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

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MJPhD, LLC

14 September 2021

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

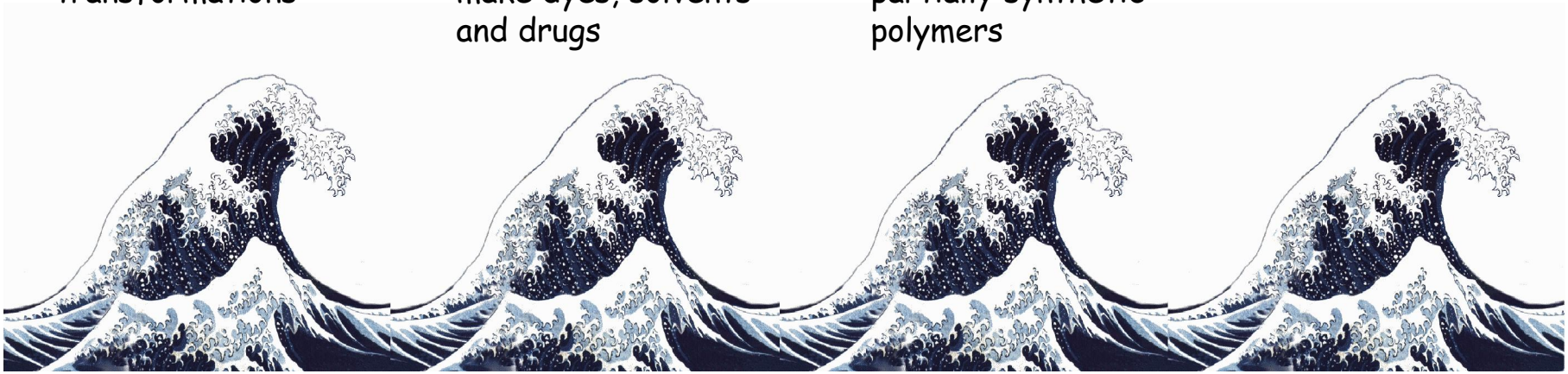
Chemical Industry Technology Waves

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

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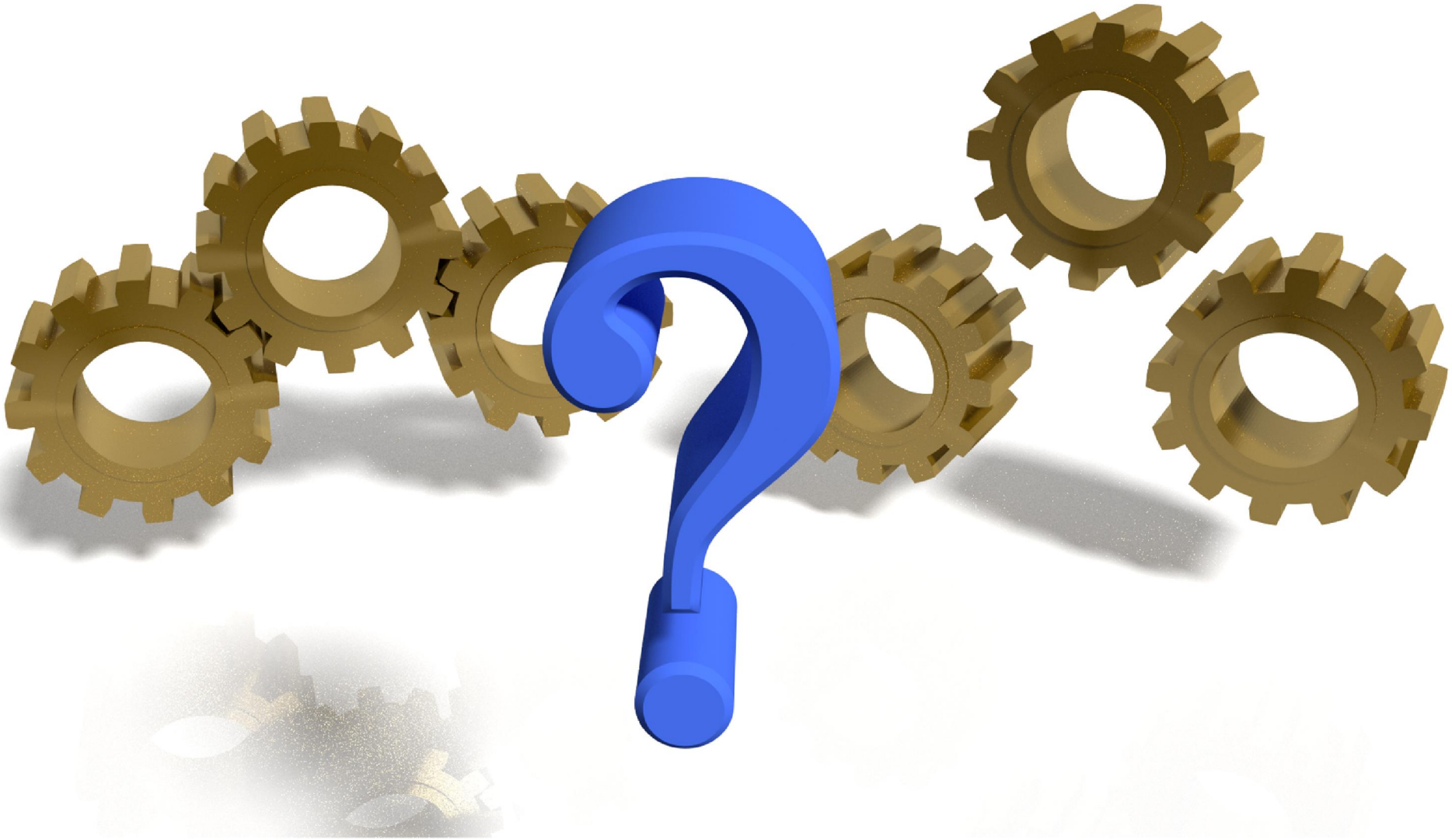
What is Integration?



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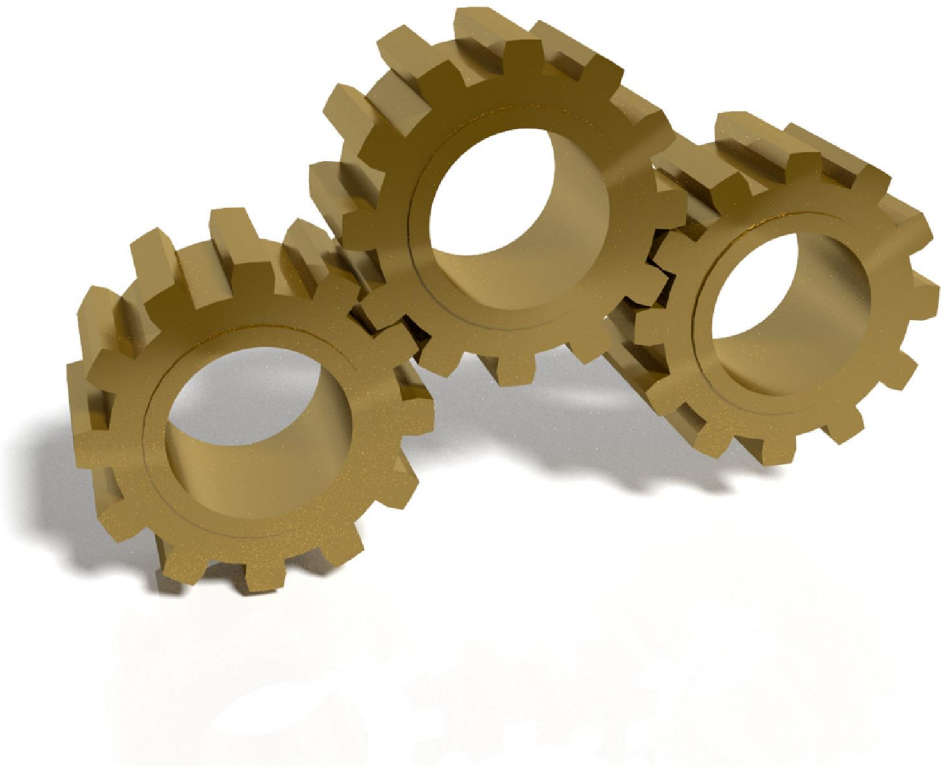
Integration



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

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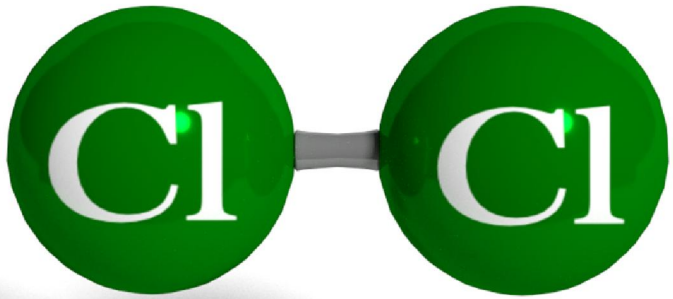

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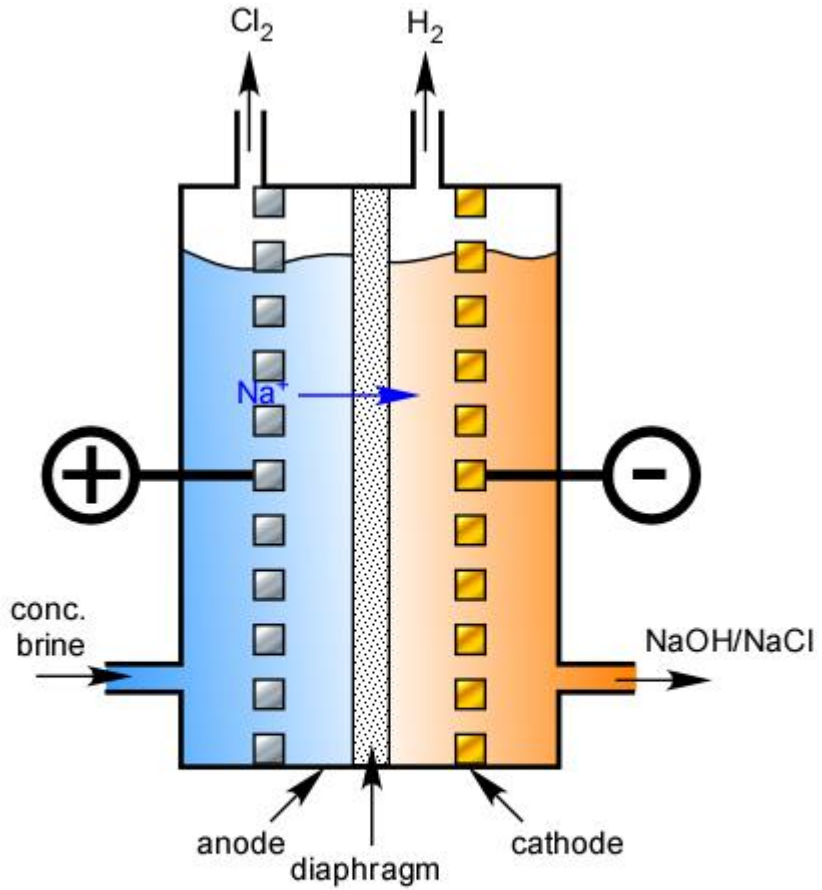
Chlor-Alkali



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

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

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

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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

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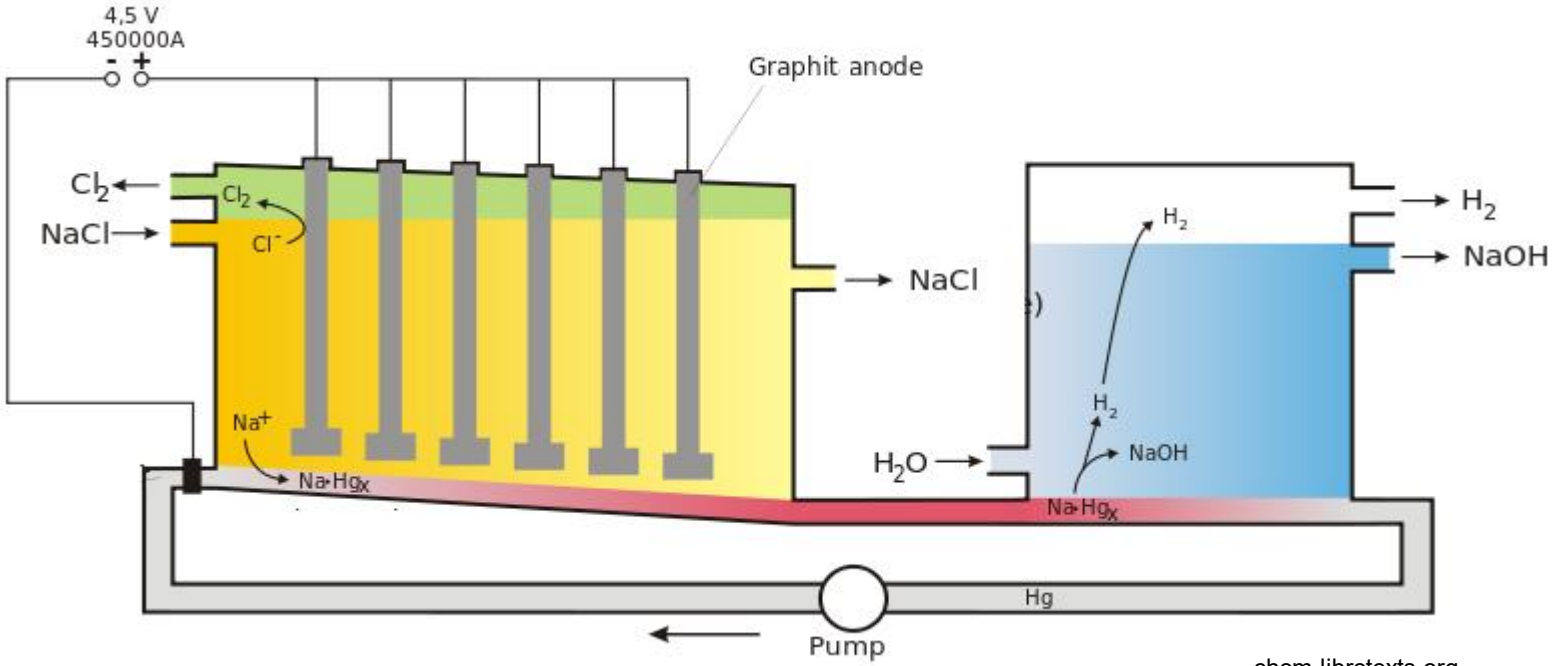
Mercury Cells



chem.libretexts.org

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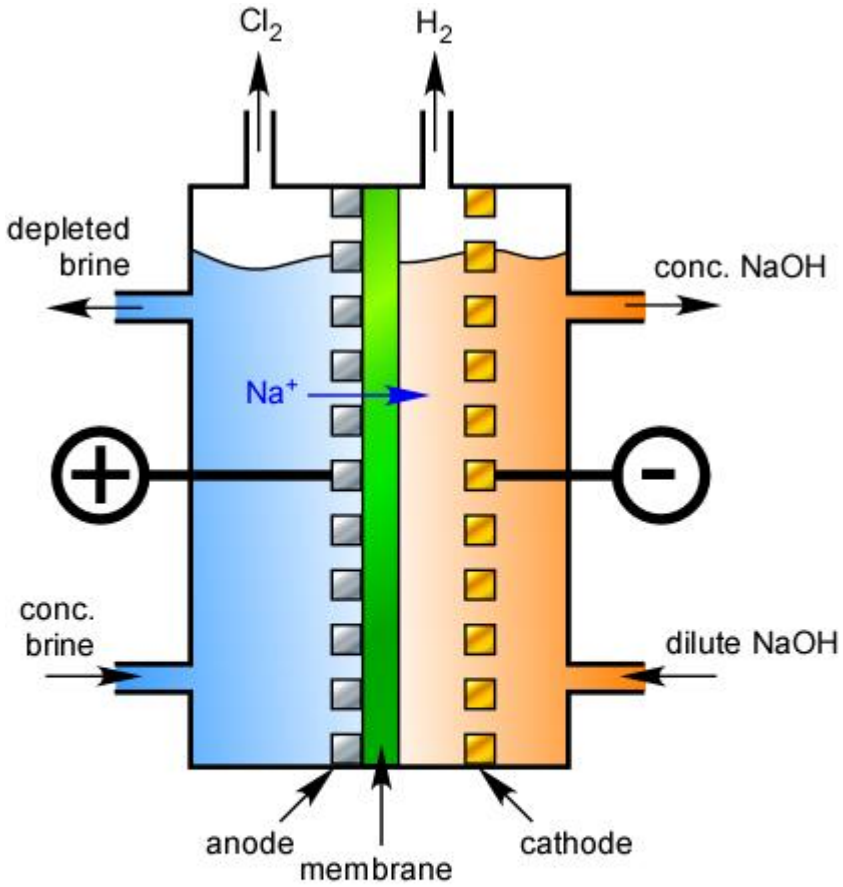
Membrane Cells



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

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

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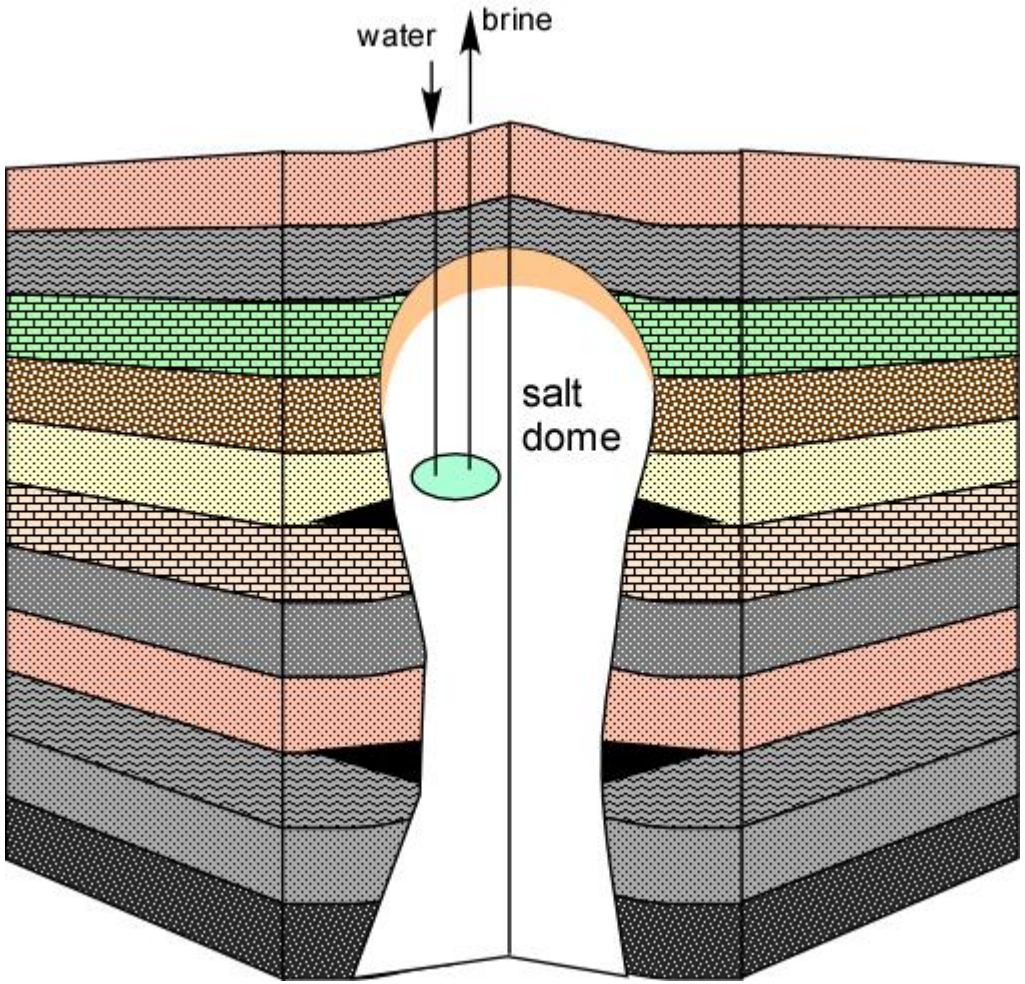
Solution Brine Mining



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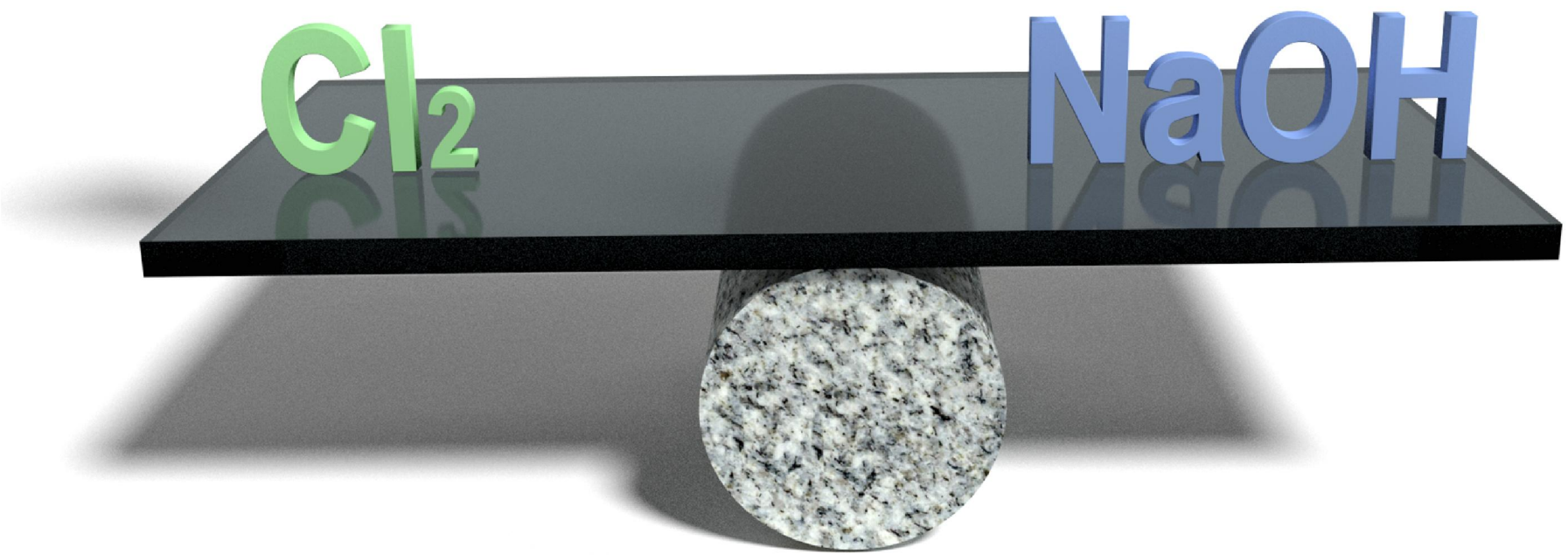
Balancing the ECU



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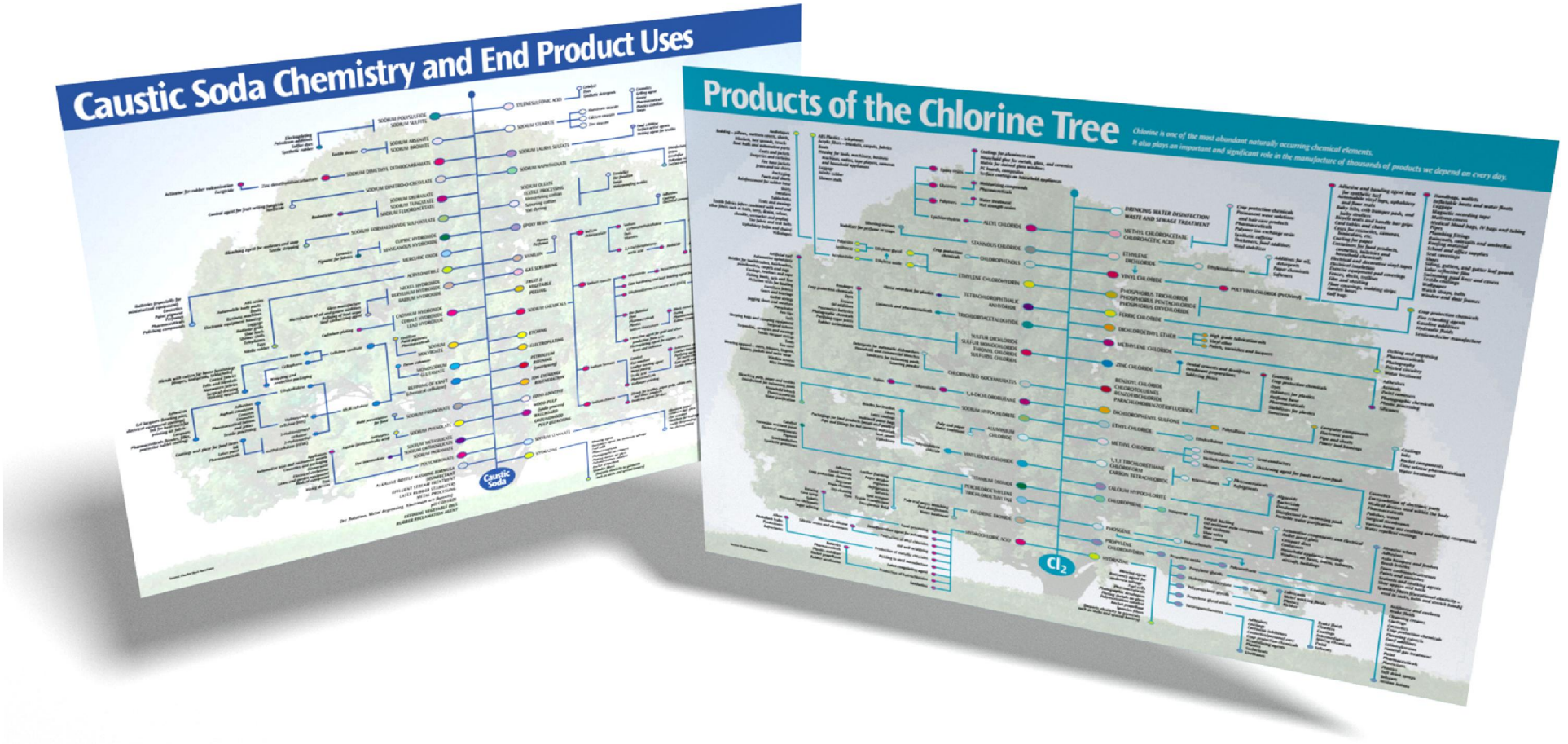

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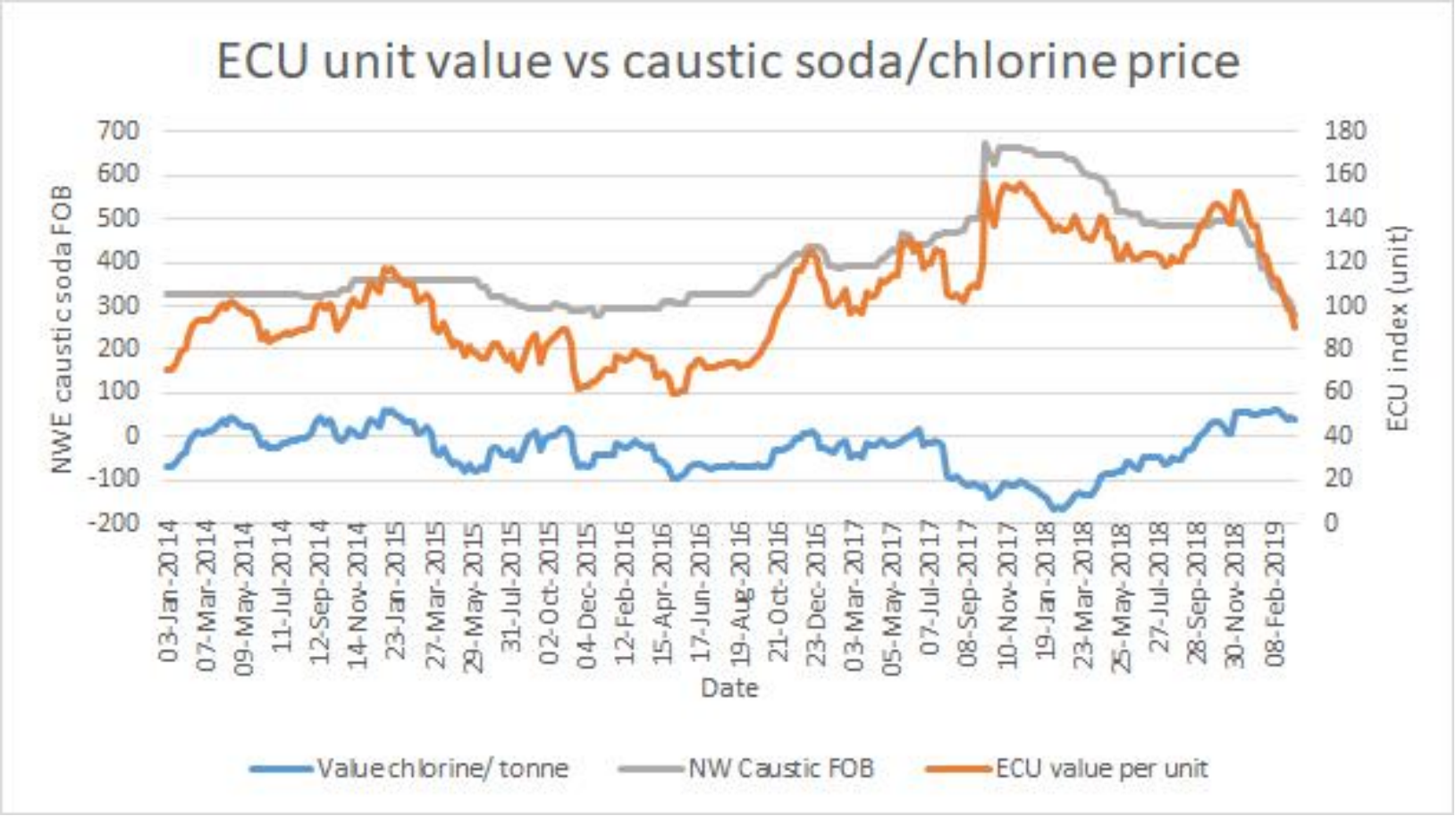
American Chemistry Council

ECU Pricing



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

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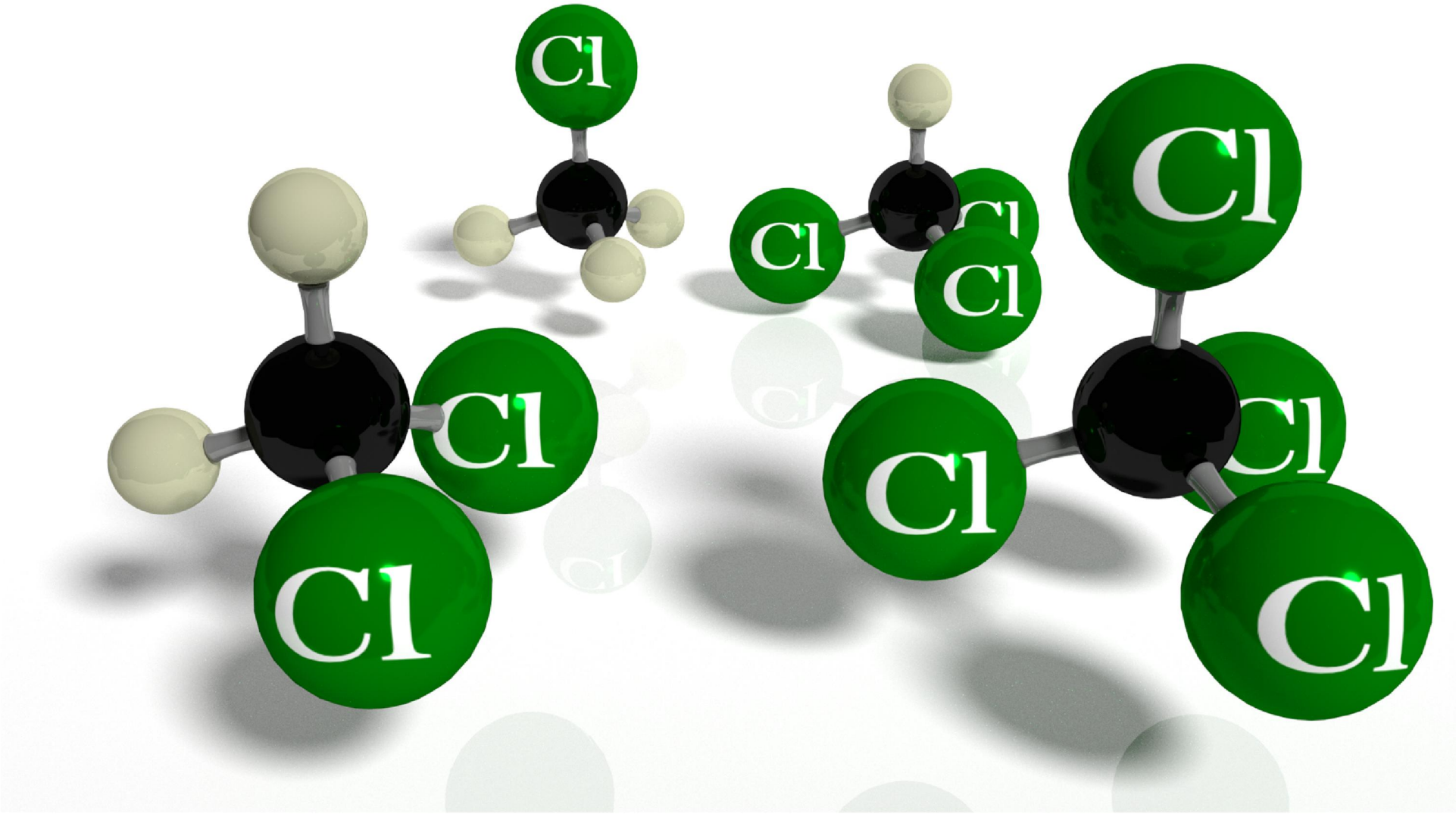
Organochlorides



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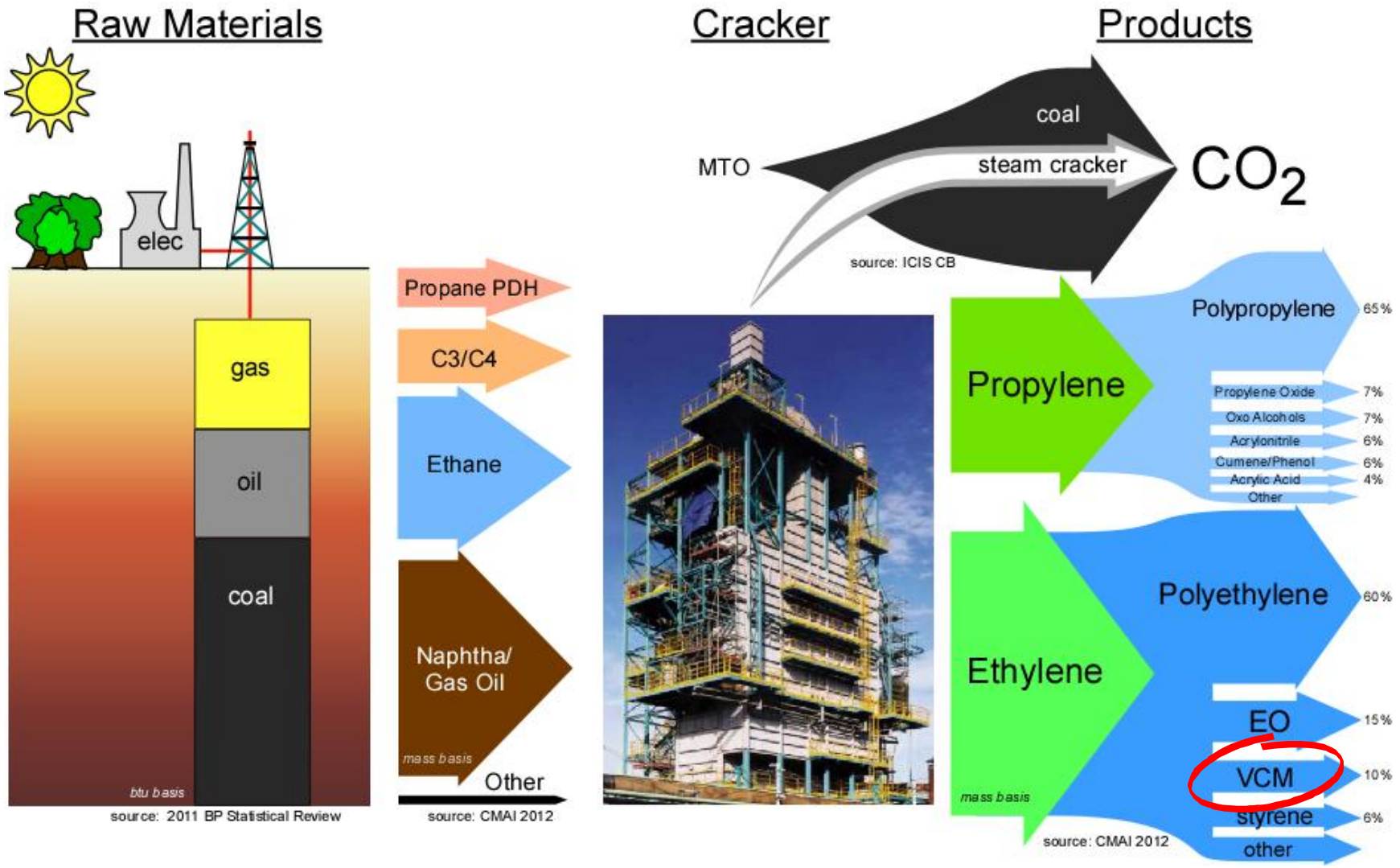
Chemical Industry Snapshot



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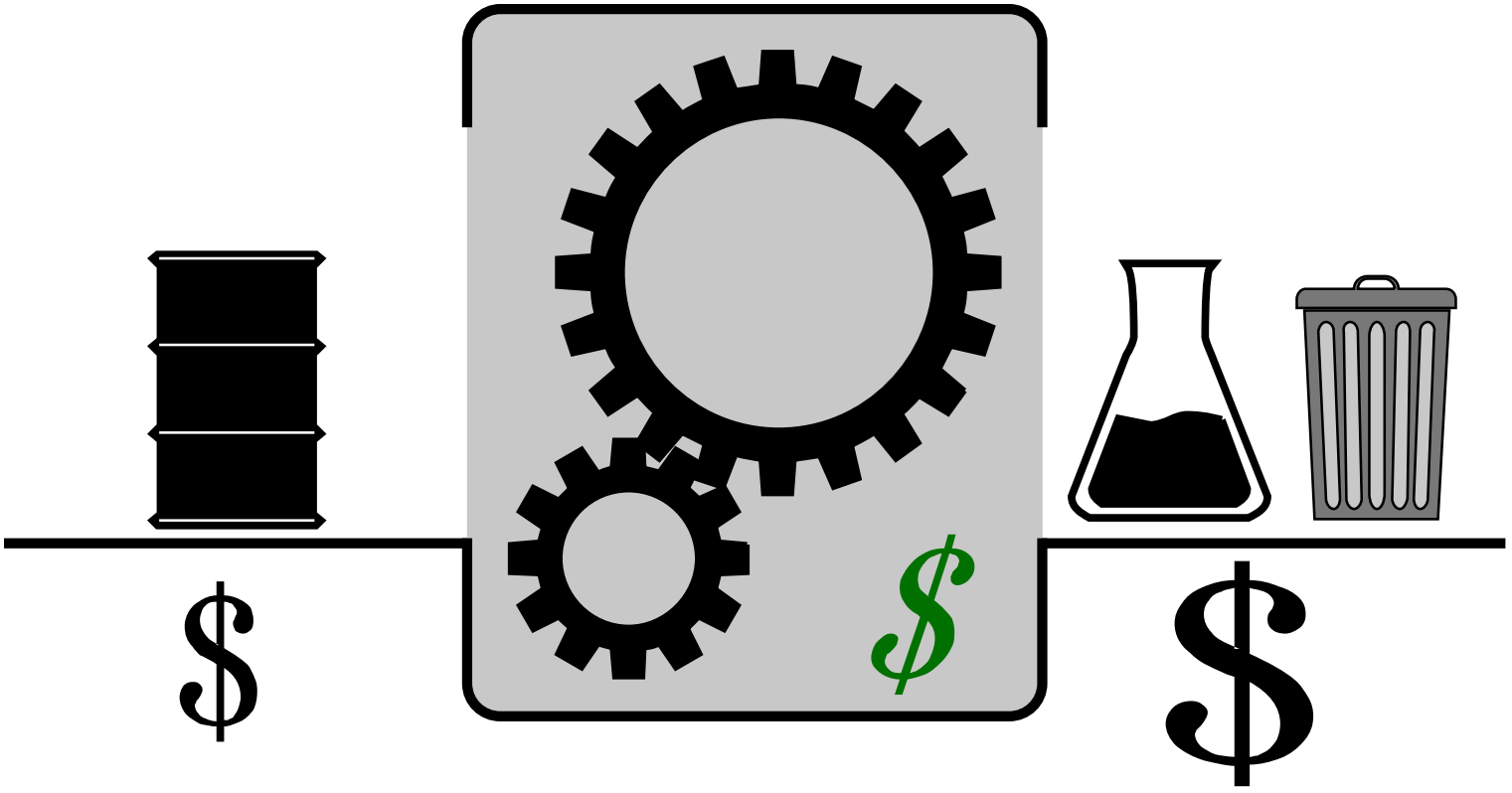
Simplified Chemical Industry



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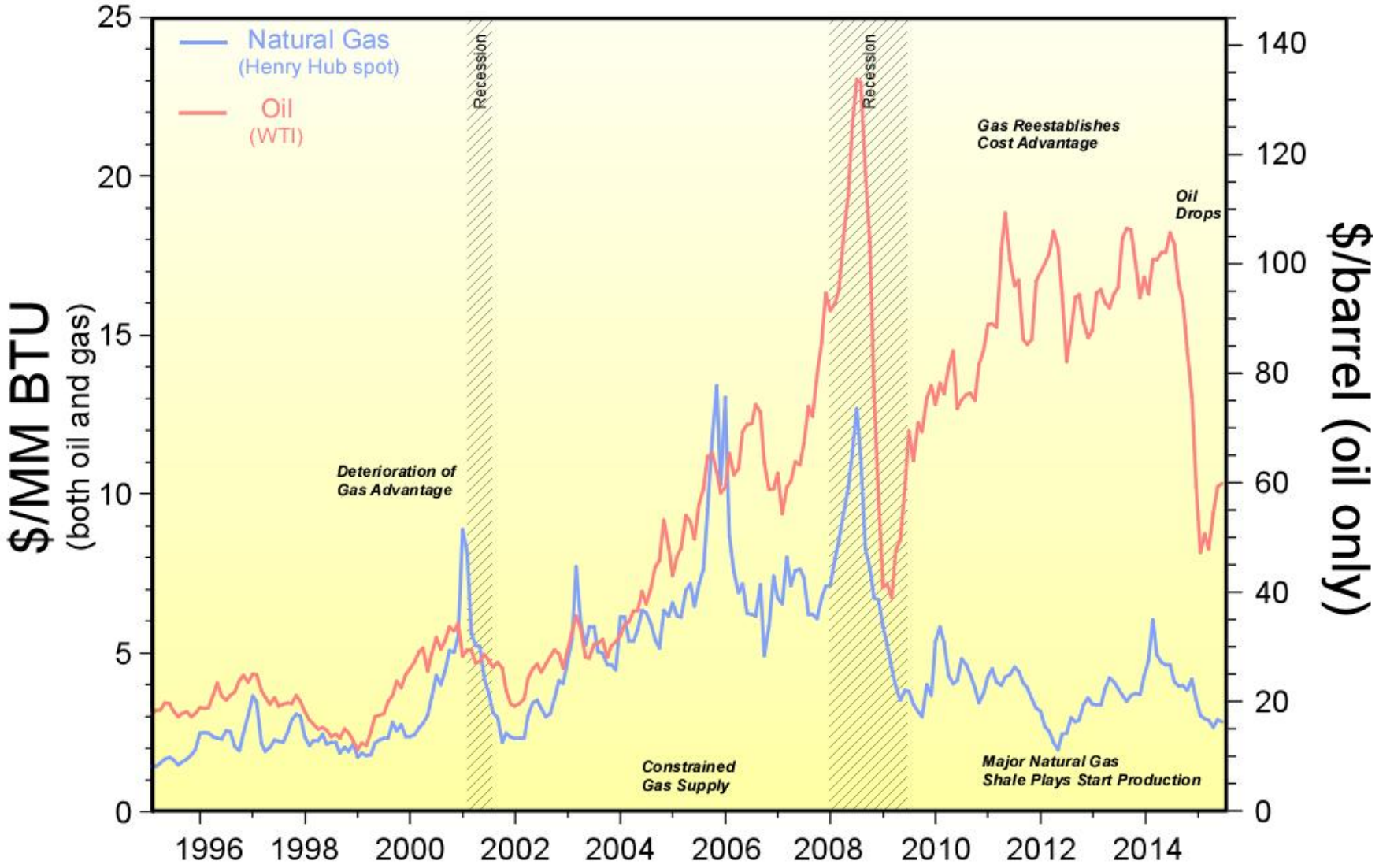
Recent Industry History



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Ethane Price Now Tracks Gas

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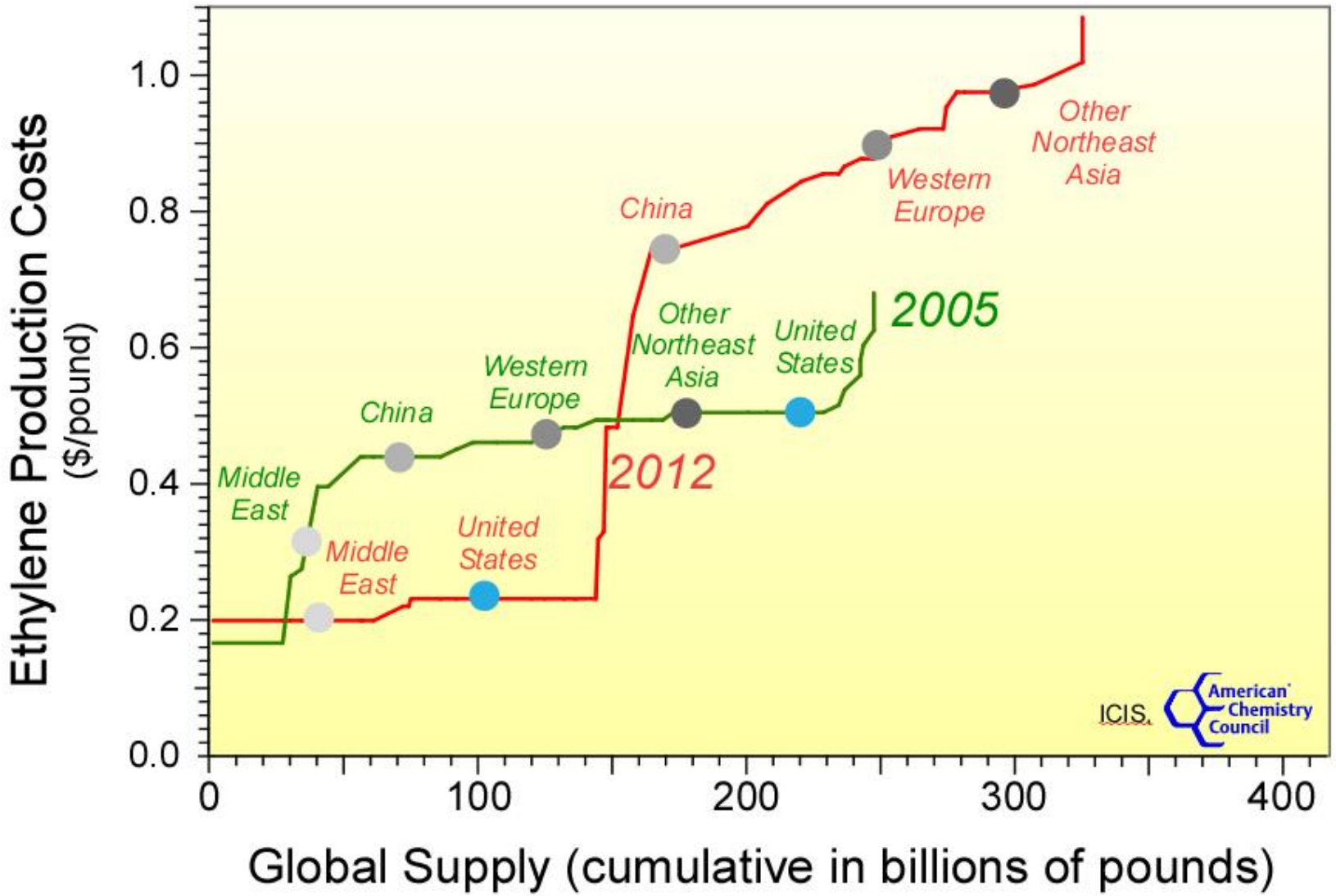
Impact of Low Gas Prices



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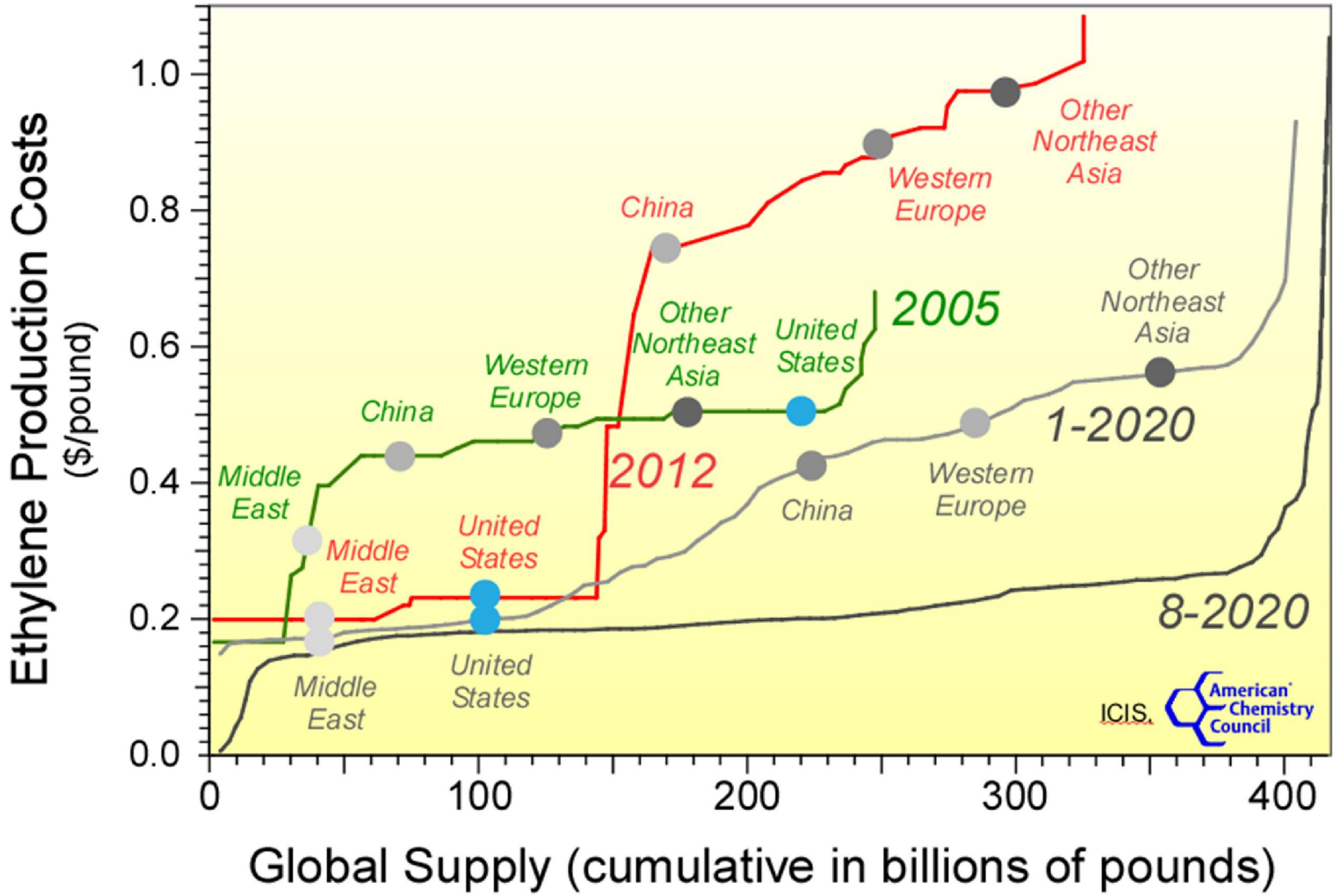
Impact of Low Gas Prices



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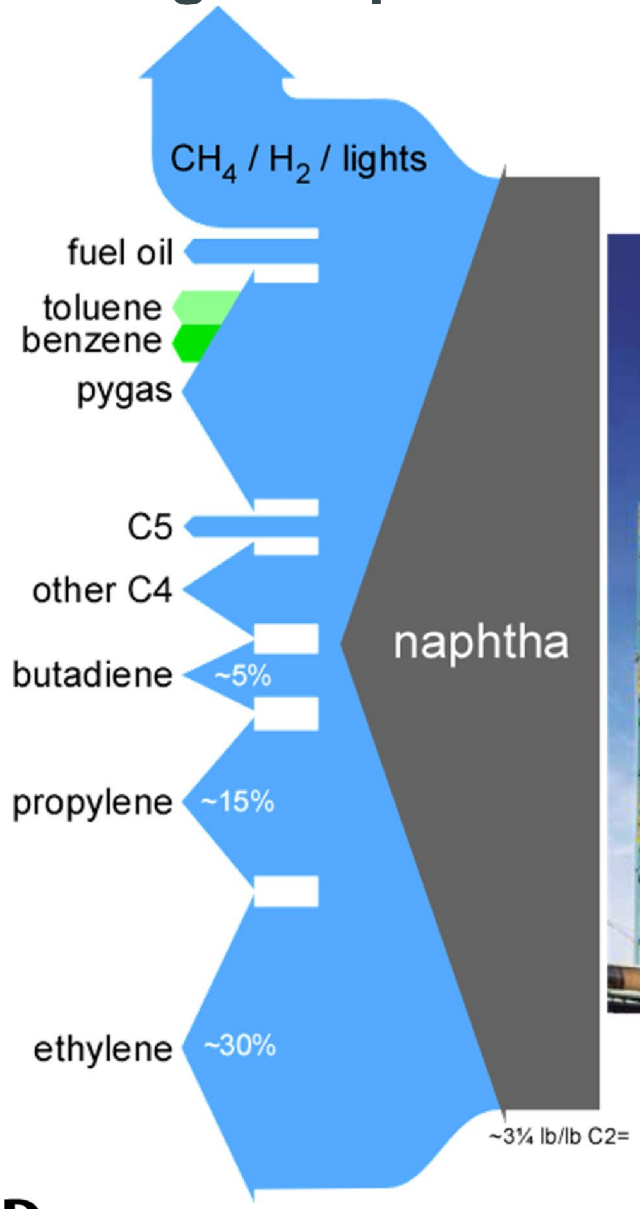
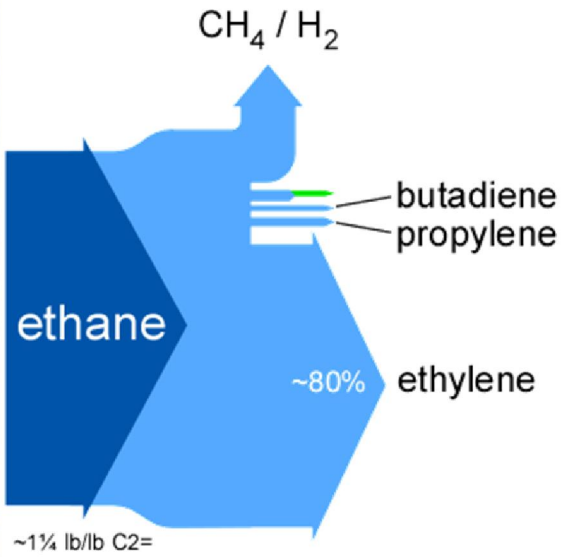
Cracking Comparison





same amount of ethylene

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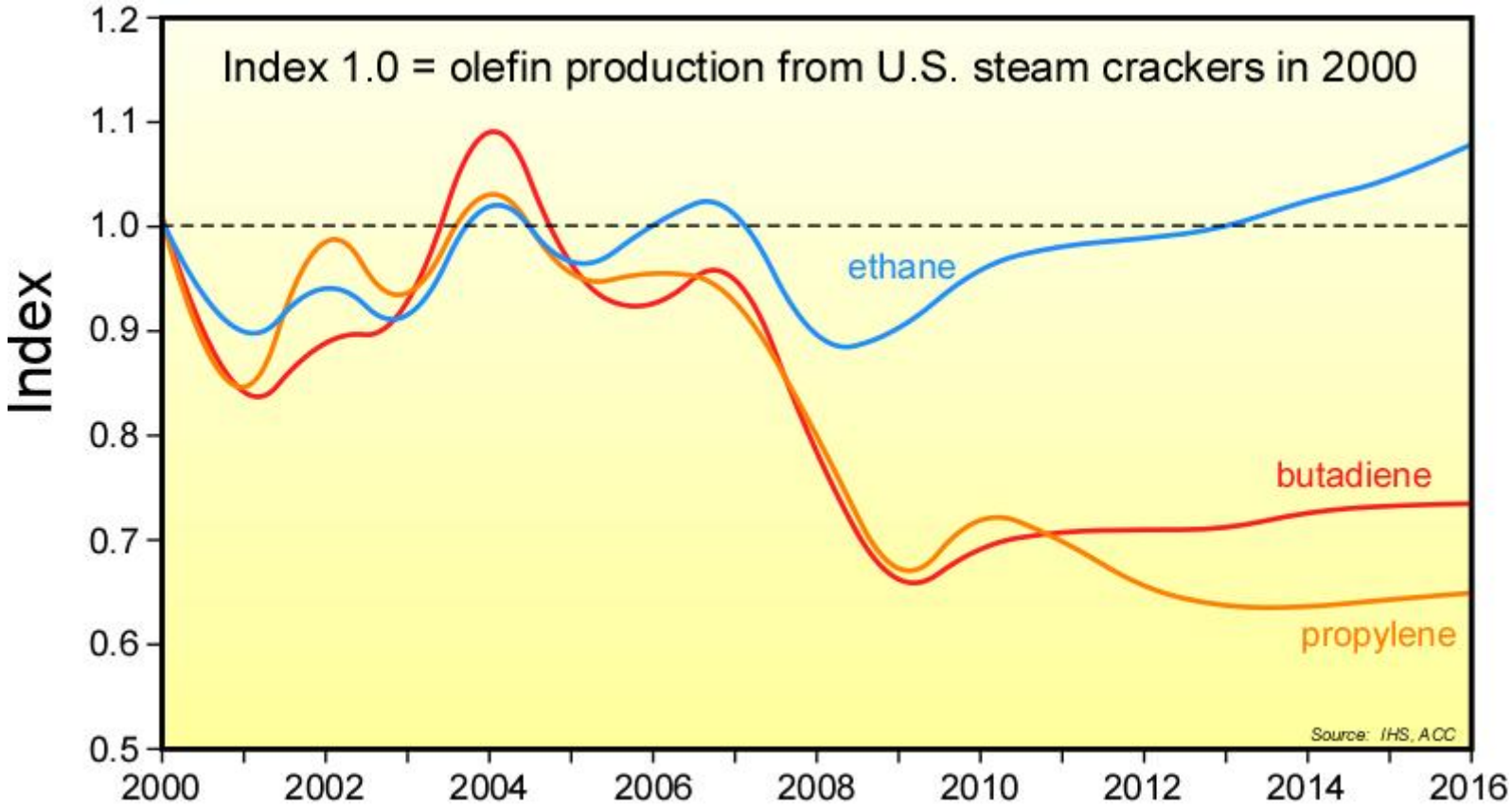
Production of C3/C4 Dropped



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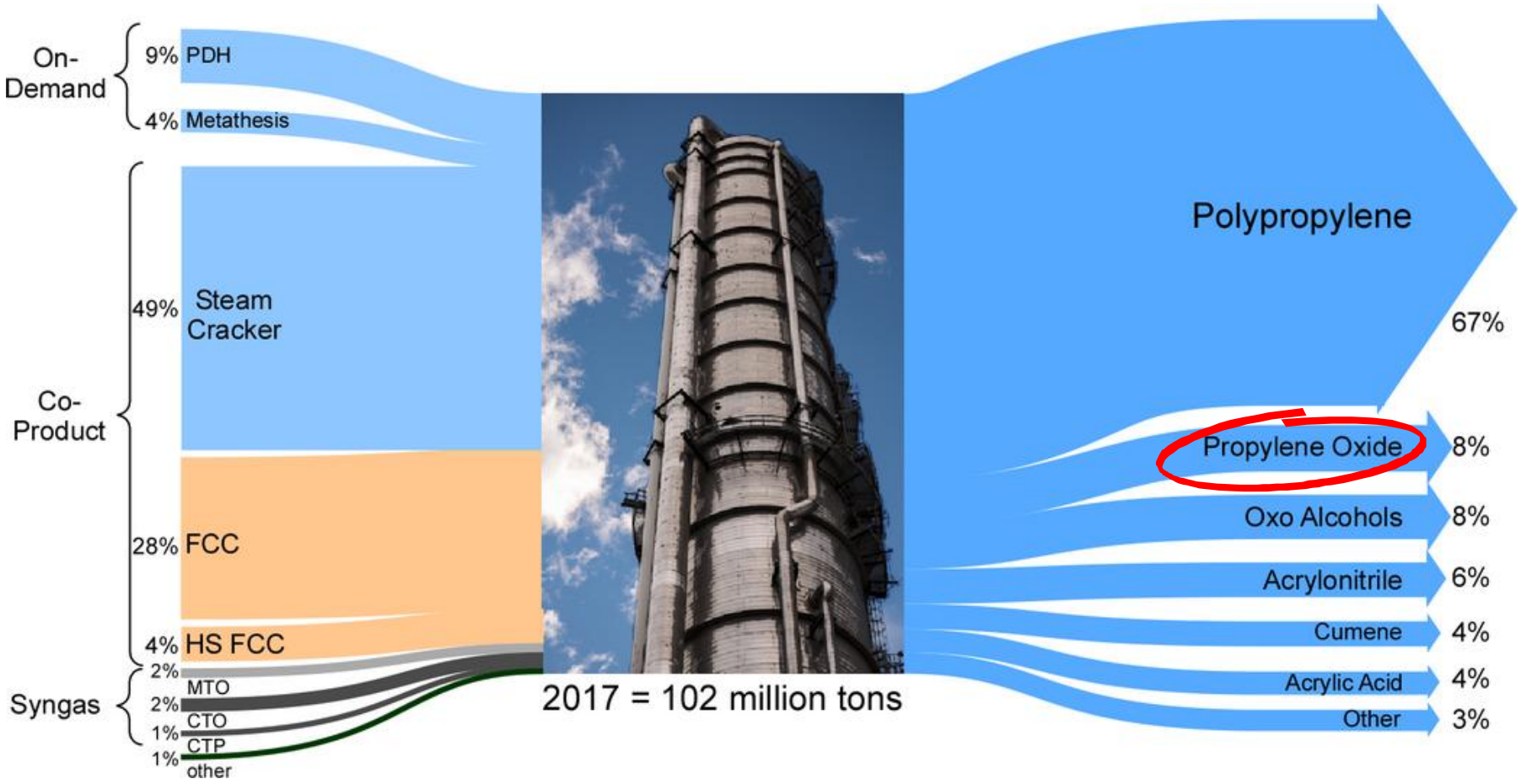
World Propylene



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Scale Is Important

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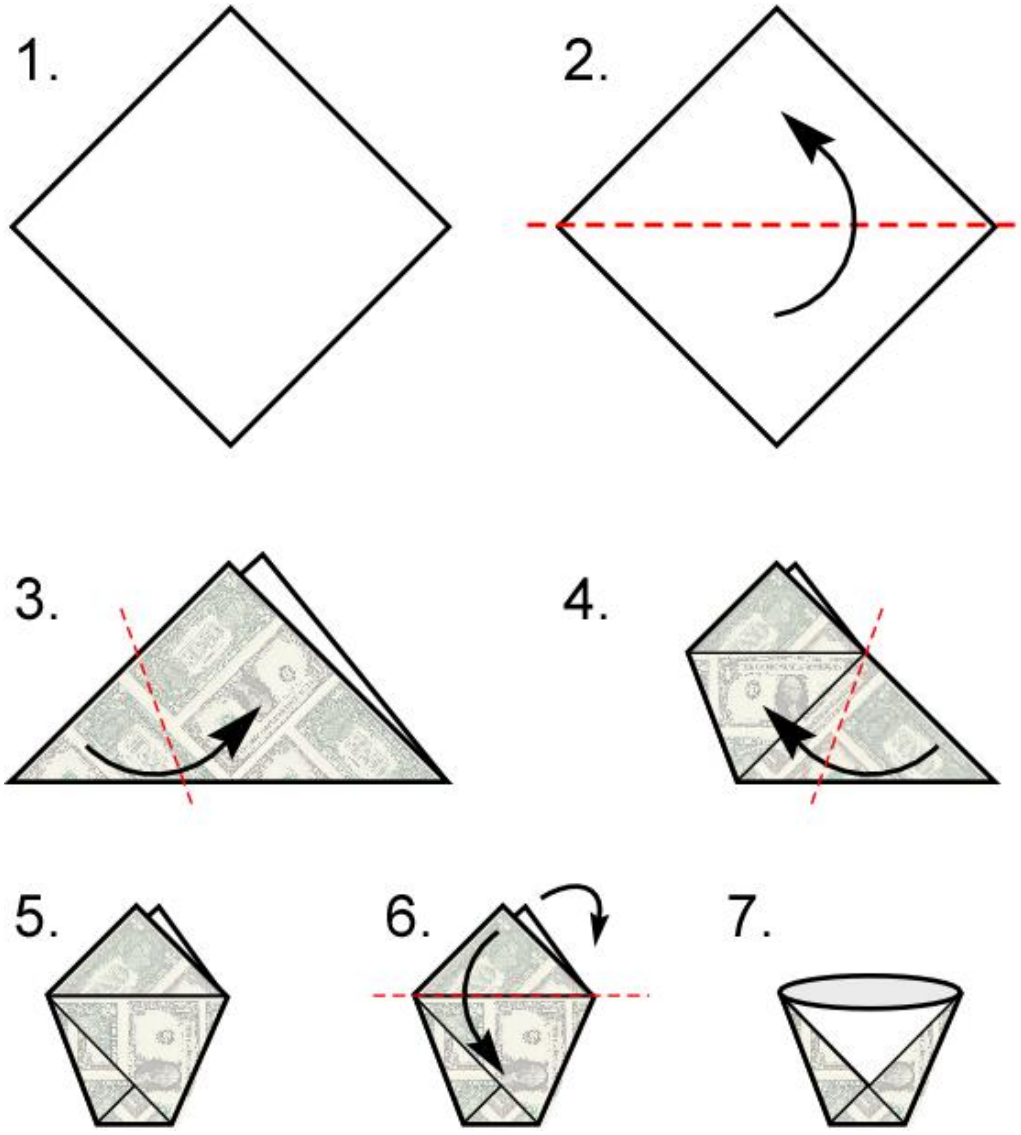
Scale Demo



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

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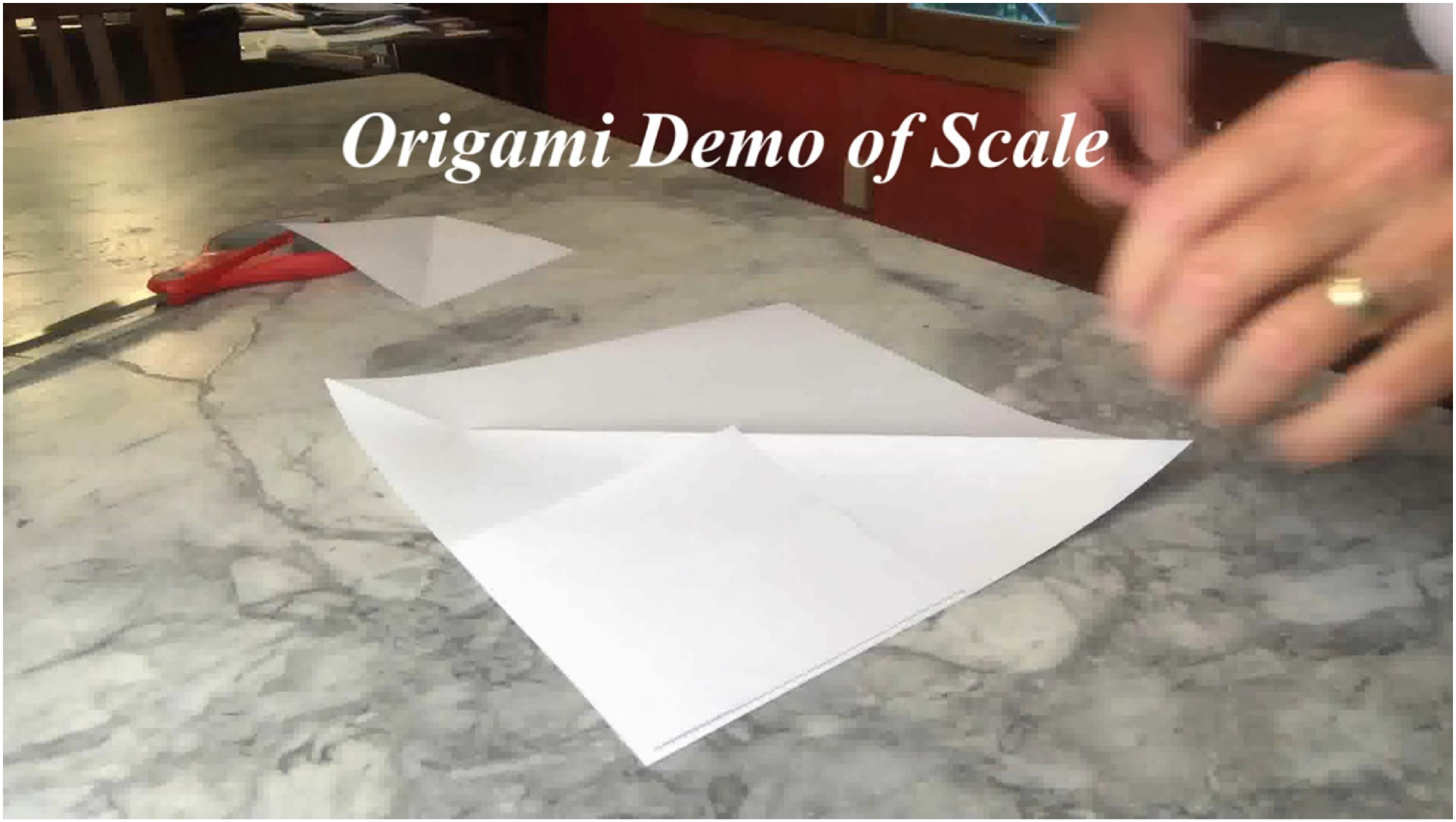

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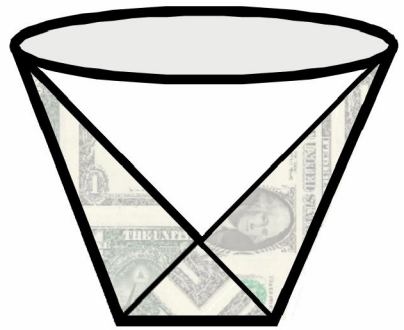
https://www.mjphd.net/OrigamiDemo.html

Impact of Scale to Contain Same Volume

>2X material
~9X labor to construct



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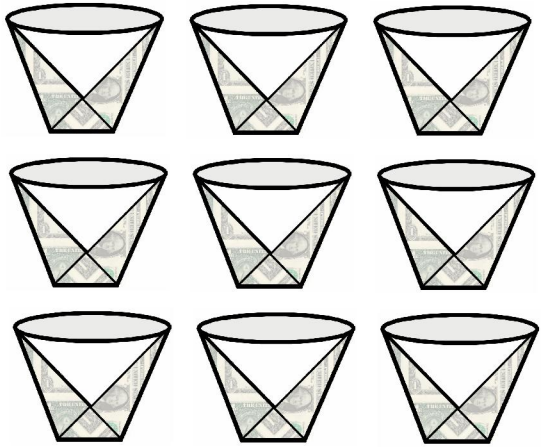

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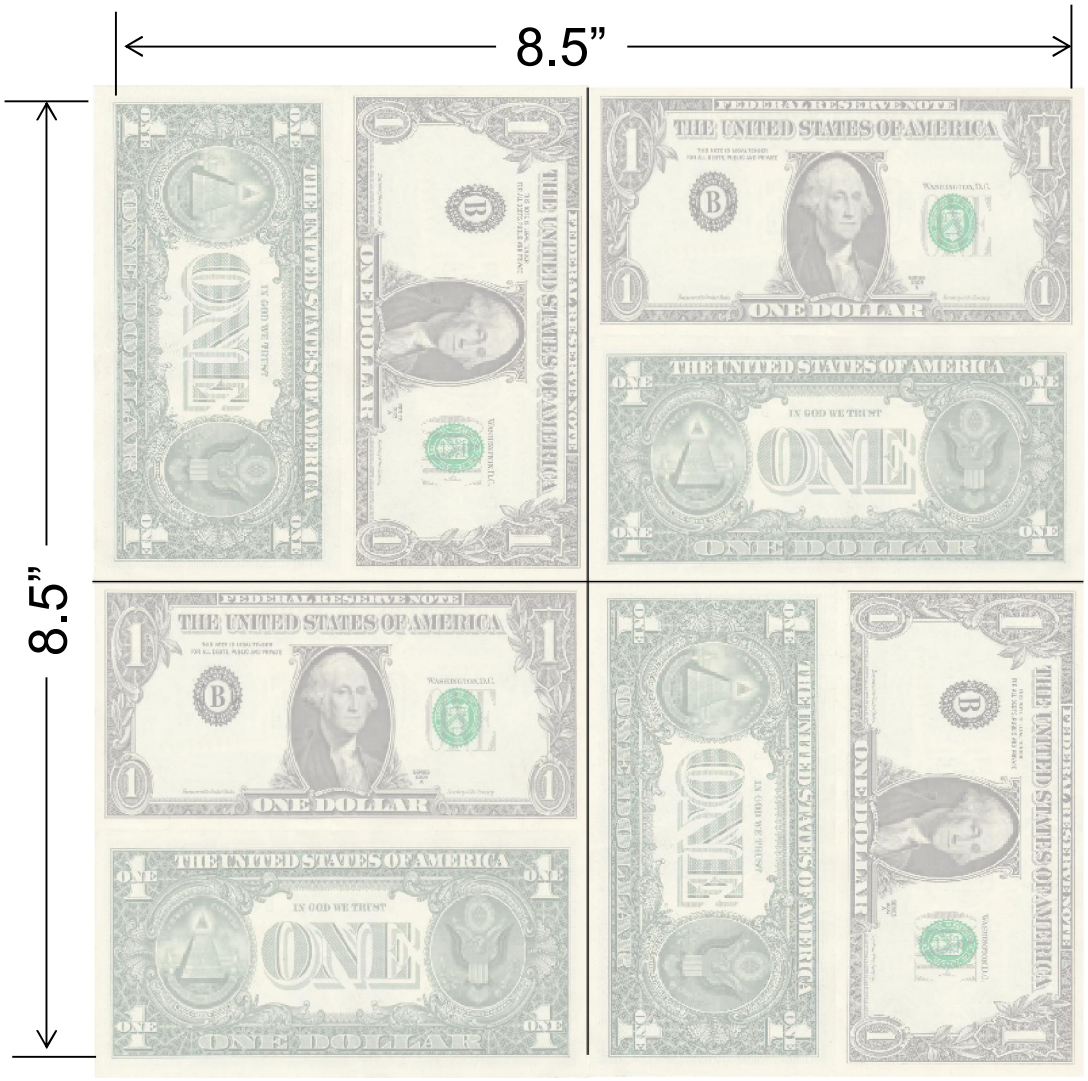
Video Demo



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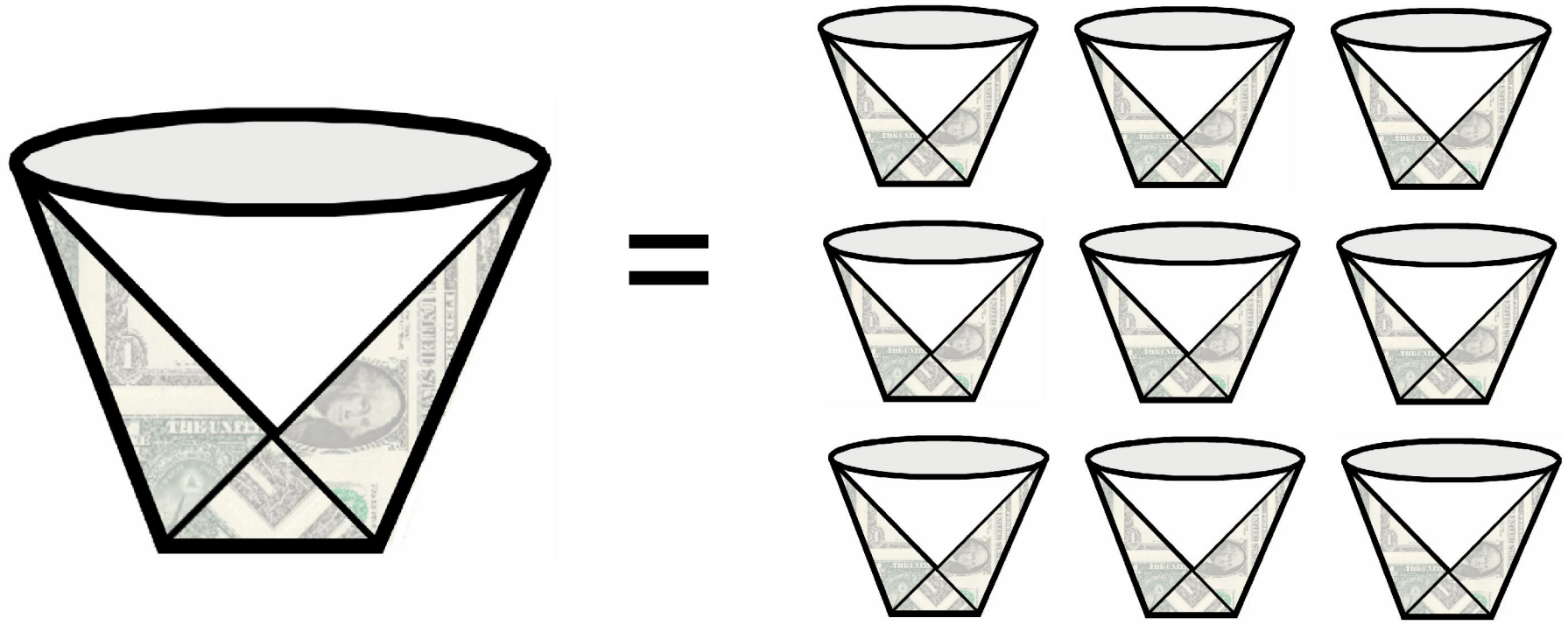
Scale Wins



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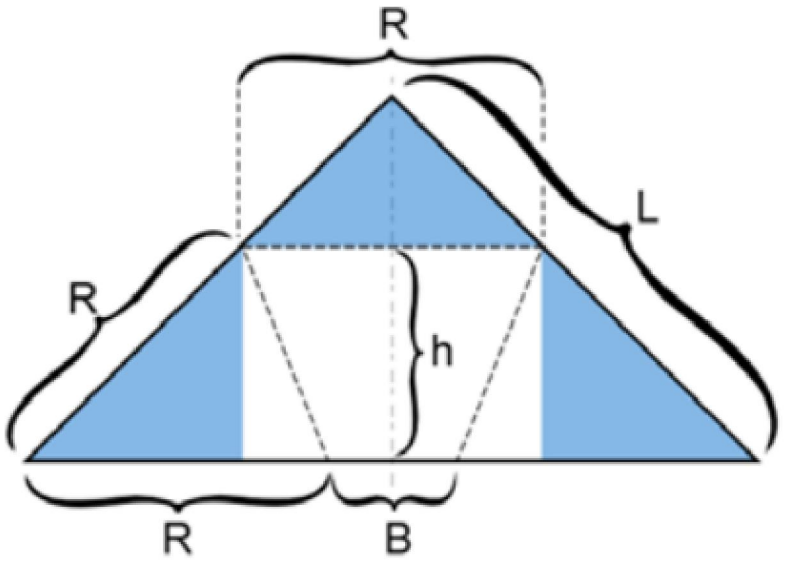
Demo Math



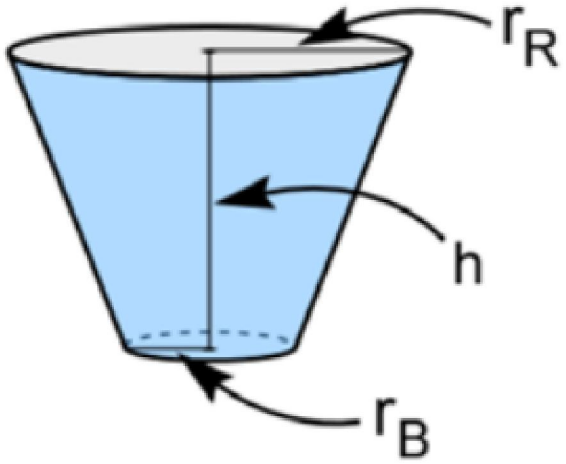
$$A = L^2$$

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

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

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

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



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

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

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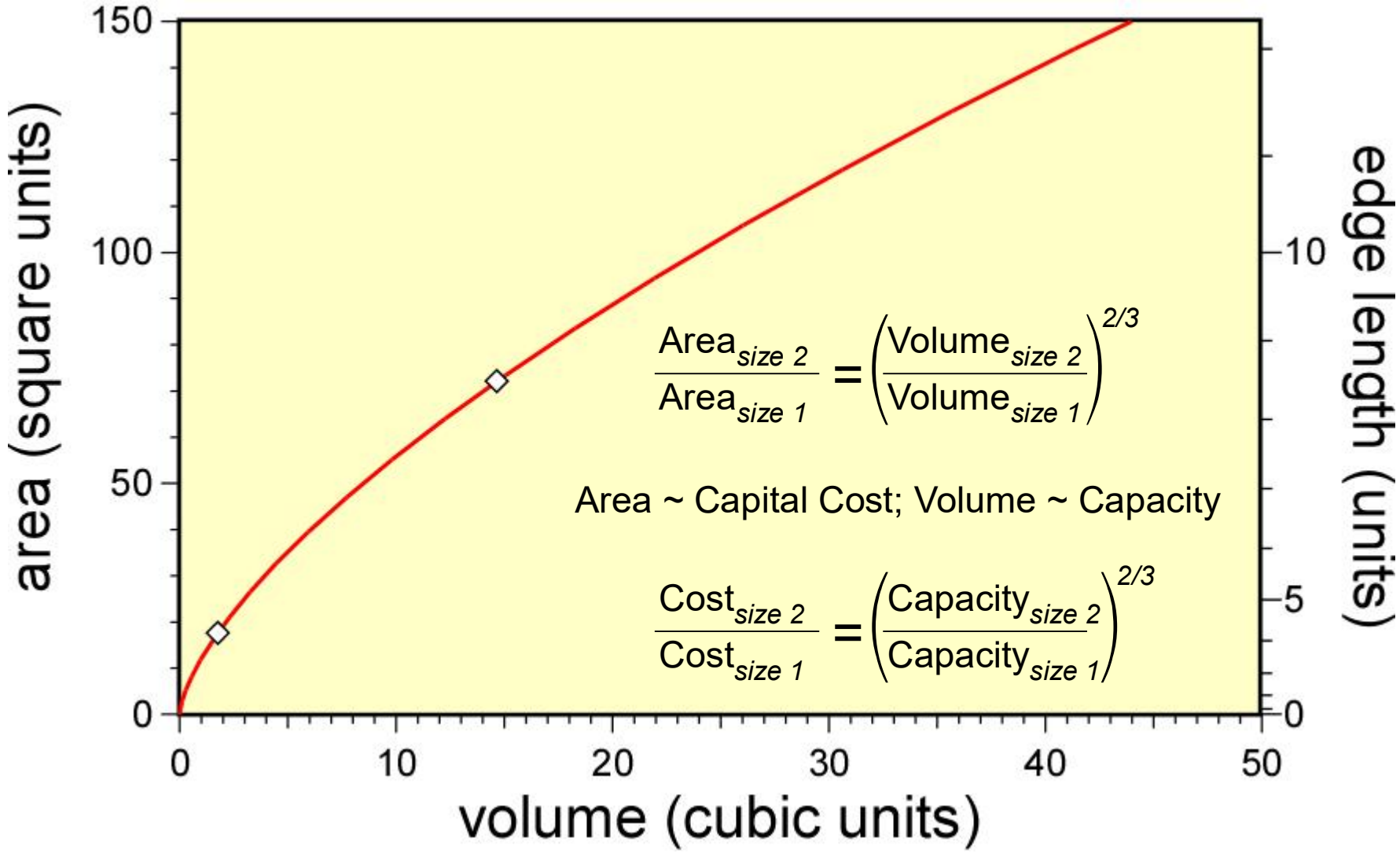
Power Law



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Scale Always Wins

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

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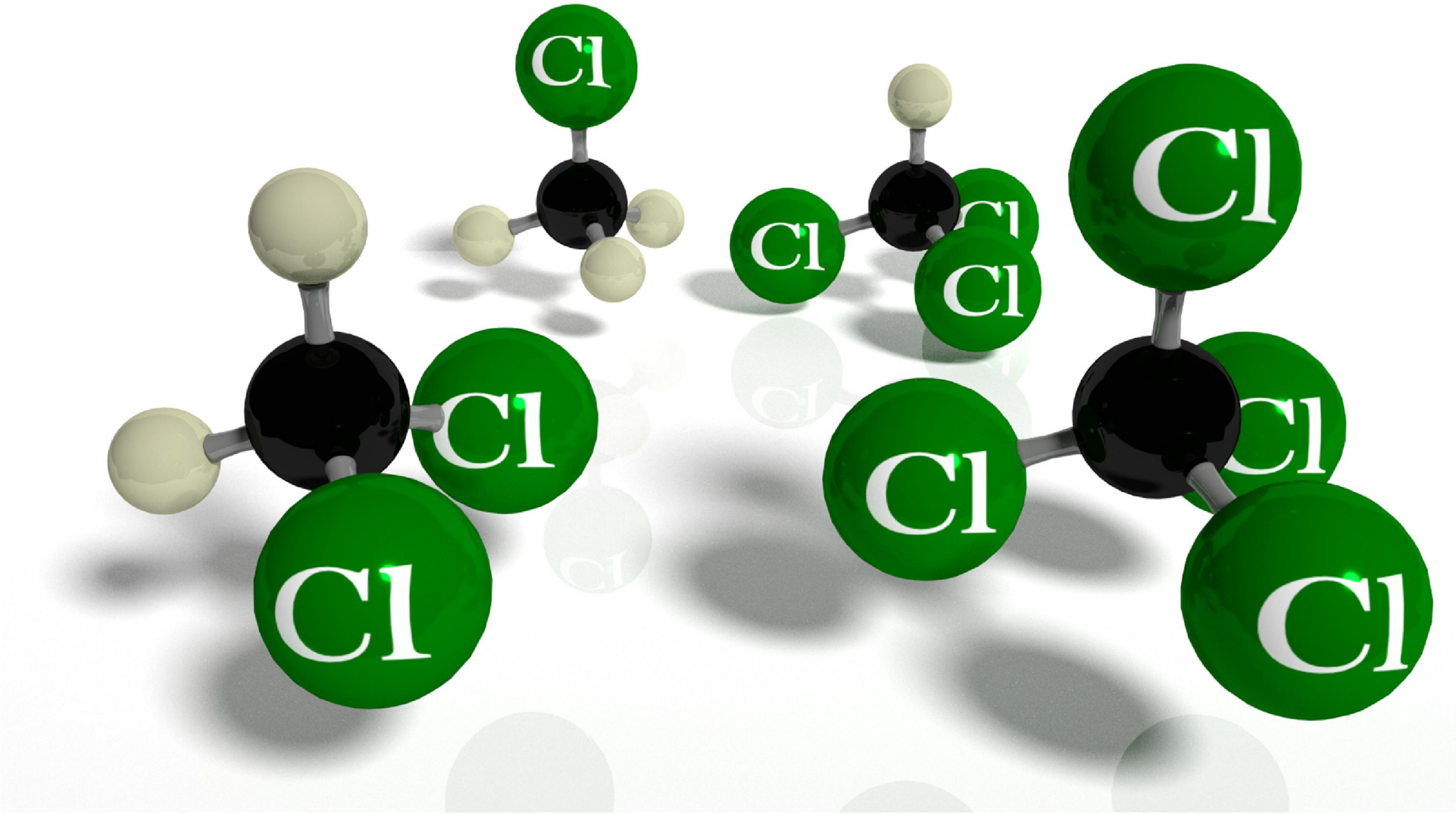
Organochlorides



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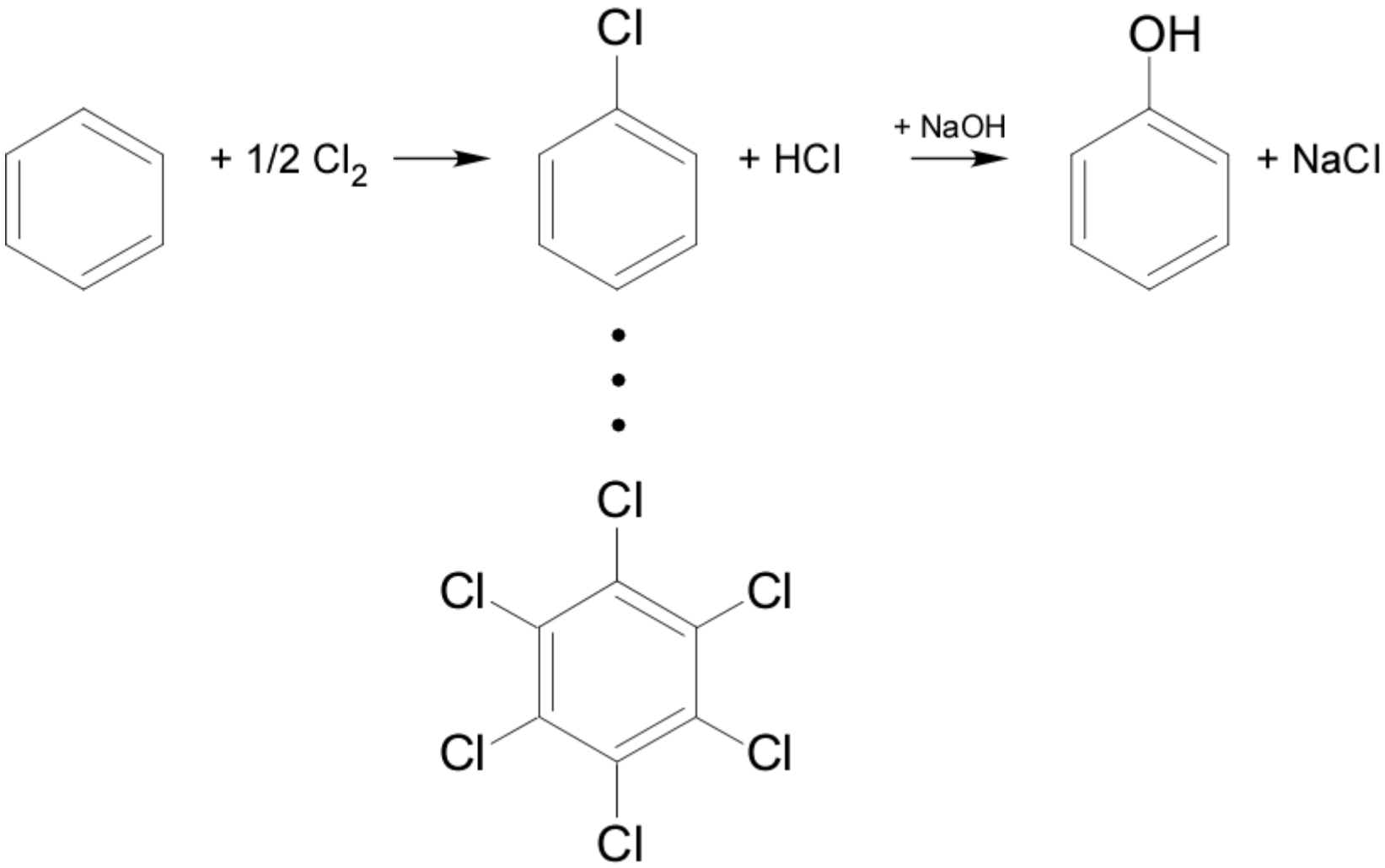
Chlorine as an Oxidant



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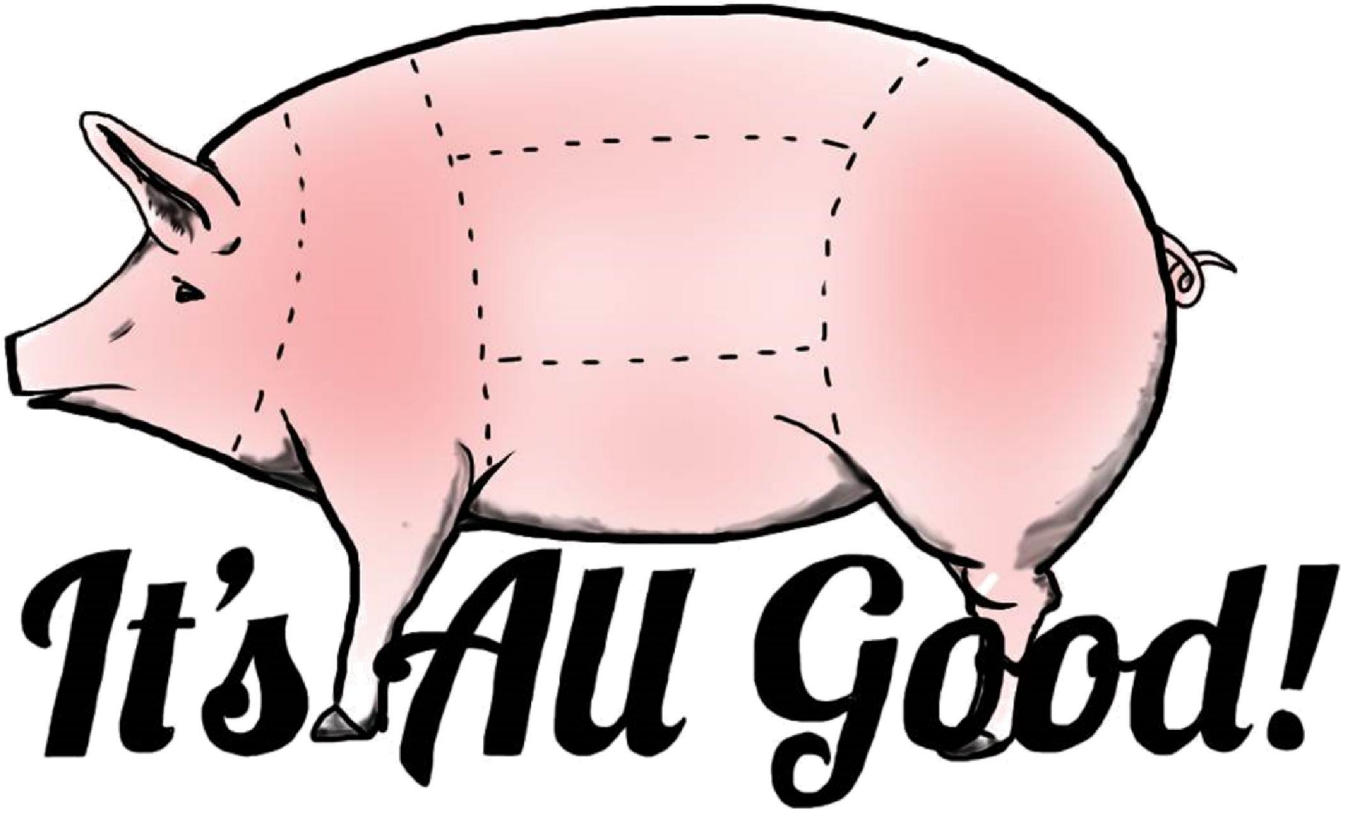
All Reaction Products Find Uses



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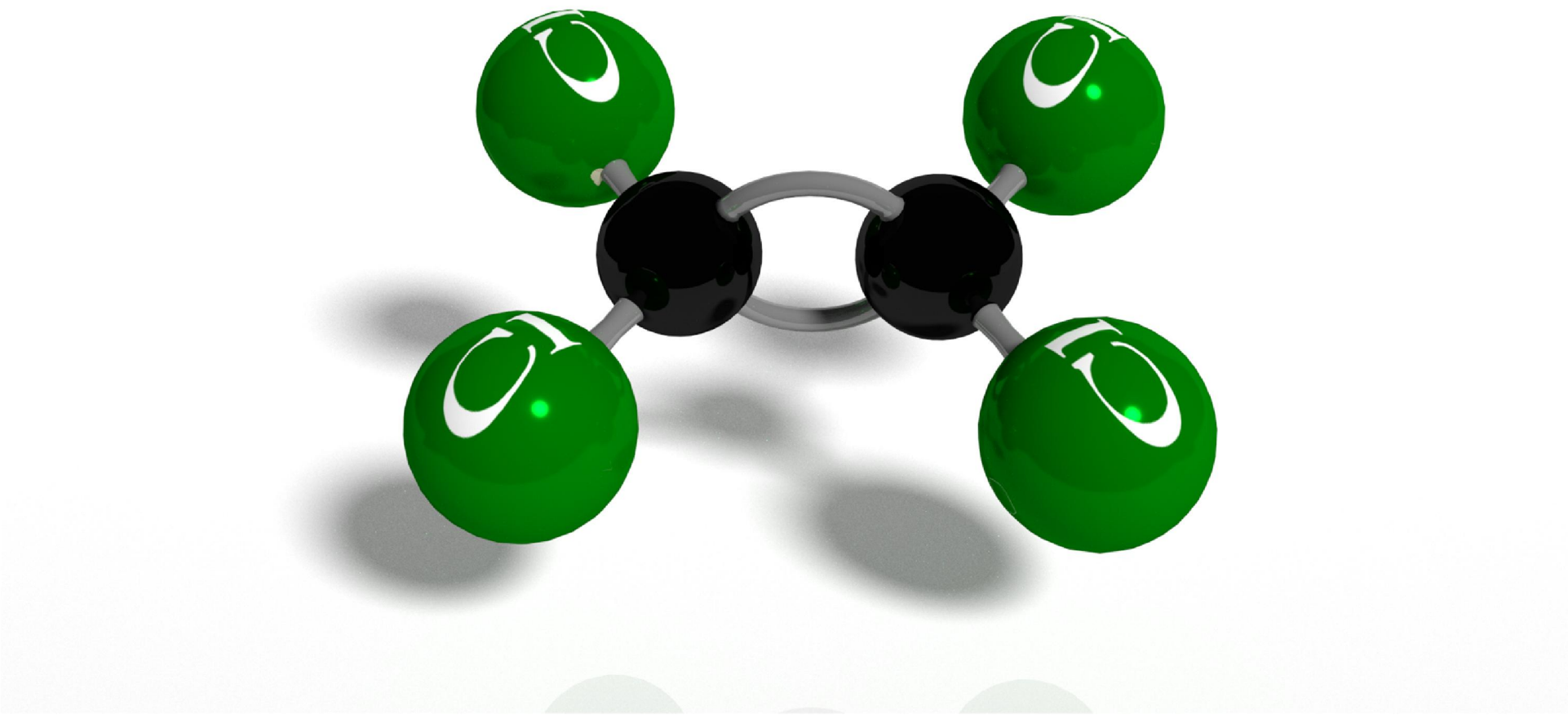
Perchloroethylene



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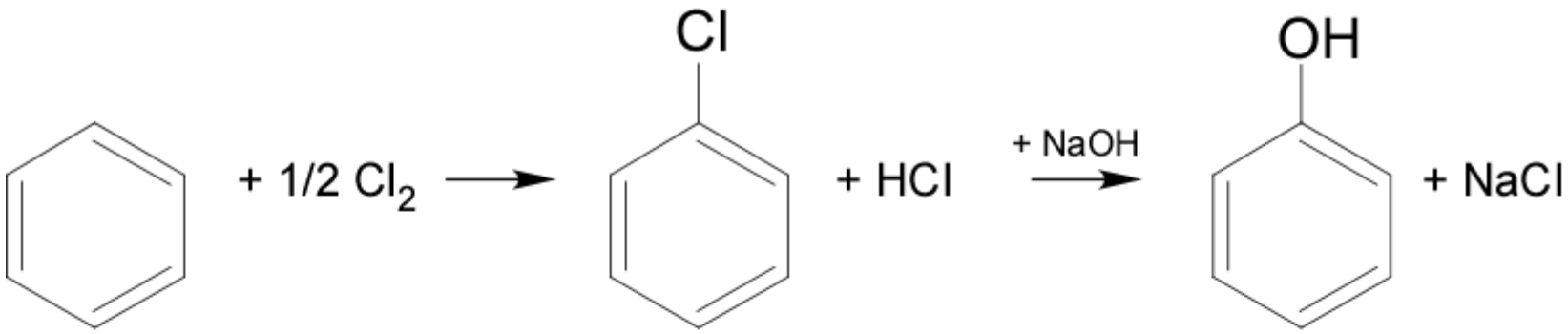
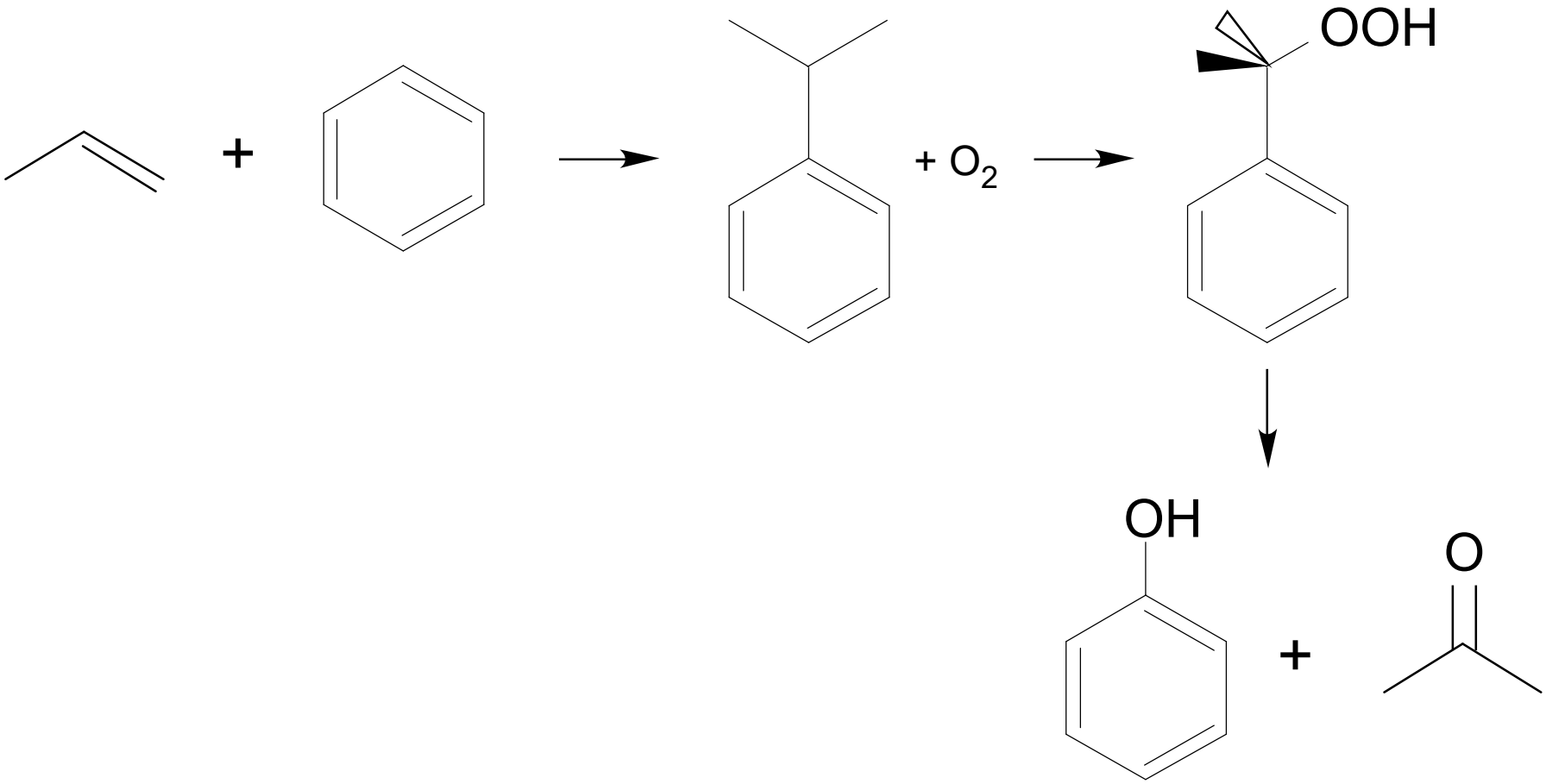
Chlorine as an Oxidant



Phenol Today



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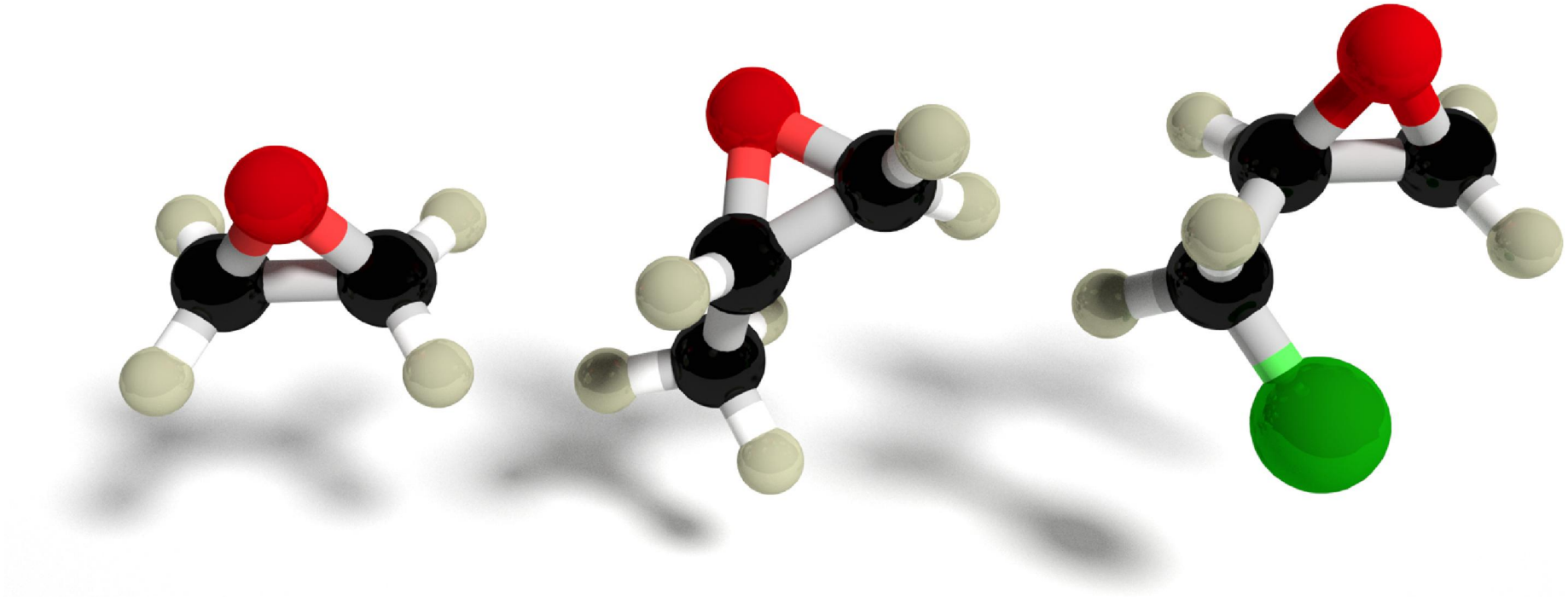
Epoxides

EO
ethylene oxide

PO
propylene oxide

EPI
epichlorohydrin



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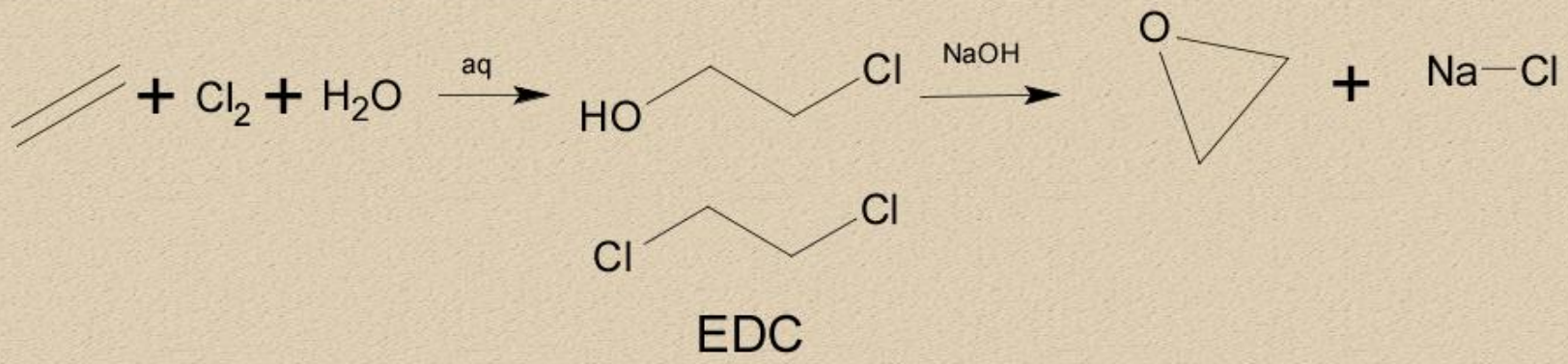
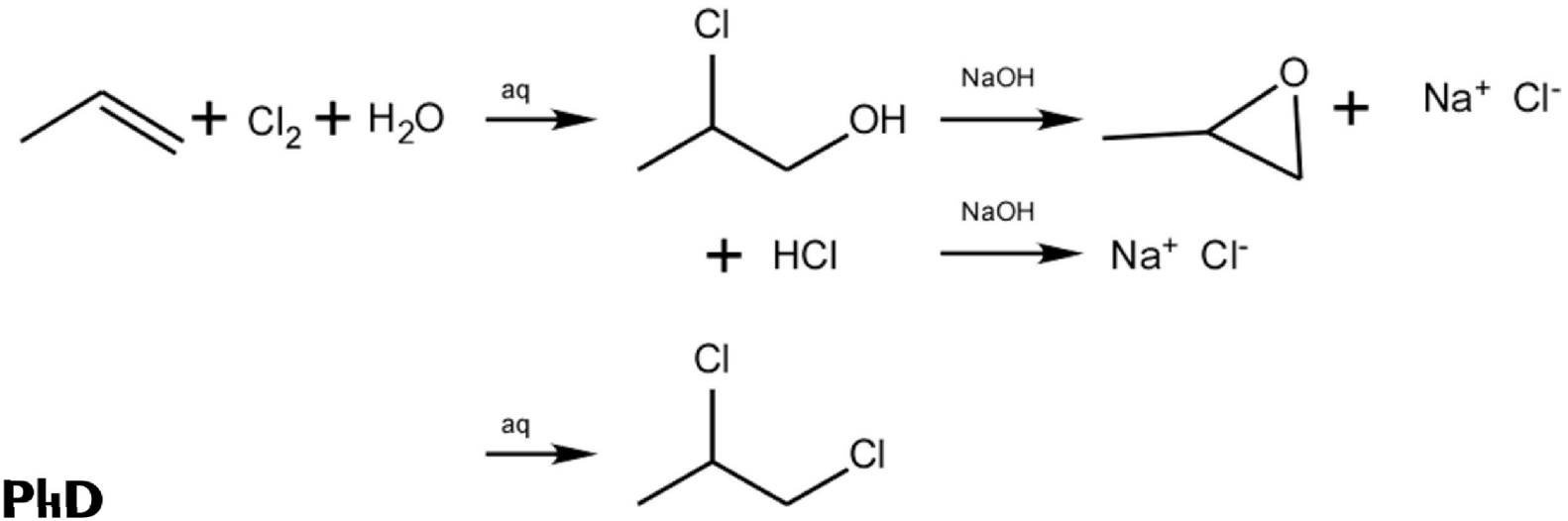
Chlorohydrin Chemistry

Clorohydrin Ethylene Oxide



1915-1975

Chlorohydrin Propylene Oxide



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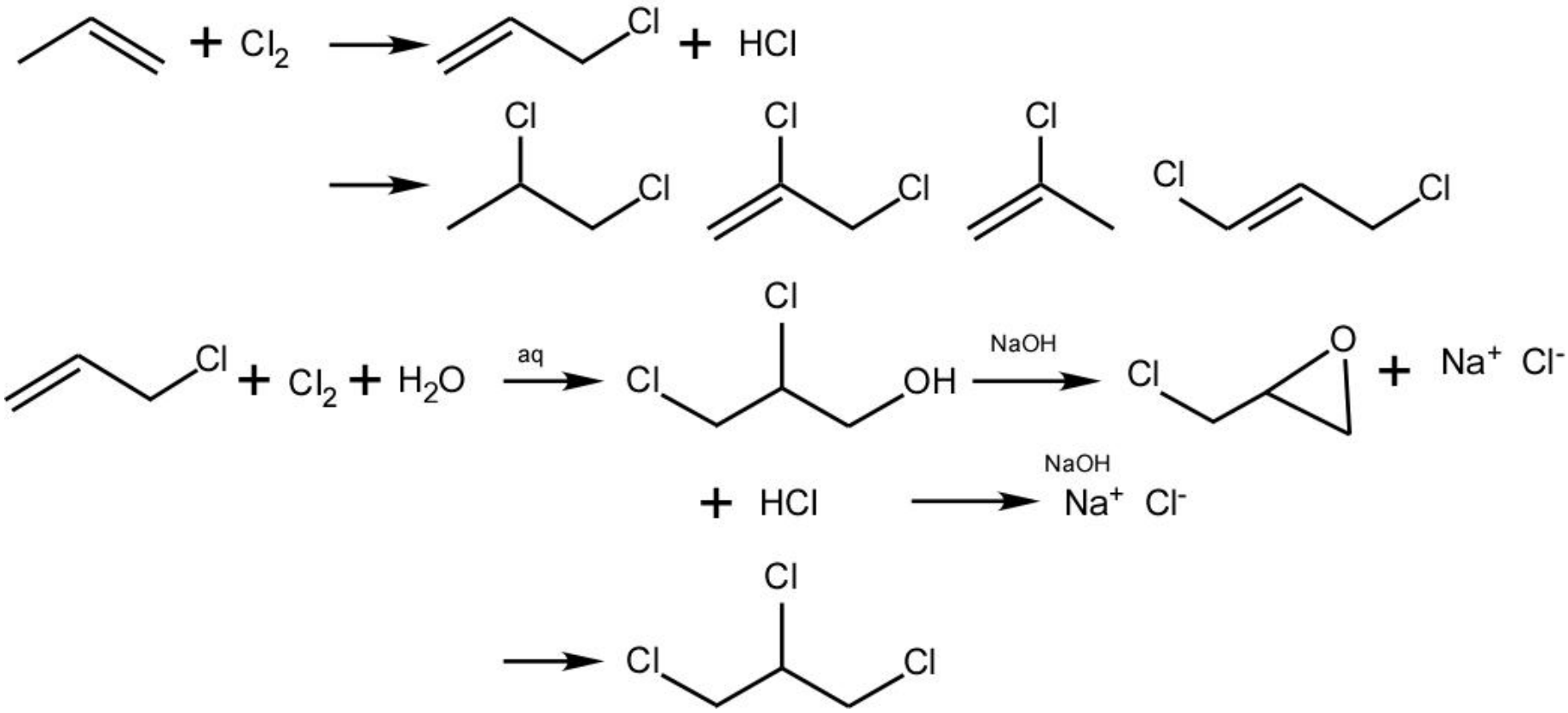
More Chlorohydrin Chemistry

Chlorohydrin Epichlorohydrin



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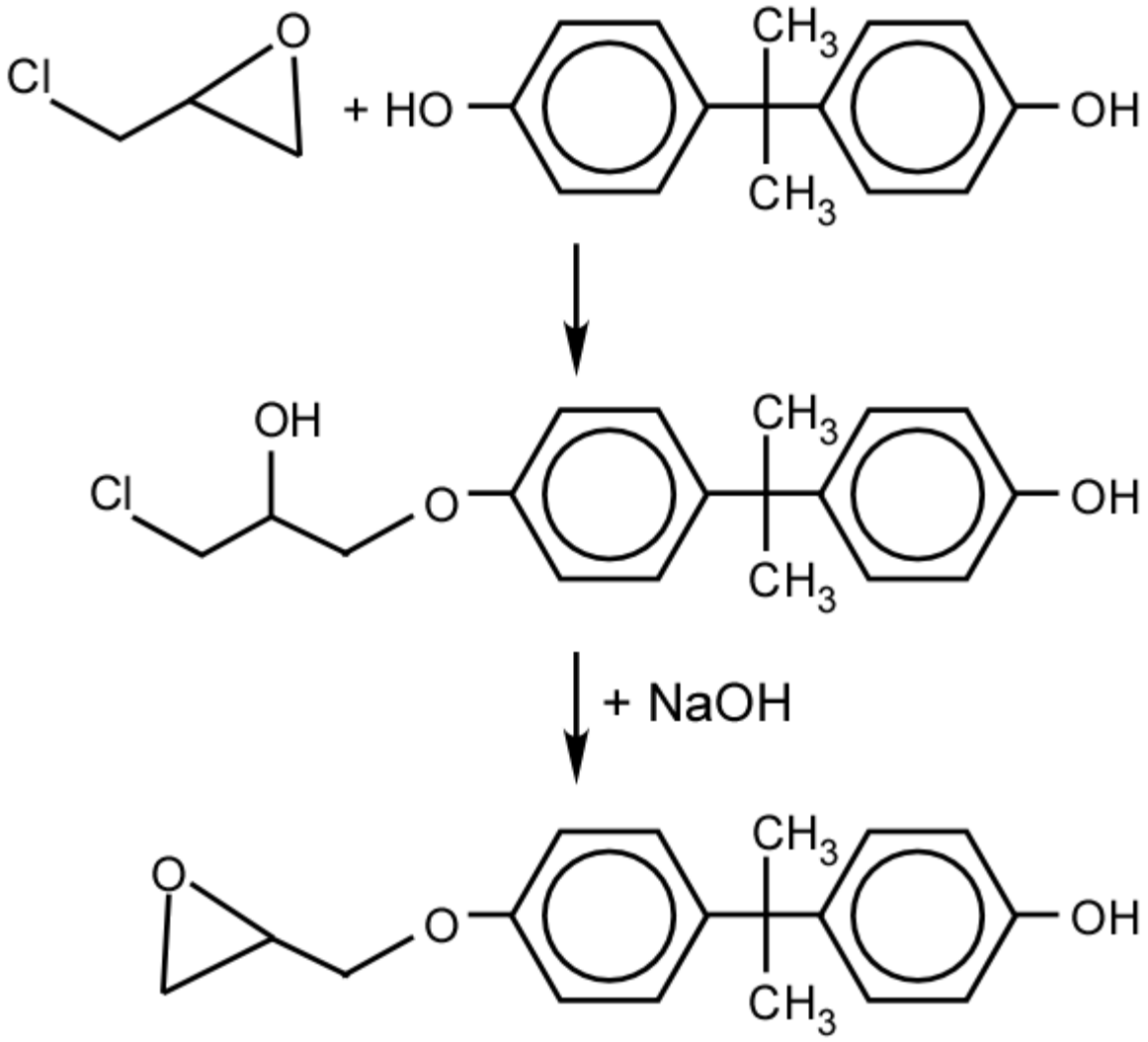
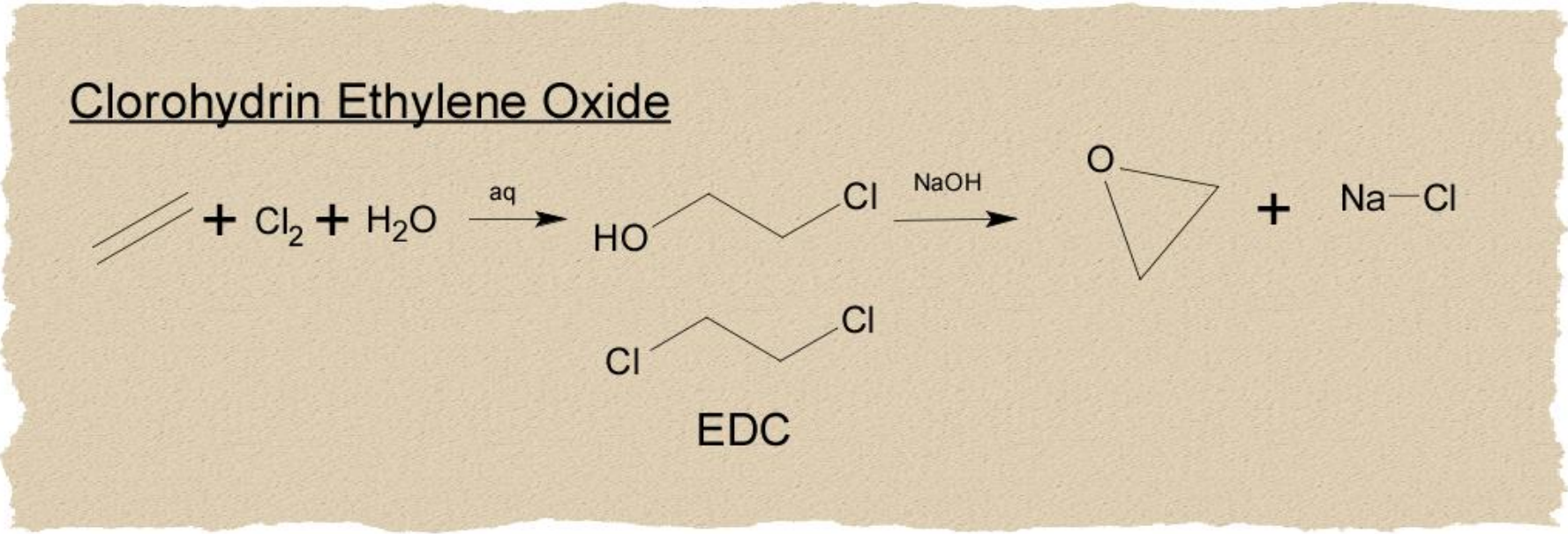
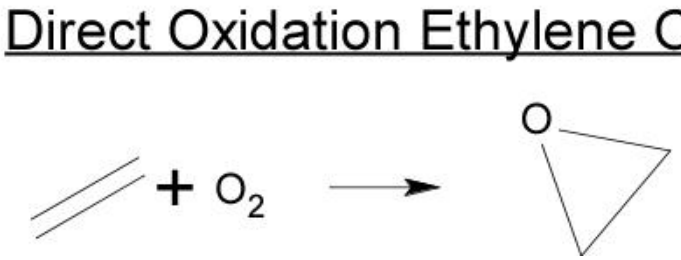
Epoxy Resins



Direct Oxidation





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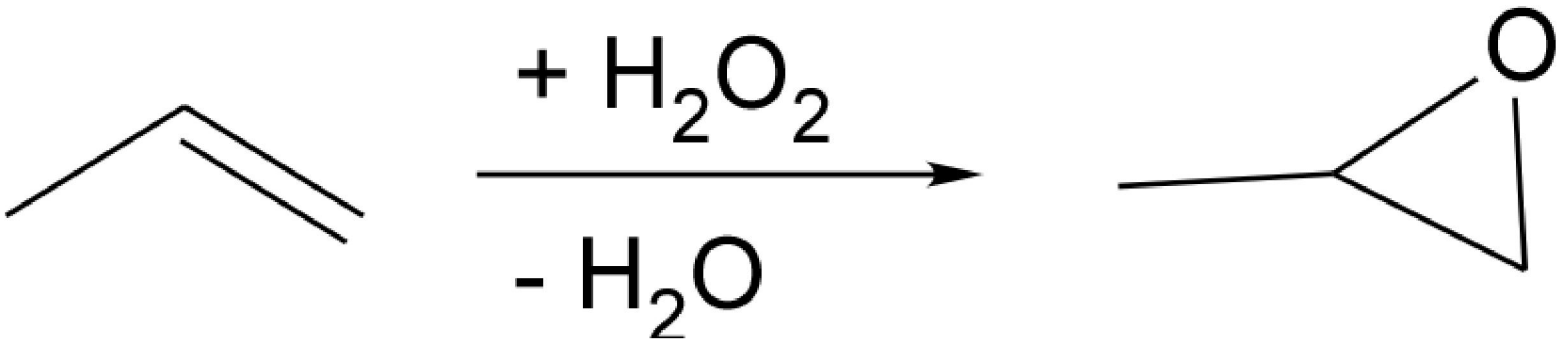
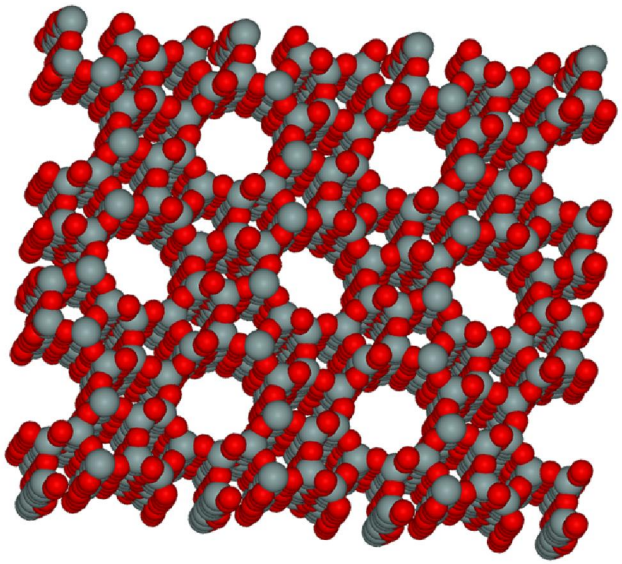
Hydroperoxidation





titanium silicate catalyst

0.5 nm pores

suitable for packed bed reactor

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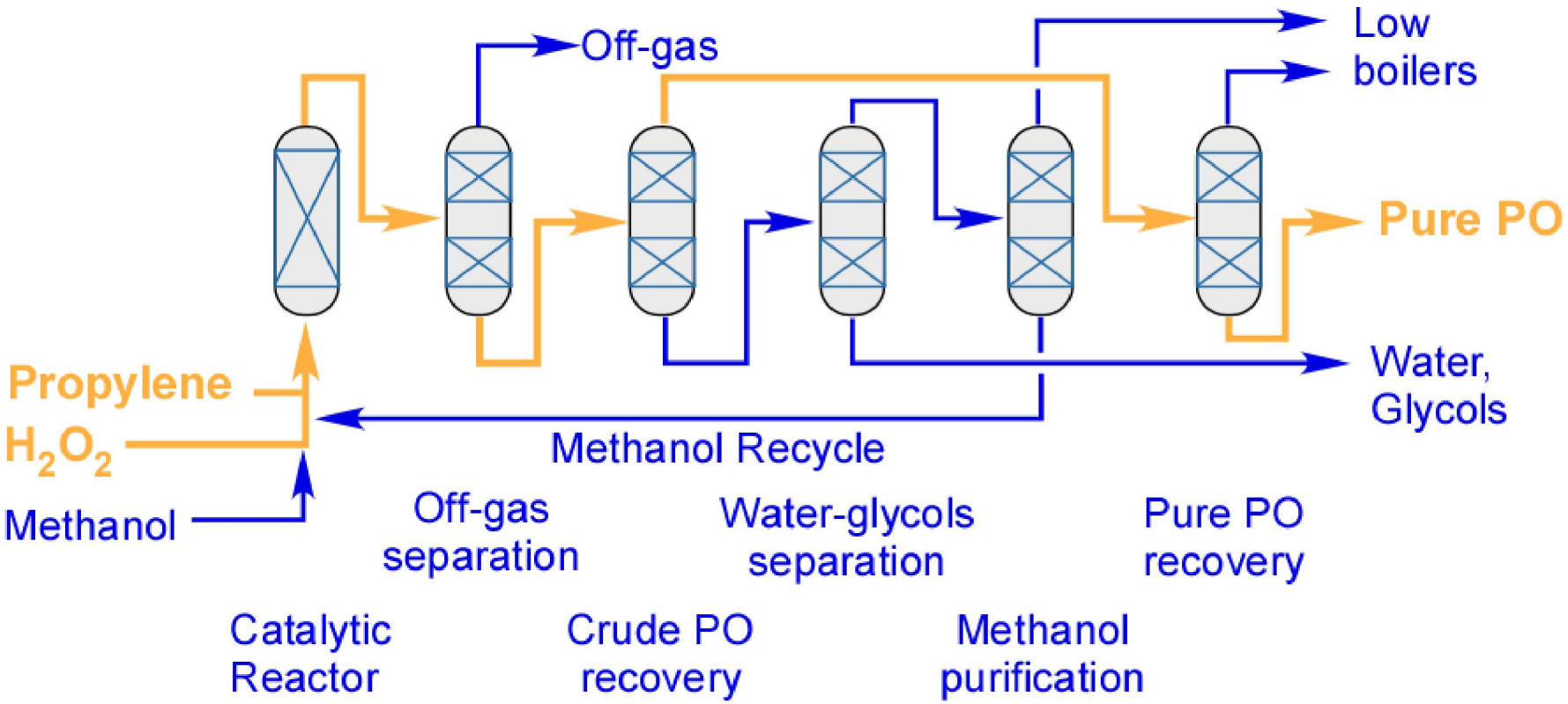
Simplified Process Flowsheet



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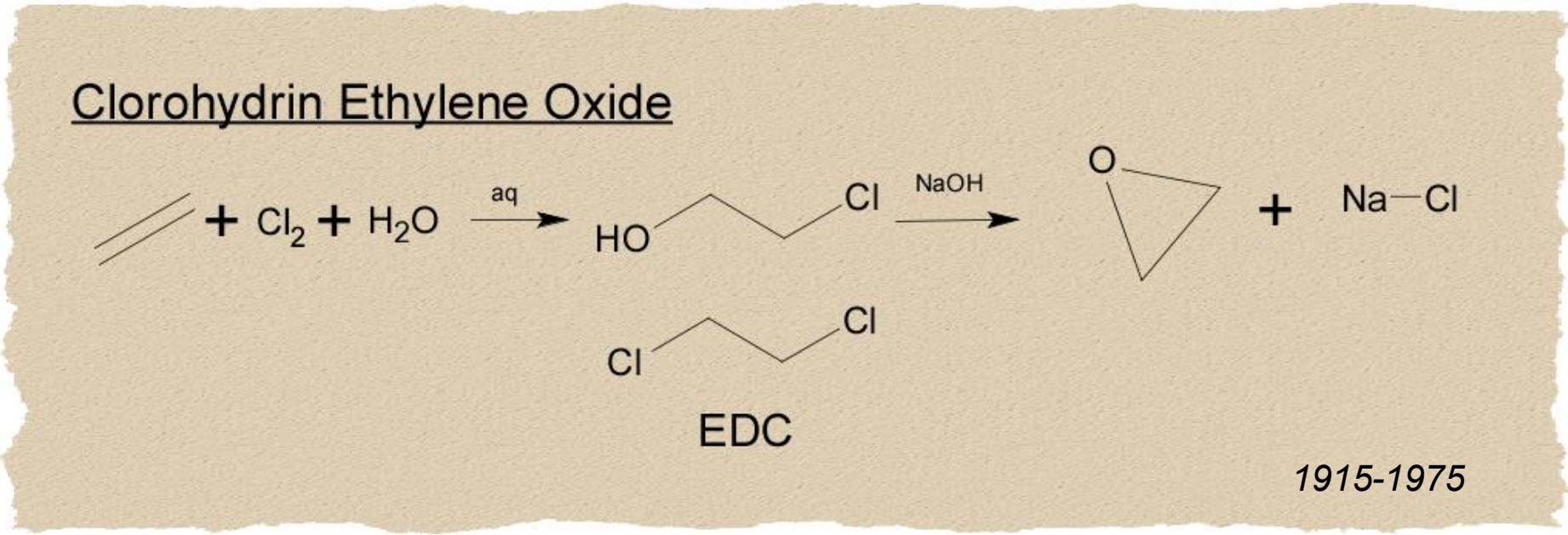
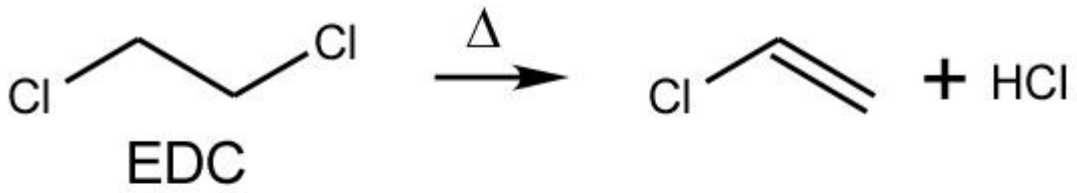
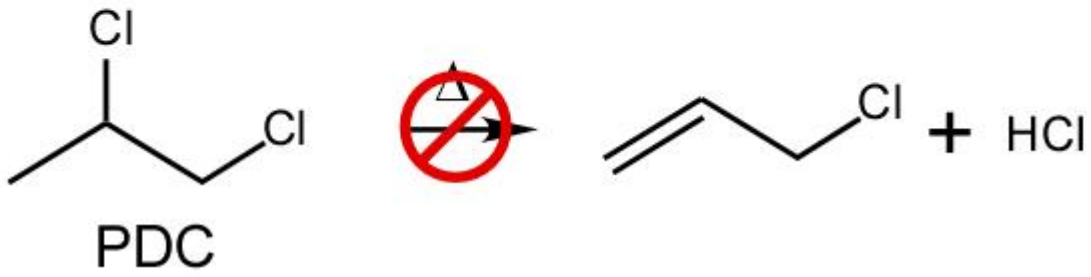
Chlorohydrin Chemistry







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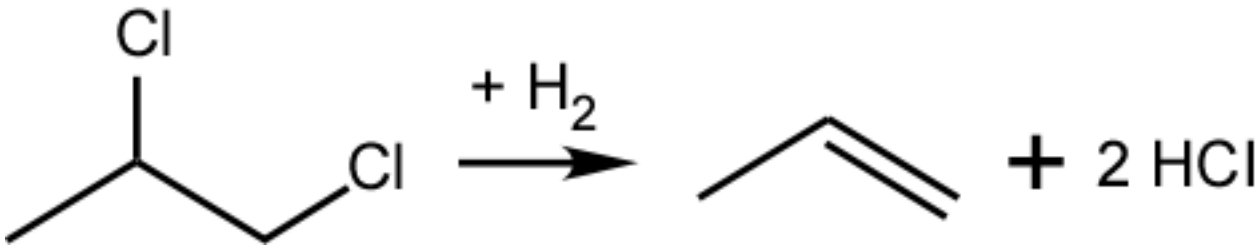
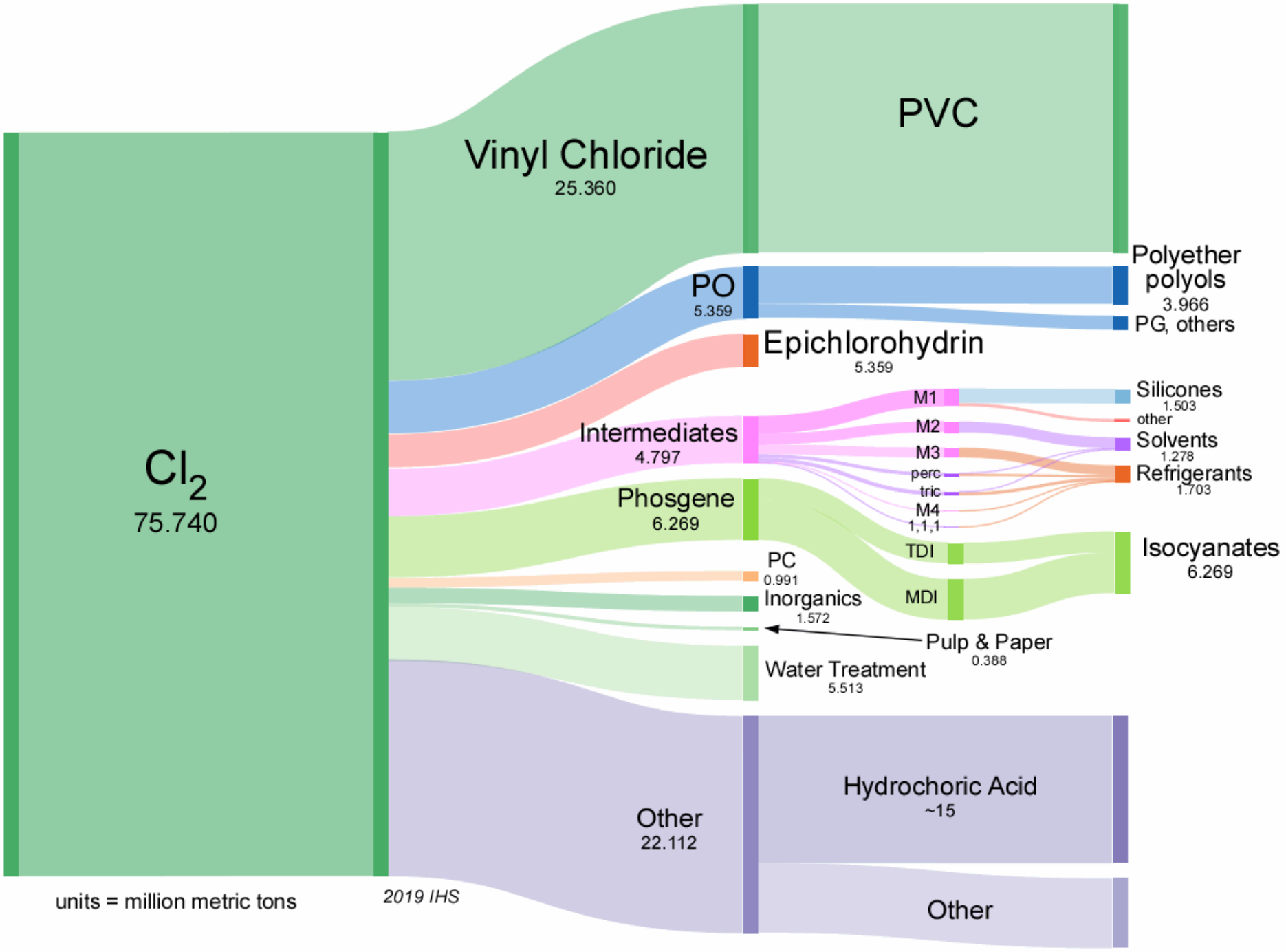
PDC Hydro

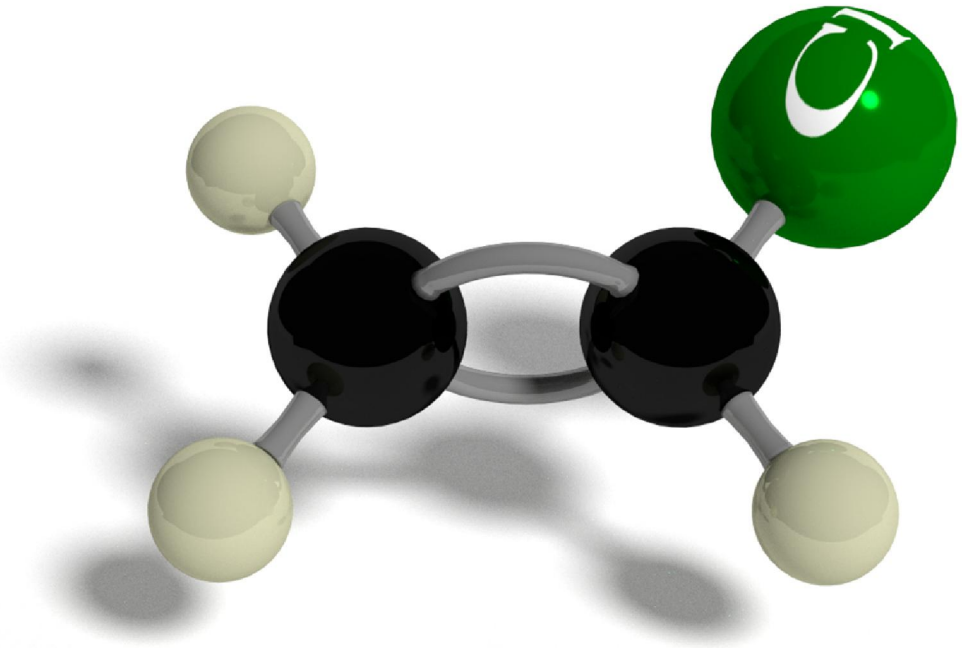


PtCu catalyst developed by Larry Ito

Carbon supported


Cl_2
75.740
Vinyl Chloride
25.360
PVC
PO
5.359
Epichlorohydrin
5.359
Intermediates
4.797
Phosgene
6.269
PC
0.991
Inorganics
1.572
Pulp & Paper
0.388
Water Treatment
5.513
Other
22.112
Hydrochoric Acid
~15
Other
Polyether polyols
3.966
PG, others
M1
M2
M3
perc
tric
M4
1,1,1
TDI
MDI
Silicones
1.503
other
Solvents
1.278
Refrigerants
1.703
Isocyanates
6.269
units = million metric tons
2019 IHS

Vinyl Chloride



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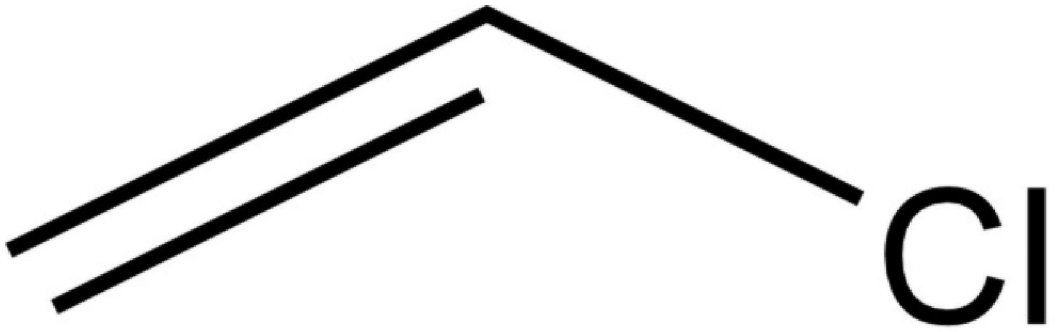

Vinyl Chloride Monomer(VCM)

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

Source: Chemical Week product focus

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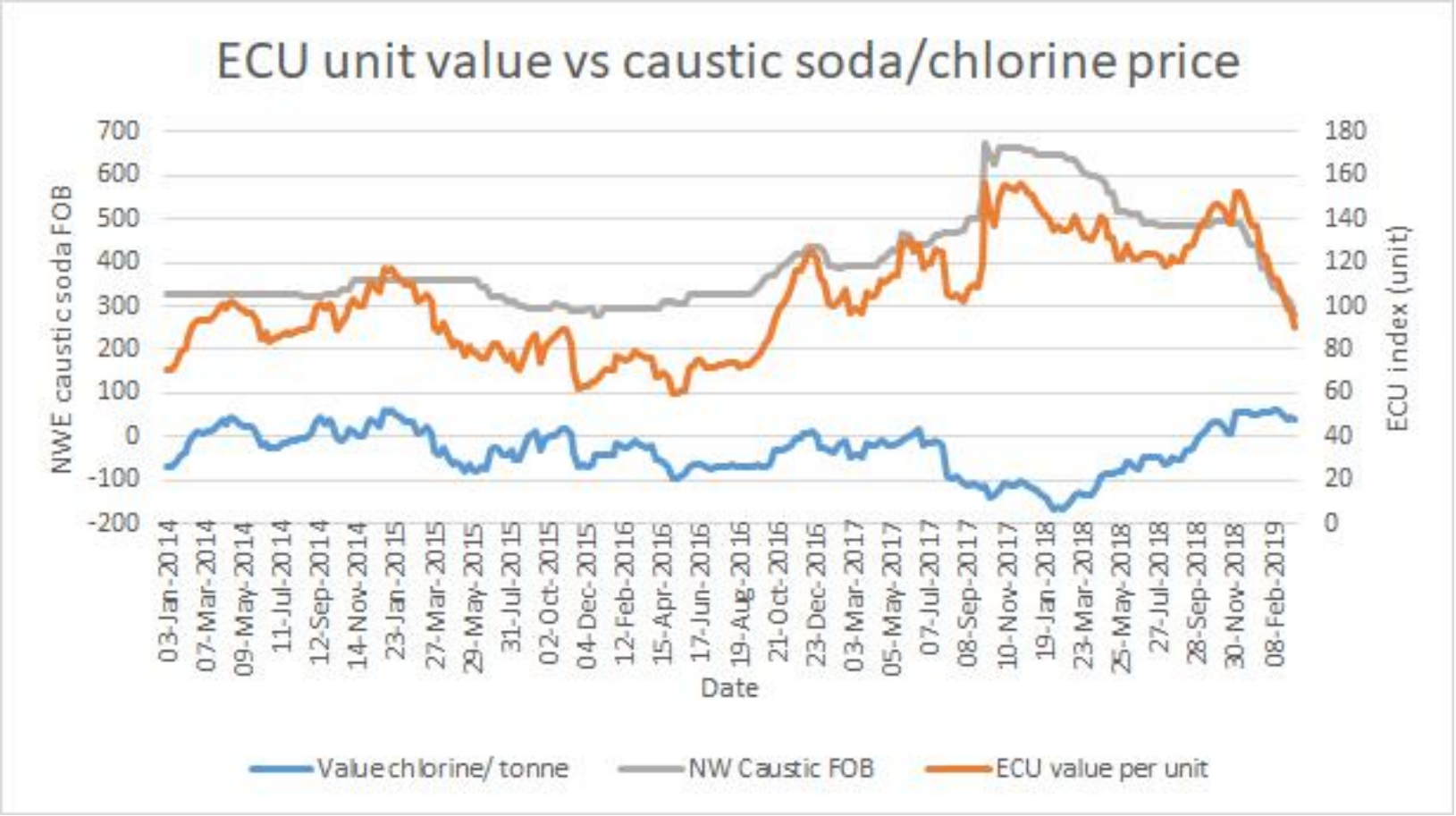
ECU Pricing



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

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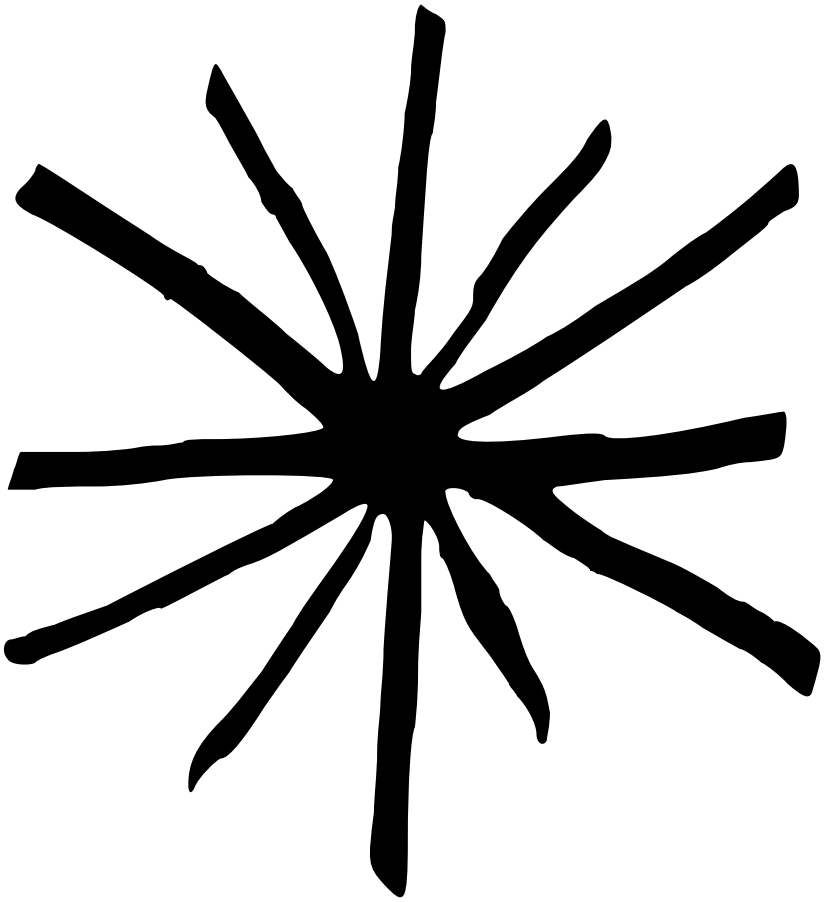
Breakfast of Champions



see Vonnegut's *Breakfast of Champions*
or
Pete Davidson's *The King of Staten Island*

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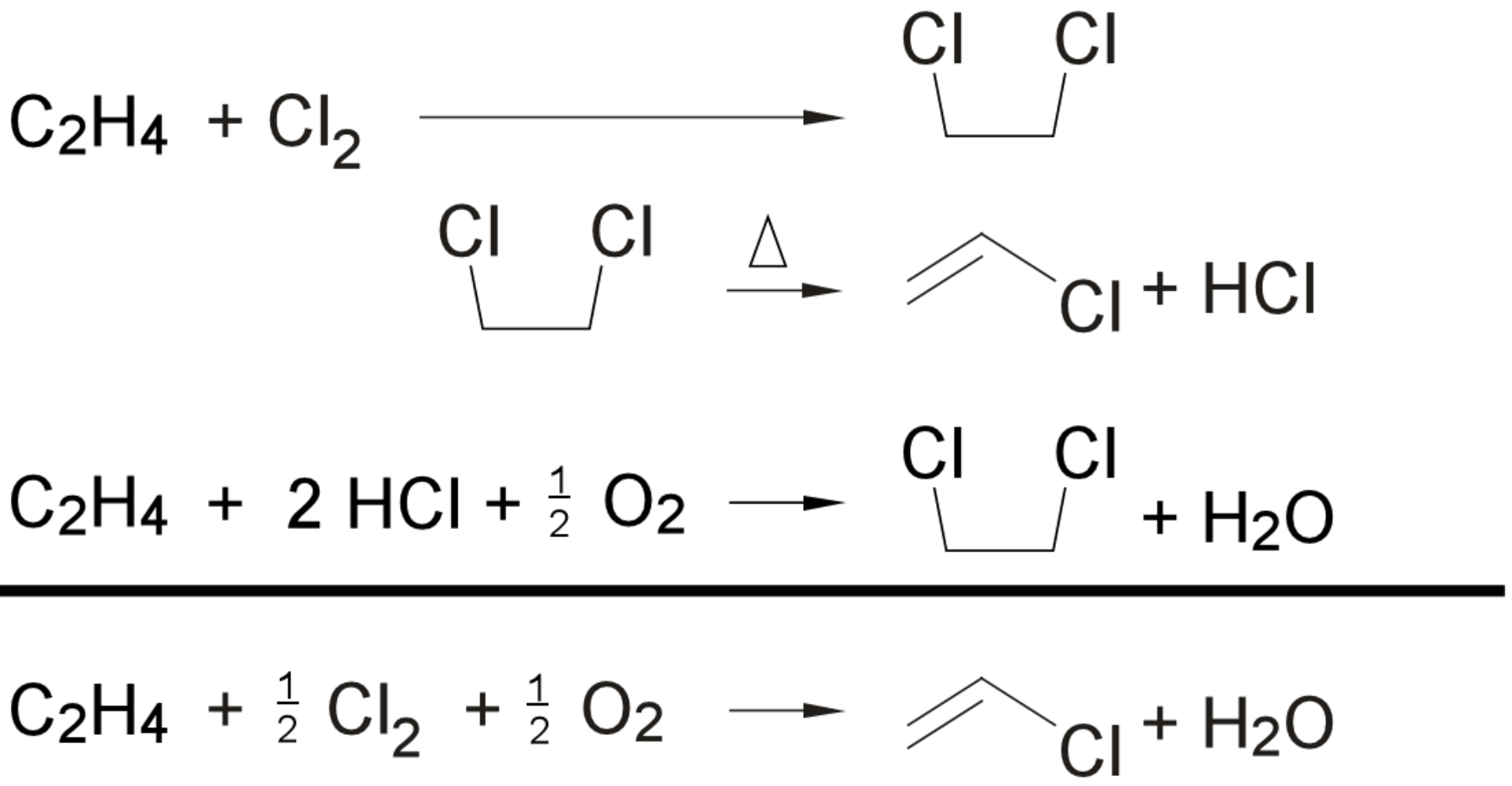
Conventional Production



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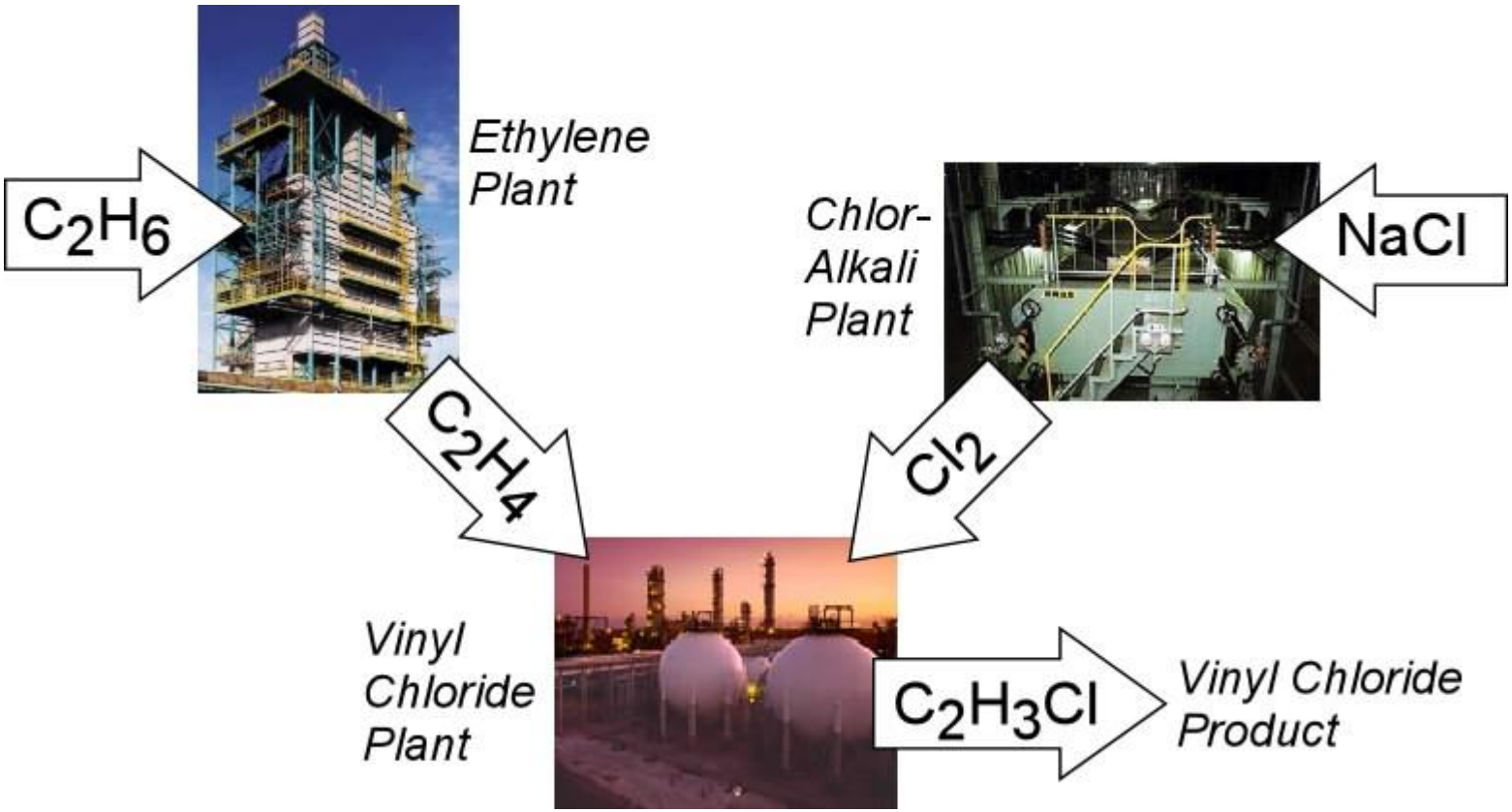
Conventional VCM



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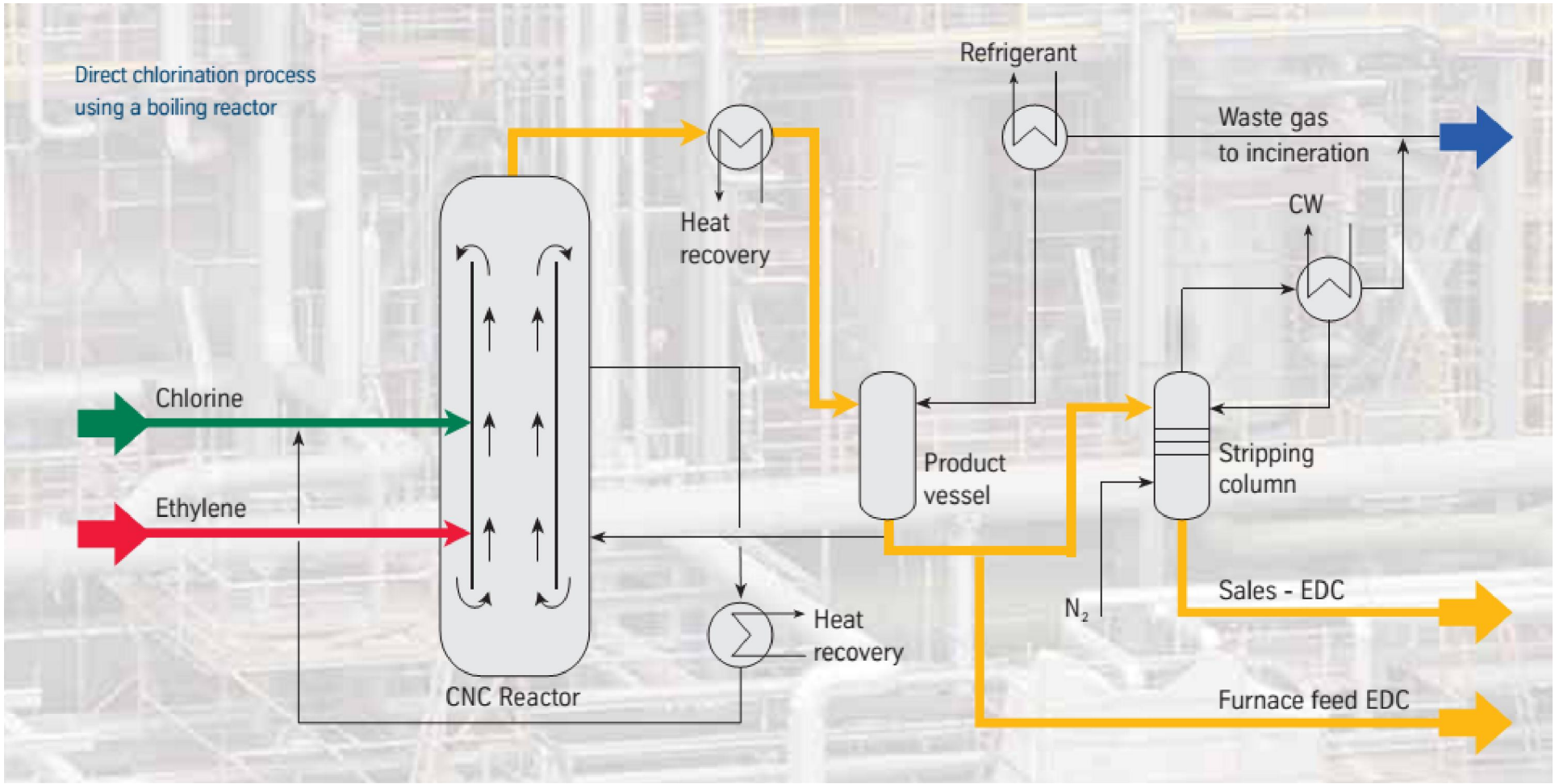
Direct Chlorination



Vinnolit

Uhde
ThyssenKrupp

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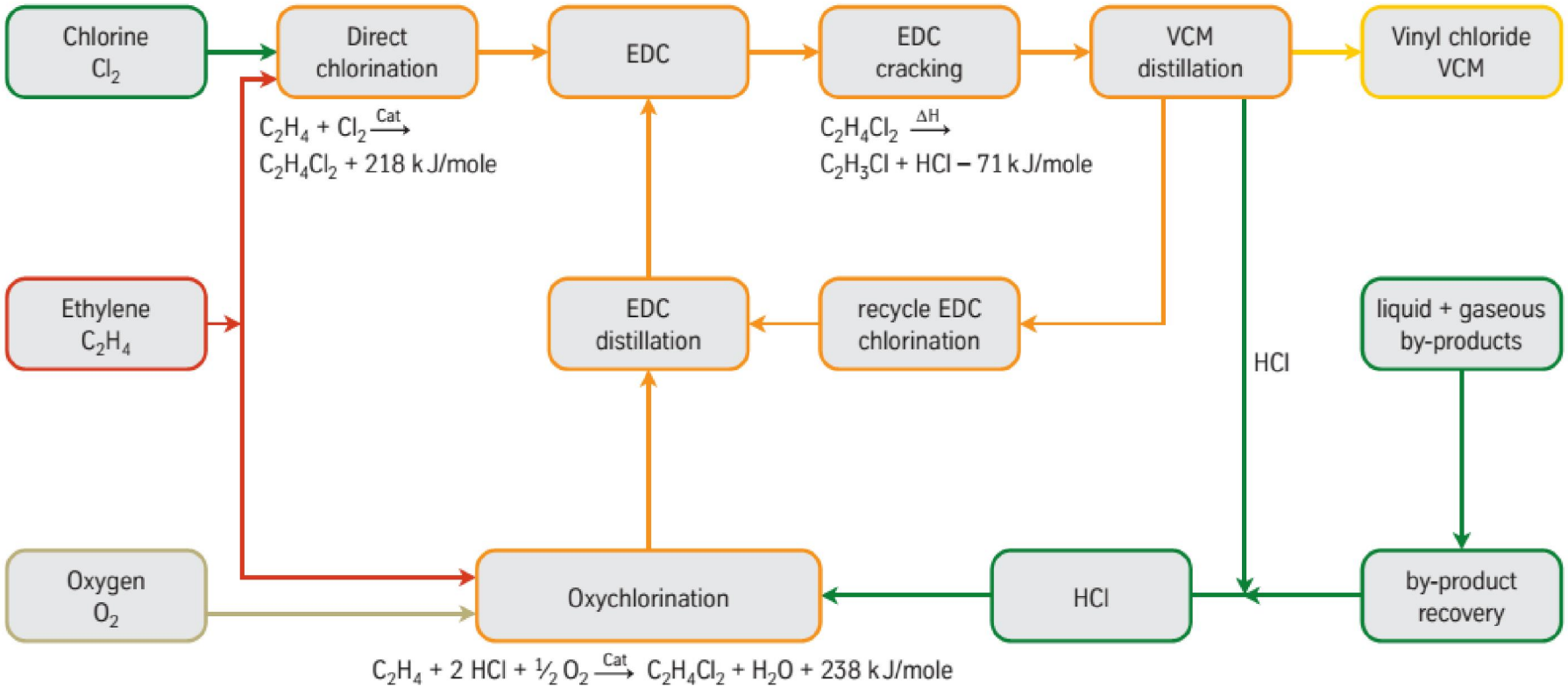
More Detail

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

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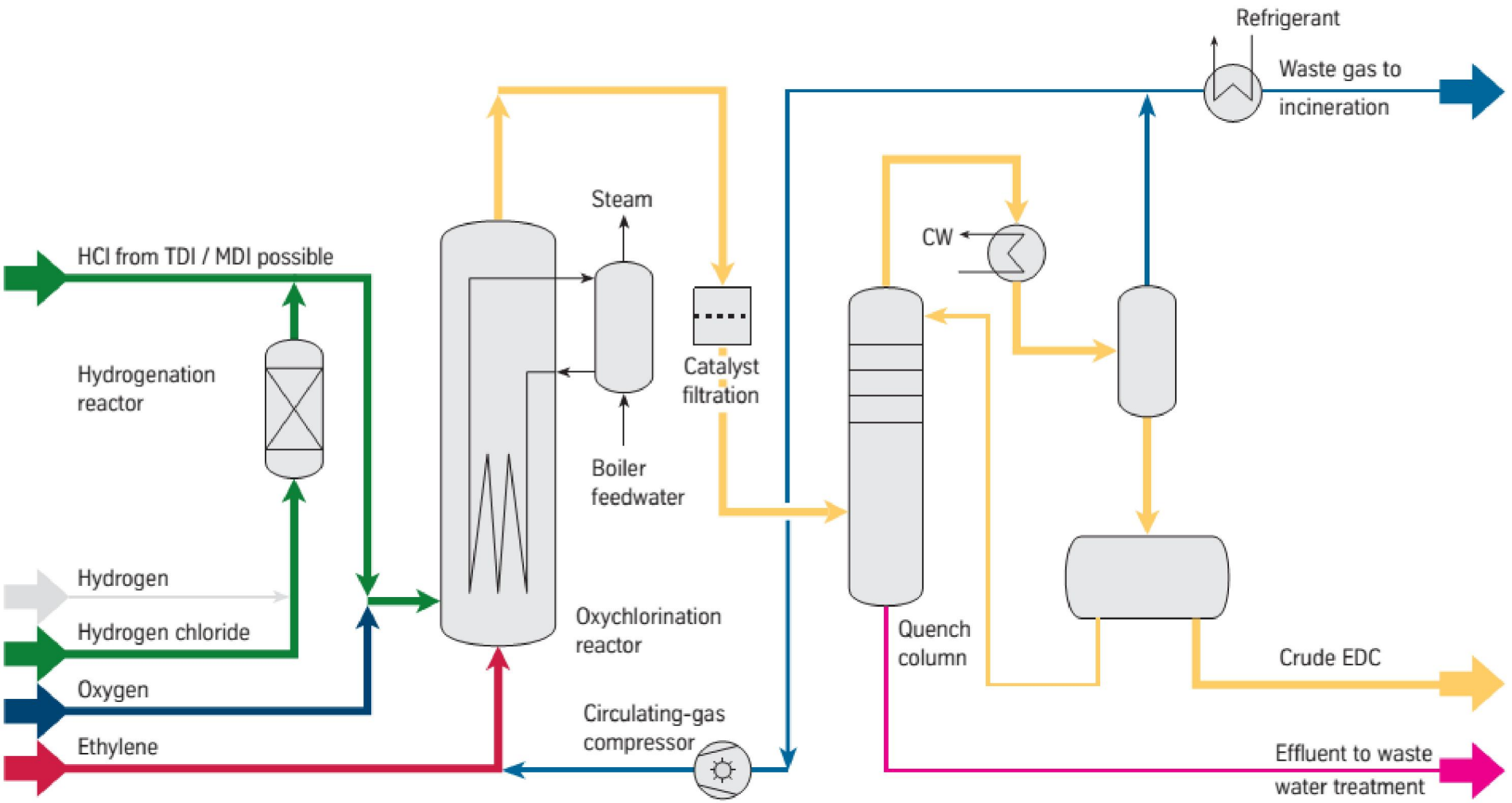
Oxychlorination



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Uhde
ThyssenKrupp

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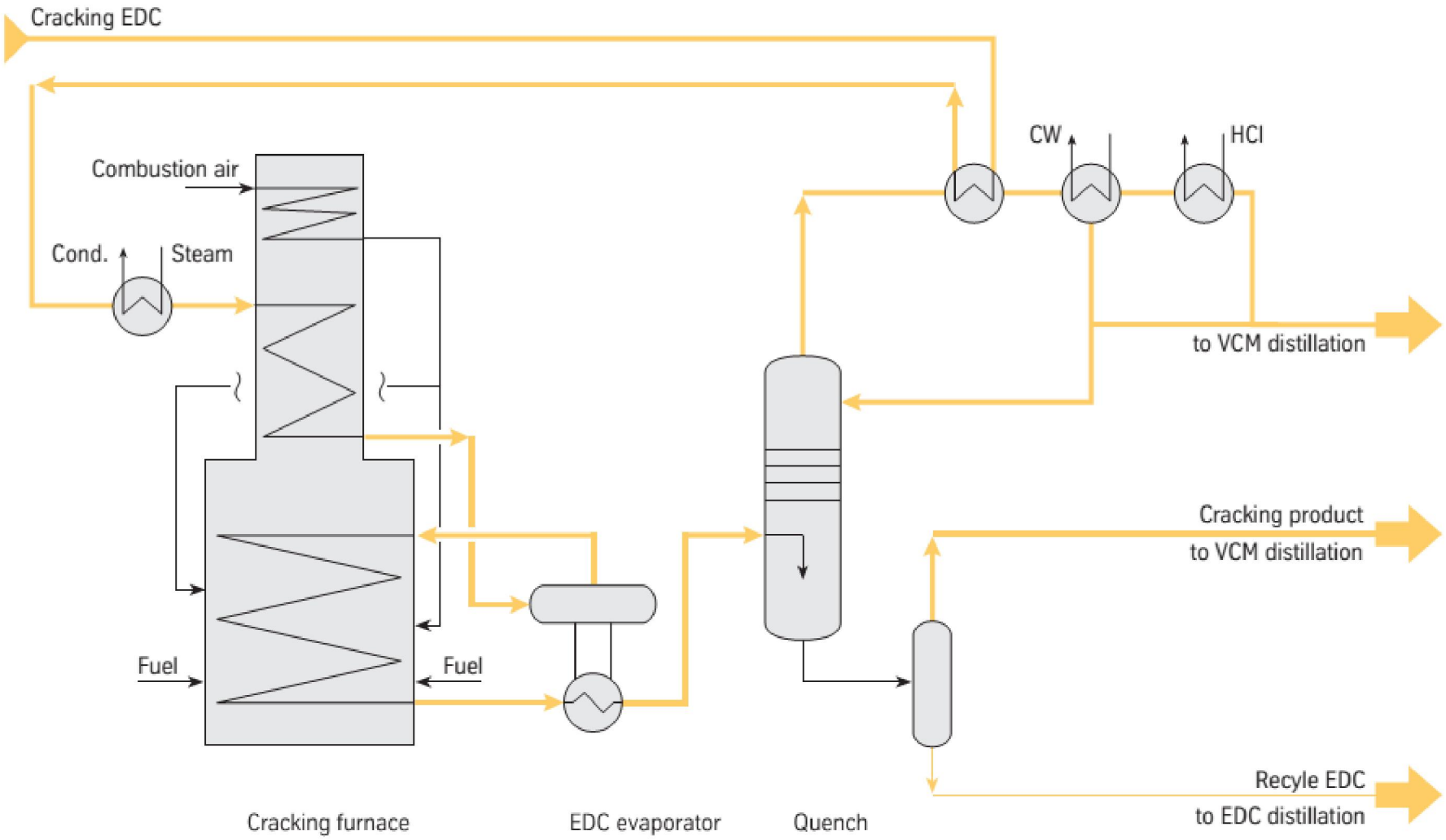
Cracking



Vinnolit Uhde ThyssenKrupp

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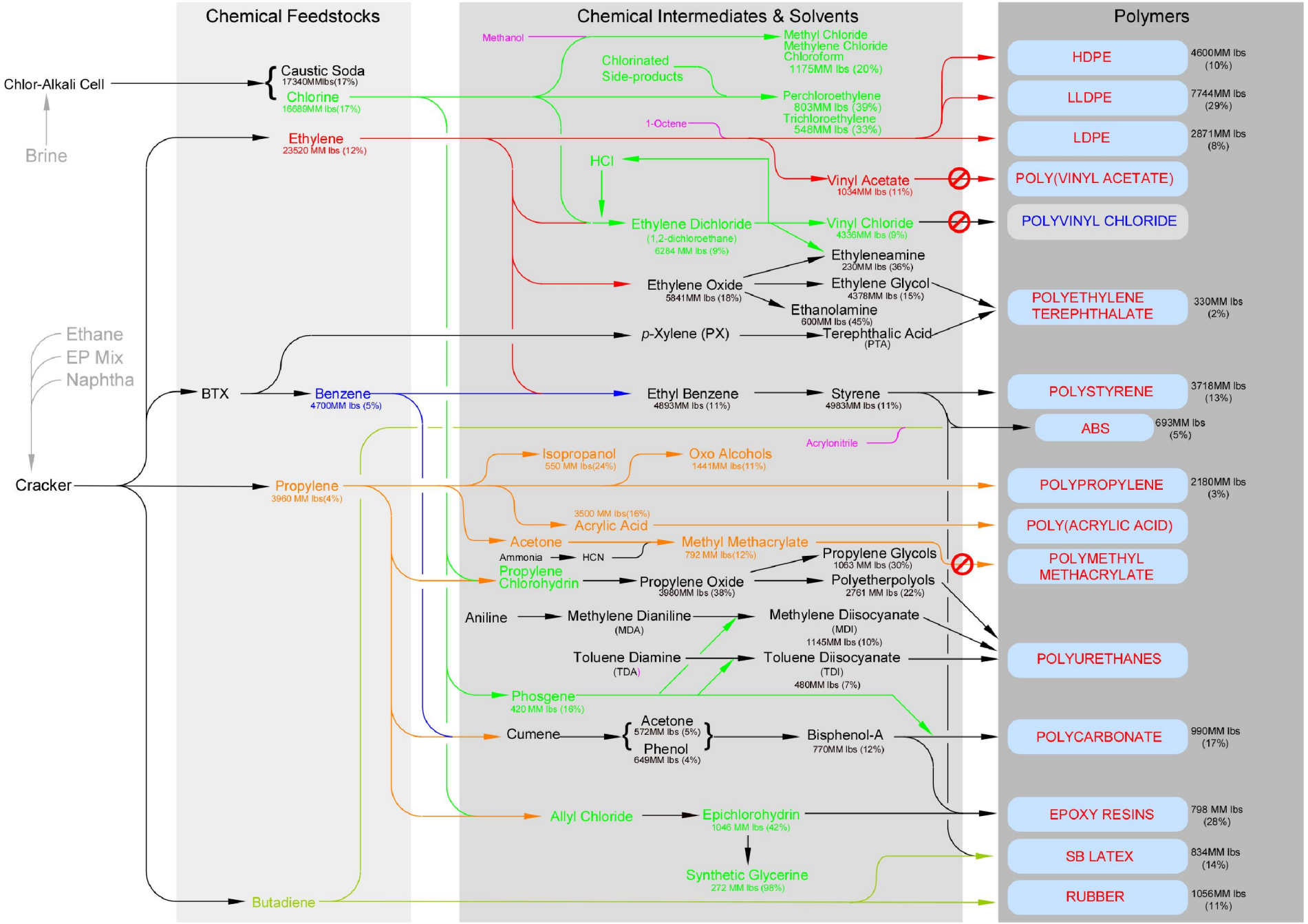
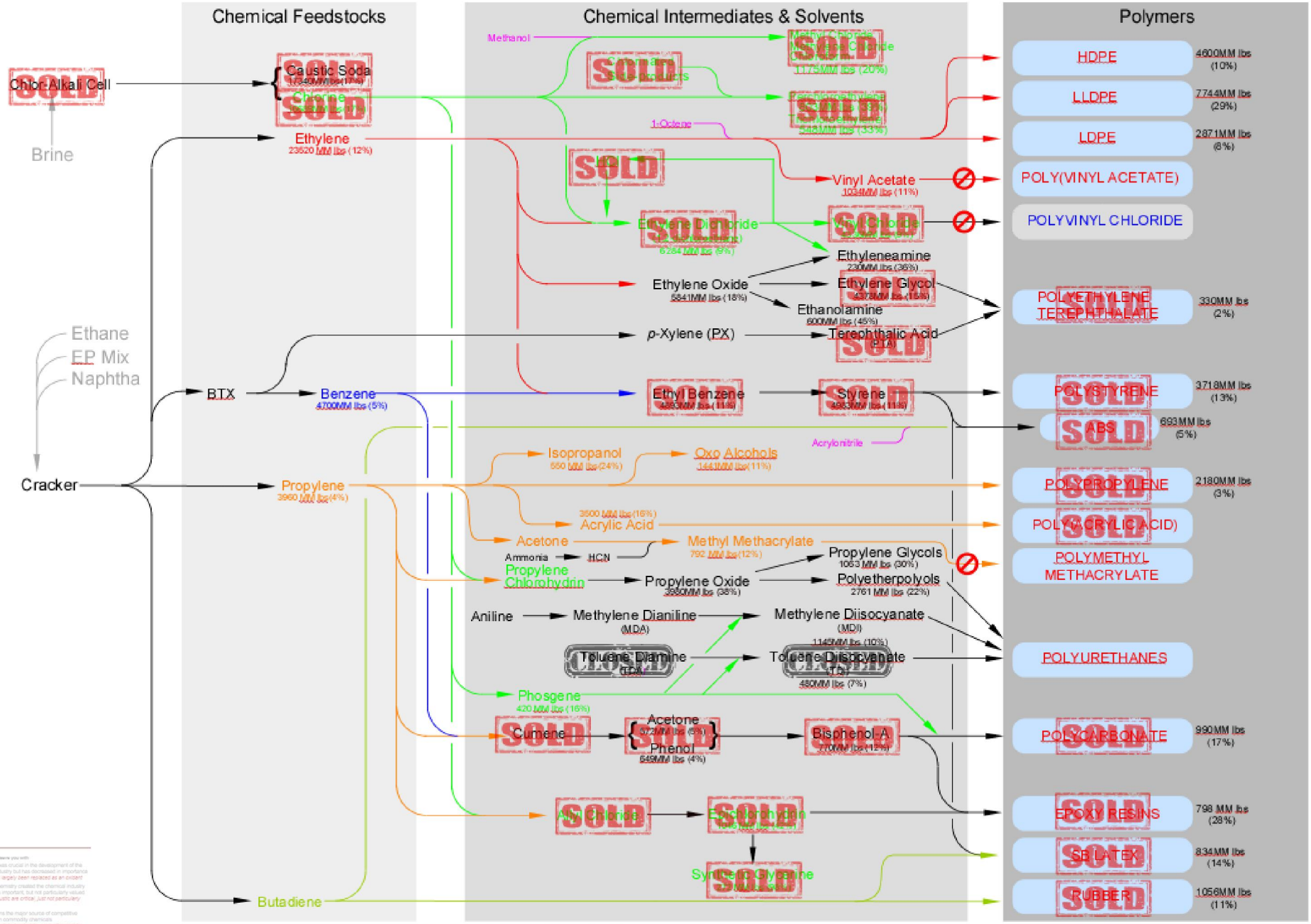

Chemical Feedstocks
Chemical Intermediates & Solvents
Polymers
Chlor-Alkali Cell
Brine
Caustic Soda
17340MMlbs(17%)
Chlorine
16689MM lbs(17%)
Ethylene
23520 MM lbs (12%)
Ethane
EP Mix
Naphtha
Cracker
BTX
Benzene
4700MM lbs (5%)
Propylene
3960 MM lbs(4%)
Butadiene
Methanol
Methyl Chloride
Methylene Chloride
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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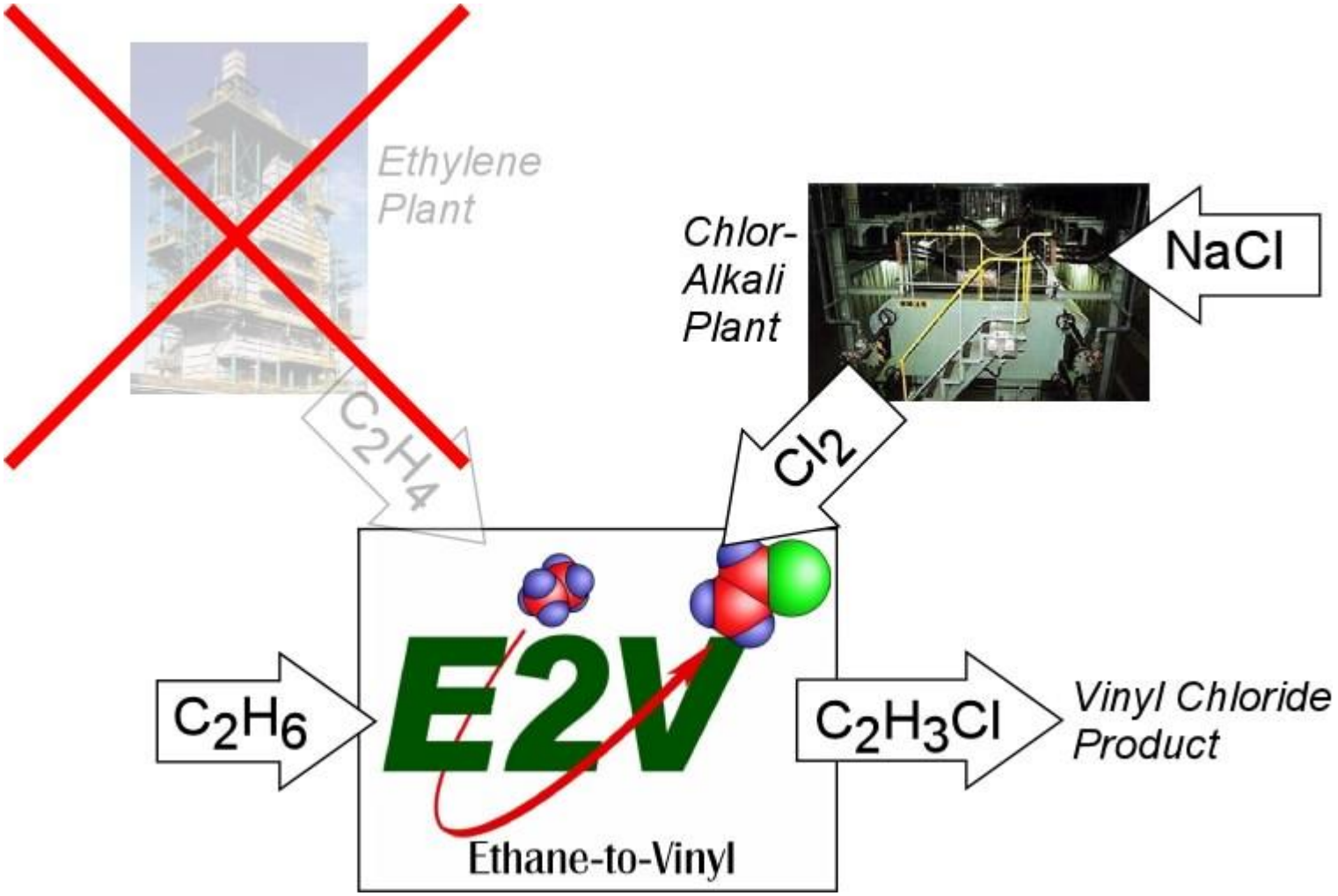
MEJ-2/2003

E2V


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

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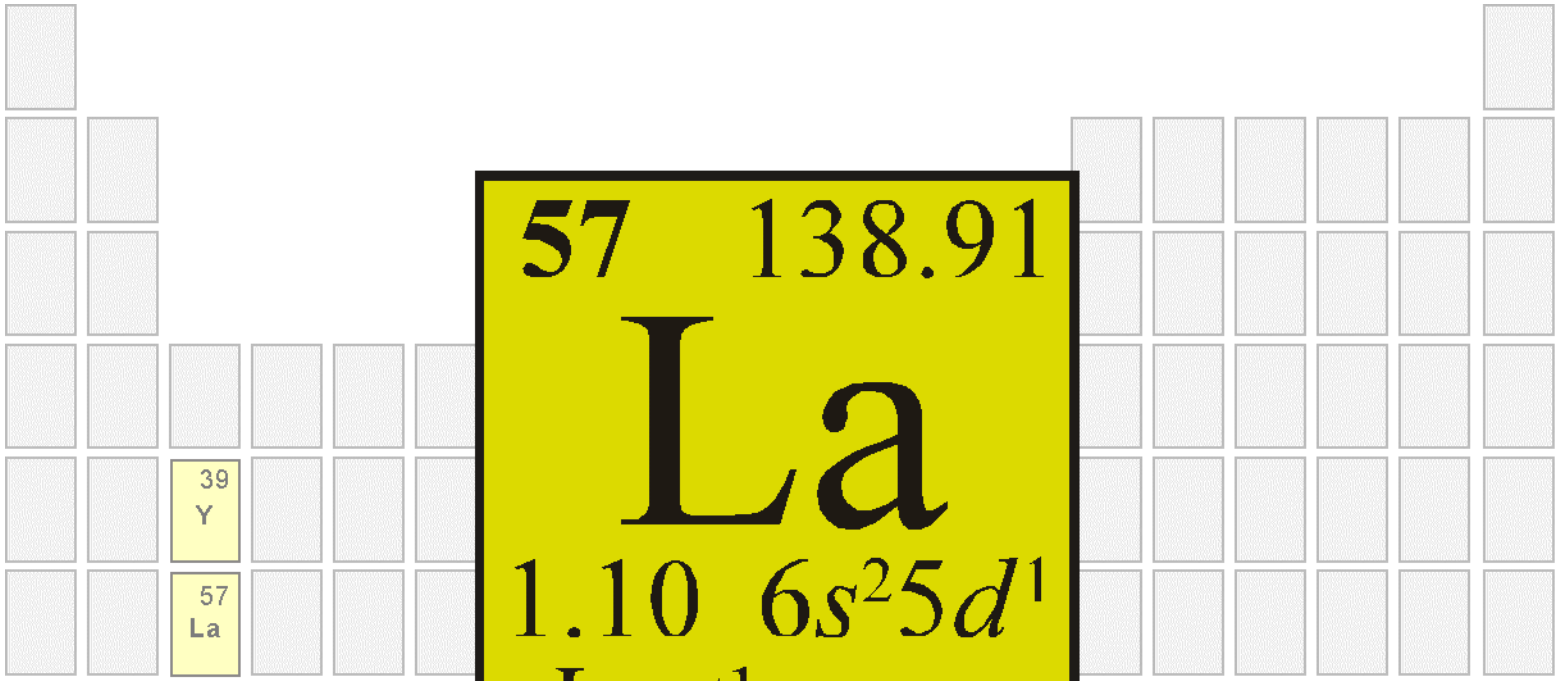
Lanthanide Catalyst



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

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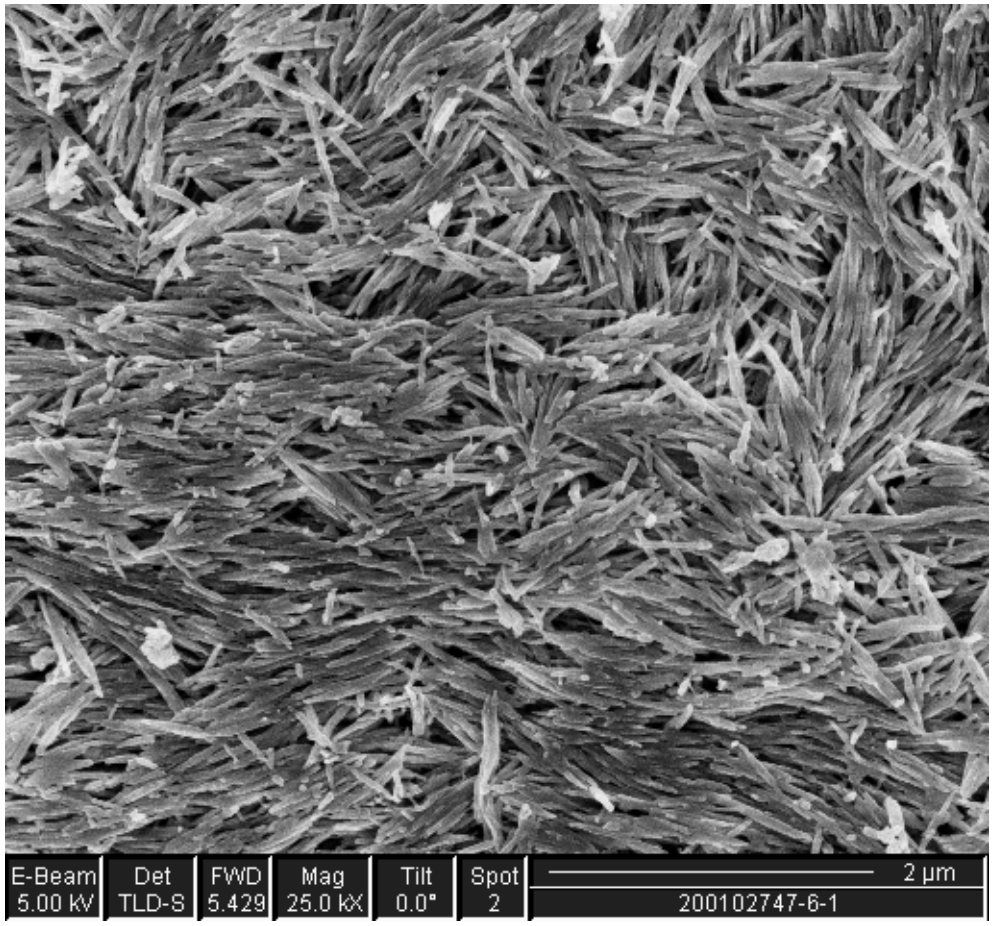
LaOCl


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

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Fluidized Bed

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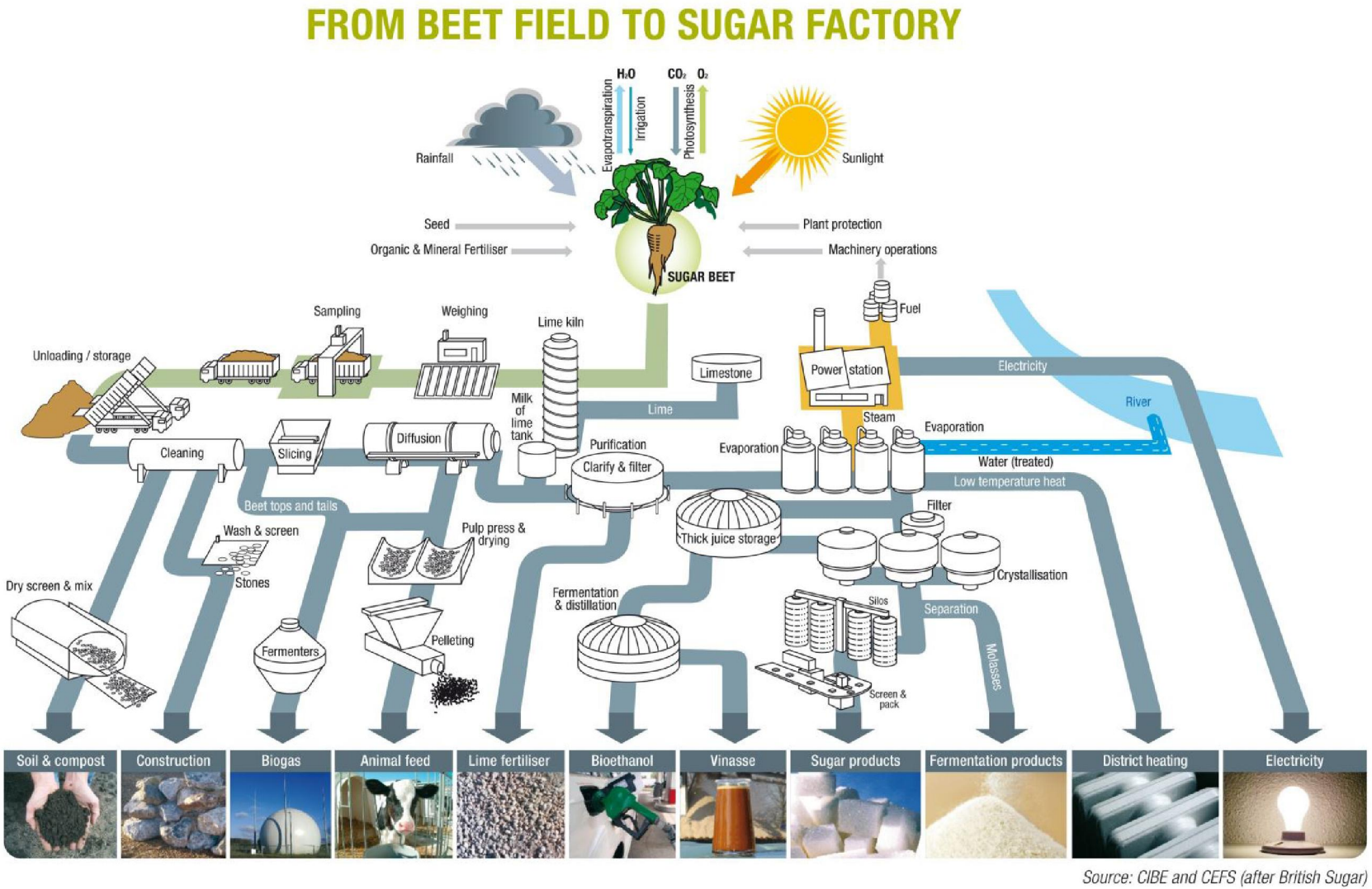
What I hope to leave you with

- Integration was crucial in the development of the chemical industry but has decreased in importance
  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/

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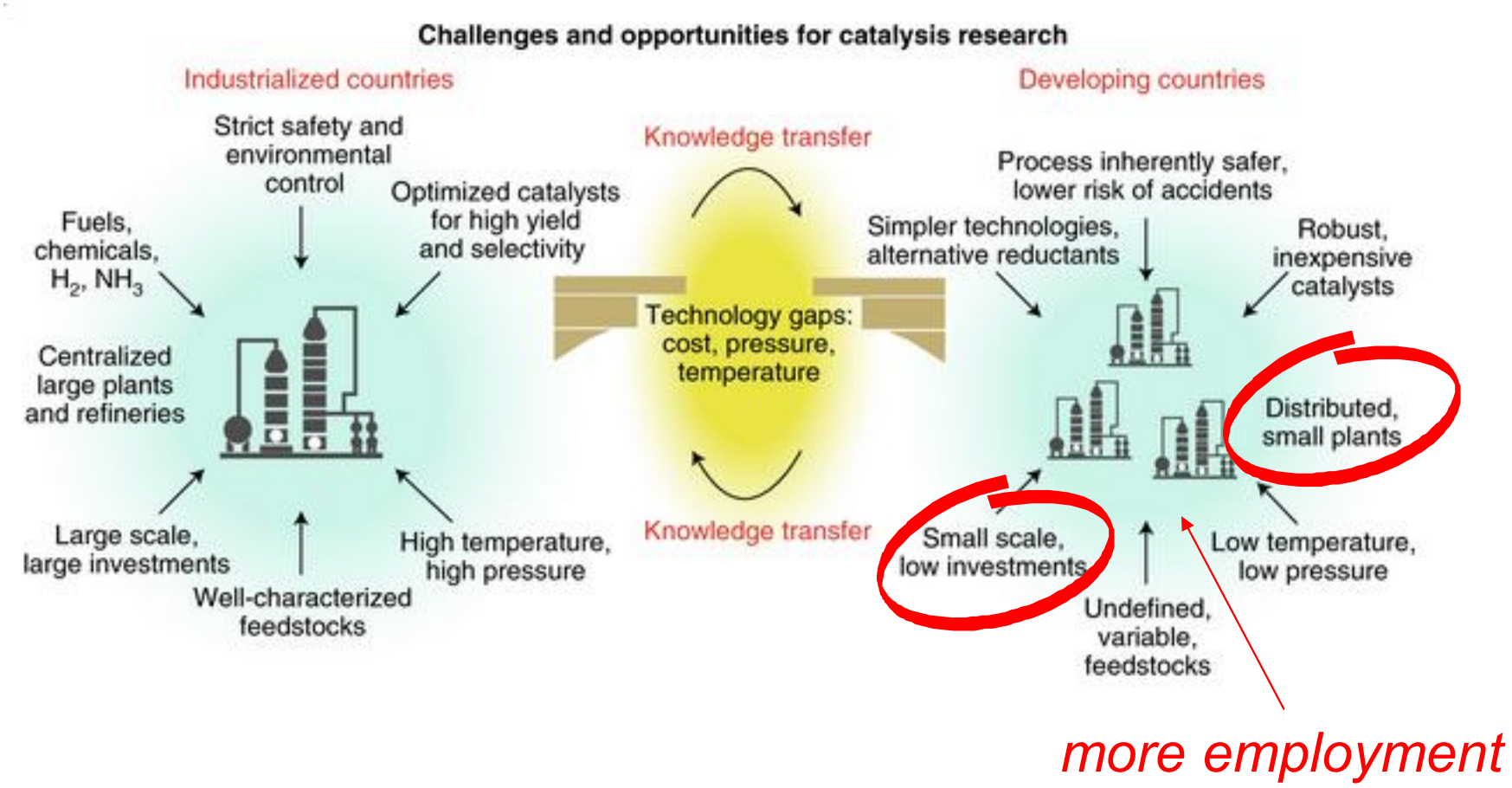
Distributed Manufacturing



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

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