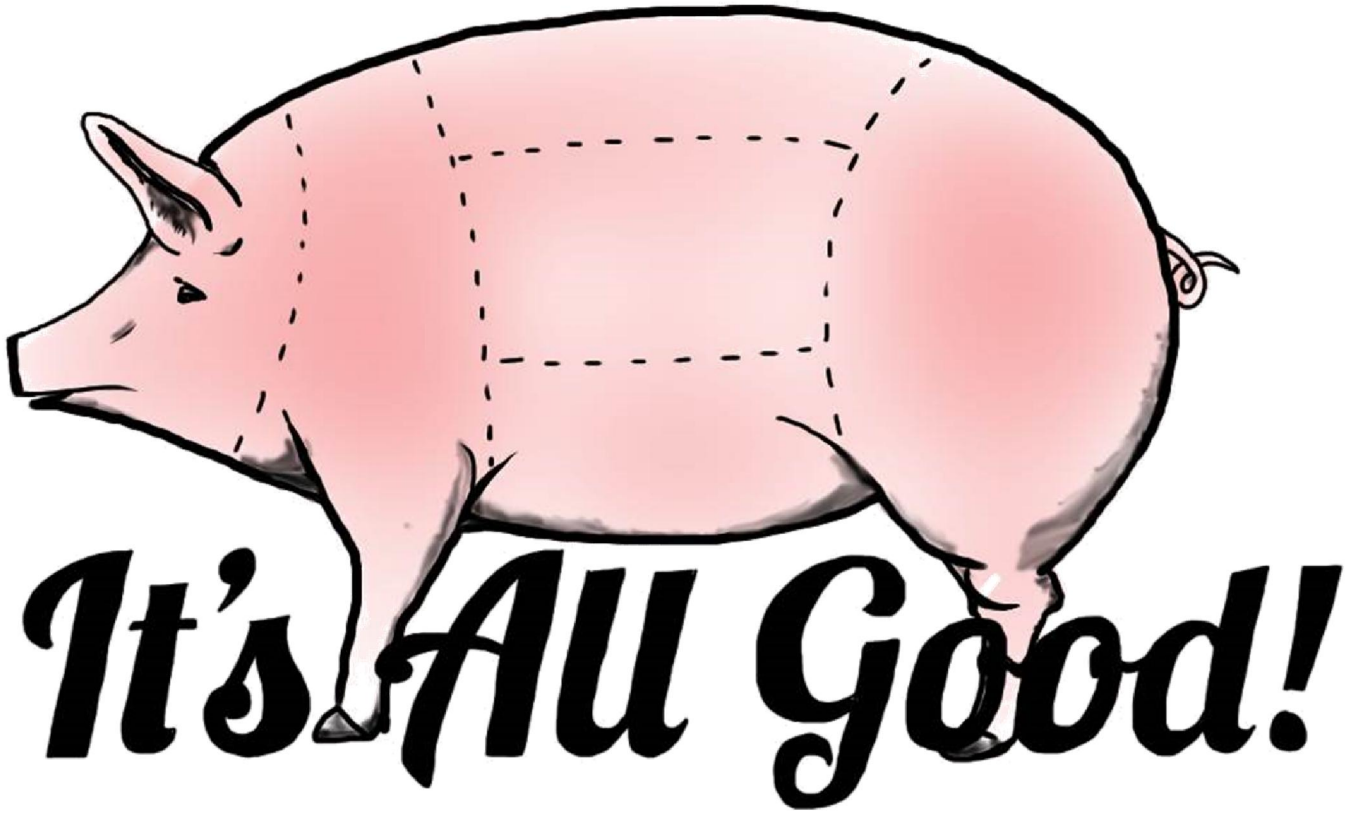
Organochlorides



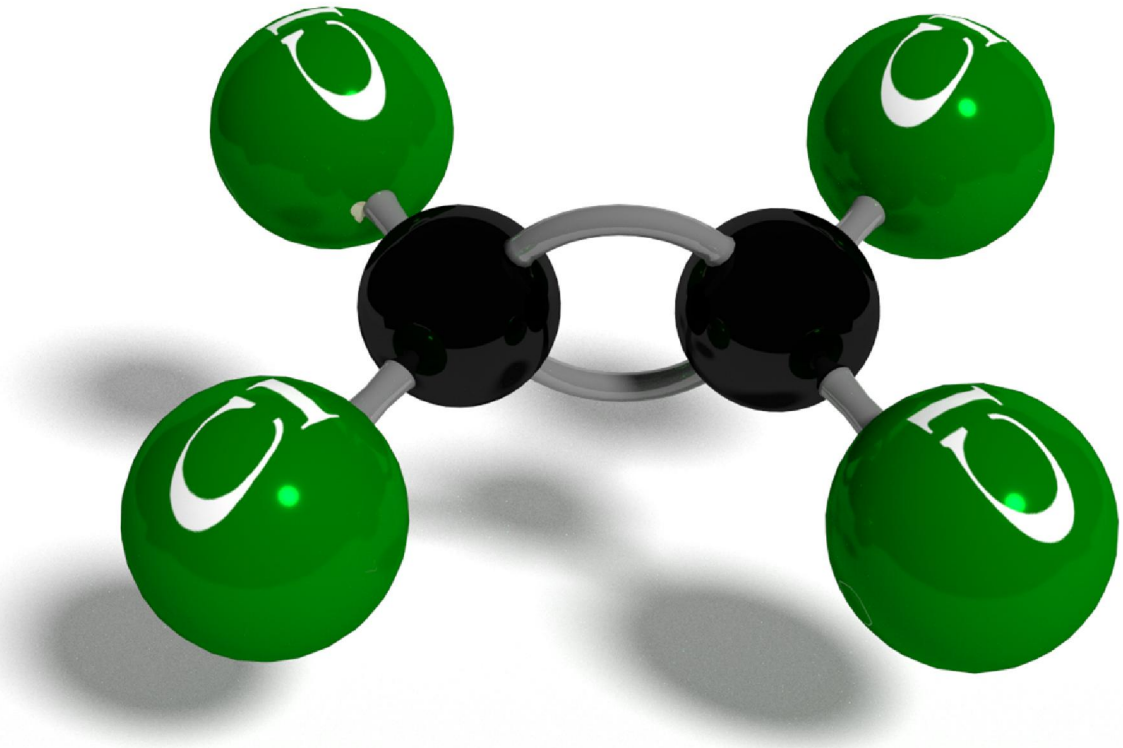
Chlorine as an Oxidant



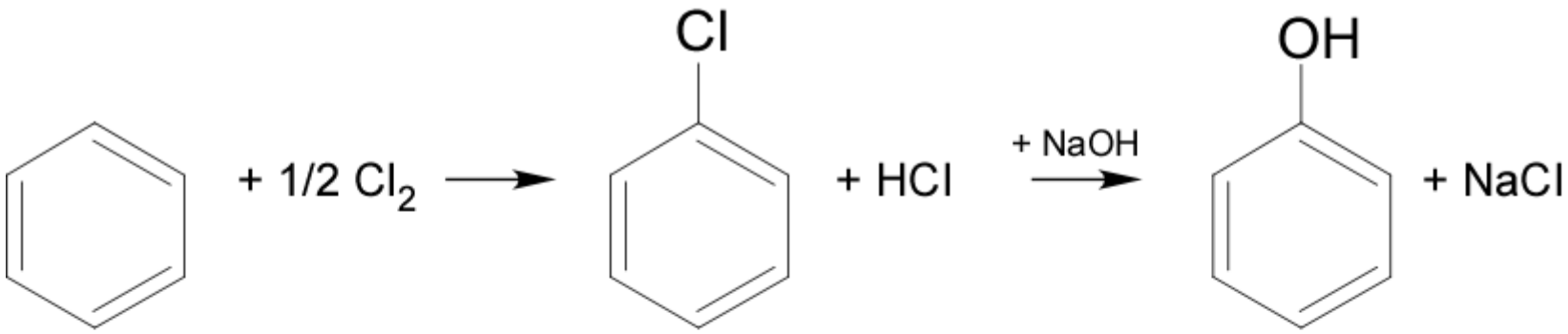
All Reaction Products Find Uses



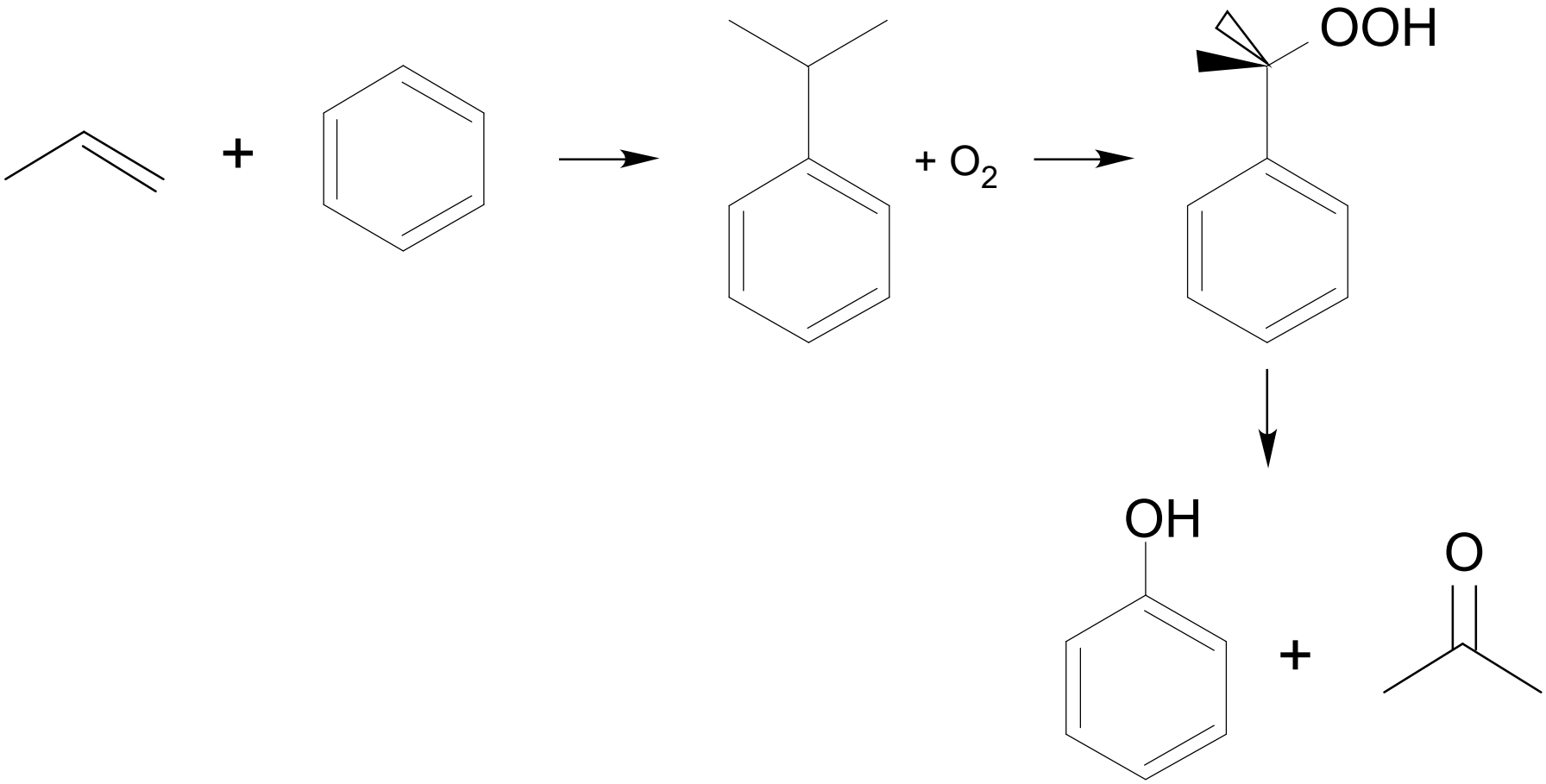
Perchloroethylene



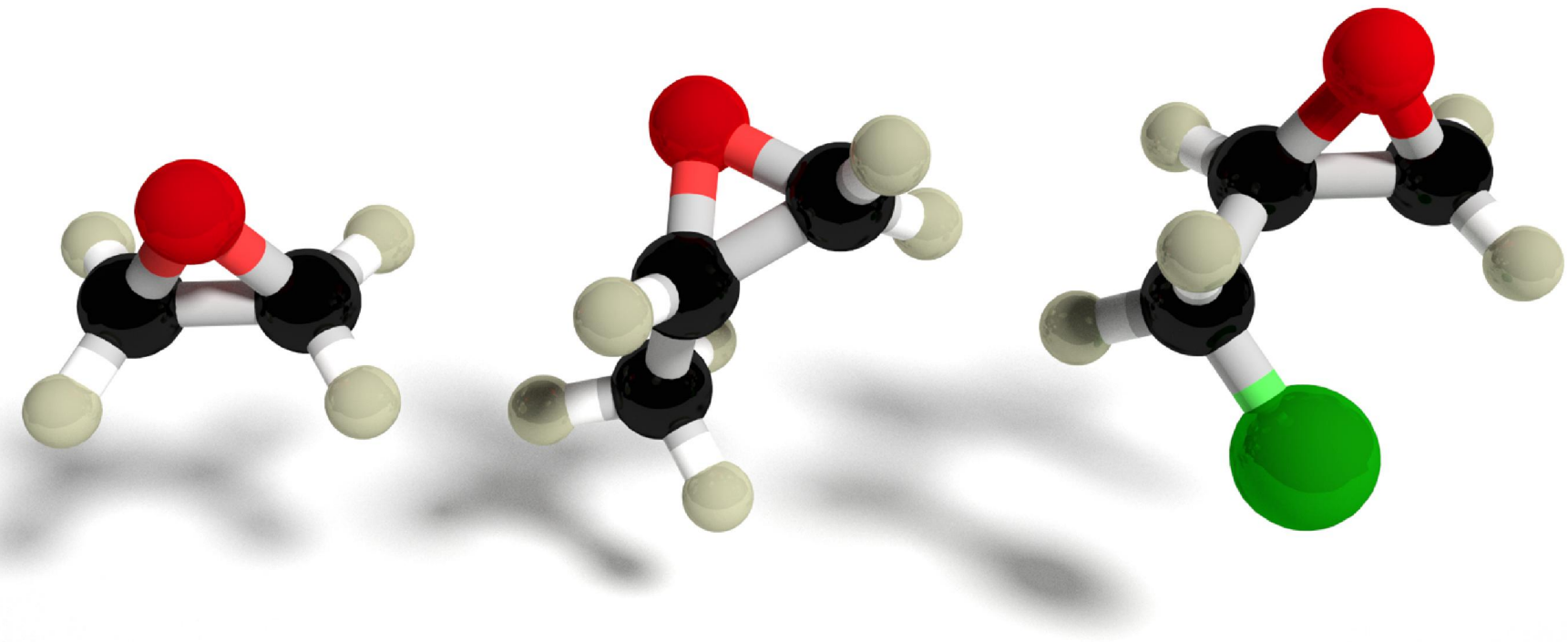
Chlorine as an Oxidant



Phenol Today

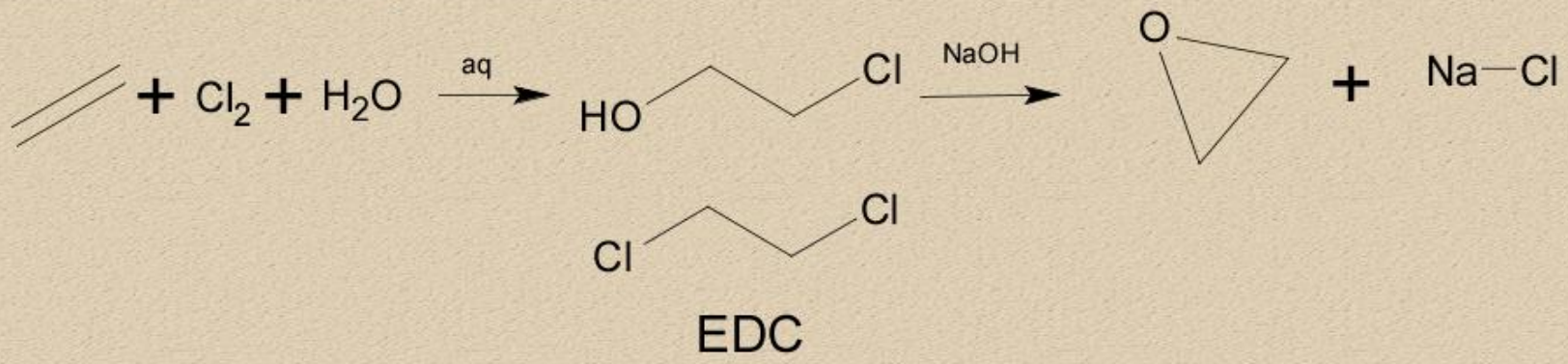


Epoxides



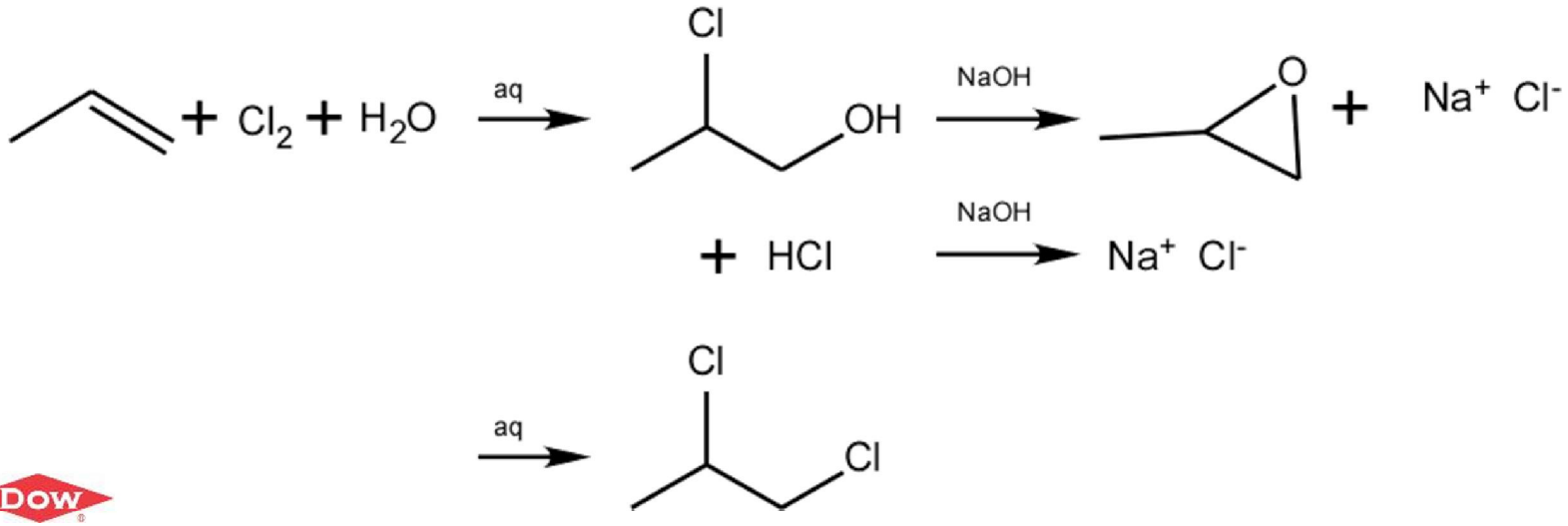
Chlorohydrin Chemistry

Clorohydrin Ethylene Oxide



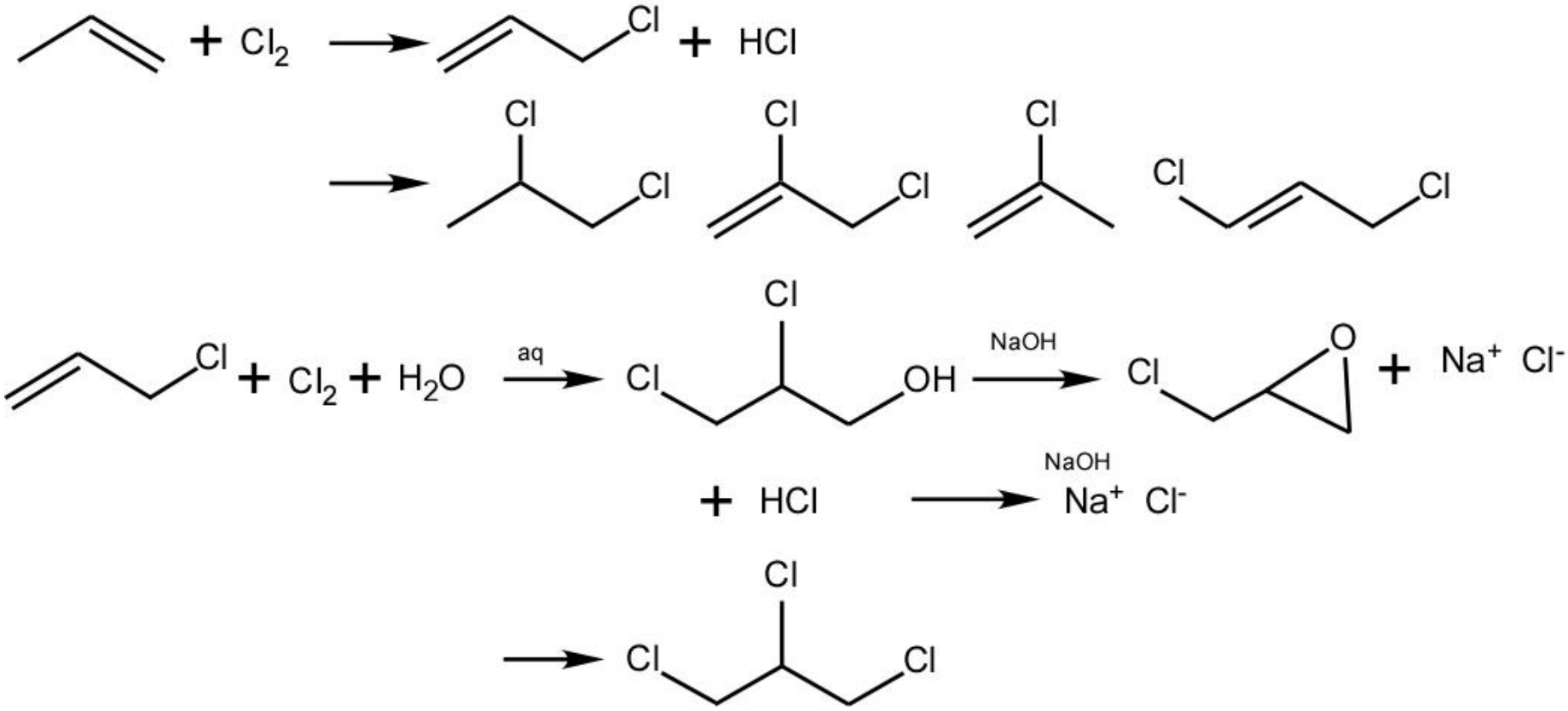
1915-1975

Chlorohydrin Propylene Oxide

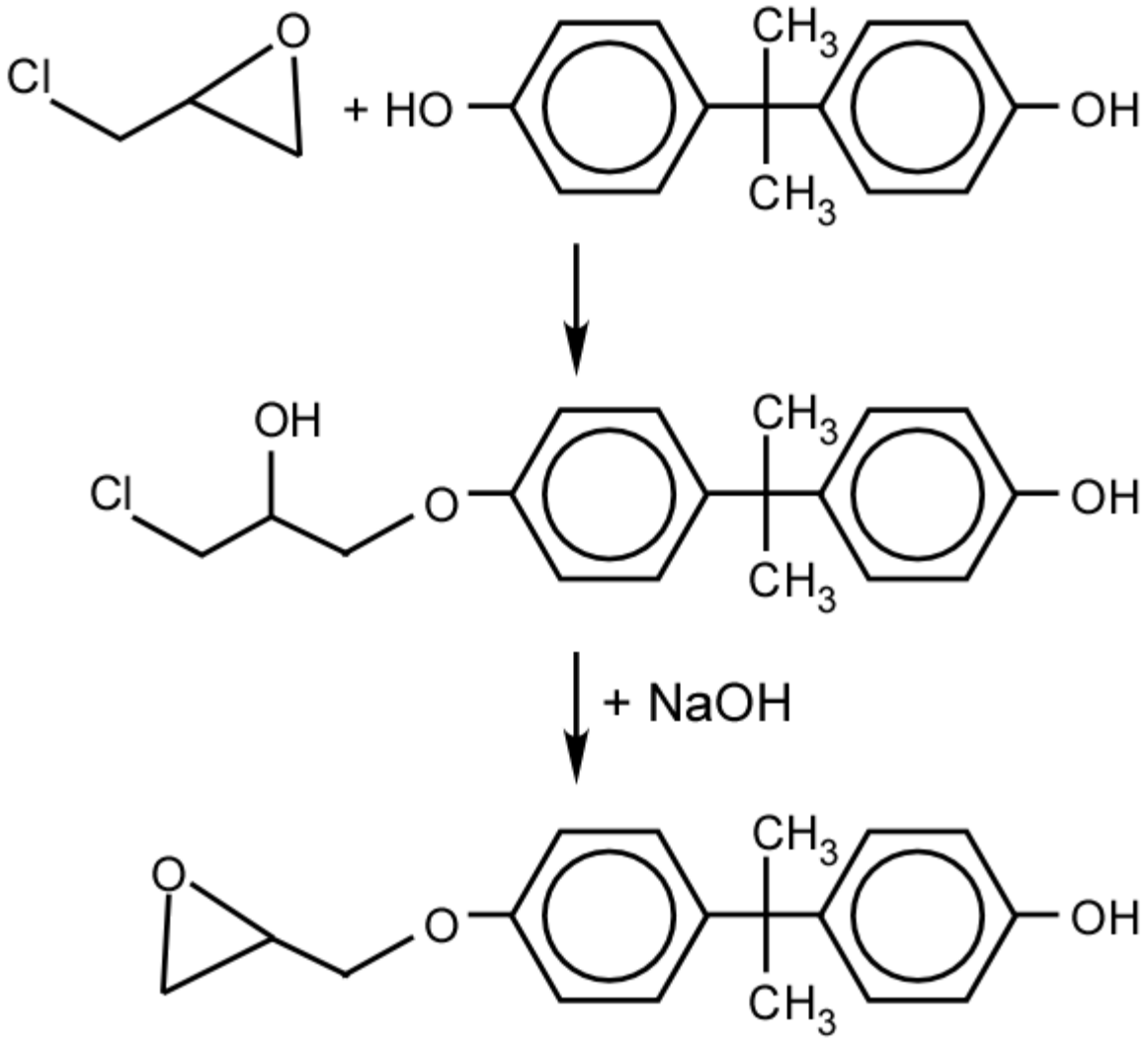


More Chlorohydrin Chemistry

Chlorohydrin Epichlorohydrin

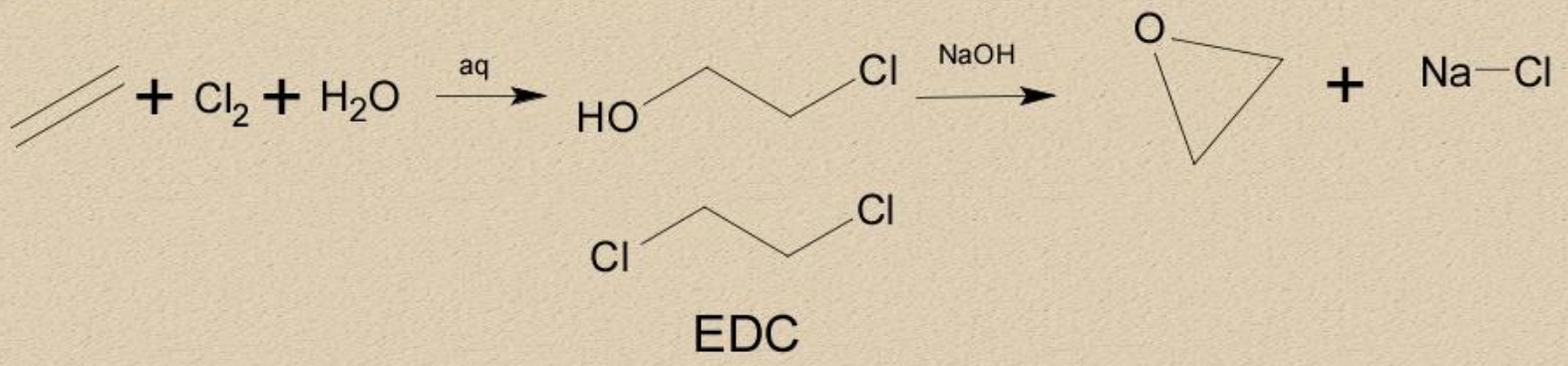


Epoxy Resins



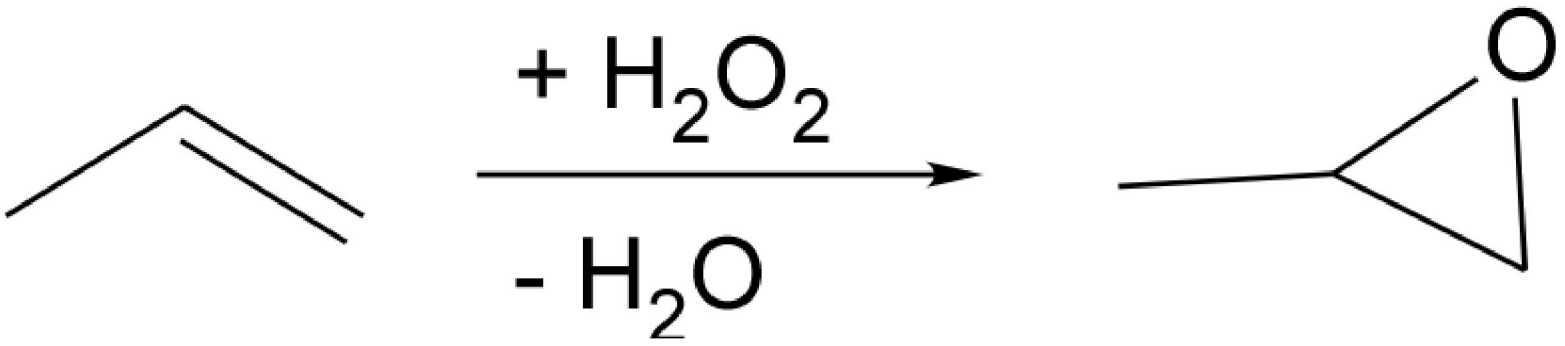
Direct Oxidation

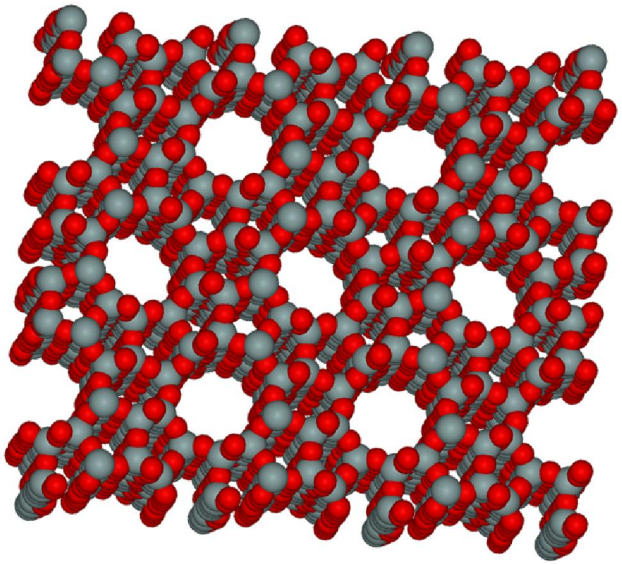
Clorohydrin Ethylene Oxide



Direct Oxidation Ethylene Oxide

Hydroperoxidation



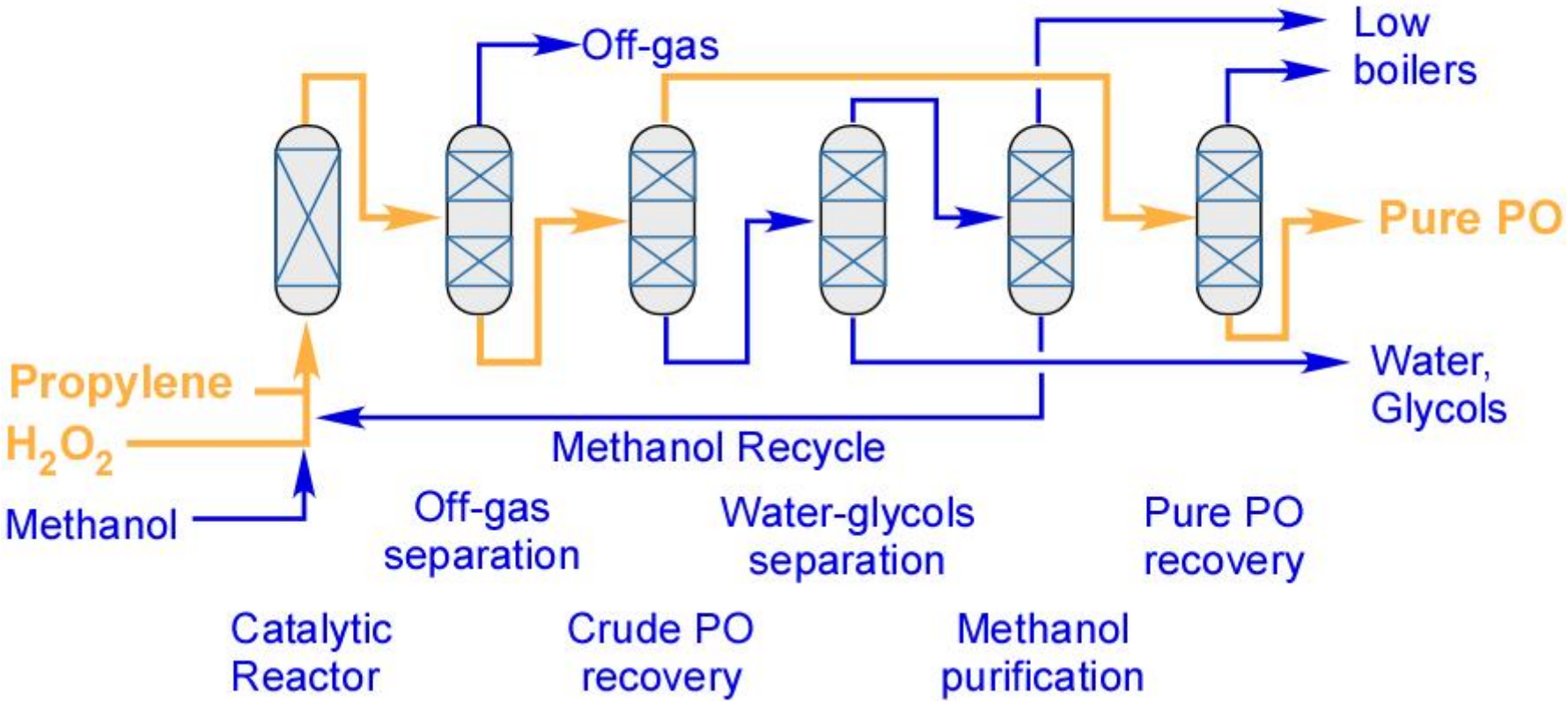


titanium silicate catalyst

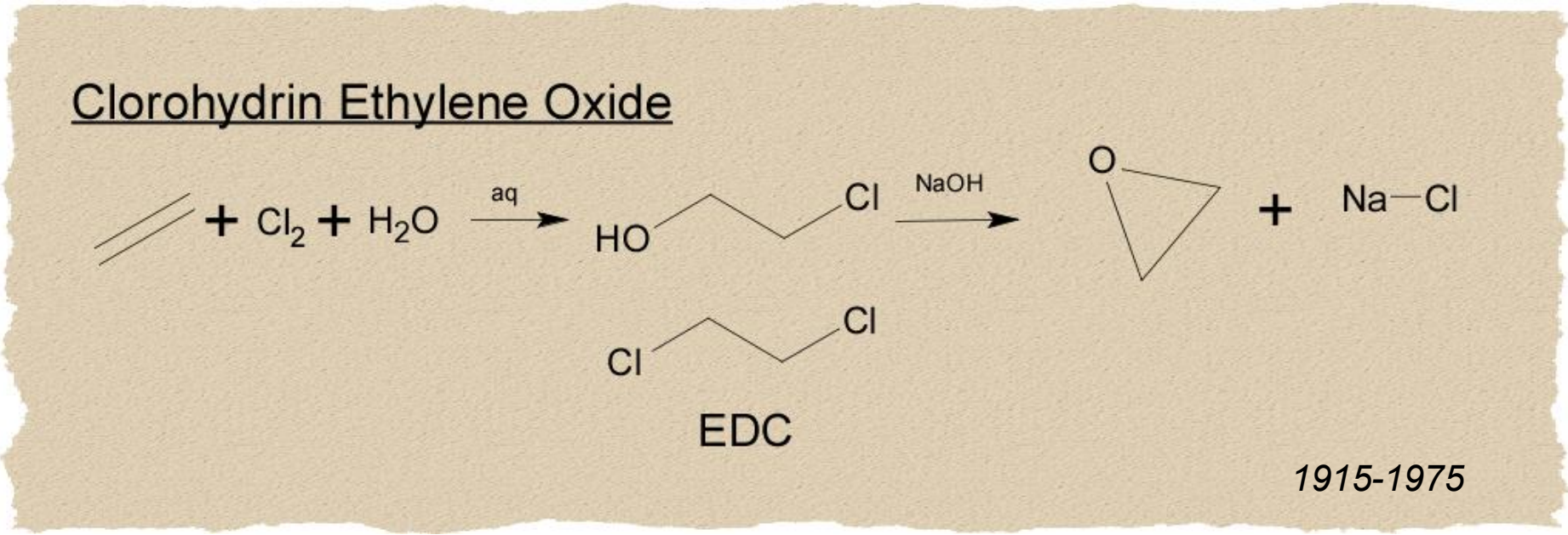
0.5 nm pores

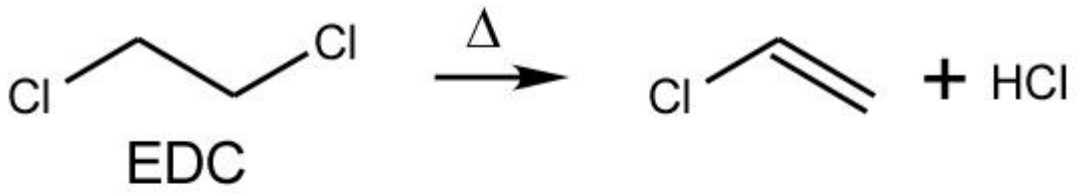
suitable for packed bed reactor

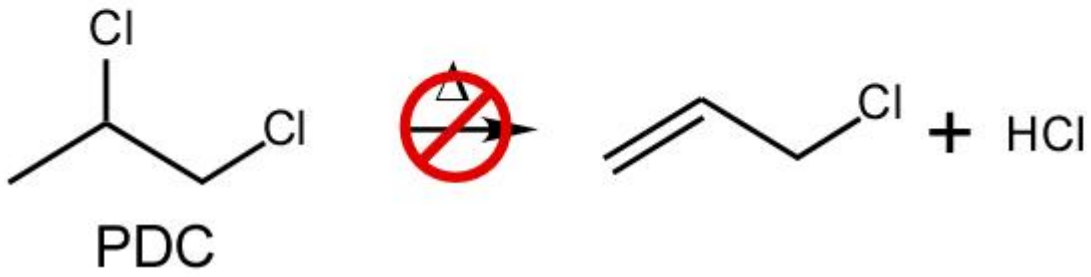
Simplified Process Flowsheet



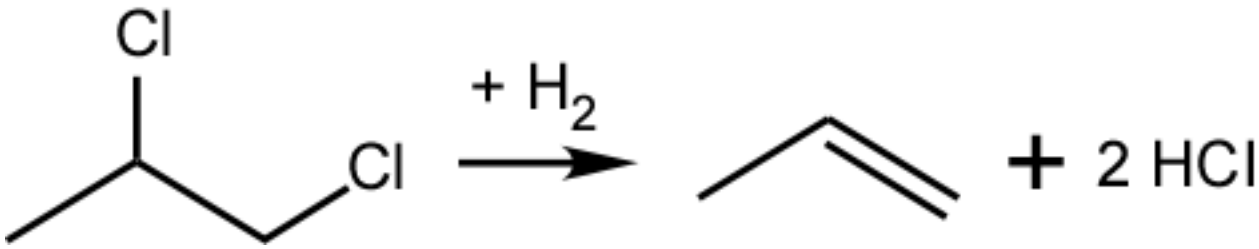
Chlorohydrin Chemistry







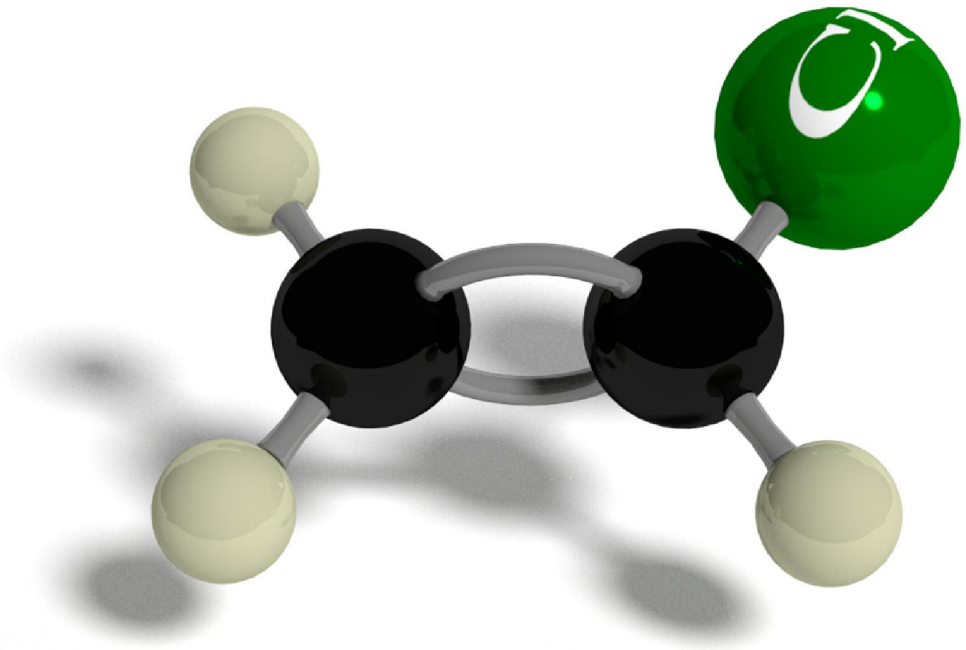
PDC Hydro

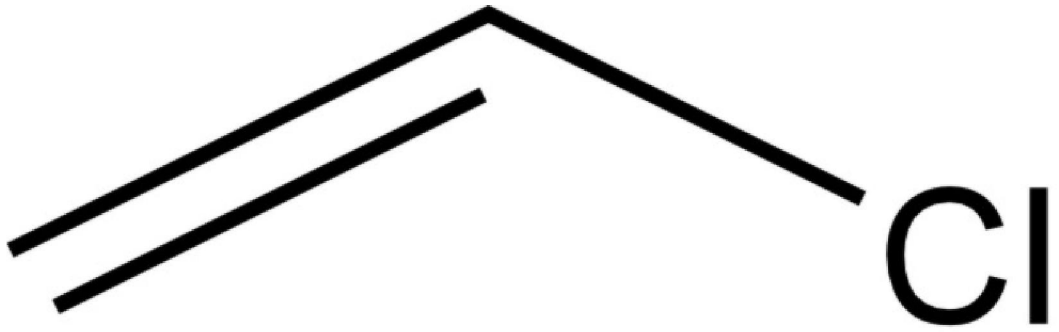


PtCu catalyst developed by Larry Ito

Carbon supported

Vinyl Chloride



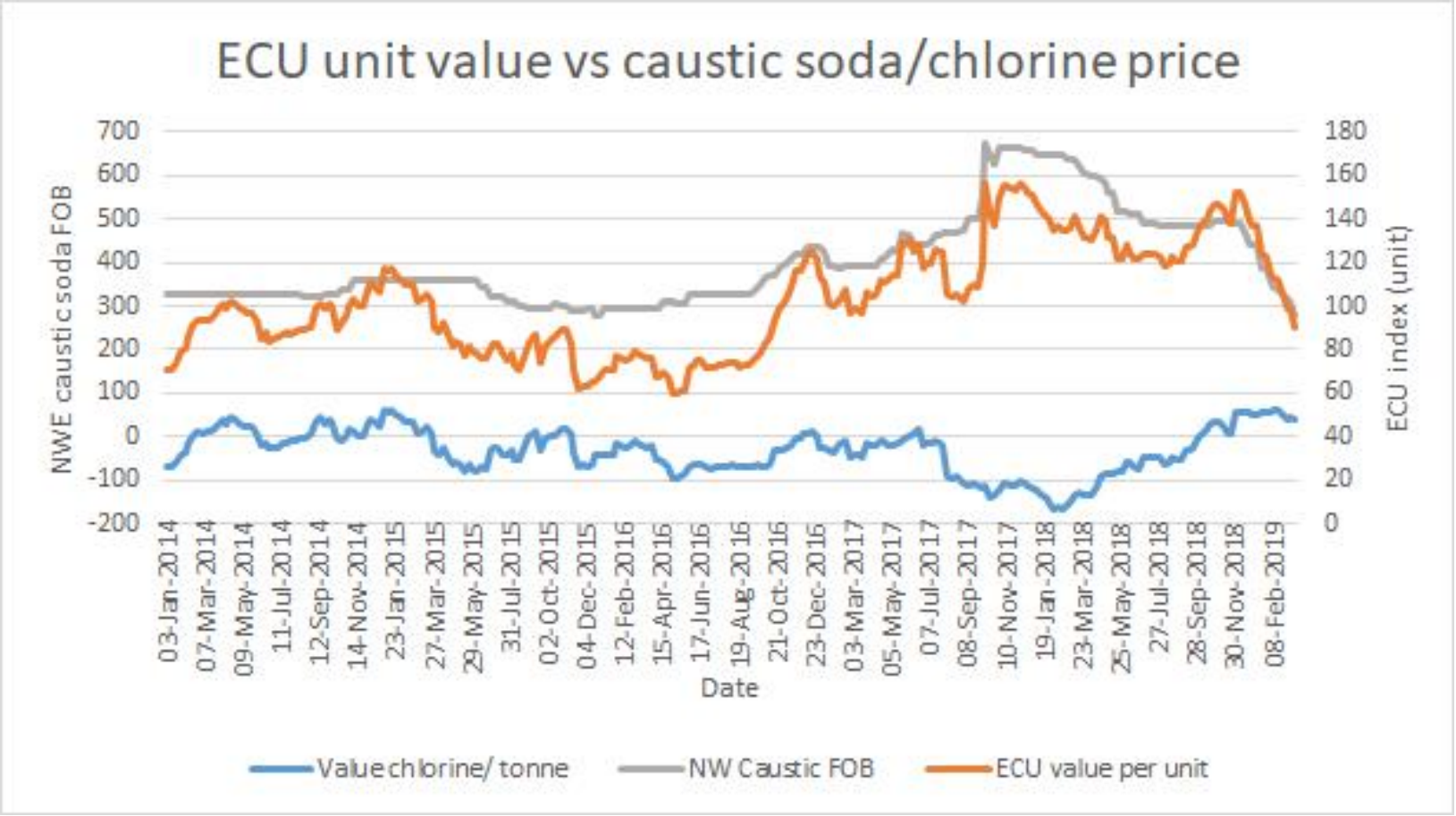


Vinyl Chloride Monomer(VCM)

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

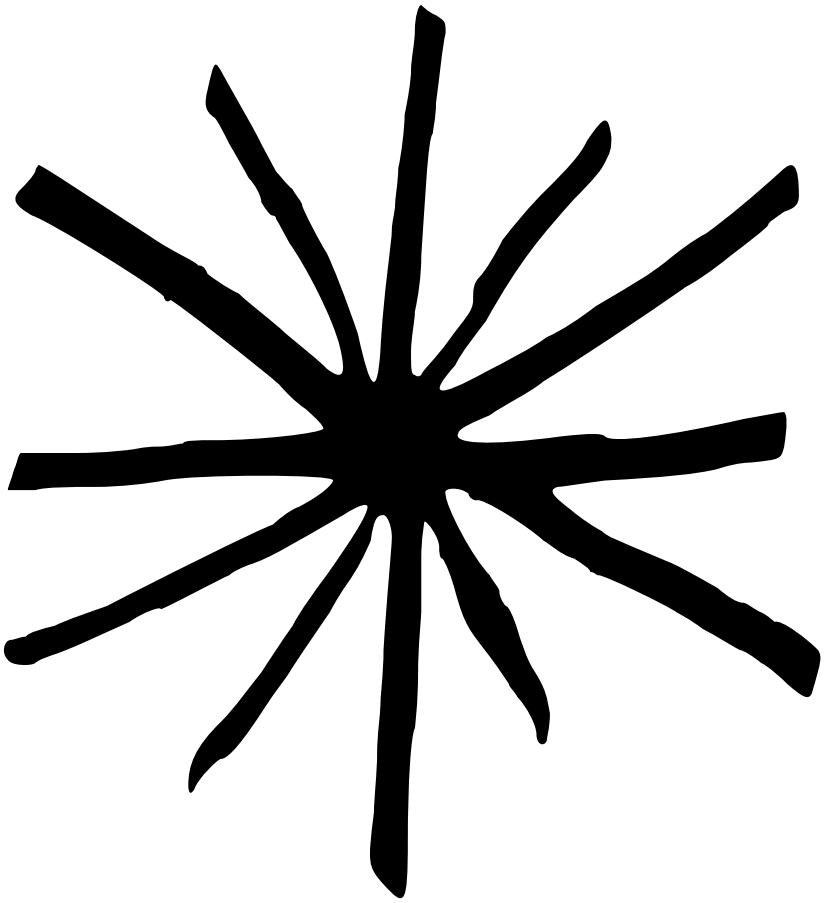
Source: Chemical Week product focus

ECU Pricing

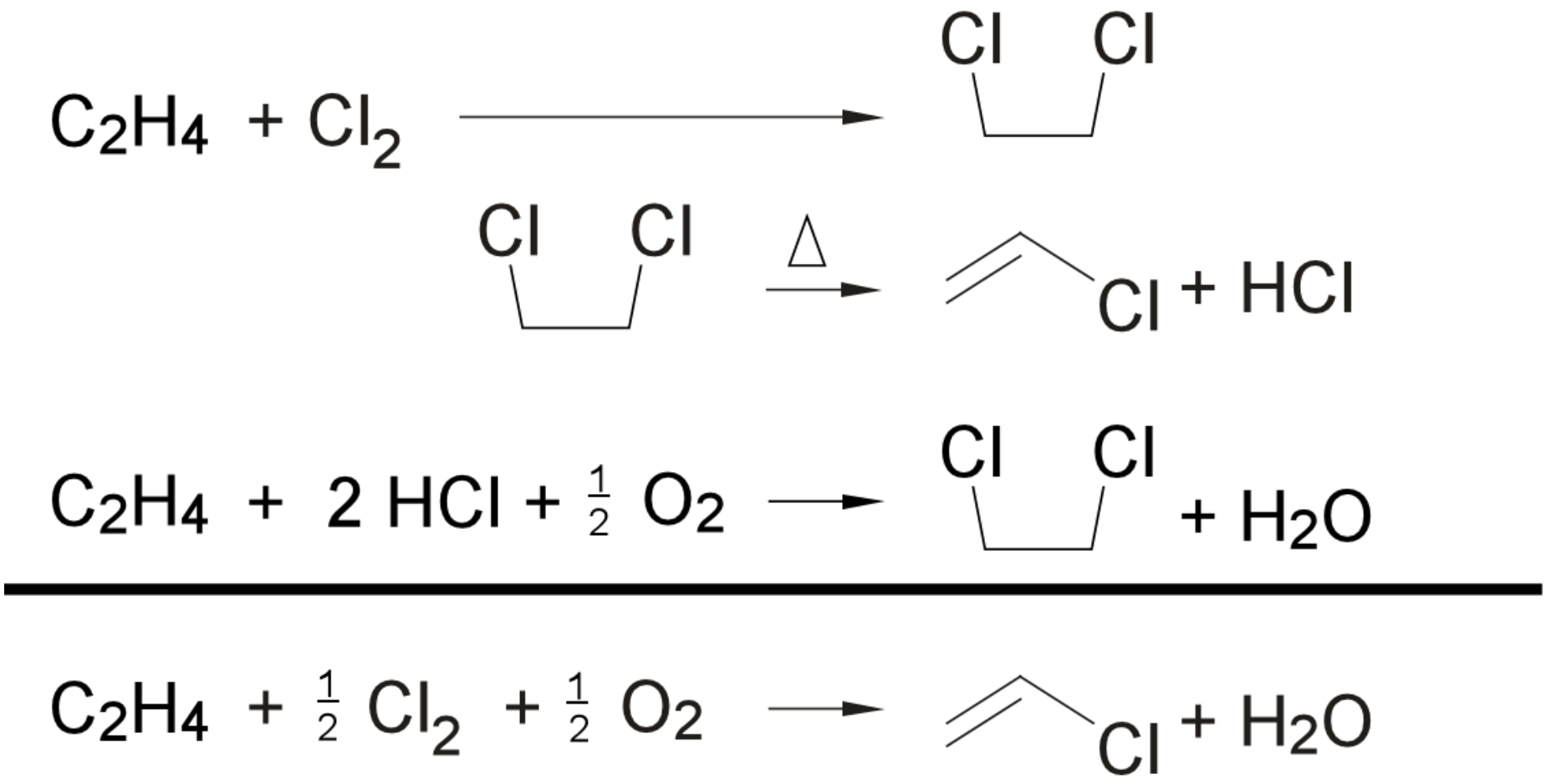


icis.com/explore/resources/news/2019/03/21/10336962/insight-european-ecu-values-fall-to-the-lowest-level-since-2016/

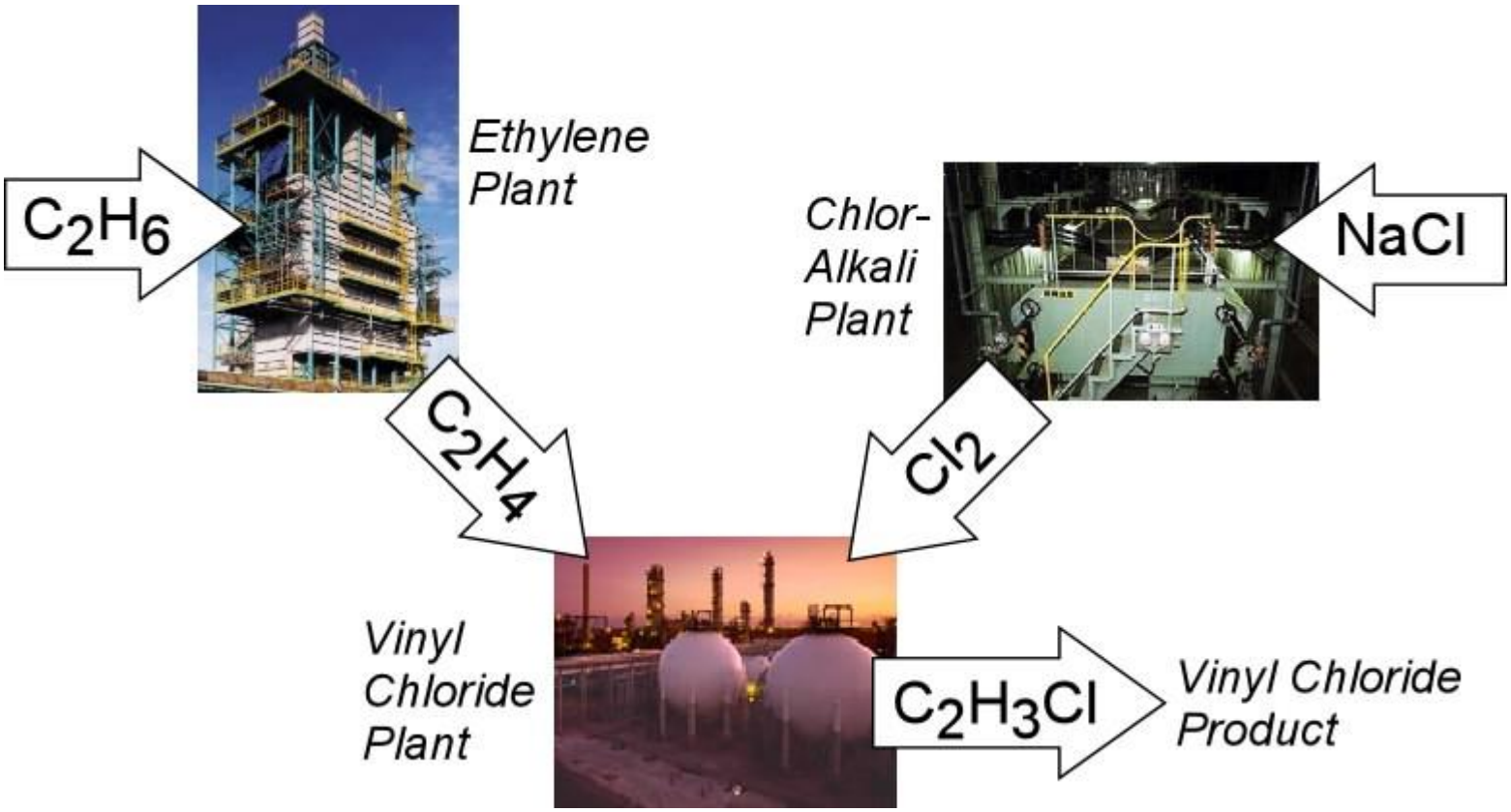
Breakfast of Champions



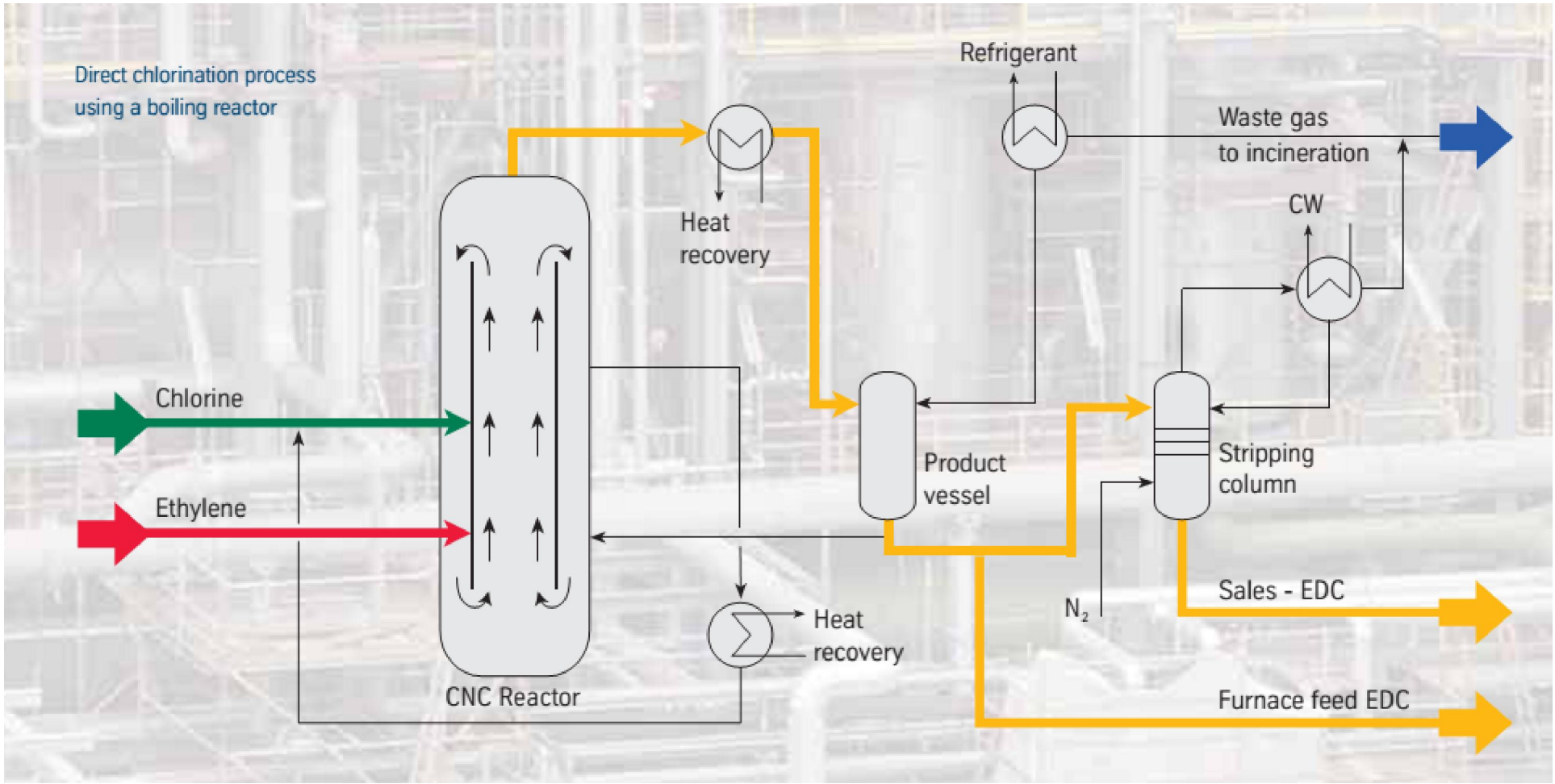
Conventional Production



Conventional VCM



Direct Chlorination



Vinnolit

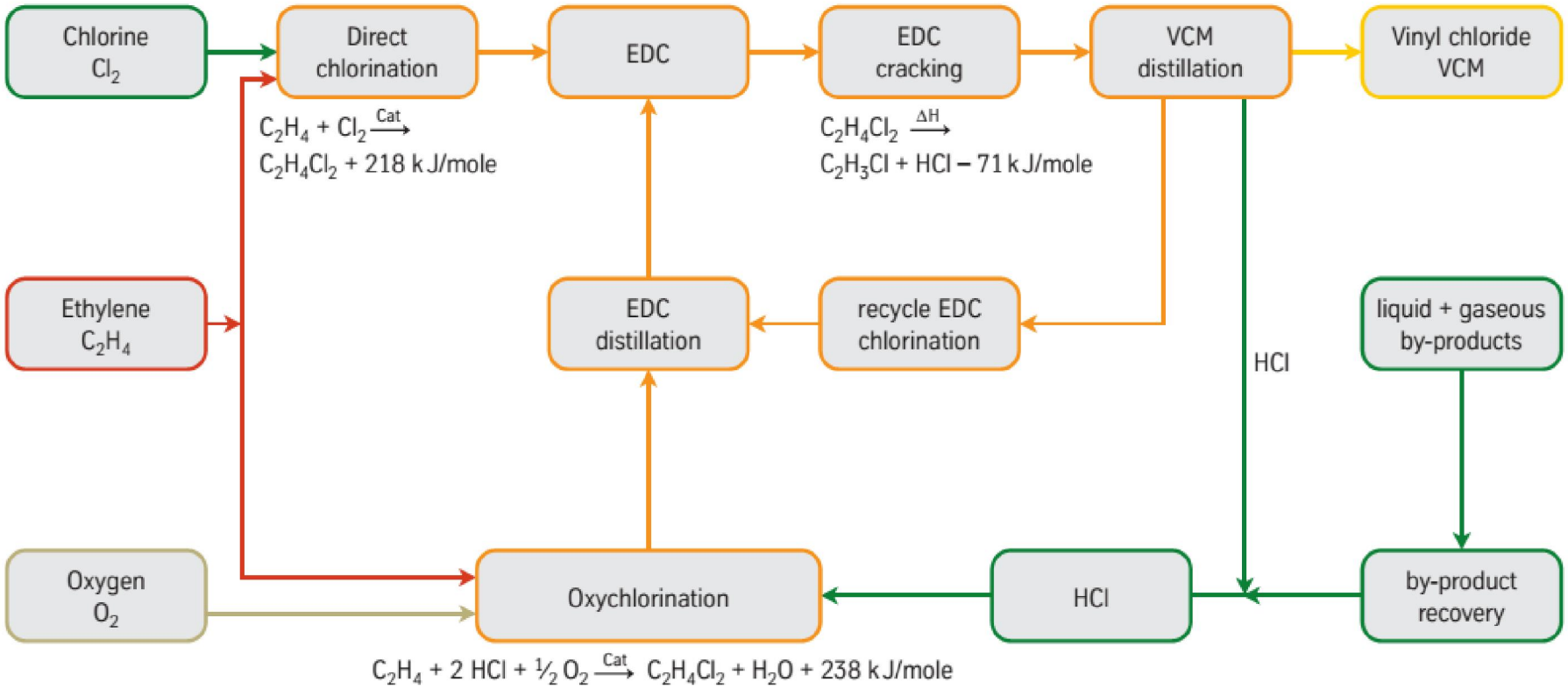
Uhde ThyssenKrupp

DOW

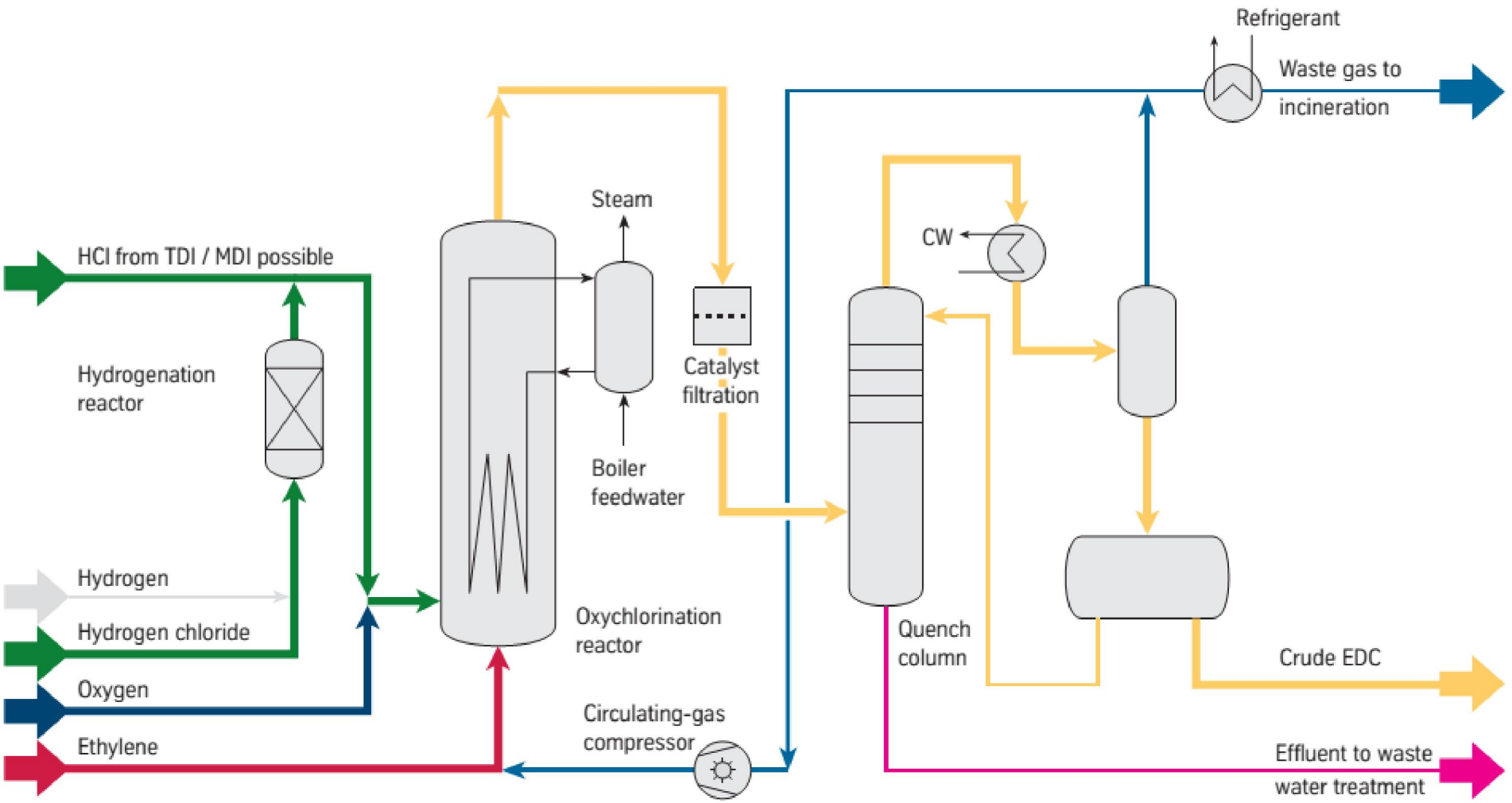
More Detail

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



Oxychlorination

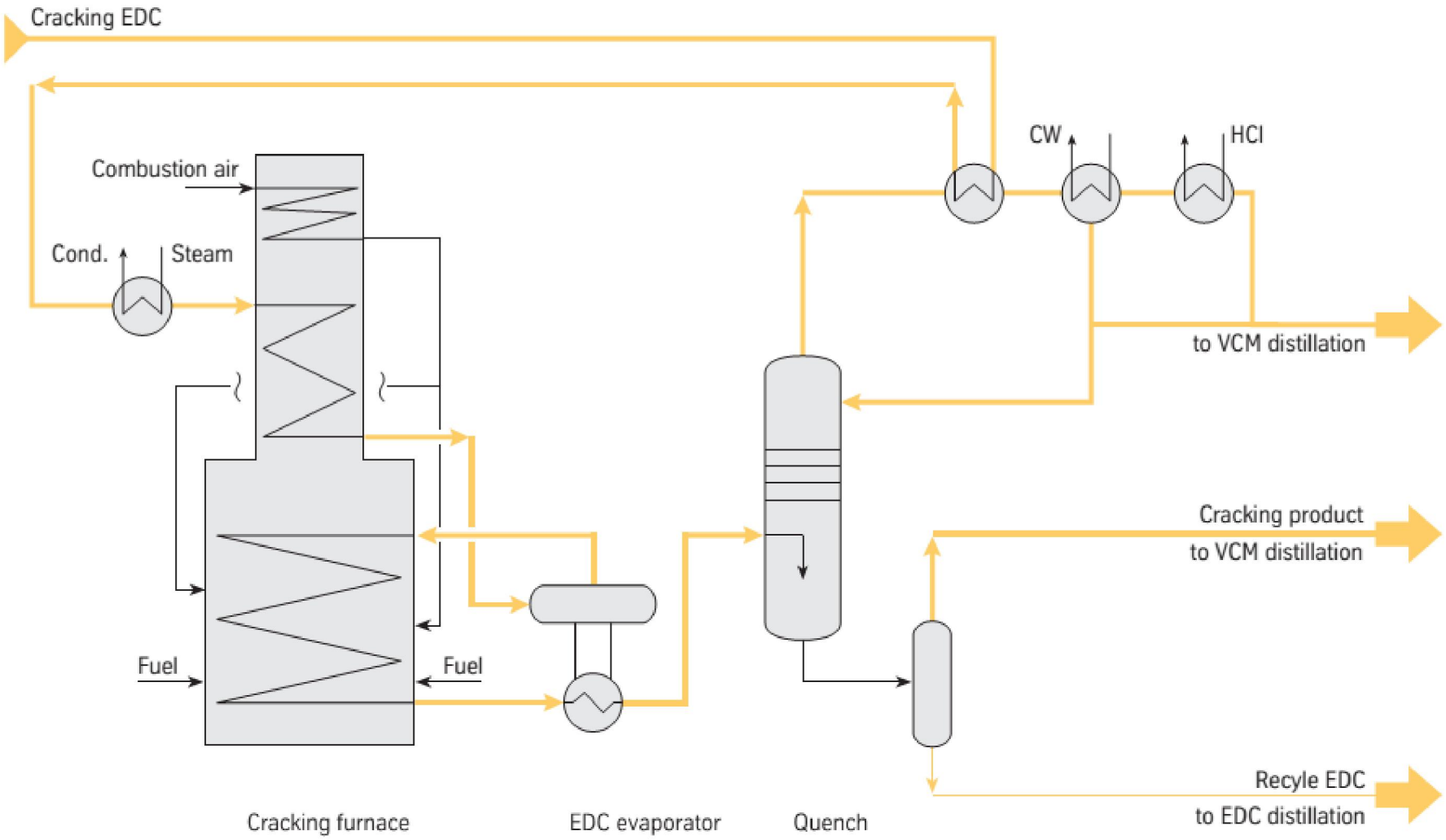


Vinnolit

Uhde
ThyssenKrupp

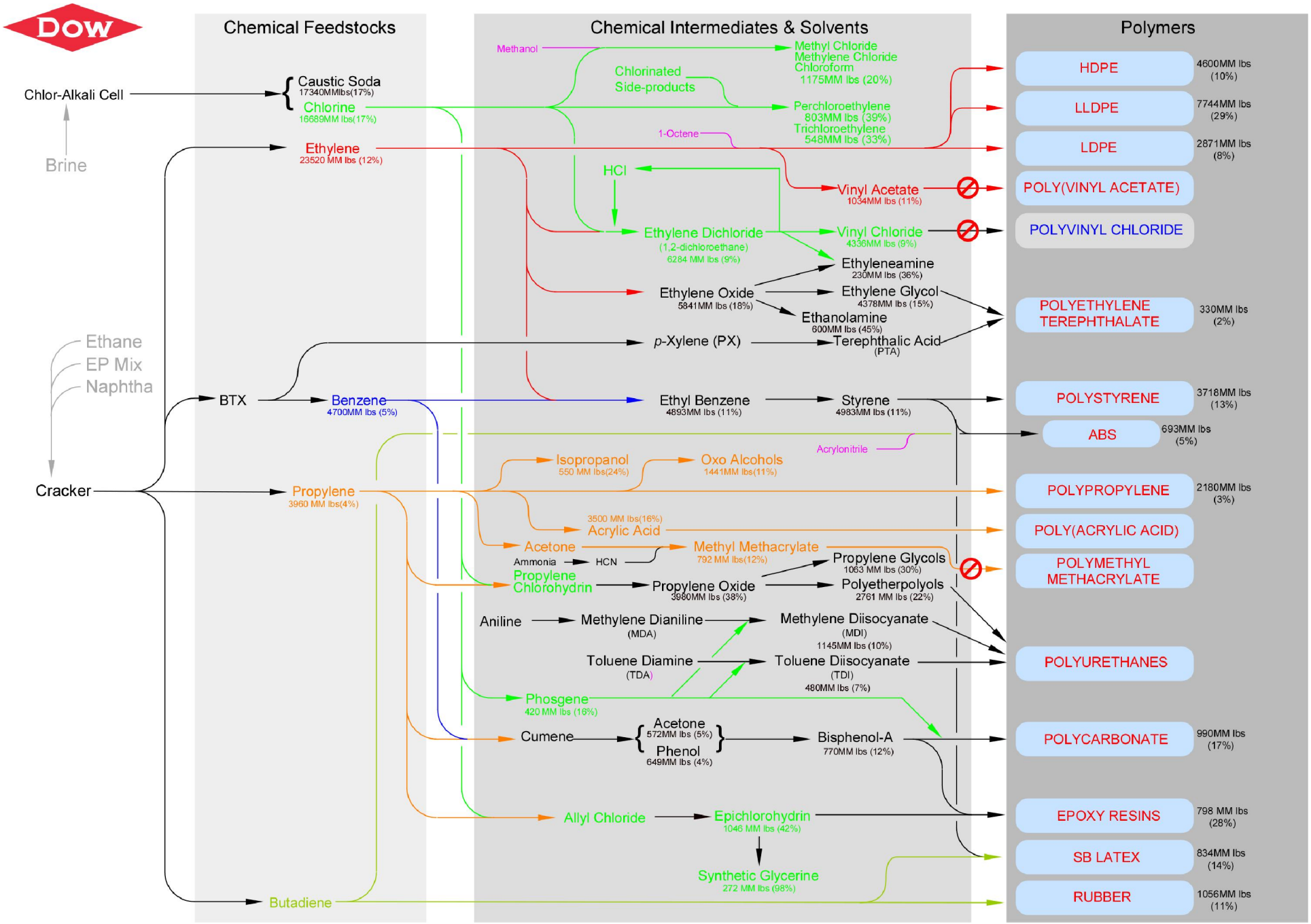
DOW

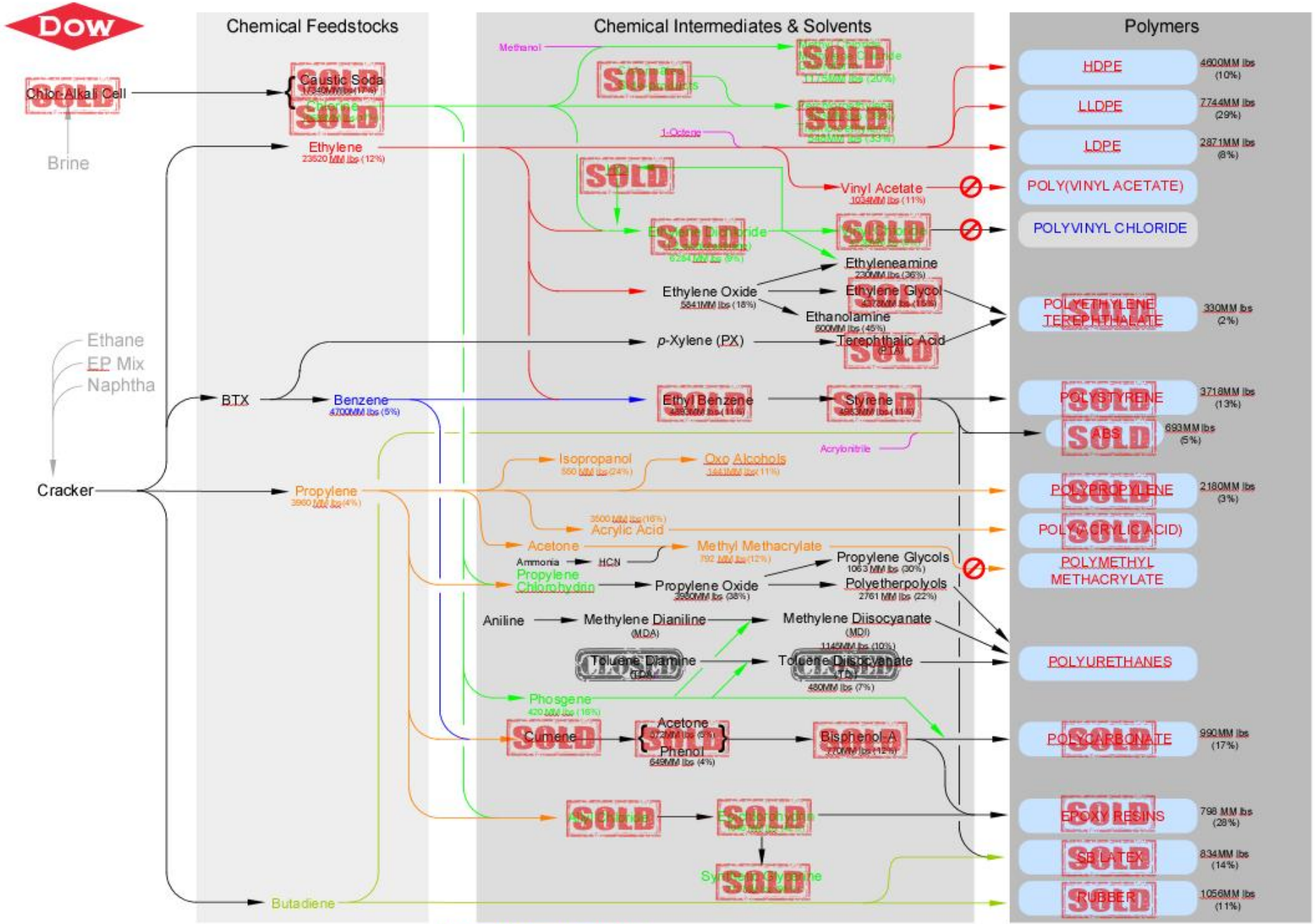
Cracking



Vinnolit Uhde ThyssenKrupp

DOW


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 Glycols
1063 MM lbs (30%)
Propylene
Chlorohydrin
Propylene Oxide
3980MM lbs (38%)
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


DOW
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Chemical Intermediates & Solvents
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Chlorine
Ethylene
23620 MM lbs (12%)
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EP Mix
Naphtha
Cracker
BTX
Benzene
4700MM lbs (5%)
Propylene
3960 MM lbs (4%)
Butadiene
Methanol
1-Octene
Vinyl Acetate
1034MM lbs (11%)
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Terephthalic Acid
(PTA)
Ethyl Benzene
Styrene
Acrylonitrile
Isopropanol
560 MM lbs (24%)
Oxo Alcohols
144MM lbs (11%)
3500 MM lbs (16%)
Acrylic Acid
Acetone
Ammonia
HCN
Methyl Methacrylate
792 MM lbs (12%)
Propylene Glycols
1063 MM lbs (30%)
Propylene Chlorohydrin
Propylene Oxide
3960MM lbs (38%)
Polyetherpolyols
2761 MM lbs (22%)
Aniline
Methylene Dianiline
(MDA)
Methylene Diisocyanate
(MDI)
1145MM lbs (10%)
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Toluene Diisocyanate
(TDI)
480MM lbs (7%)
Phosgene
420 MM lbs (16%)
Cumene
Acetone
572MM lbs (8%)
Phenol
648MM lbs (4%)
Bisphenol A
Epichlorohydrin
Styrene Butadiene
HDPE
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POLY(VINYL ACETATE)
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POLYETHYLENE TEREPHTHALATE
330MM lbs (2%)
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RUBBER
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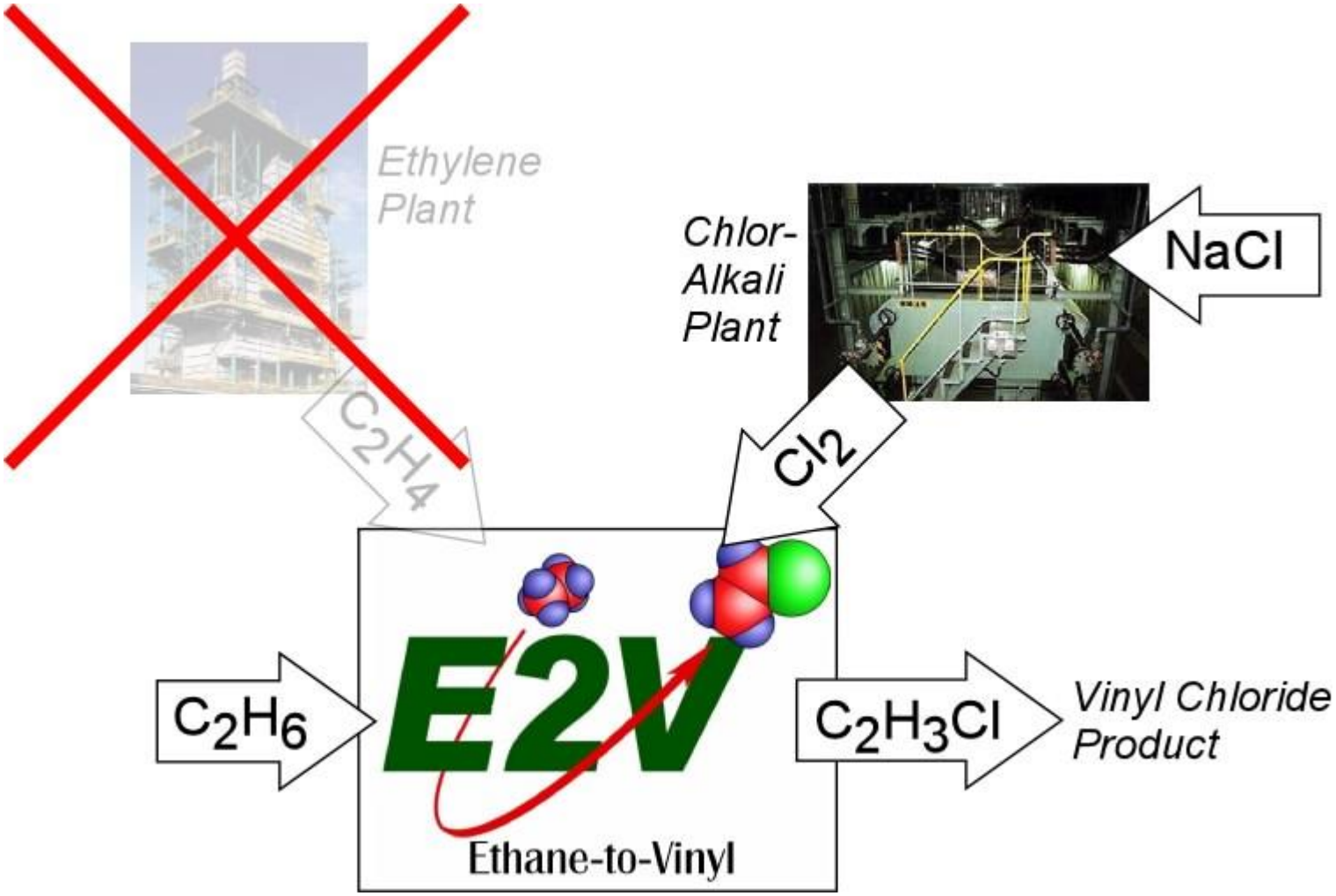
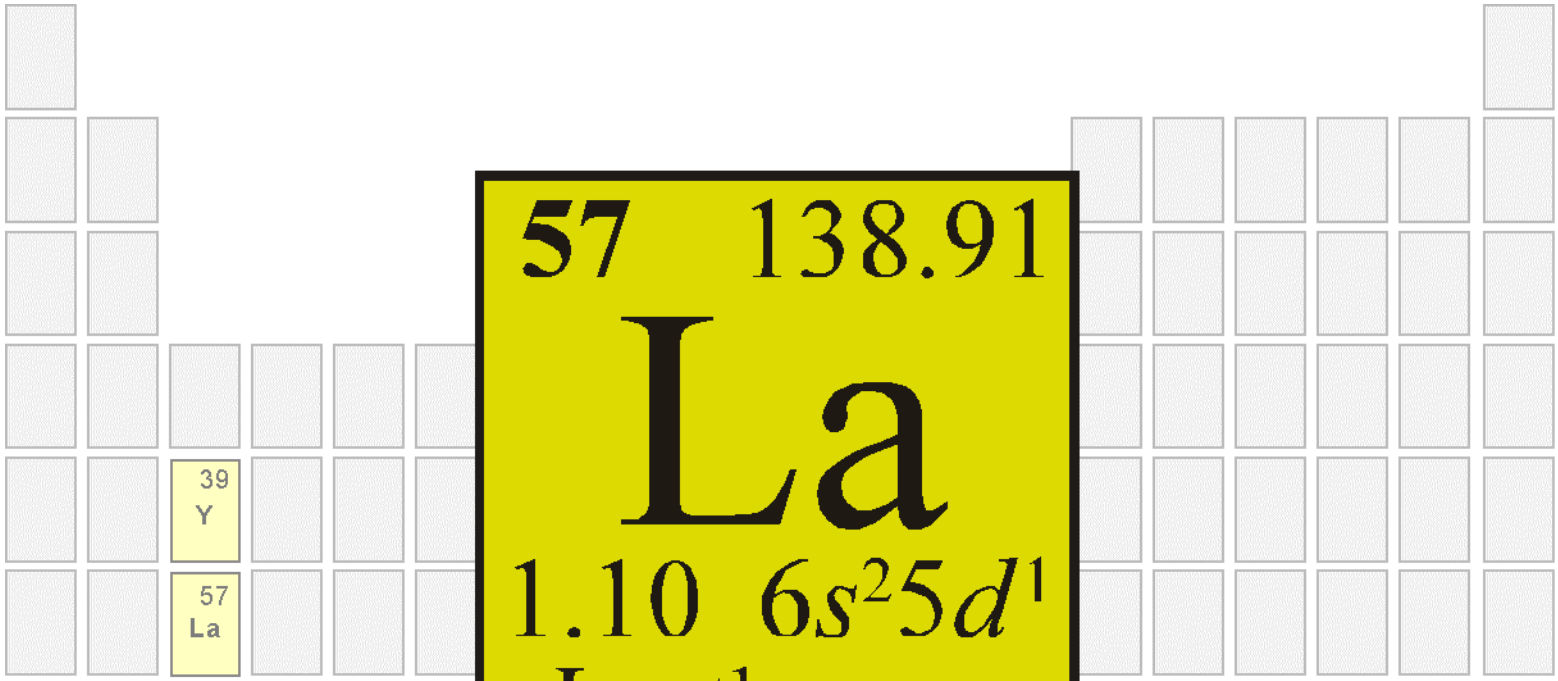
MEJ-2/2003

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

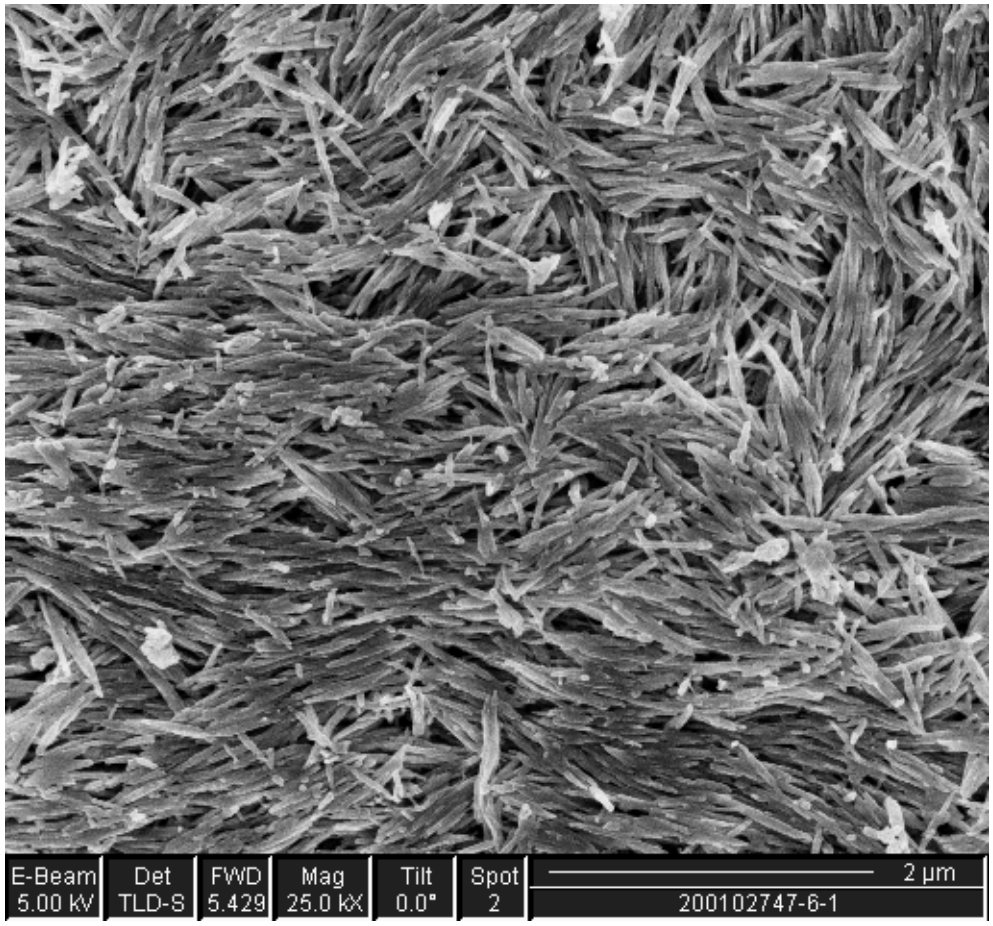
Lanthanide Catalyst



not a redox metal!

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

LaOCl

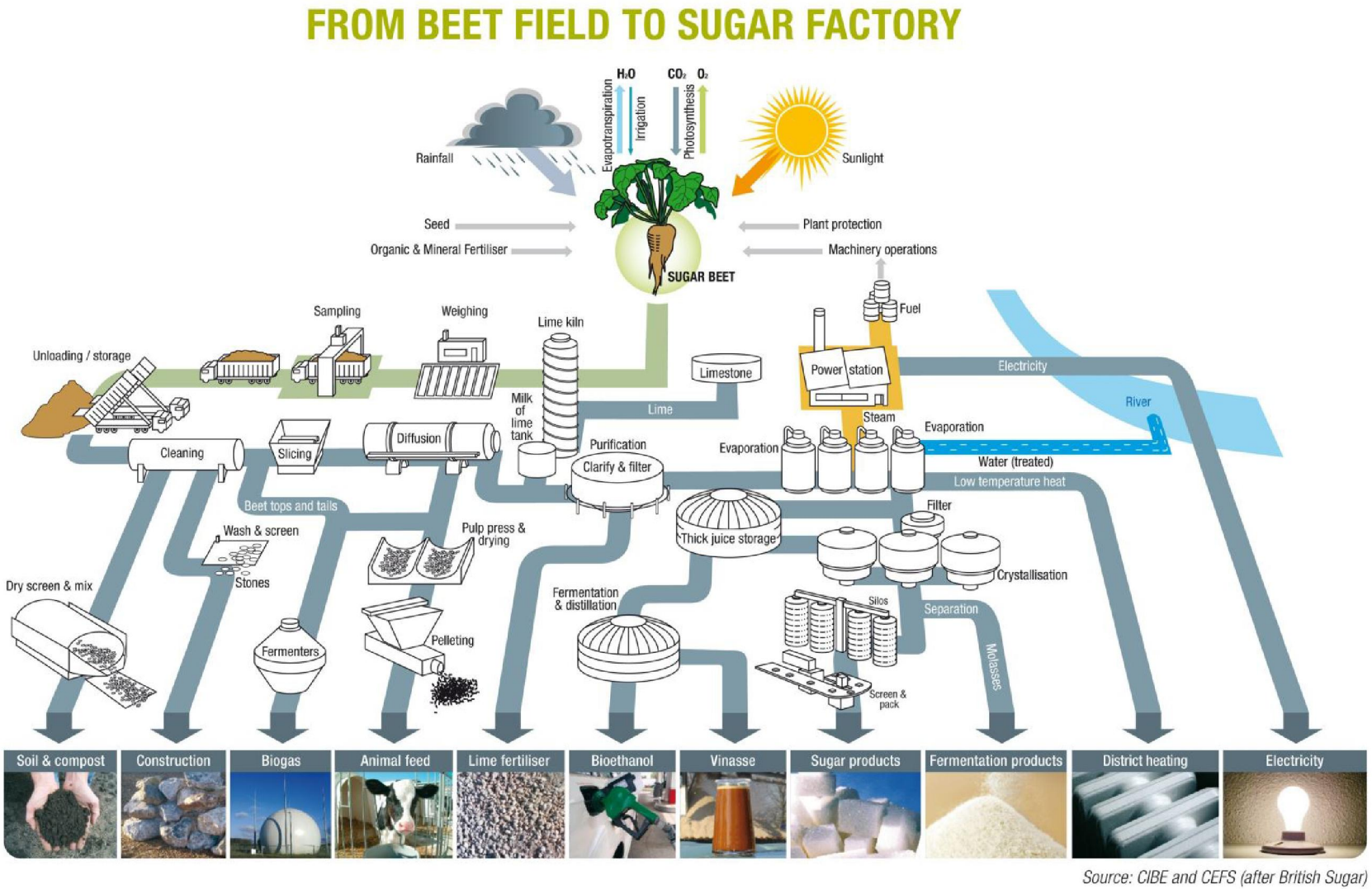

E-Beam
5.00 kV
Det
TLD-S
FWD
5.429
Mag
25.0 kX
Tilt
0.0°
Spot
2
2 µm
200102747-6-1

Fluidized Bed

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

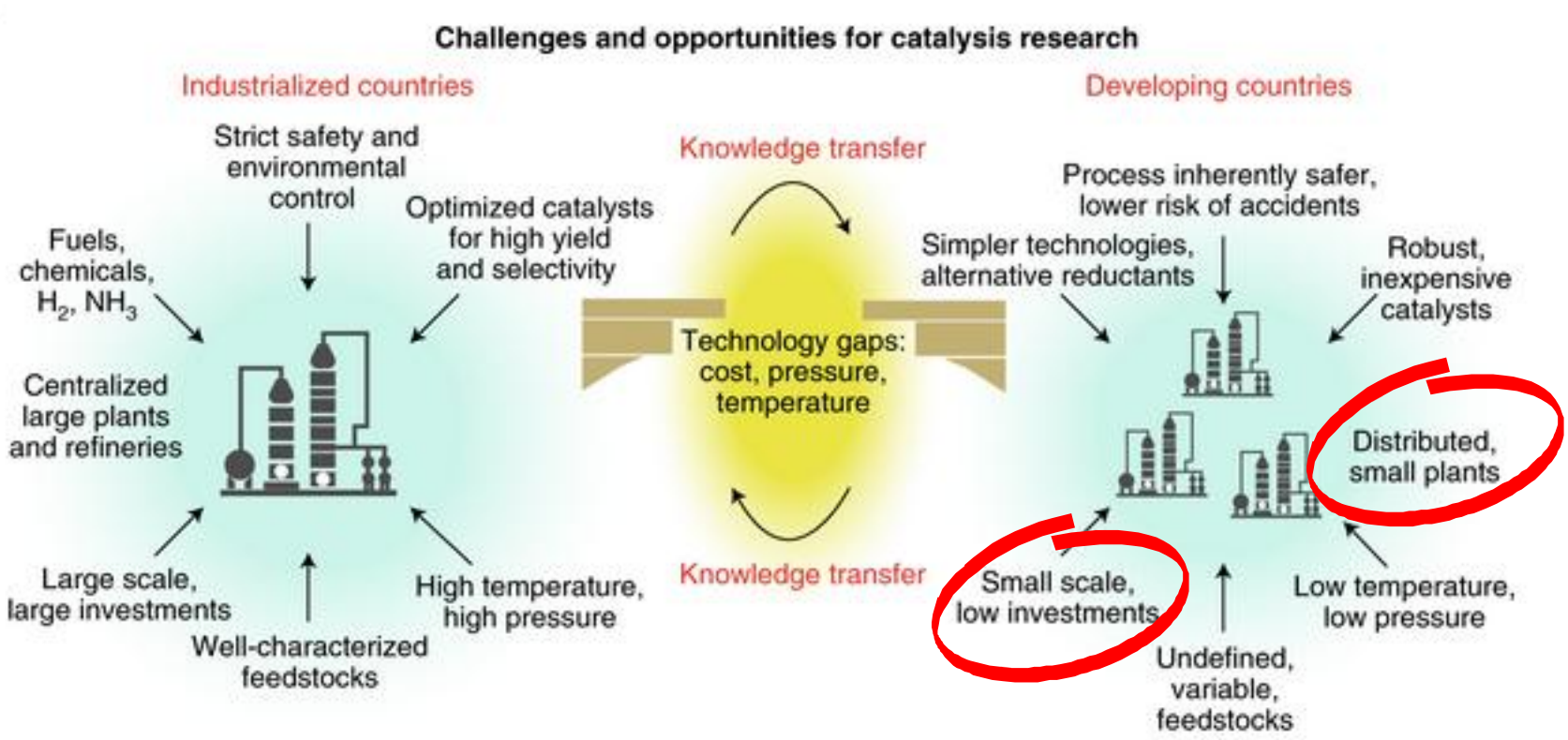
Integrated Biorefinery



Source: CIBE and CEFS (after British Sugar)

prokris.nl/production/

Distributed Manufacturing



Resasco DE, Wang B, Sabatini D. Distributed processes for biomass conversion could aid UN Sustainable Development Goals. Nature Catalysis. 2018 Oct;1(10):731.