The Impact of Mega Economic Trends on the Chemical Industry and Chemical Engineering Profession

How Chemical Engineering Fundamentals Can Change the World

William F. Banholzer, PhD
Executive Vice President & Chief Technology Officer
The Dow Chemical Company

DOW®

8
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HUMAN

Dow Sustainability - Microsoft Internet Explorer

http://www.dow.com/commitments/

Dow will reduce GHG intensity 25 percent from 2005 to 2015.

Sustainability requires making every decision with the future in mind. It is our relationship with the world around us - creating economic prosperity and social

Dow is combining the creativity of its employees with its technological expertise to provide innovative solutions to help supply cleaner and safer water to those in need.

- Commitment to the Planet
- Corporate Citizenship
- Product Responsibility
- Public Safety & Security
- Issues & Challenges
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for growth and profitability.

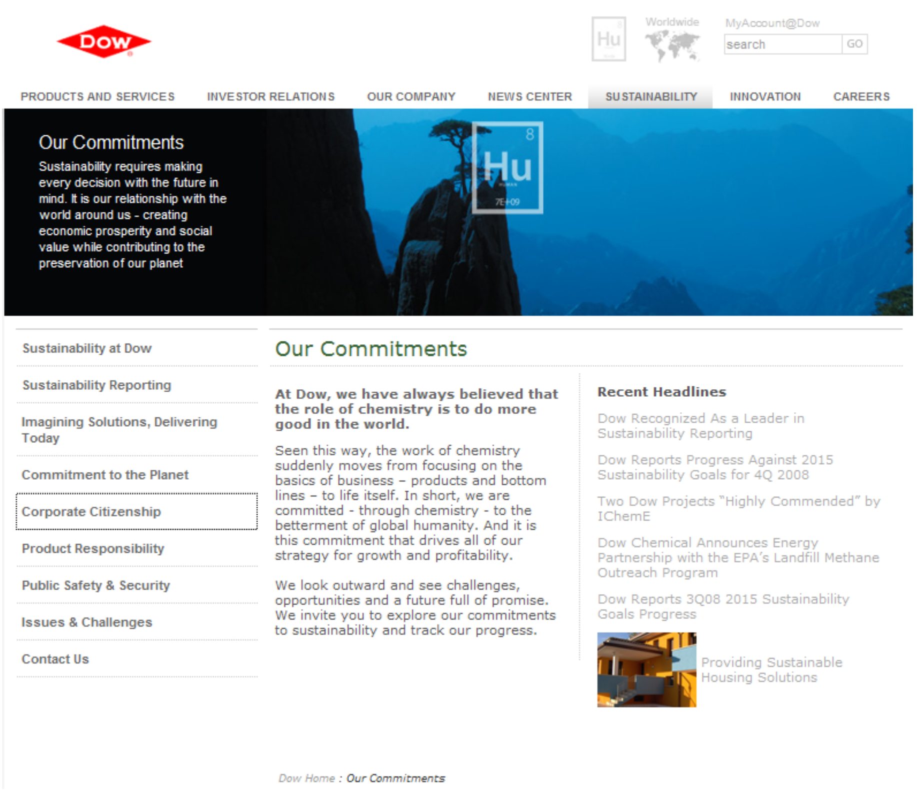
William Banholzer, MIT 2009

Technology Evaluation – **A Case Study**

In April 2008, Dow announced plans to build a 600 MW coal and gas fired power plant at its location in Stade, Germany. The 20 year old plant that is currently there can only meet 25%of the need for power.

Dow's commitment to sustainability includes a pledge to reduce GHG emissions.

We will leverage the strength of the human element in our laboratories around the world and make unprecedented financial investments in R&D to achieve breakthrough solutions that will slow, stop and reverse global warming.



In 2008, a company by the name of Skyonic contacted us with a proposal to completely eliminate carbon dioxide emissions from our proposed power plant in Stade.

- ***WHO WE ARE:***
  Skyonic is a for-profit Intellectual Property corporation dedicated to the proliferation of the internationally patented SkyMine™ process. SkyMine™ was developed with the intent to reduce global CO2 emissions and halt the advancement of global climate change without impacting development. Skyonic is based in Austin, Texas, with laboratory and field operations throughout the state.

Power Plant Waste Used to Make Cookies!

Cookies from Coal?

Technology Evaluation – **Skyonic Process**

Founded in 2005. Has raised $4.5MM from 15 investors including TXU Corp (NYSE: TXU).

$NaOH$		CO_2		$NaHCO_3$
Caustic	**+**	**Carbon Dioxide**	$\longrightarrow$	**Baking Soda**

This technology appears to be a natural fit for Dow, the world's leading manufacturer of caustic soda.

Should Dow:

1. **Collaborate with Skyonic to implement this technology at the Stade plant?**
2. **Ignore the offer?**

What questions would you ask?

Technology Evaluation – **Skyonic Process**

How is **caustic** made?

NaCl Salt	+	H_2O Water	→	NaOH Caustic	+	½ Cl_2 Chlorine	+	½ H_2 Hydrogen

How much NaOH is needed to capture the CO_2 from our power plant?

7 billion lb/yr — *This is 5% of the world market.*

Capital required to build this NaOH capacity?

$4 billion — *This is 4 times the capital required to build our power plant.*

How much electricity is required to make this NaOH?

1000 MW plant — *This is 400 MW more than our plant will produce.*

How much chlorine byproduct is made?

7 billion lb/yr — *This is 50% of Dow's annual production.*

William Banholzer, MIT 2009

The **Fundamentals** are…**FUNDAMENTAL**

You can NEVER lose sight of these considerations:

•**Thermodynamics**	In Your Favor
•**Kinetics**	Fast
•**Catalysis**	Controlled
•**Separations/Transport**	Easy/Lower Energy
•**Unit Operations**	Lower Capital

There isn't a useful process in the world that is exempt from these **fundamentals**

William Banholzer, MIT 2009

Breakthrough Capture Research

Dow is a global gas treating and technology leader

-World's largest producer of amines

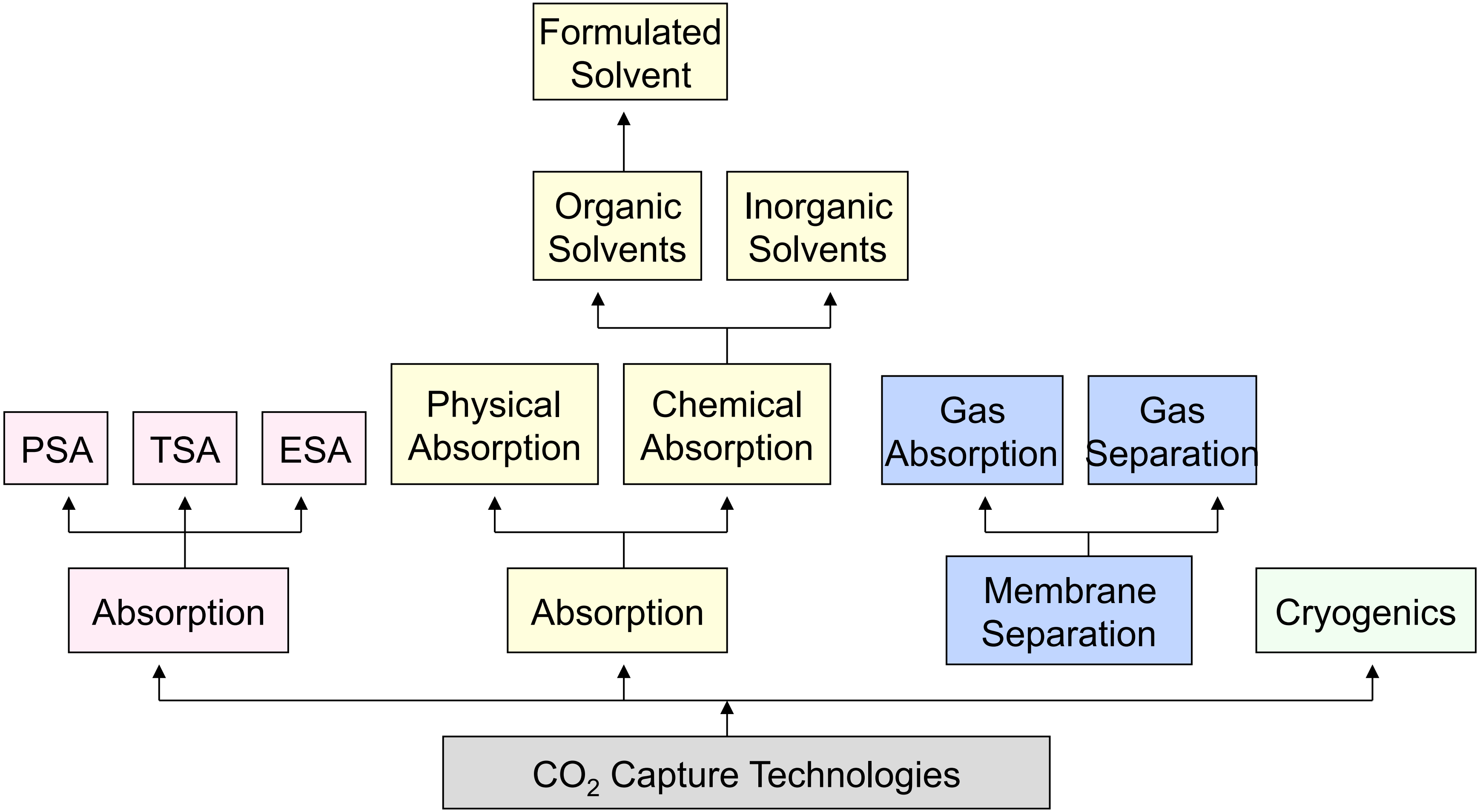
Alstom is at the forefront of carbon capture technology development

- Leadership and experience in power plant technologies

"A joint development (JDA) and commercialization agreement for advanced amine scrubbing technology for the removal of CO_2 from low pressure flue gases particular to fossil fuel fired power plants and other major industries."

February 13, 2008

Potential CO_2 Capture Technologies



<u>**The CANiCAP Program: Planning Options for Technology and Knowledge Base Development for the Implementation of Carbon Capture and Transportation Research, Development and Deployment in Canada**</u>, W.D. Gunter, Bob Mitchell, I. Potter, Brent Lakeman and Sam Wong, 122 pages, (2005)

Technology Challenge – Concentration

Capture Technology	CO_2 Conc (%)	Feed Gas Pressure (MPa)	Operating Temperature (*C)
Adsorption	>30	Moderate	Low to Moderate
Cryogenic	>90	Moderate	Low
Membrane	>15	>0.7	Feed temperature
Physical Absorption	>20	>2	Low (-10)
Amine Absorption	>3	>0.1	50

Wong et.al 2002)

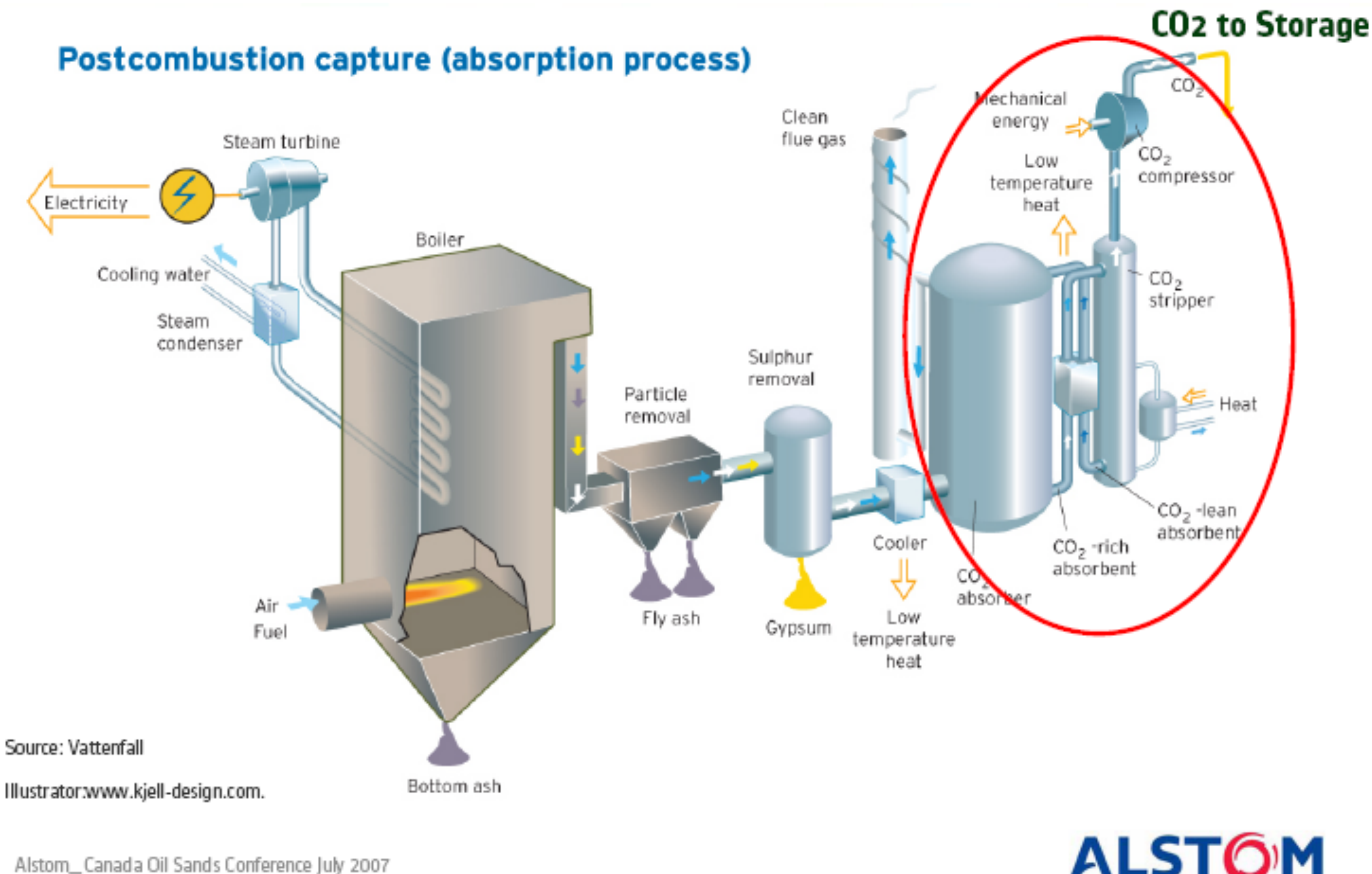
Why Amine Absorption?

•Easily multistaged and operated as a continuous process

•Does not require compression of flue gas prior to treatment

•Best compromise of operating and capital cost with proven robustness in industry.

The Process



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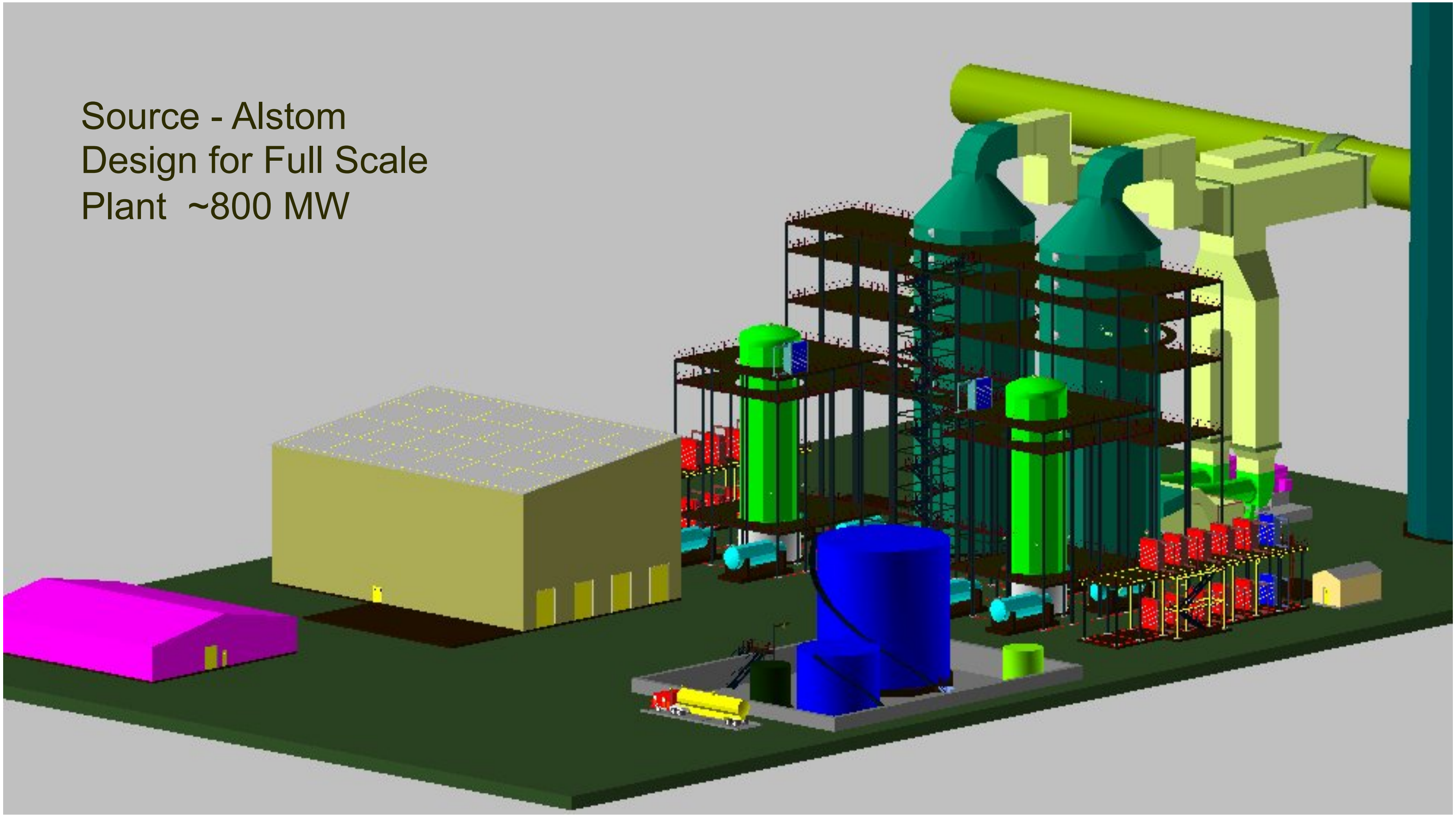
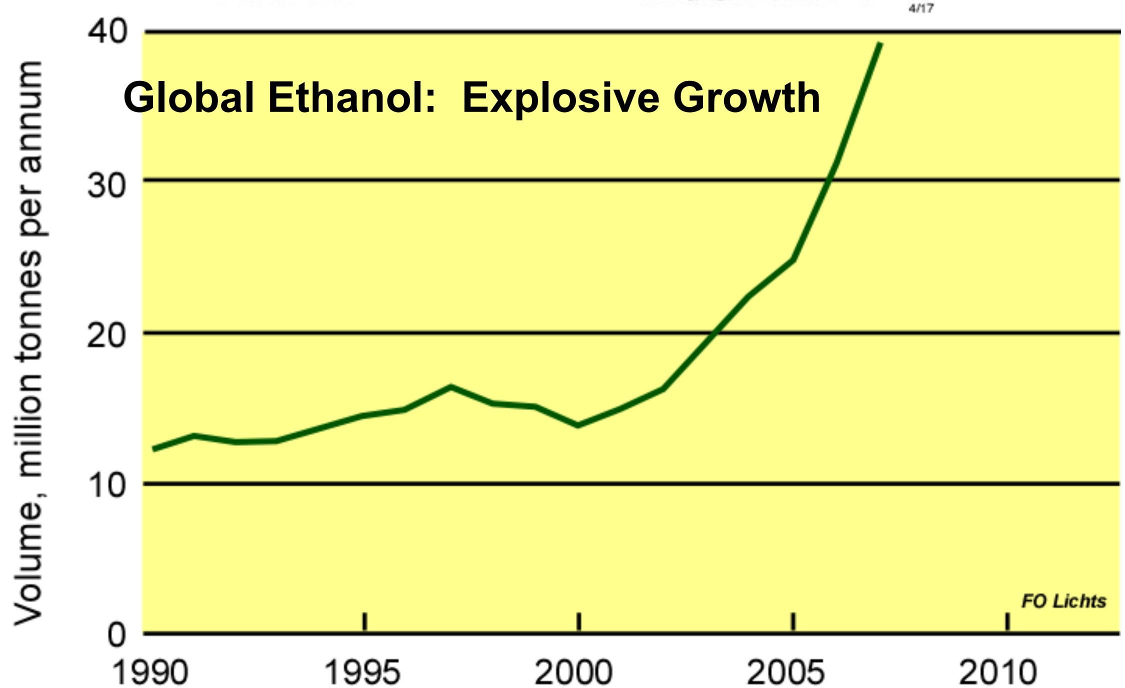
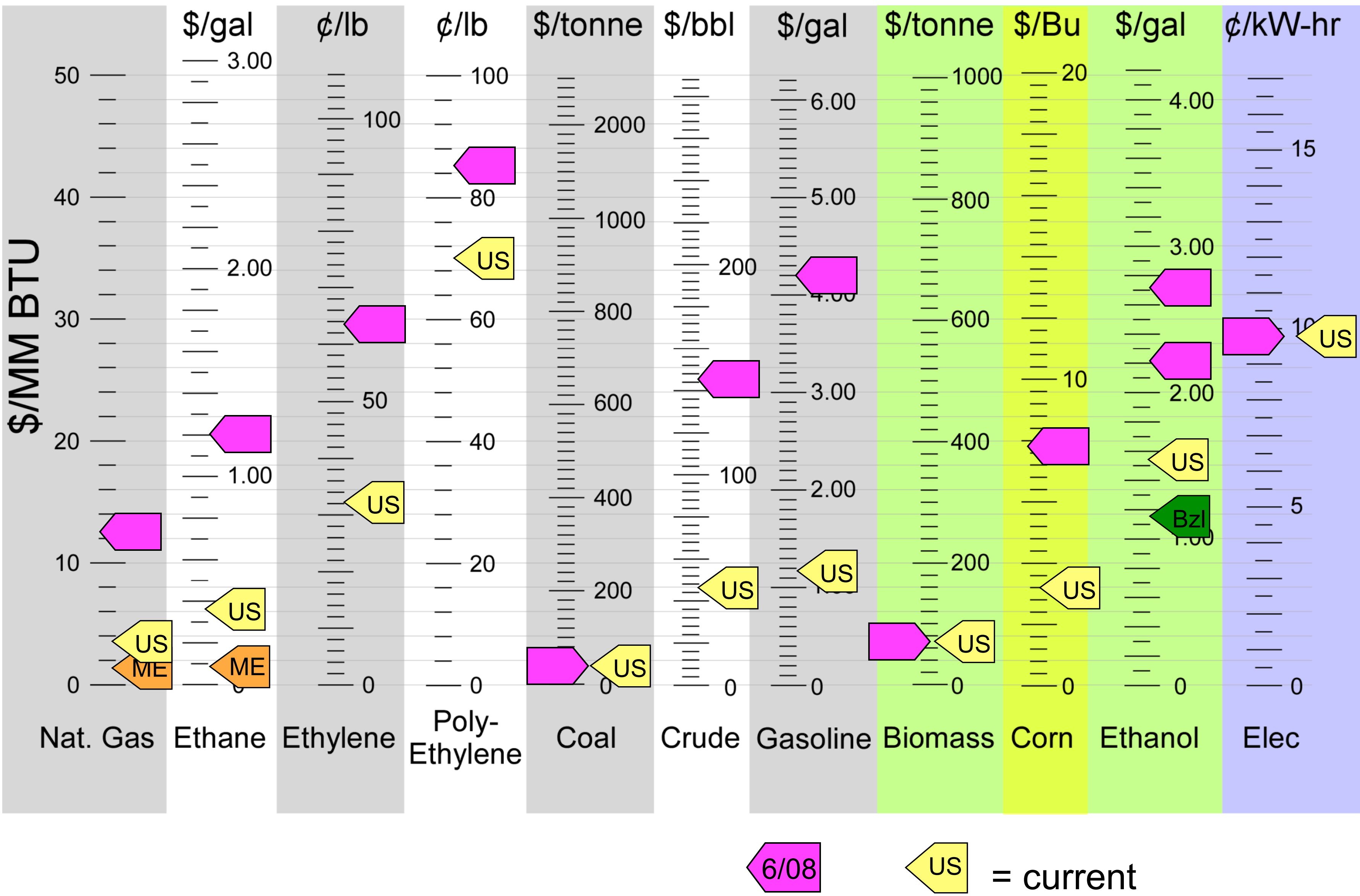
CO_2 Capture Unit



Corn Ethanol **Debate**



Energy Cost



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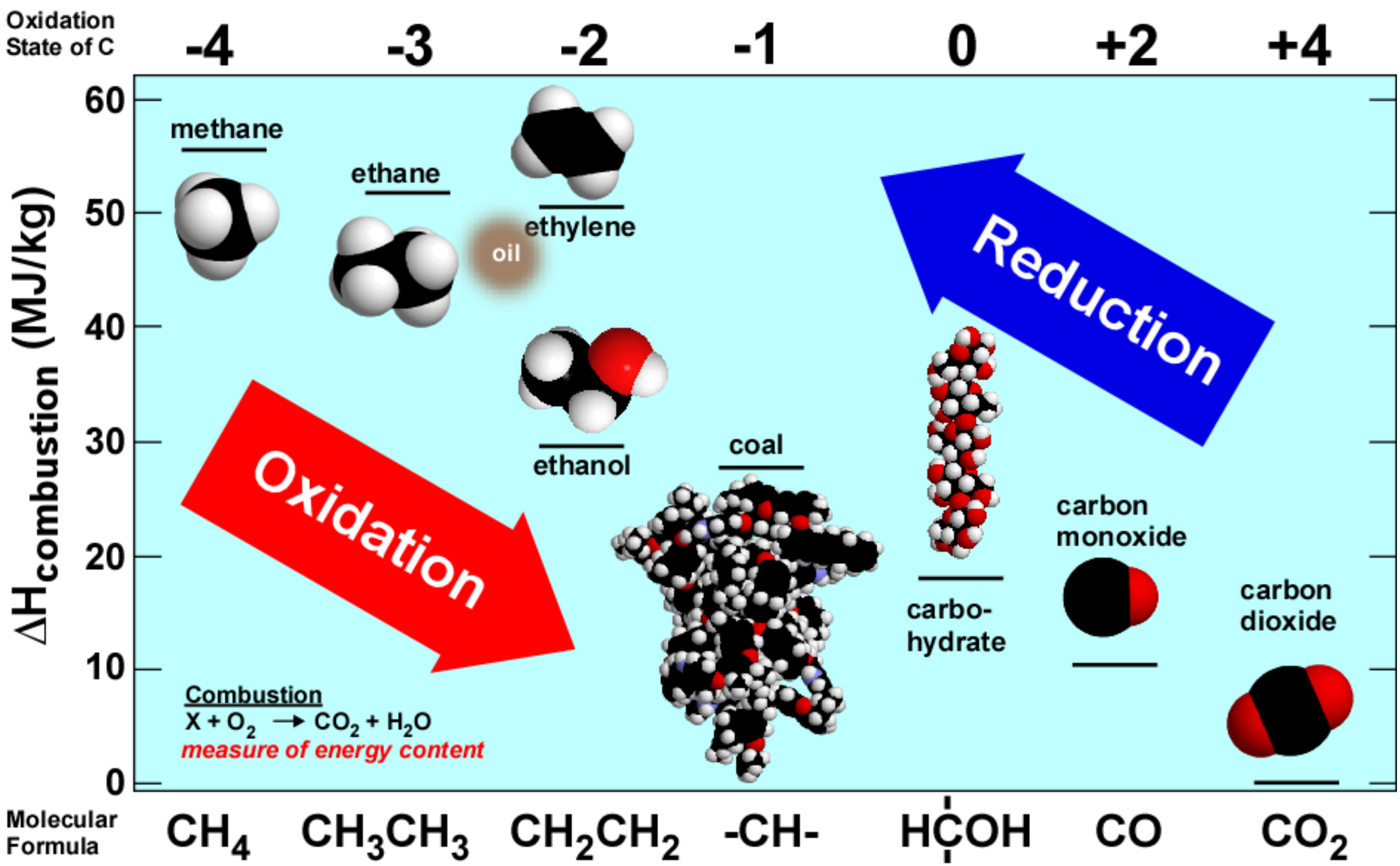
Feedstock **Oxidation States**



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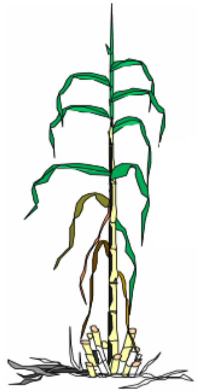
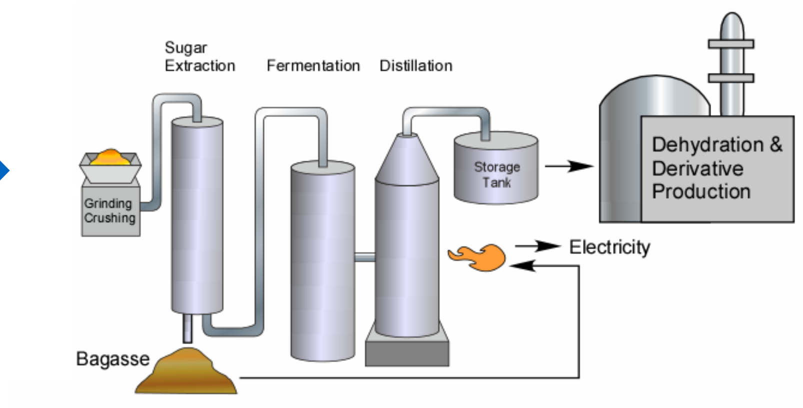
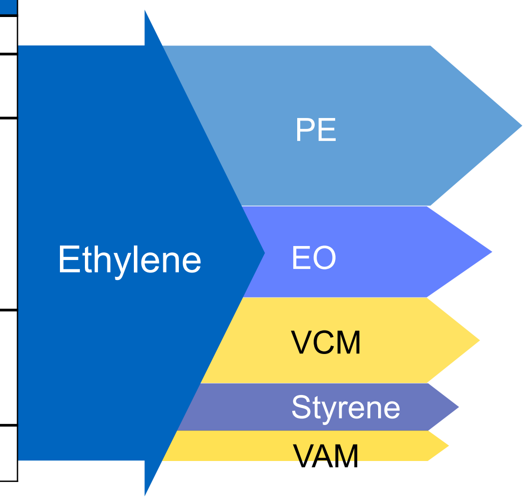
Ethanol to **Polyethylene** in Brazil

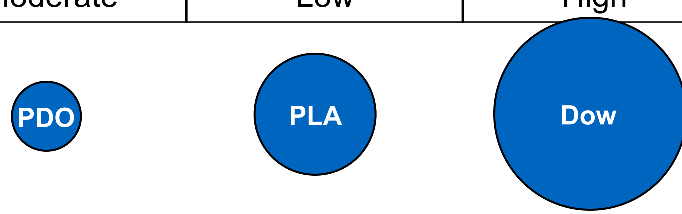
CO_2





	DuPont Bio-PDO (Serona®)	NatureWorks™ PLA	Dow
Plant Scale	45 kTA	140 kTA	**350 kTA**
Fermented Product	1,3-Propanediol	Lactic Acid	Ethanol
Key Processes	Fermentation, Condensation Polymerization	Fermentation, Oligomerization, Ring-Closing, & Ring-Opening Polymerization	Fermentation, Dehydration, Polymerization
Initial Product	PDO/TPA Copolymer	Polylactic acid	Ethylene, Polyethylene, Copolymers
Flexibility	Moderate	Low	High





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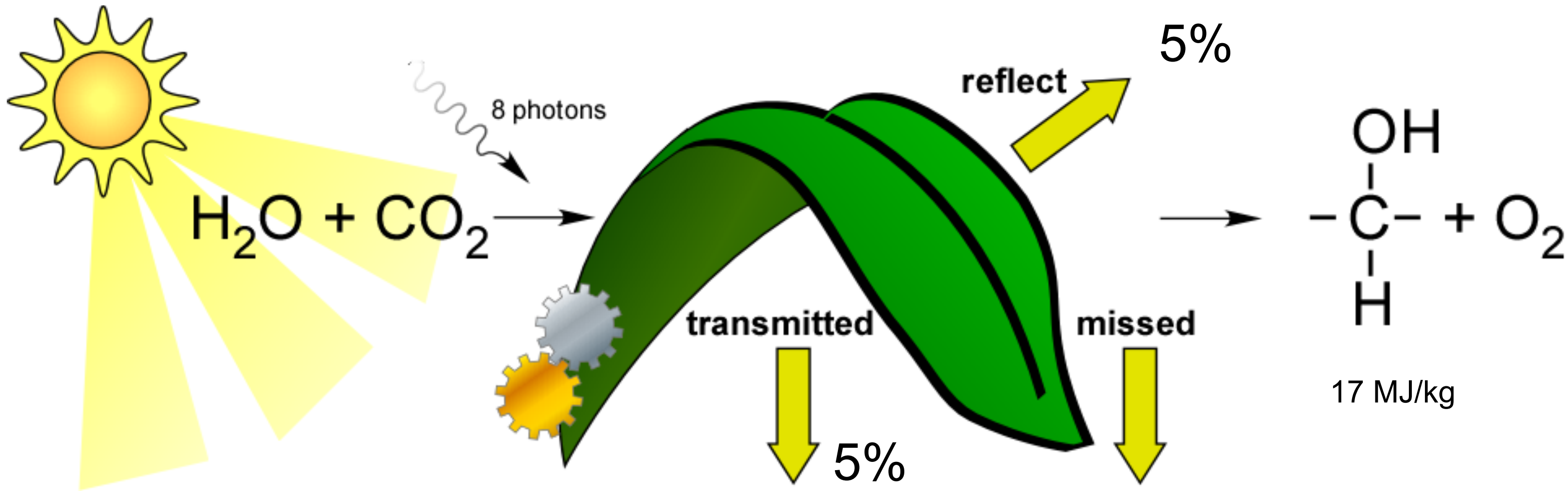
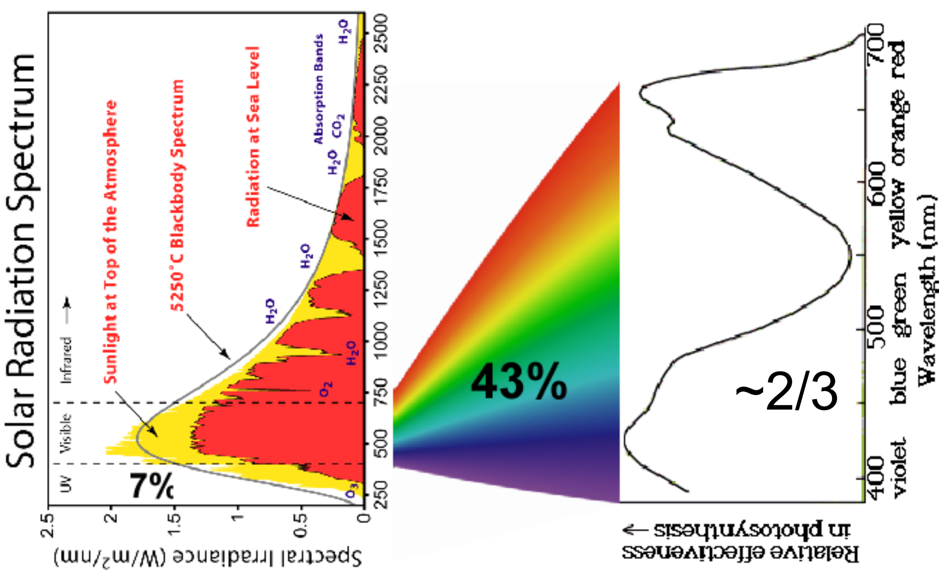
Limits to Photosynthesis





Efficiency

Cane ~ 1 %

Corn < 0.4%

(Ideal conditions)

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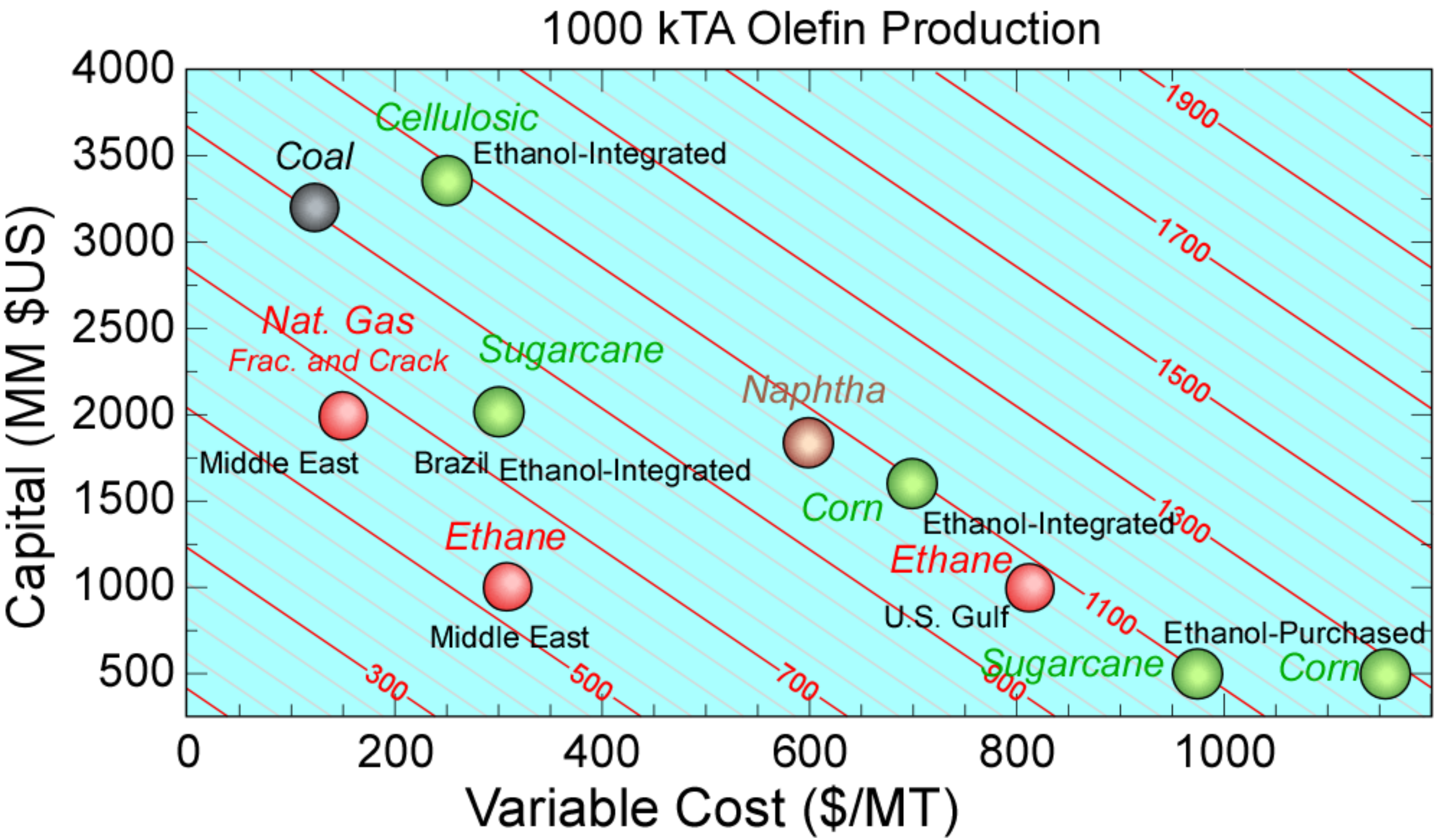
Capital v. Variable Cost



Fall of 2007

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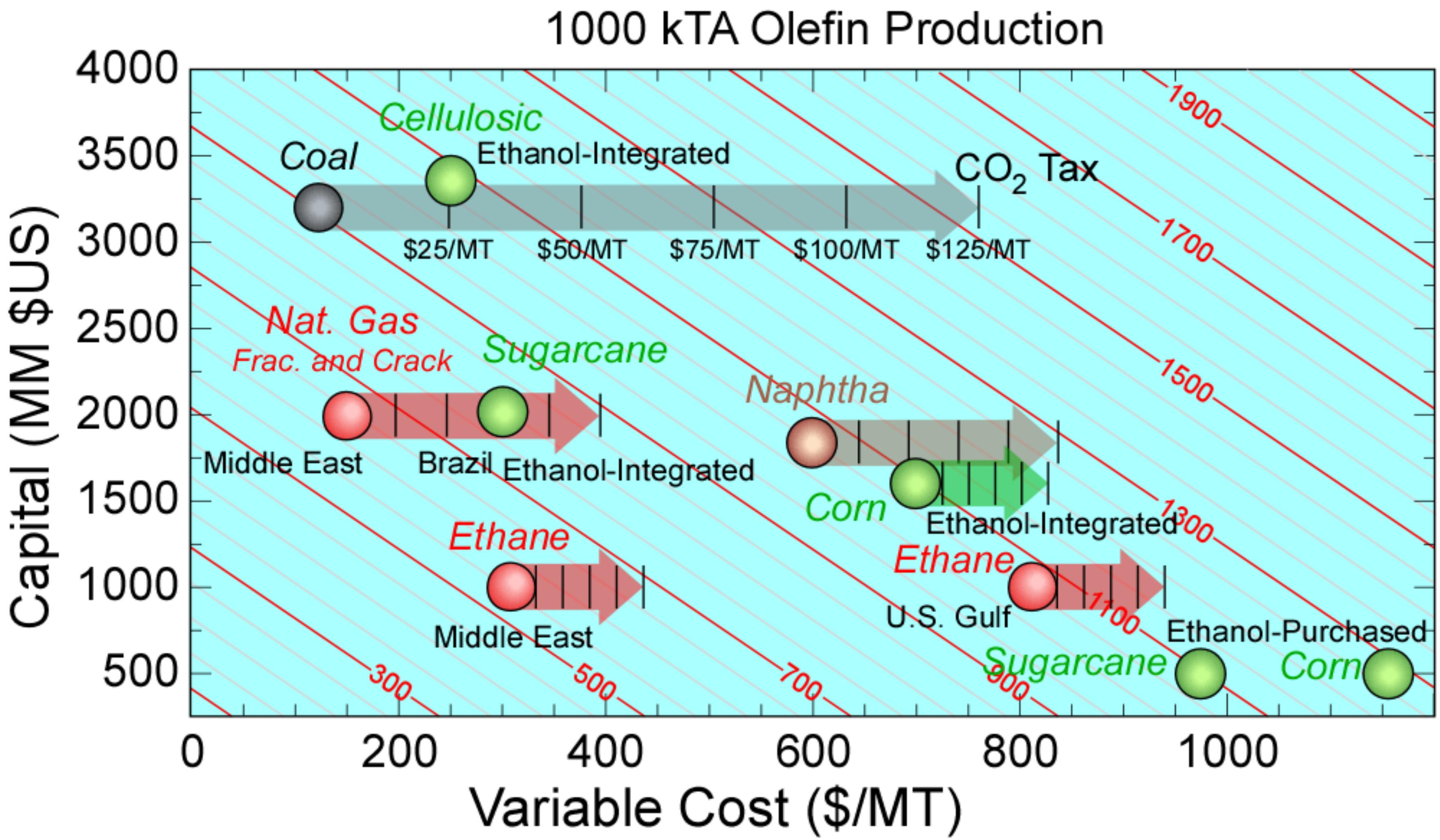
Capital v. Variable Cost



Fall of 2007

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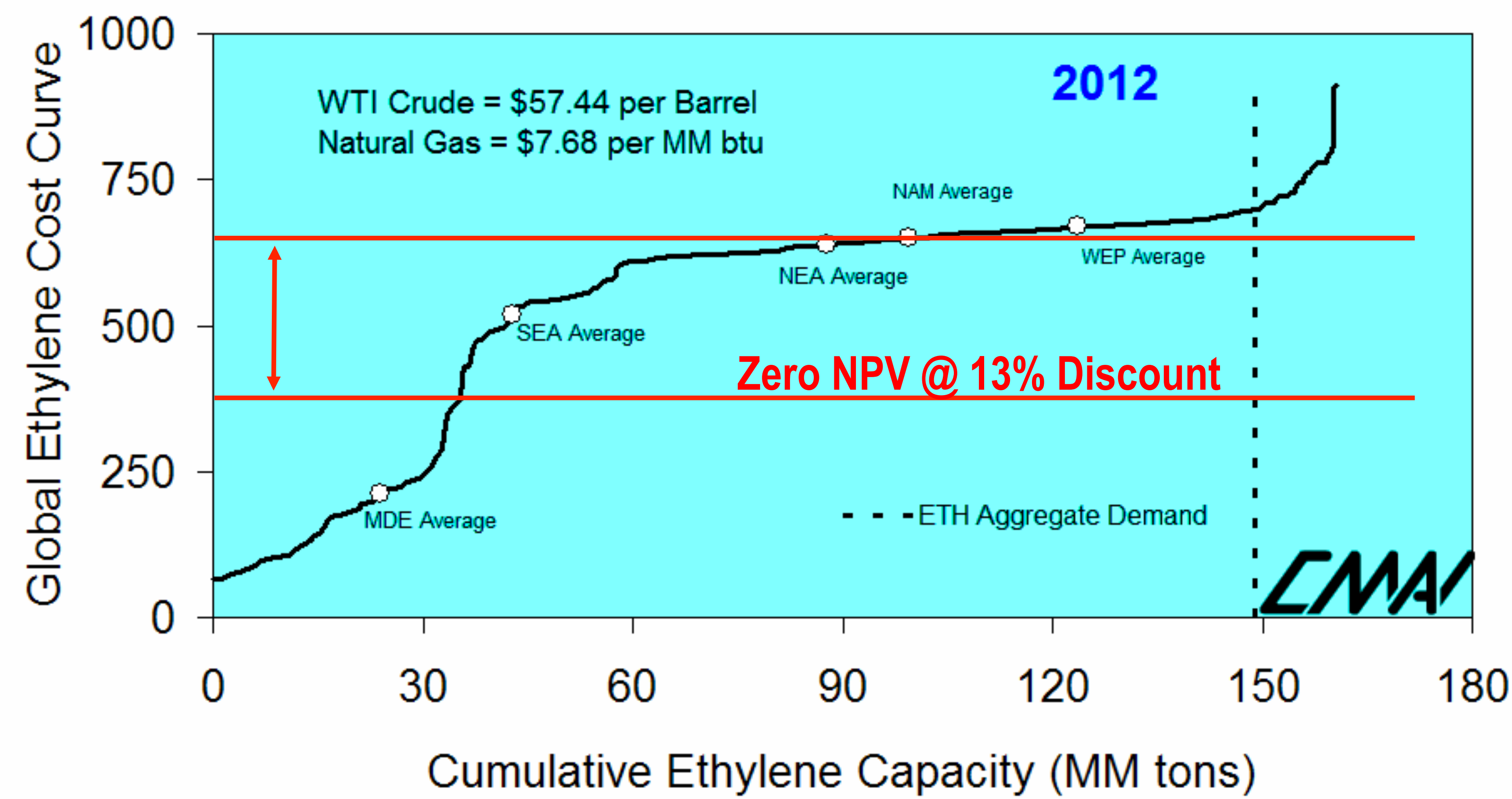
Ethylene Cost Curve

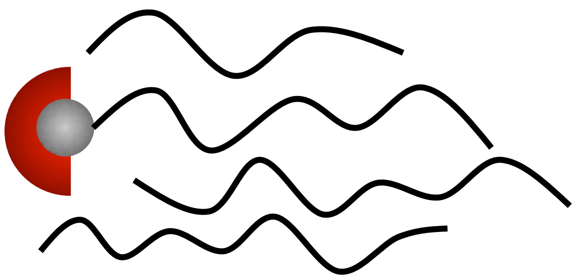


To replace a $1.5B plant producing 1 MM tons per year with a cash cost of $650/ton (NA average) with a new $1.5B plant requires a cash cost of $375/ton or less*

*13% discount factor

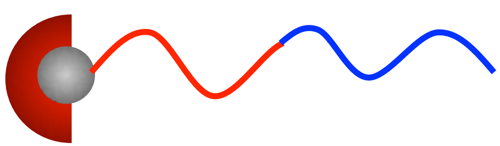
INFUSE™ Olefin Block Copolymers

Homogeneous Catalysis



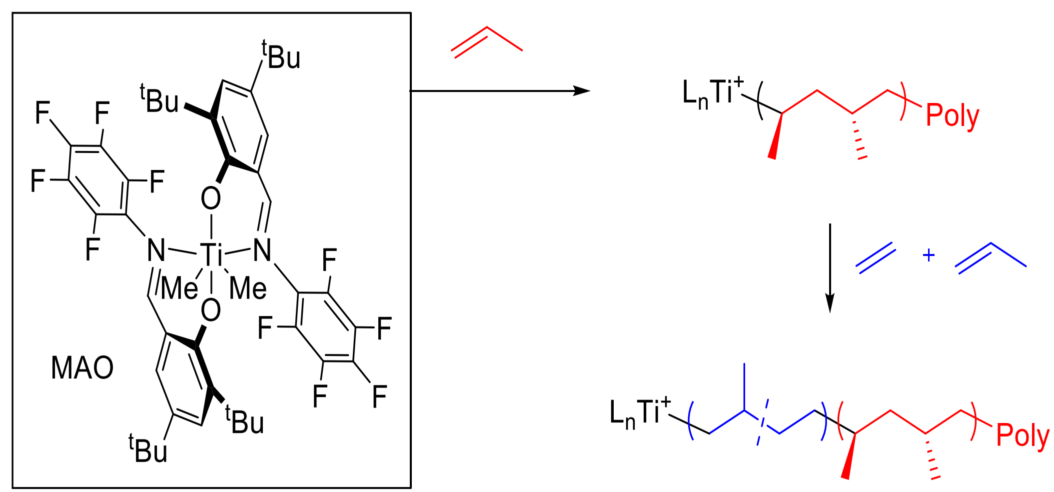
- efficient process
- many chains per catalyst

Living Coordination Catalysis



- enable block copolymers
- one chain per catalyst
- very inefficient processes

State of the art in living olefin polymerization

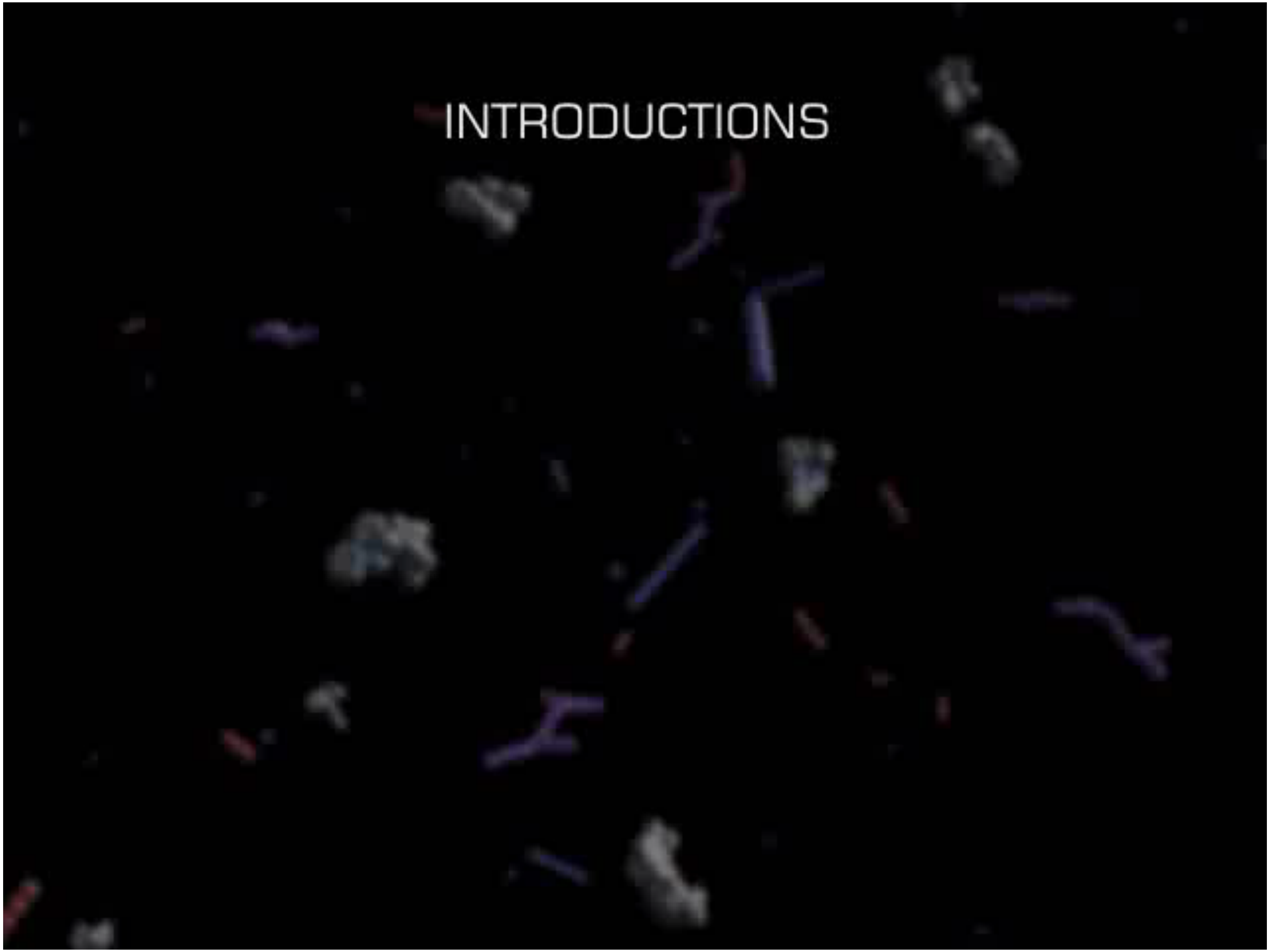


For a review of living polymerization systems, see:

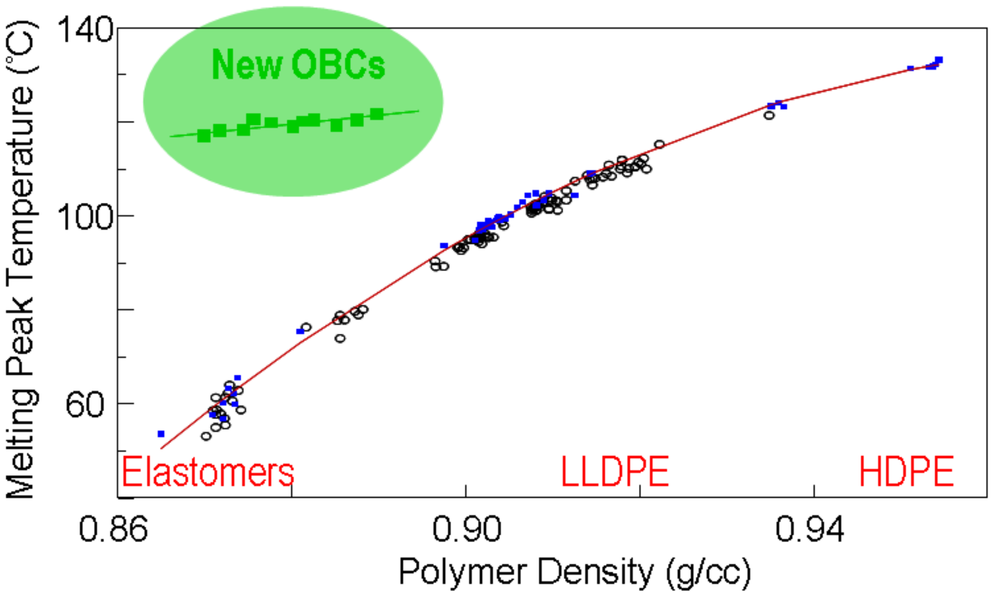
Coates, Hustad, & Reinartz, Angew. Chem. Int. Ed. ***2002****, 41, 2236*

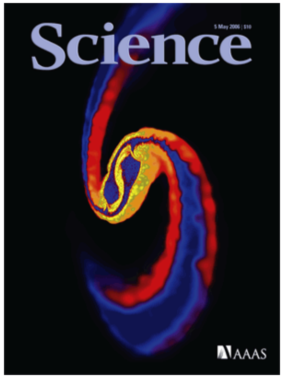
William Banholzer, MIT 2009

INFUSE™ Olefin Block Copolymers



INFUSE™ Olefin Block Copolymers





RESEARCH ARTICLE

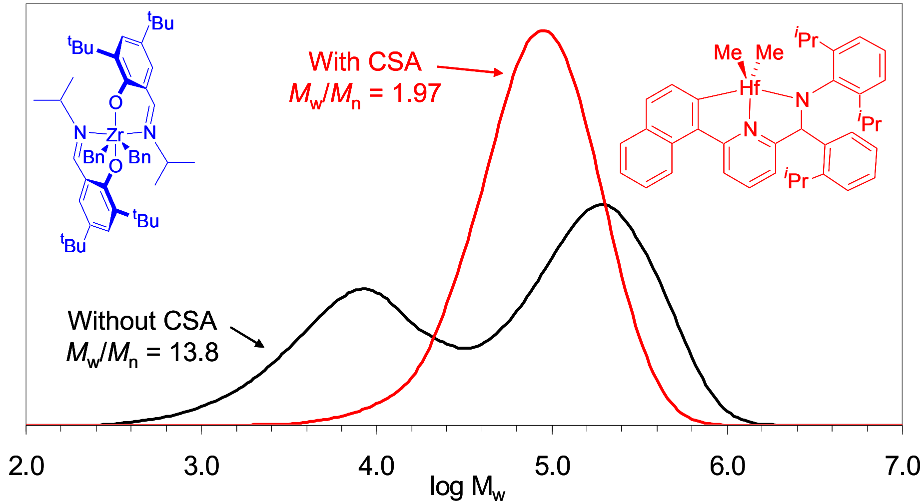
Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization

Daniel J. Arriola,[1*] Edmund M. Carnahan,[2*] Phillip D. Hustad,[2*] Roger L. Kuhlman,[2*] Timothy T. Wenzel[1*]

We report a catalytic system that produces olefin block copolymers with alternating semicrystalline and amorphous segments, achieved by varying the ratio of α-olefin to ethylene in the two types of blocks. The system uses a chain shuttling agent to transfer growing chains between two distinct catalysts with different monomer selectivities in a single polymerization reactor. The block copolymers simultaneously have high melting temperatures and low glass transition temperatures, and therefore they maintain excellent elastomeric properties at high temperatures. Furthermore, the materials are effectively produced in economically favorable, continuous polymerization processes.

From lead article in Science to commercial launch in the same calendar year!

Kinetics!



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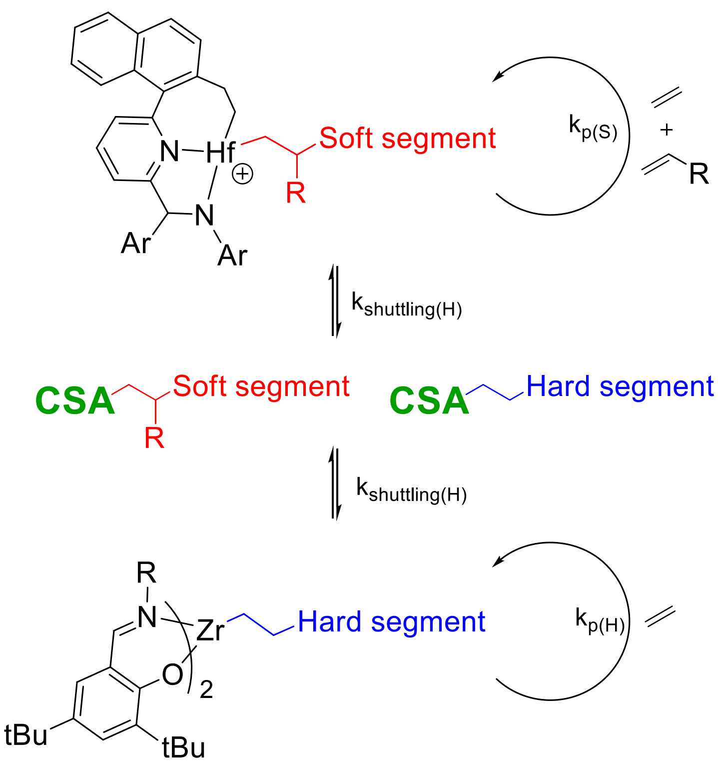
Material Properties by Design

- Many reactor variables exist in OBC process
- Products can be tailored to meet specific customer needs
    - Catalyst ratio → modulus
    - [CSA]/[monomer] → blockiness

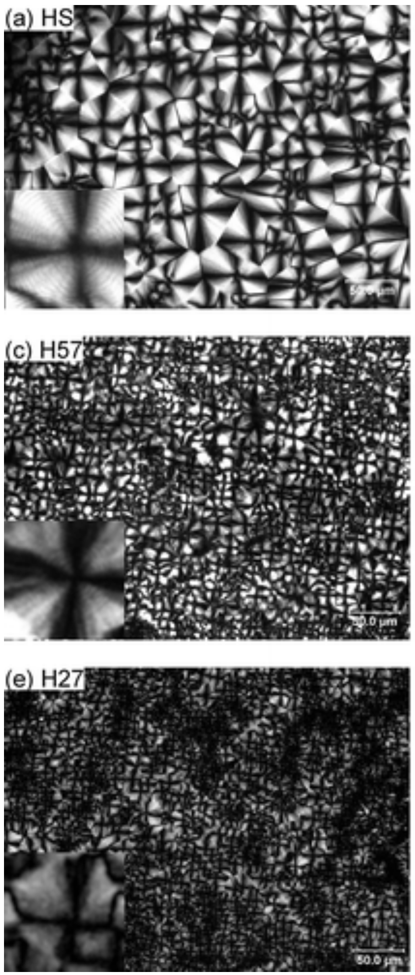


Rate(soft) ~ [catalyst][ethylene][octene]

Rate(shuttling) ~ [CSA]/[ethylene]

Rate(hard) ~ [catalyst][ethylene]

High Hard Segment



High Soft Segment

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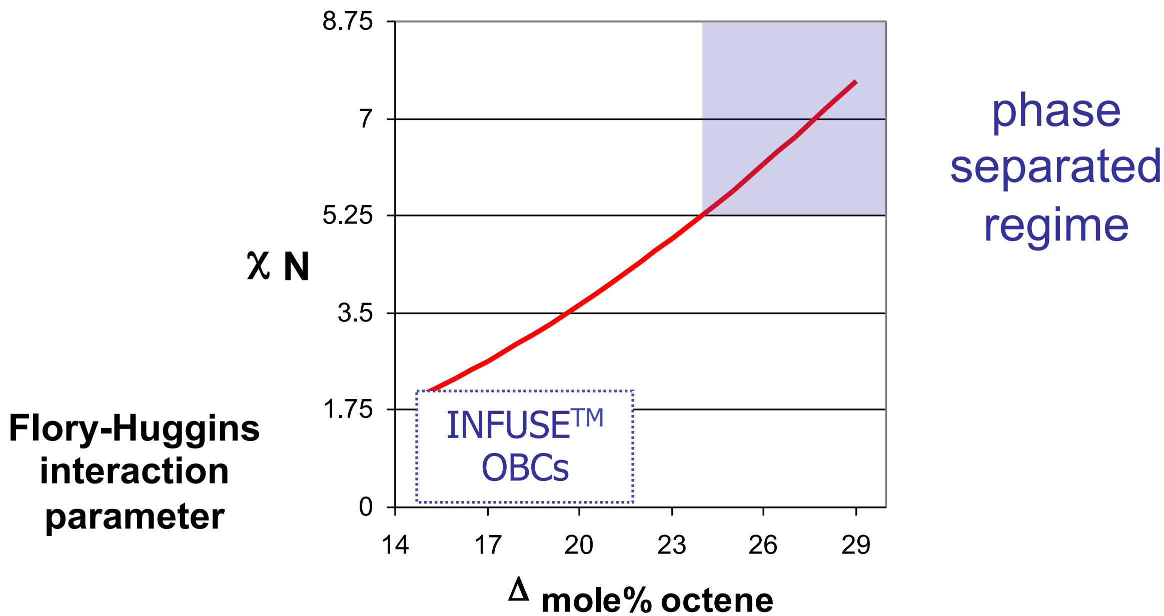
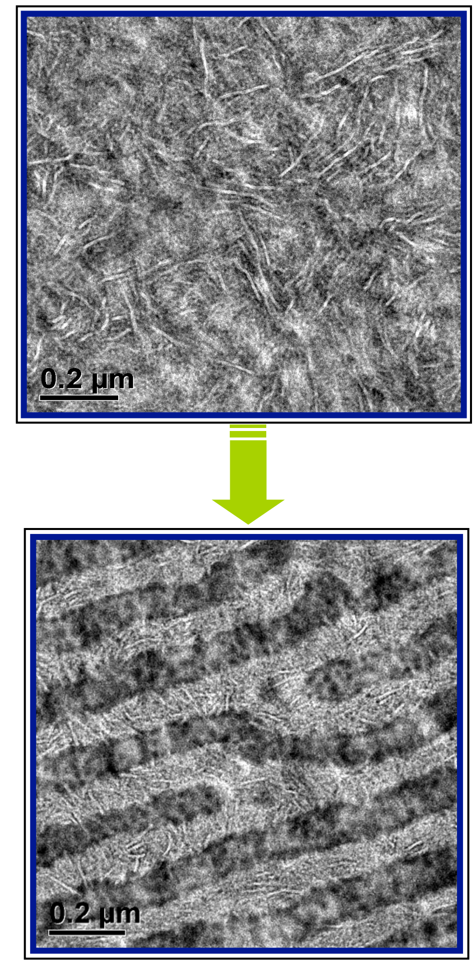
INFUSE™ Olefin Block Copolymers

- Morphology control might also be possible if we can further tailor OBC microstructure to give phase separated materials



increasing composition difference in soft and hard blocks

Typical OBC morphology



Phase-separated OBC morphology

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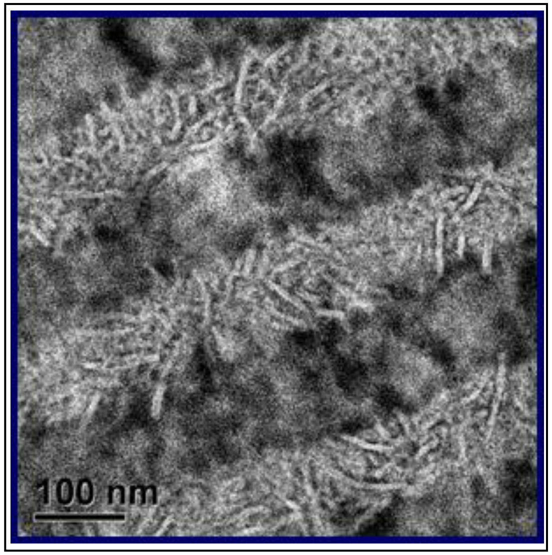
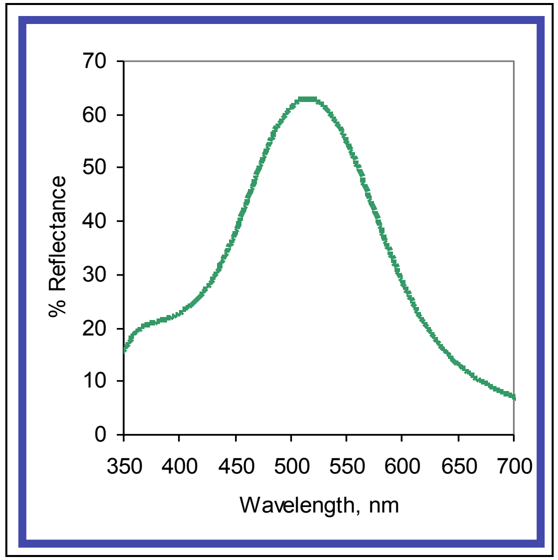
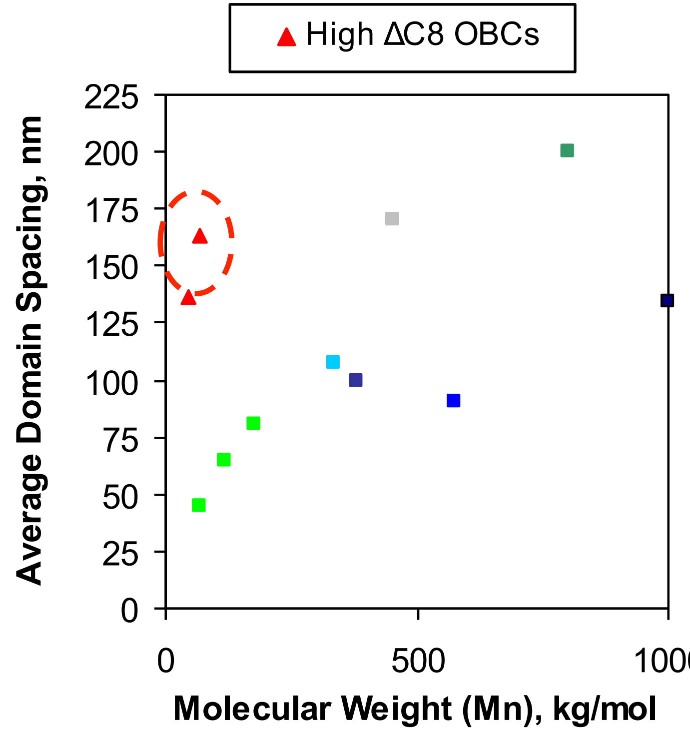
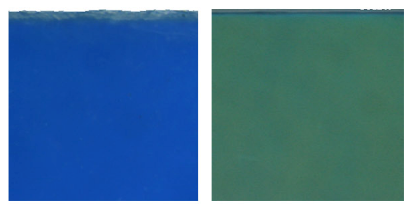
Manipulating Light with Self-Assembled Polyolefins



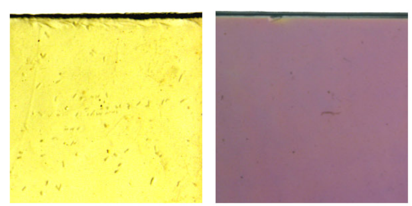




High octene OBC
M_n = 48,000 g/mol



reflected colors

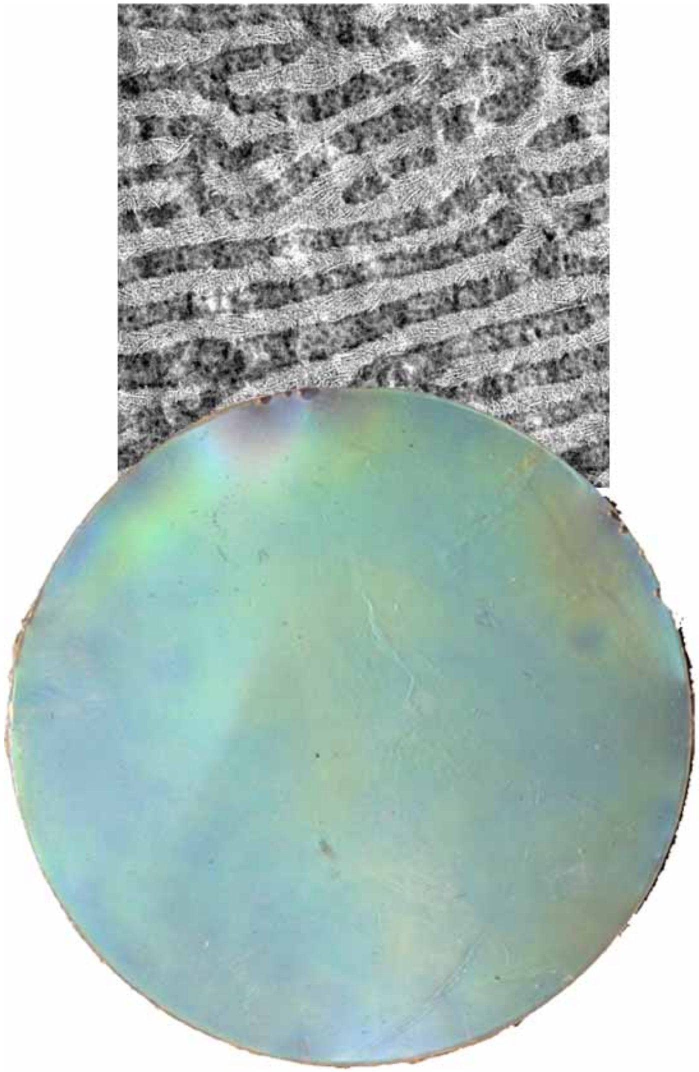


transmitted colors

$$\lambda = 2(n_a d_a + n_b d_b)$$

Hustad, Garcia-Meitin, Marchand, Roberts,Weinhold. *Macromolecules*, in press.

INFUSE™ Olefin Block Copolymers



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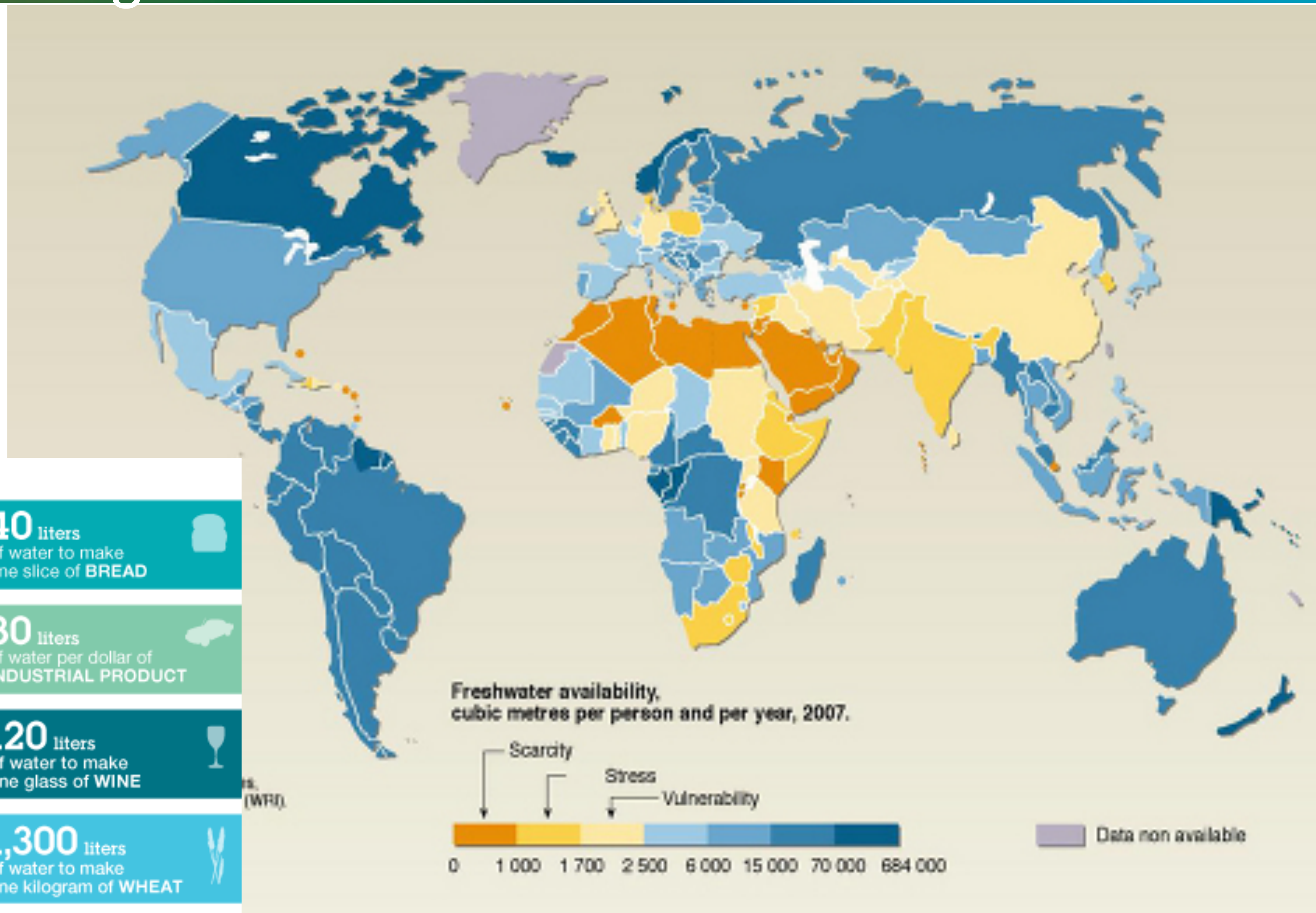
Thank you!

World Challenge – **Water**



It takes...

- **10** liters of water to make one sheet of **PAPER**
- **40** liters of water to make one slice of **BREAD**
- **70** liters of water to make one **APPLE**
- **80** liters of water per dollar of **INDUSTRIAL PRODUCT**
- **91** liters of water to make one pound of **PLASTIC**
- **120** liters of water to make one glass of **WINE**
- **140** liters of water to make one cup of **COFFEE**
- **1,300** liters of water to make one kilogram of **WHEAT**
- **4,800** liters of water to make one kilogram of **PORK**
- **10,855** liters of water to make one pair of **JEANS**
- **15,500** liters of water to make one kilogram of **BEEF**
- **16,600** liters of water to make one kilogram of **LEATHER**

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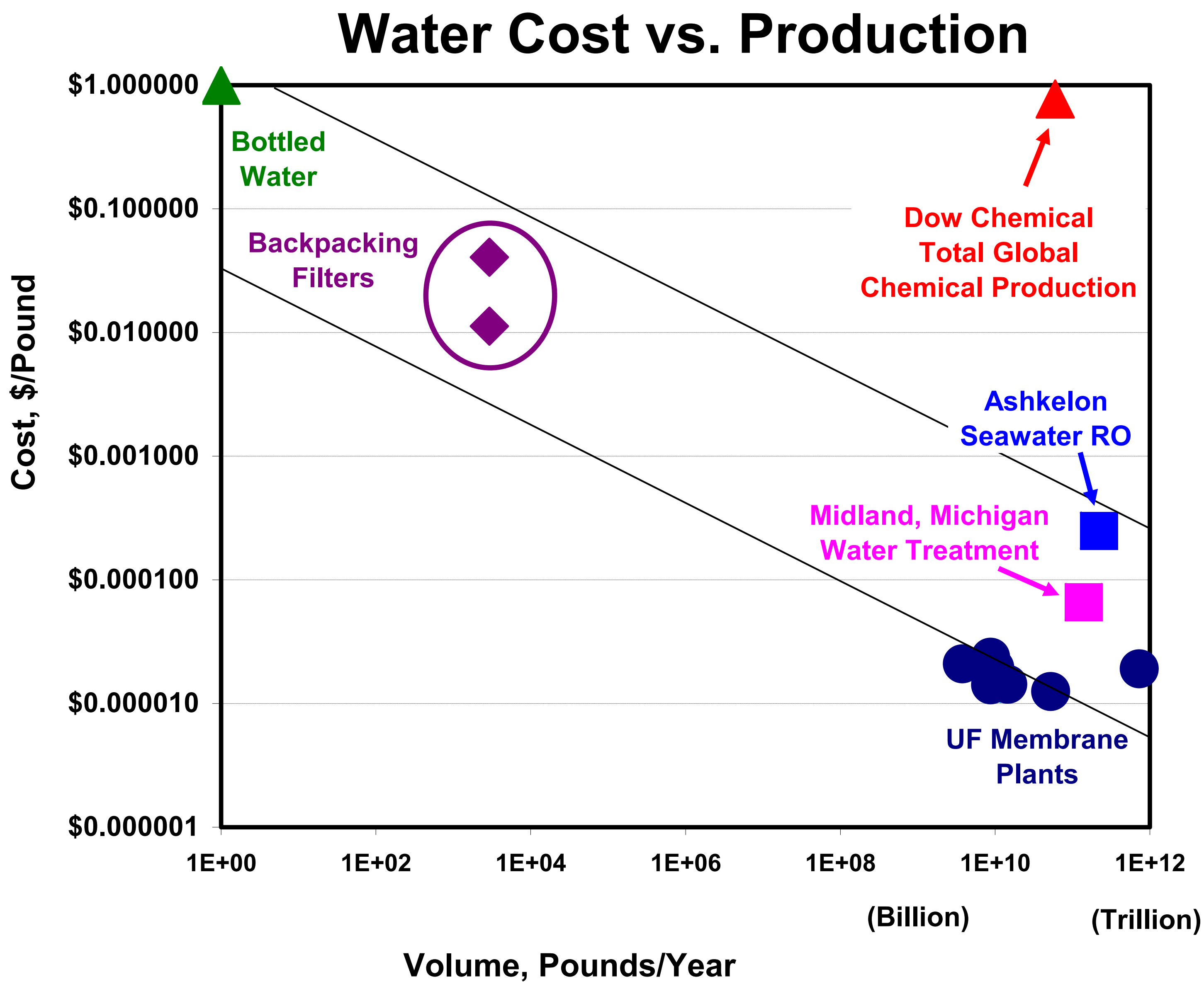
Water Desalination Plants – **Massive Scale**



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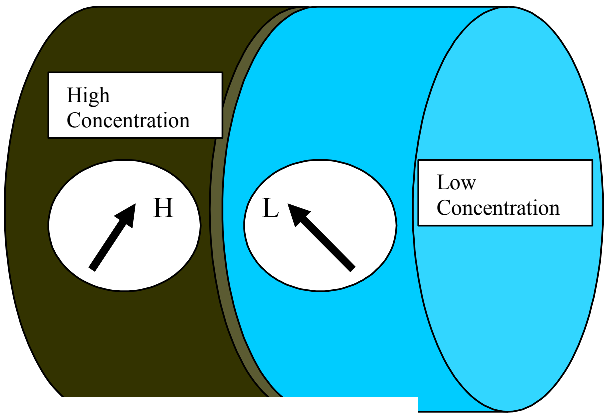
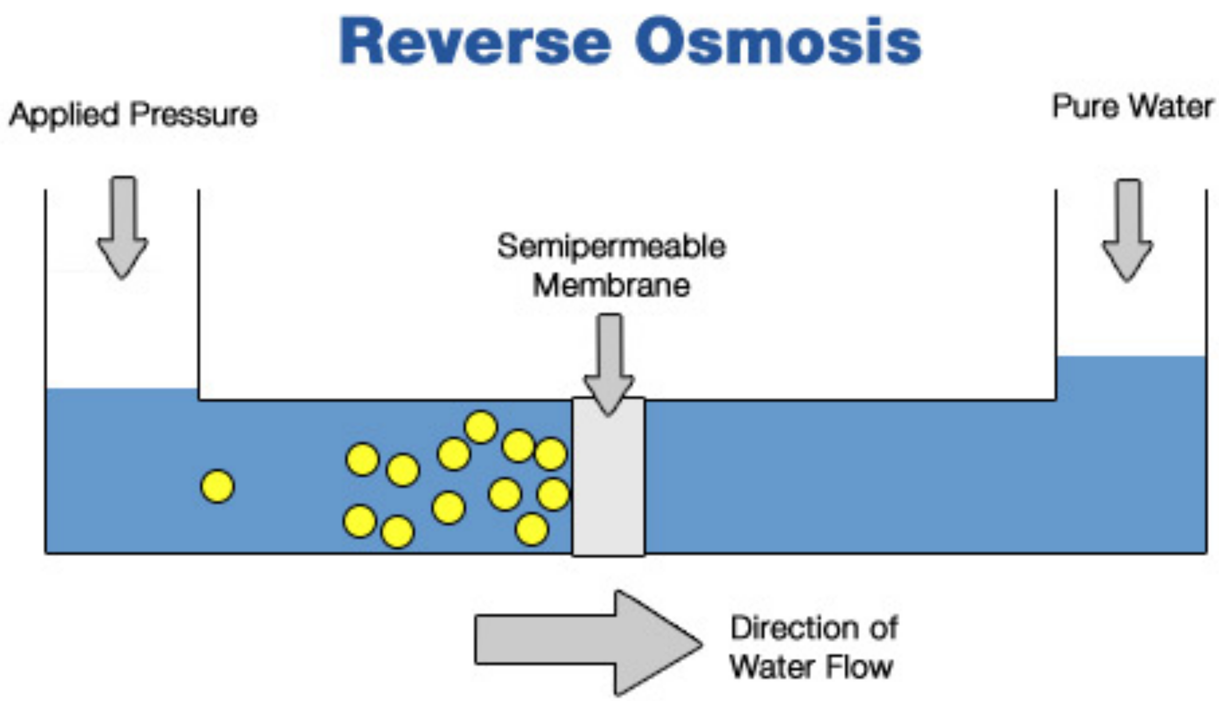
Osmotic Pressure

- Simple Osmotic Pressure

$$\Phi = \frac{-m_A \ln(a_A)}{m_B}$$



- Activity (a) is dependent on concentration, temperature, other ions



Control of Solute (Salts) Passage

Solution Diffusion (Londsdale, 1965)

Water Flux

$J_w = A(\Delta \text{Pressure} - \Delta \text{Osmotic Pressure})$

Solute Flux

$J_s = B(\Delta[\text{Solute Feed}] - \Delta[\text{Solute Permeate}])$

Coupled Solute Water Fluxes Irreversible Thermodynamics (Kedum, 1968)

Water Flux

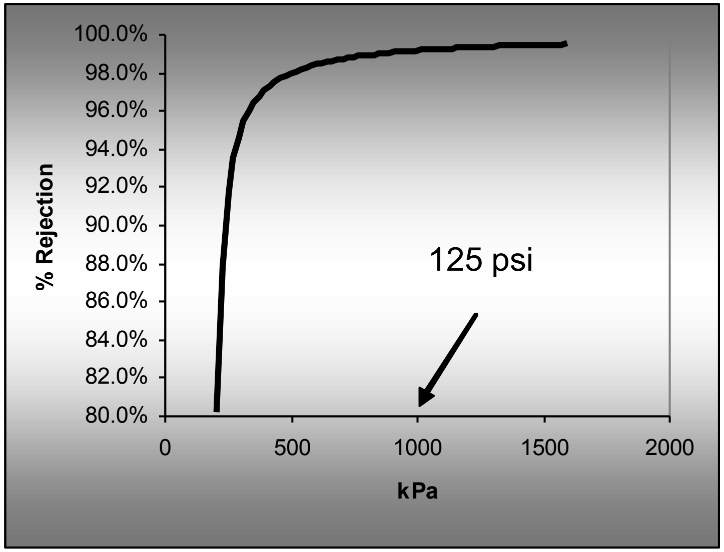
$J_w = A\,(\,\Delta \text{ Pressure} - \sigma\, \Delta \text{ Osmotic Pressure})$

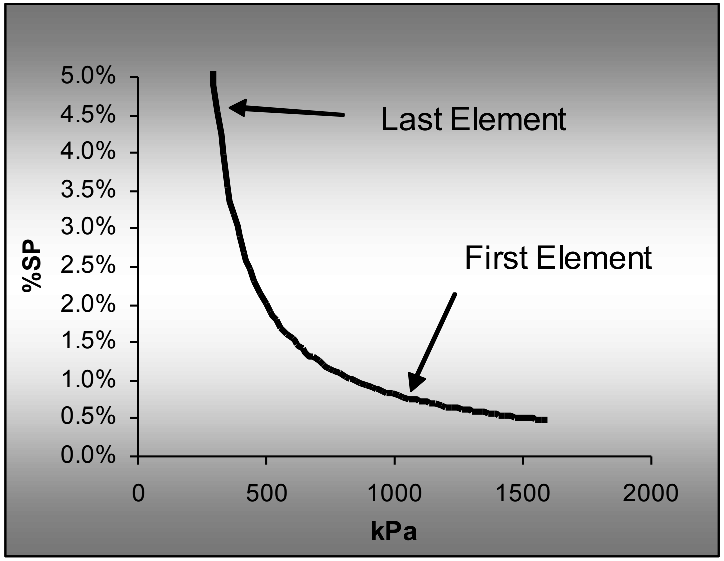
Solute Flux

$J_s = (\,c_m)_{avg}\,(1\text{-}\sigma)\, J_w +$

$B(\,\Delta[\text{Solute Feed}] - \Delta[\text{Solute Permeate}])$

Passage is very NON-Linear!



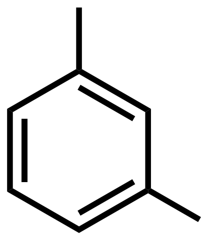


Where are the Losses?

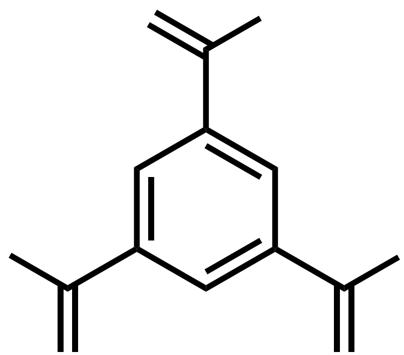
Quantity	**RO**
Exergy input, kW/cubic m	**76.95**
Min work of separation	**1.224**
Total exergy destruction, kW	**70.82**
Mechanical energy of product water, kW	**4.91**
2^{nd}-law efficiency	**8.0%**
Exergy destruction in various components:	
-Discharged raw water -Bag filters -Static mixer **-Separation unit (RO)** -Throttling of bypass water -Blending with bypass water **-Mech. exergy of discharge brine** -Pumps and piping system	0.93 (1.3%) 1.66 (2.4%) 0.60 (0.8%) **25.62 (36.2%)** 7.49 (10.6%) 0.43 (0.6%) **5.97 (8.4%)** 28.11 (39.7%)

Source: Kahraman et. al. *Desalination* **171** (2004) 217-232

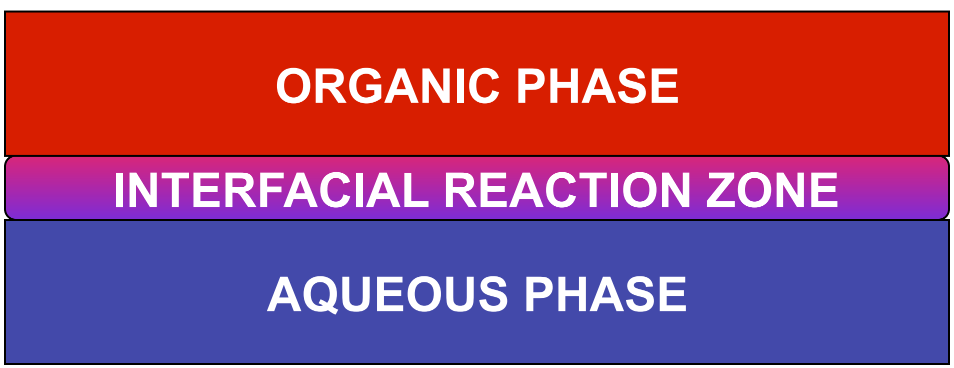
FILMTEC™ Reverse Osmosis Membranes

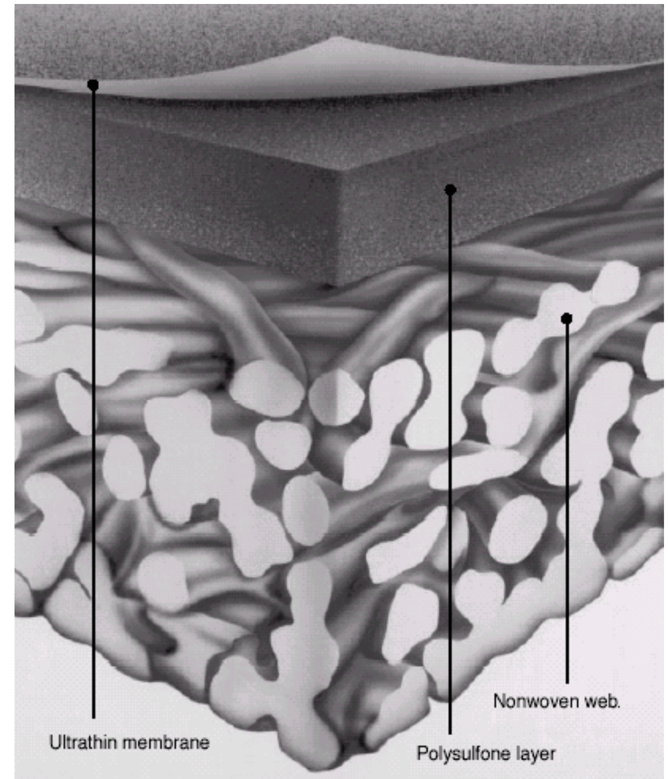


m-Phenylene Diamine
Aqueous Phase



Trimesoyl Chloride
Organic Phase





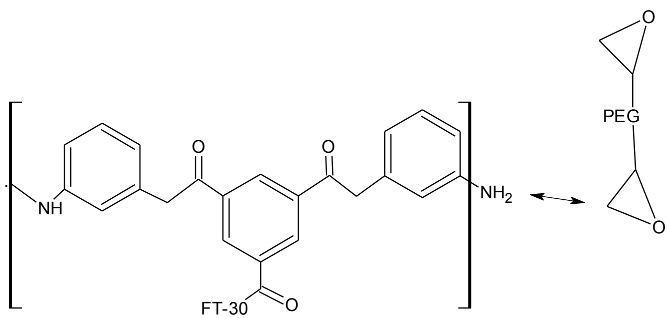
Film formation stops mixing of monomers & stops reaction.
Allows formation of ultrathin pinhole-free films.

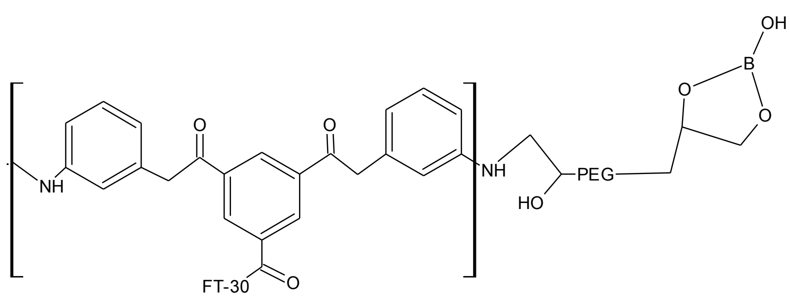
RO Was Used to Clean up **Salt** From Water

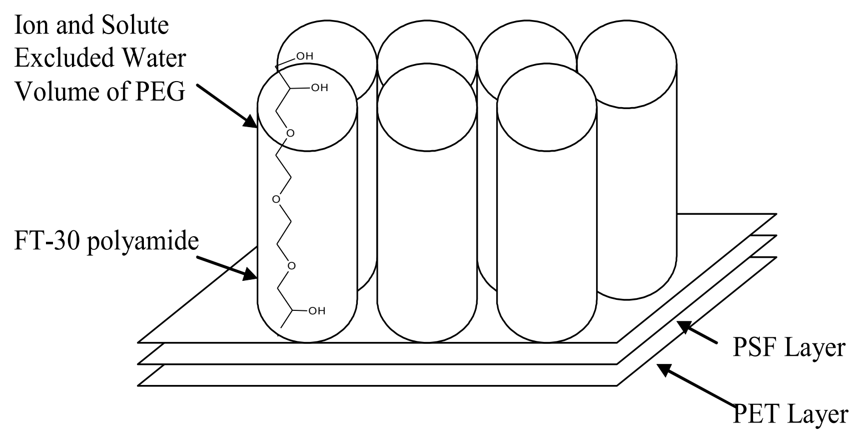
Now it is used to remove **Toxic Contaminants**

- **Boron**: The World Health Organization requires lower than 1 ppm boric acid. Seawater RO often can't meet that.
- **Ag Chem**: Contaminated ground water often contains high nitrate, silica, As, and organics. RO often can't remove these to the requested level.

Modifying FT-30 can allow us to produce pure water from these contaminated streams.



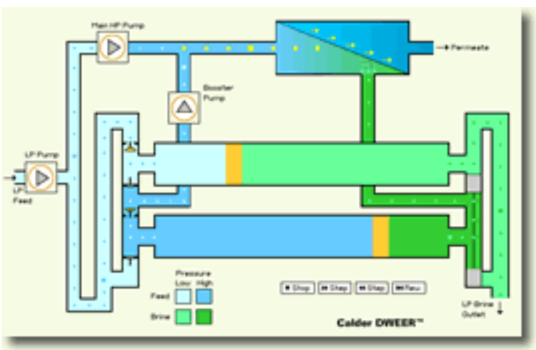




William Banholzer, MIT 2009

Dual Work Exchanger Energy Recovery

Cylindrical vessel alternately filled with hp brine and lp feed
Brine and feed separated by a piston
DWEER has two cylinders so there is constant flow of hp feed to membranes
Flow is controlled via valves at both ends of cylinders



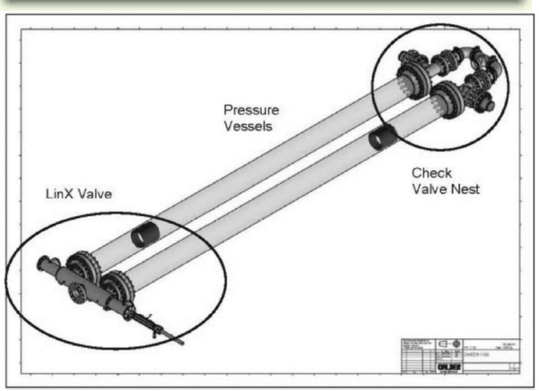
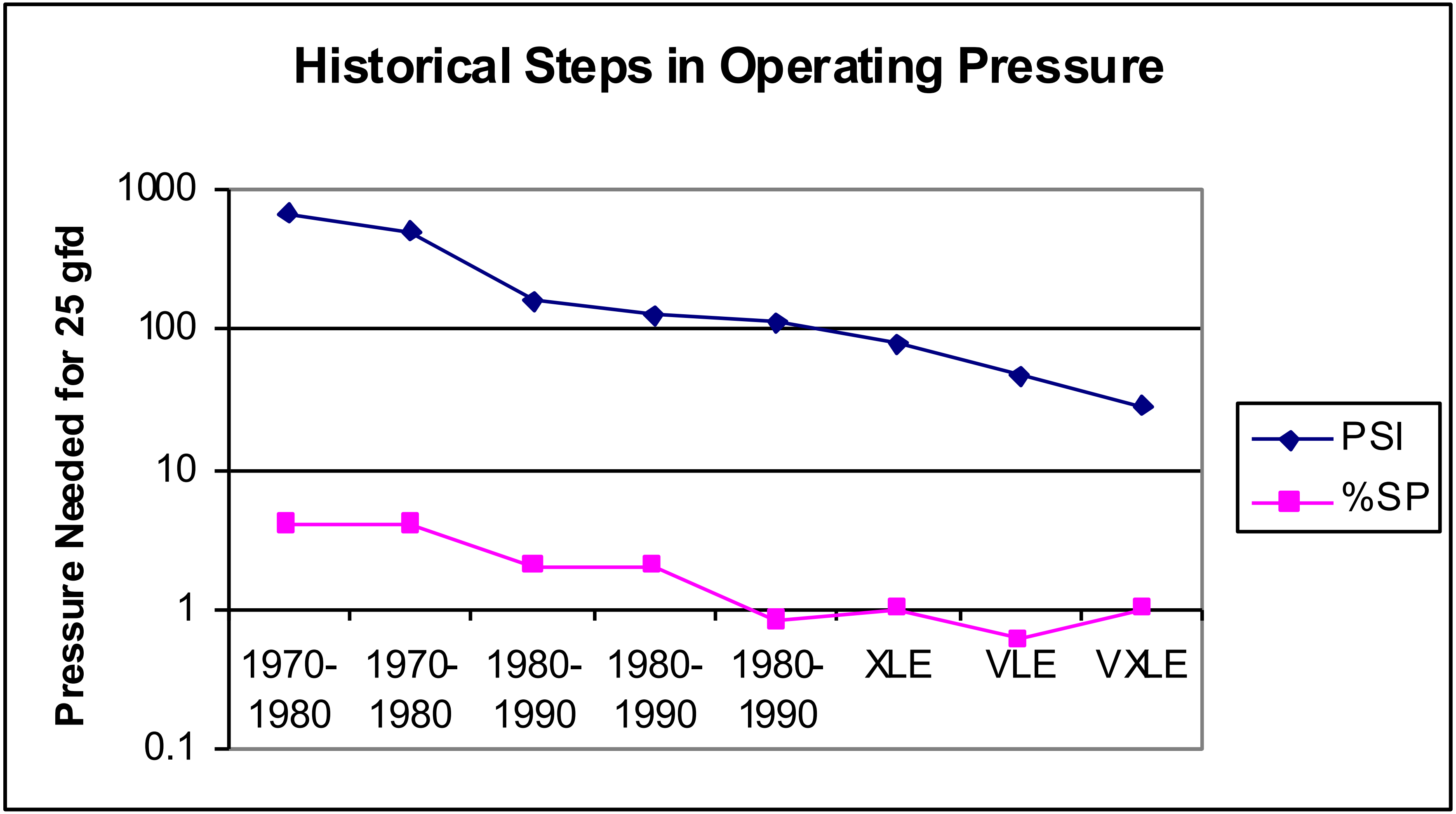


Fig. 3. The DWEER™ work exchange.

Improvements in RO Operating Pressure



William Banholzer, MIT 2009