

# **Green Engineering: Principles and Practice**

Jennifer L. Anthony

Department of Chemical Engineering  
Kansas State University

Adapted from presentations by E. Beckman (U. Pitt) and J. Brennecke (U. Notre Dame)

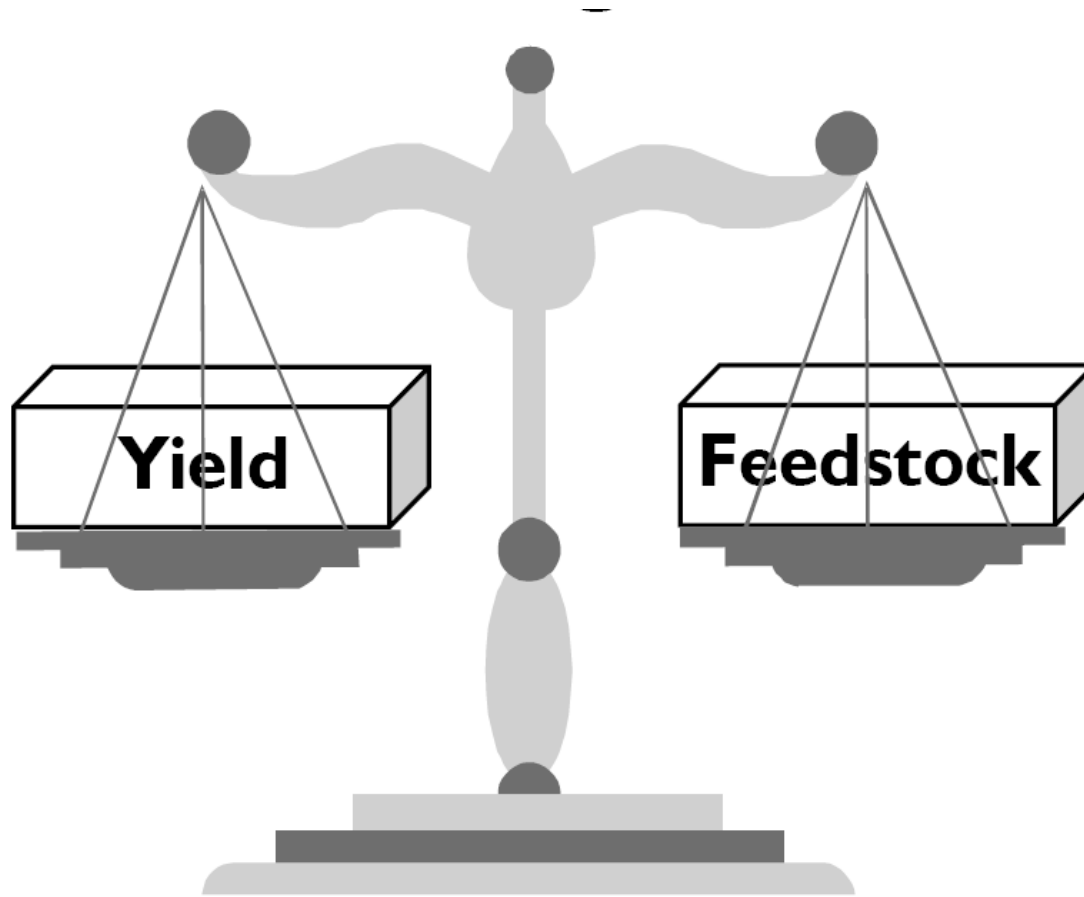
*“Green chemistry is a multidisciplinary field involving fundamental sciences, business, law, and engineering.”*

*Green chemistry, green engineering, environmental design, sustainability, industrial ecology, natural capitalism...*

# Engineering Role

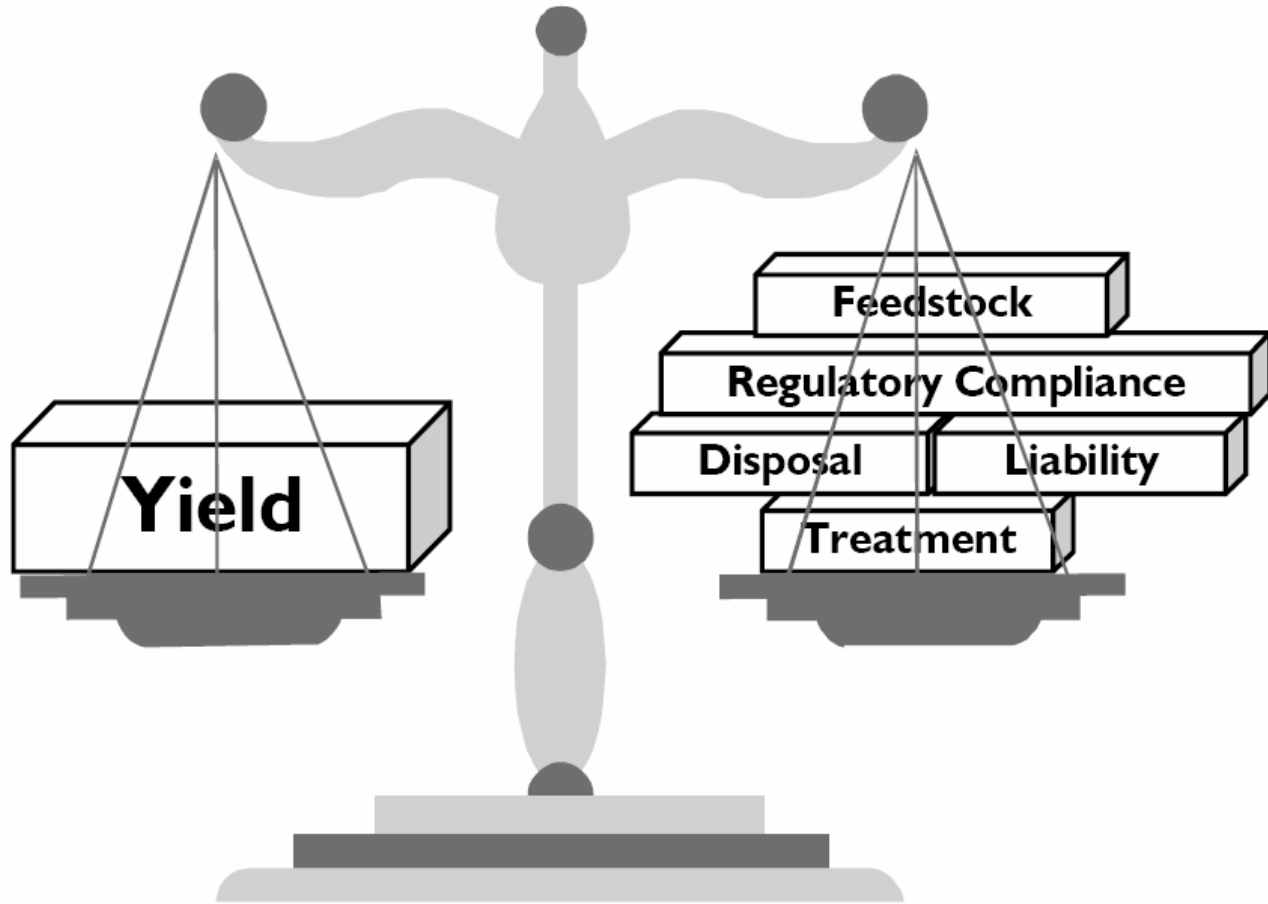
- Environmental remediation
  - Air
  - Water
  - Soil
- Design / Development / Implementation
  - Industrial processes
  - Research
  - Classroom / Laboratory

# Balance in Design



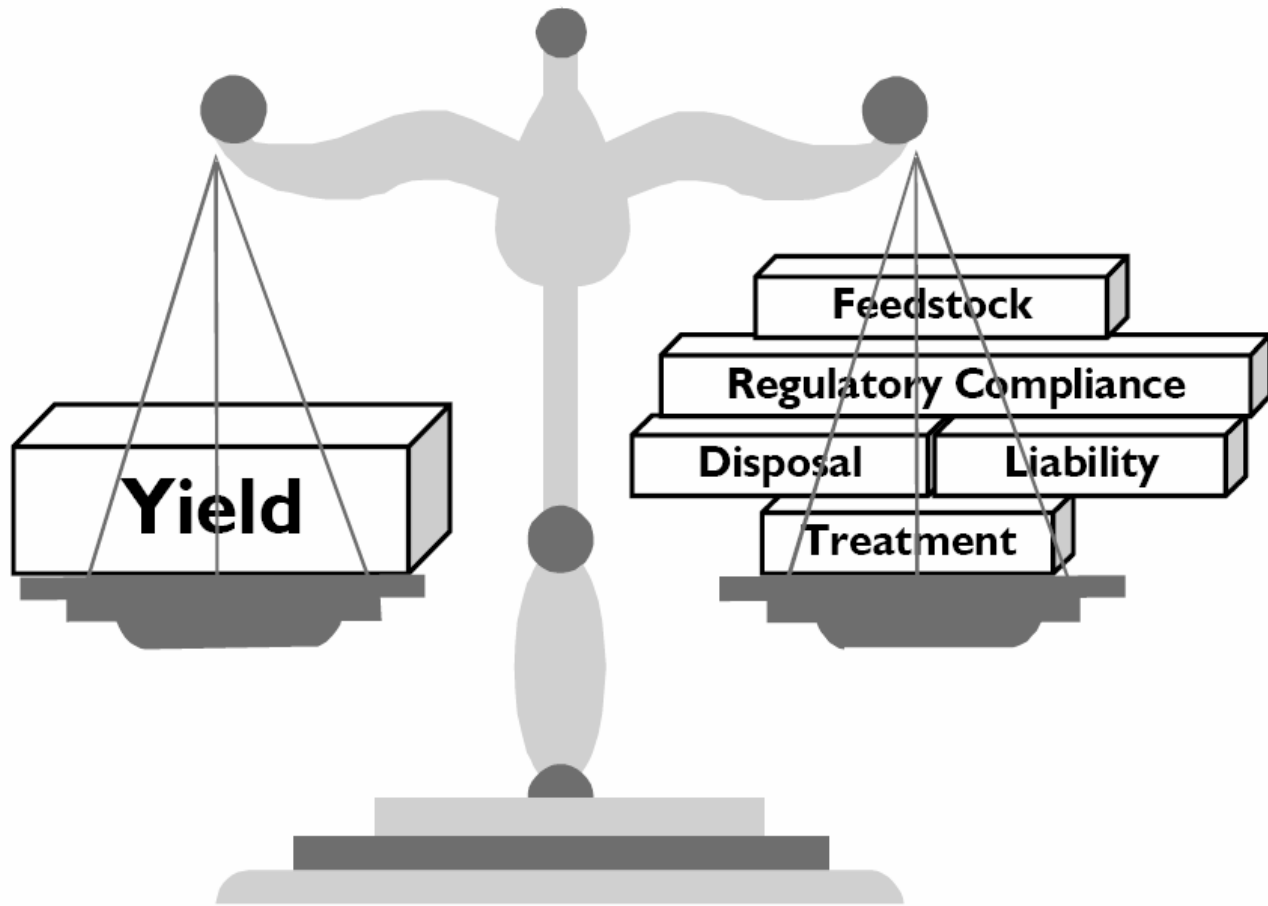
**Past**

# Balance in Design



**Present**

# Balance in Design



**Economical vs. Environmental**

# 12 Principles of Green Engineering

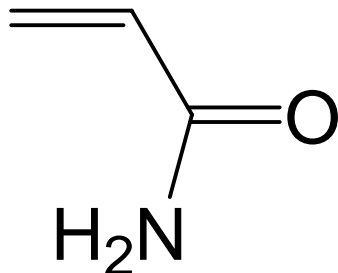
1. Inherent rather than circumstantial
2. Prevention rather than treatment
3. Design for separation
4. Maximize mass, energy, space, and time efficiency
5. Output-pulled versus input-pushed
6. Conserve complexity
7. Durability rather than immortality
8. Meet need, minimize excess
9. Minimize material diversity
10. Integrate local material and energy flows
11. Design for commercial afterlife
12. Renewable rather than depleting

# Principle 1

- Inherent rather than circumstantial  
*“designers should evaluate the inherent nature of the selected material and energy inputs to ensure that they are as benign as possible as a first step toward a sustainable product, process, or system”*

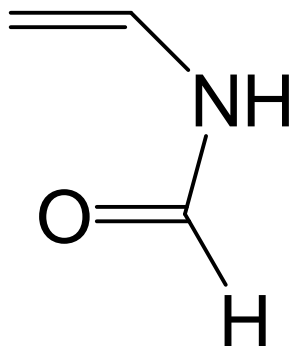


# A Case Study: Acrylamide vs. N-vinyl Formamide



→ Polyacrylamide, used in papermaking, oil recovery, personal care, water treatment

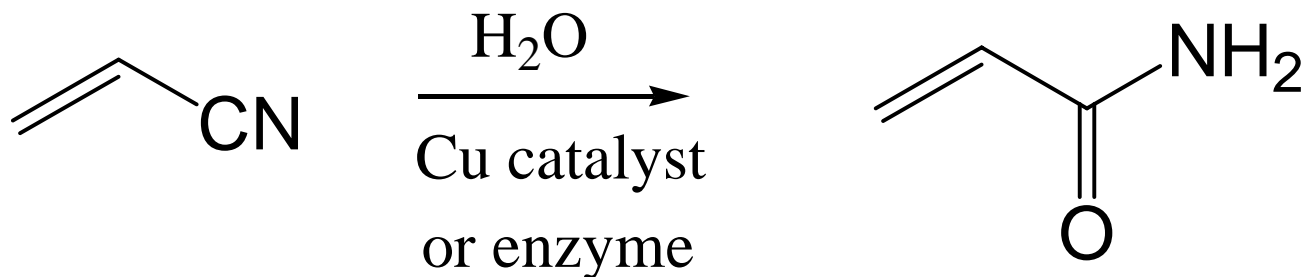
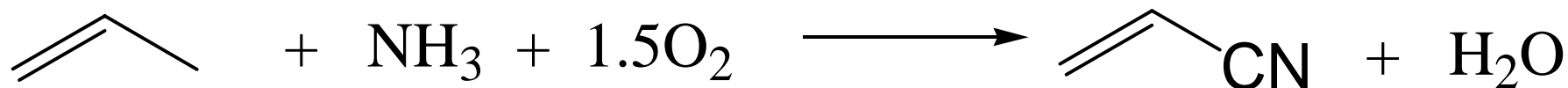
Highly toxic, causes CNS paralysis ~ \$1/kg



→ Poly(N-vinyl formamide), many of the same uses, hydrolyzed to polyvinyl amine.

Acute oral, > 1400 mg/Kg, not a neurotoxin ~ \$4.50/kg

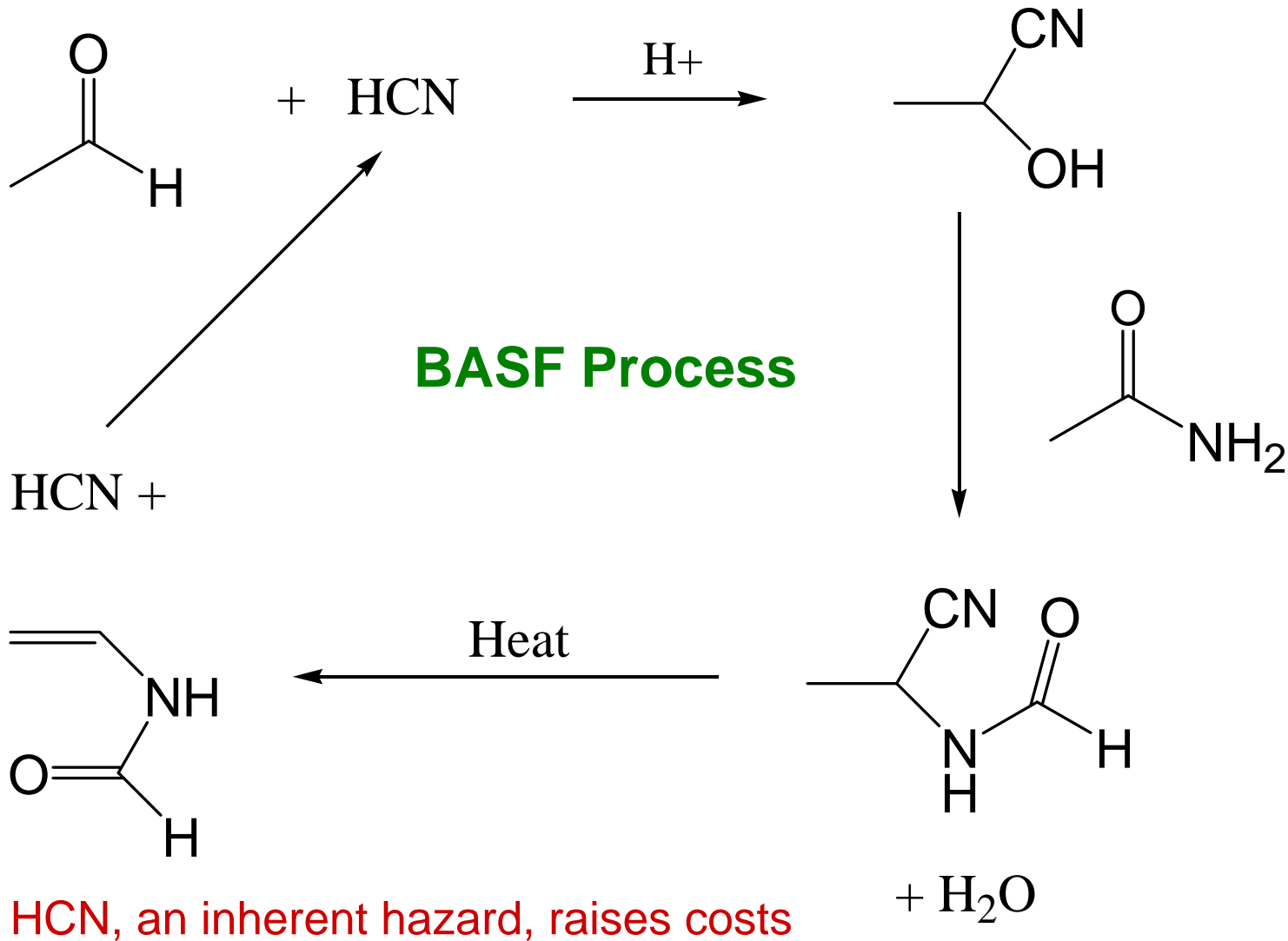
## Acrylamide Synthesis



Enzymatic route newest, greenest approach

Process green, Product not

# NVF Production



**Product green, Process not**

## Principle 2

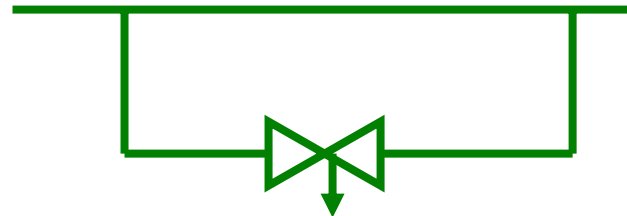
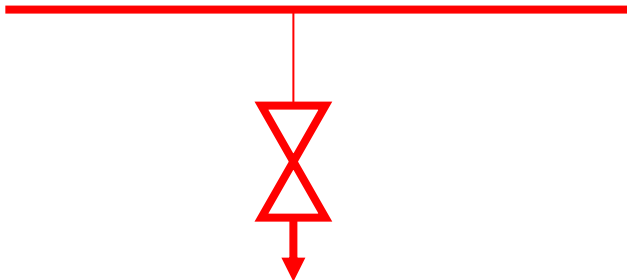
- Prevention rather than treatment  
*“it is better to prevent waste than to treat or clean up waste after it is formed”*
- Tremendous \$\$ spent on waste treatment, disposal and remediation; in the past not always considered in cost of plant - full cost accounting (life cycle analysis)
- Usually requires extra unit operations
- Industrial mindset is changing

## 2 example: how to prevent pollution?

- Implementation of new technology
  - solvent substitution
  - eliminate toxic intermediates
  - new reaction paths/new chemistry

## 2 example: how to prevent pollution?

- Simple (no/low cost) solutions
  - sloping piping downwards to cut wash solvent use
  - short, fat pipes reduces drag, lower energy use
  - paint storage tanks white
  - no dead-end sample points



## 2 example: how to prevent pollution?

- Engineering changes
  - raw materials; pretreatment of water for refinery to cut down on sludge waste
  - increase selectivity in reactors (reactor type, residence time, T, P, conc., mixing, catalysis)
  - separation processes
    - choice of mass separating agent
    - LLE vs. distillation
    - combined reaction/separation
    - membrane, adsorption....

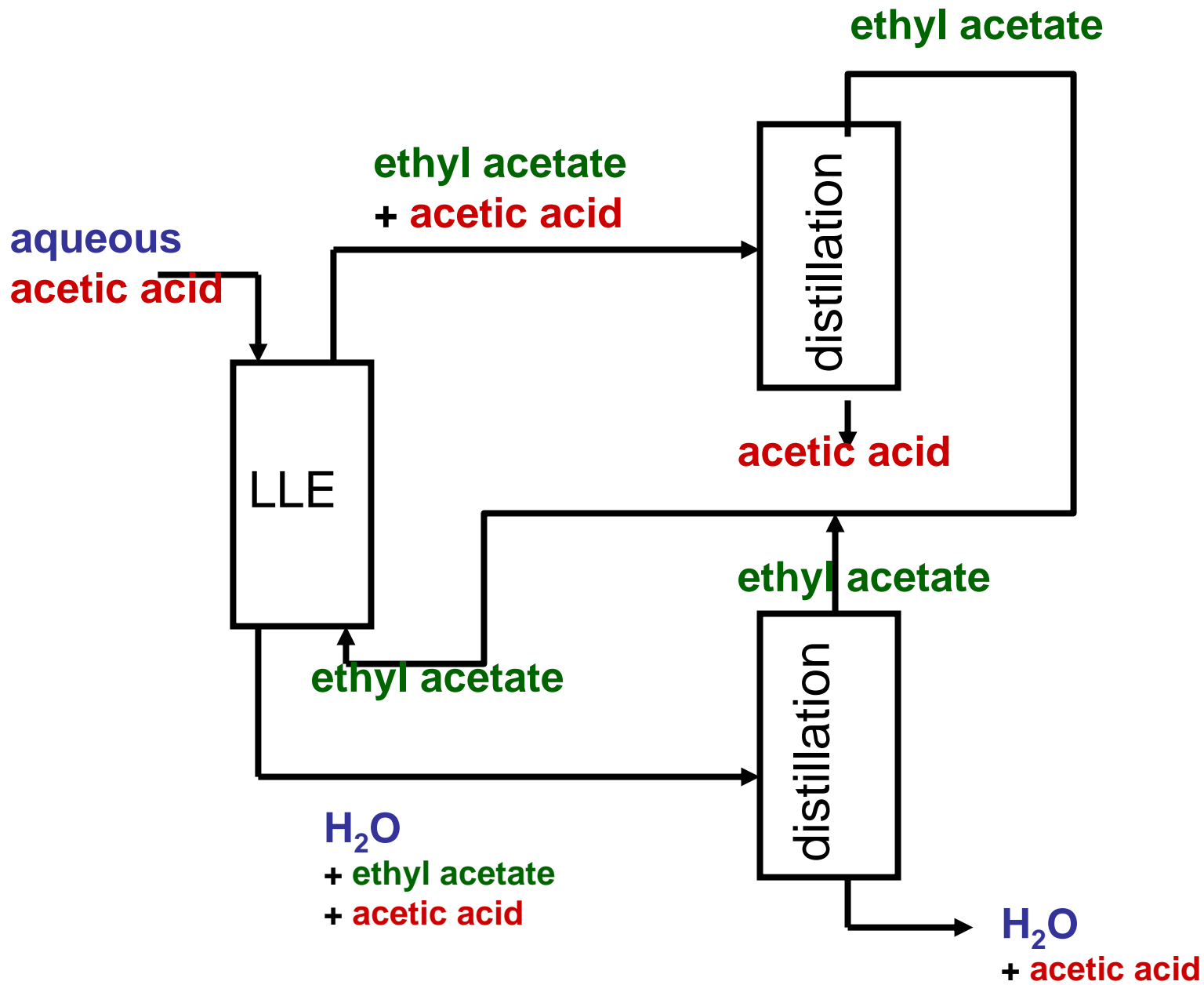
# LLE vs. Distillation: acetic acid/water separation

Acetic Acid     $T_b = 118.2 \text{ }^\circ\text{C}$   
 $\Delta h^{\text{vap}} = 24.39 \text{ kJ/mol}$

Water             $T_b = 100 \text{ }^\circ\text{C}$   
 $\Delta h^{\text{vap}} = 40.6 \text{ kJ/mol}$

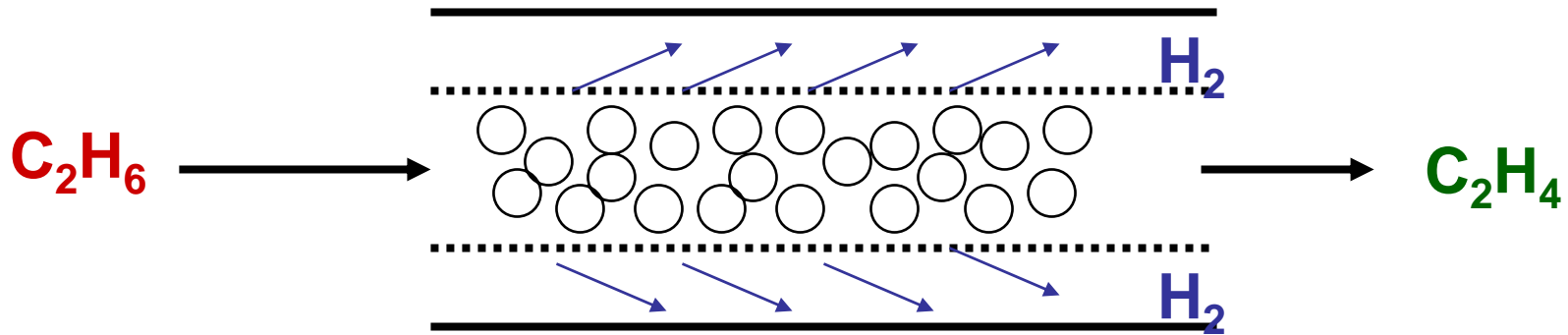
- large energy cost to vaporize all that water
- relative volatilities close to 1.0, so need lots of stages







# Combined reaction/separation



- microporous membrane
- allows  $H_2$  to pass but not  $C_2H_4$  or  $C_2H_6$
- allows close to 100% conversion
- eliminates need for energy-intensive separation process

## Principle 3

- Design for Separation;

*“many traditional methods for separation require large amounts of hazardous solvents, whereas others consume large quantities of energy as heat or pressure. Appropriate upfront designs permit the self-separation of products using intrinsic physical/chemical properties....”*

# Design for Separation, the Serendipitous Result.....



Polypropylene Cap (sometimes present...)

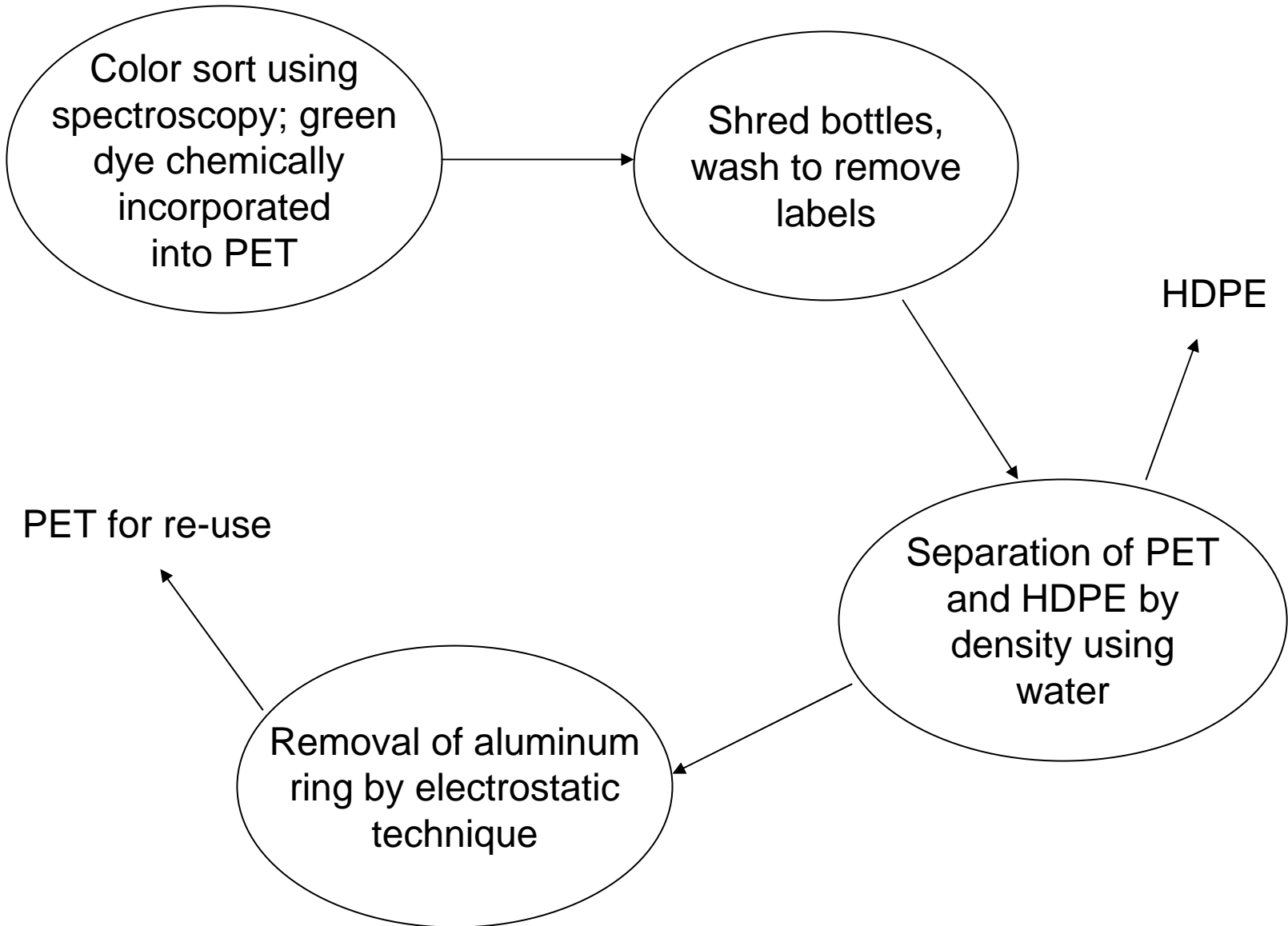
Aluminum Ring

Polyethylene Terephthalate Bottle

Paper/adhesive Label

Polyethylene Base Cup

# Recycling of PET bottles



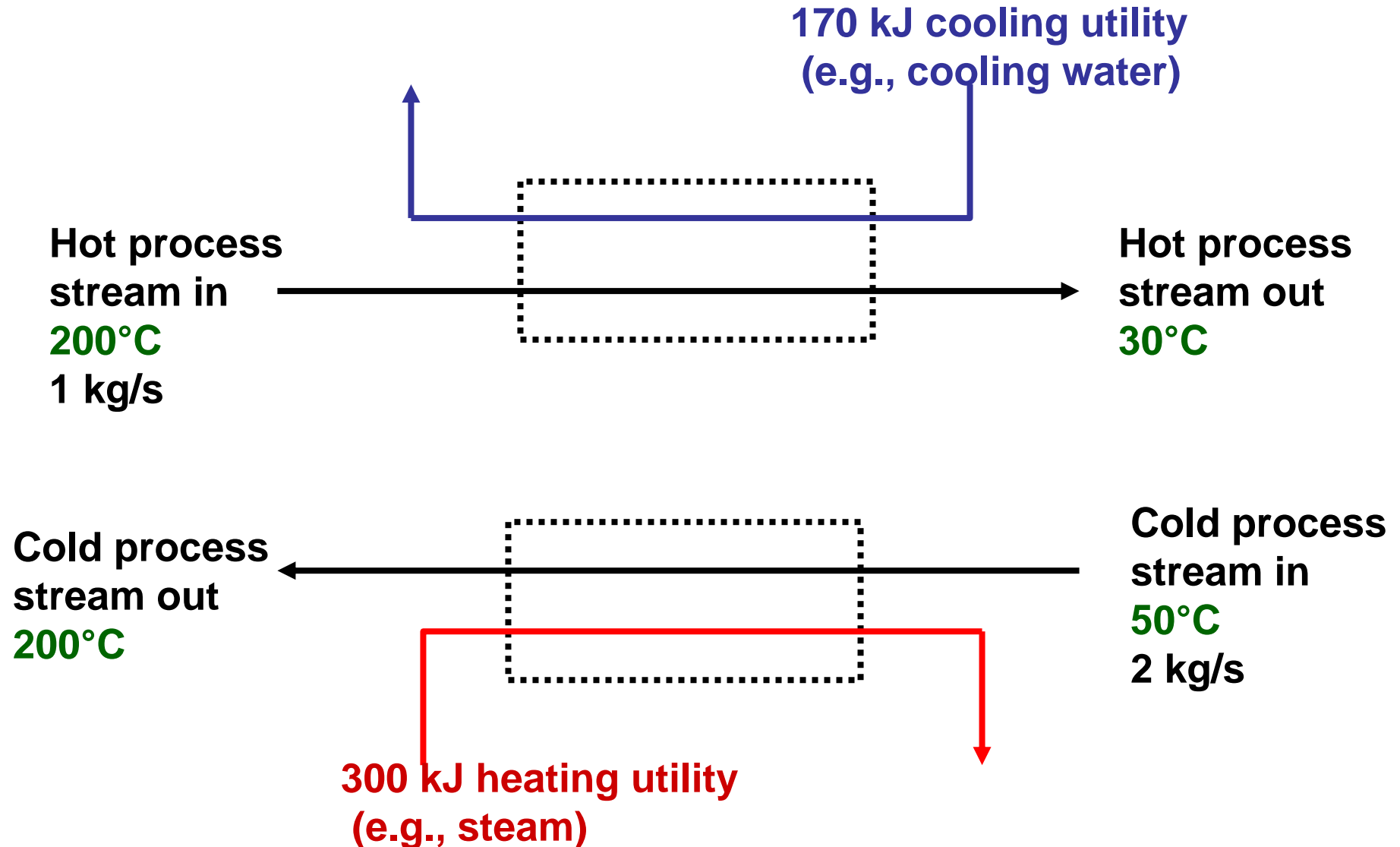
# Principle 4

- Maximize efficiency

*“products, processes, and systems should be designed to maximize mass, energy, space and time efficiency”*

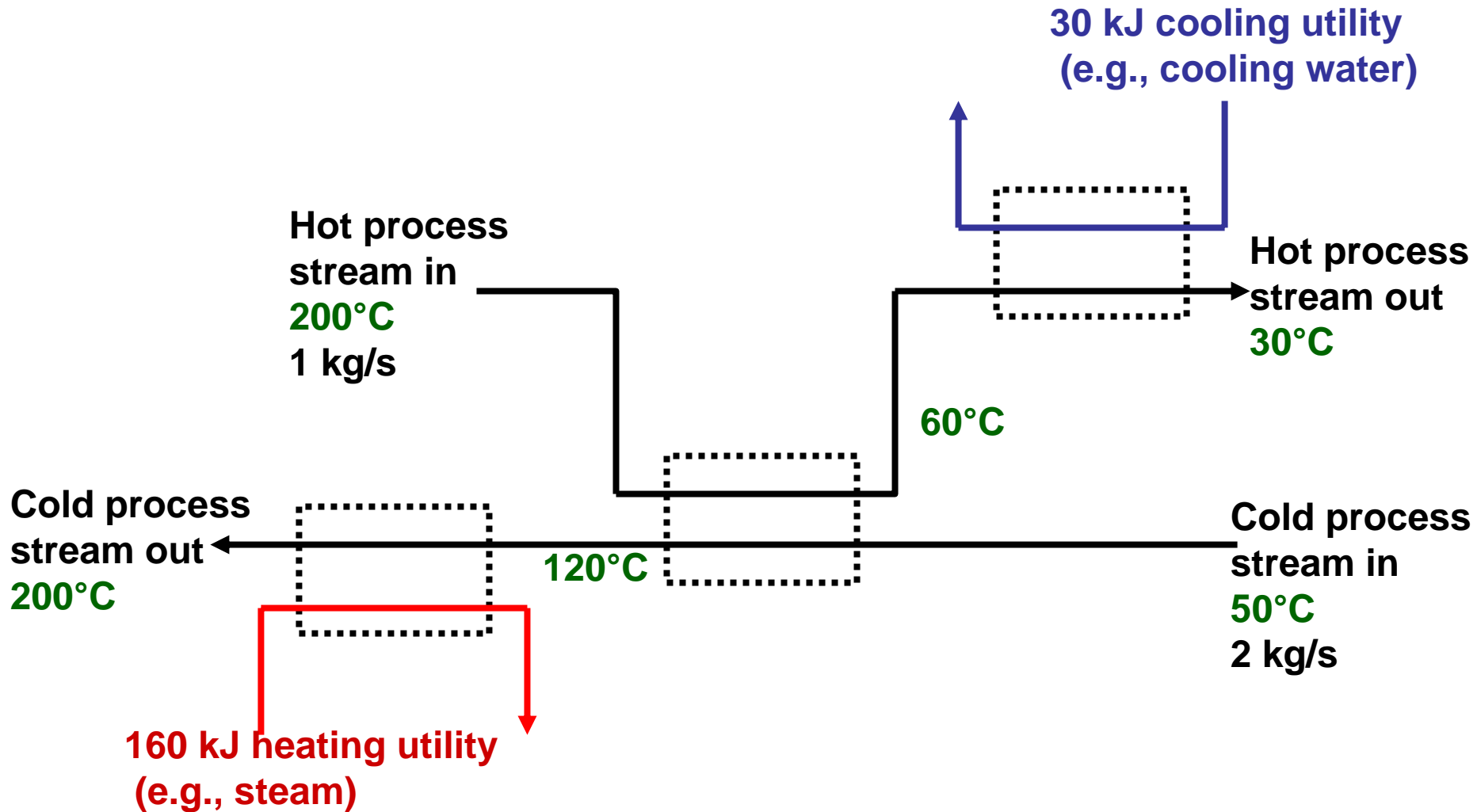
- Mass and energy efficiency is standard Chemical Engineering optimization
- Related to 8 (no overcapacity)
- Related to 10 (mass & energy integration)

# 4 example: heat integration





# 4 example: heat integration



## Principle 5

- Output-pulled rather than input-pushed  
*“approaching design through Le Chatelier’s Principle, therefore, minimizes the amount of resources consumed to transform inputs into desired outputs”*

Gap uses RFID tags to keep track of amounts on shelves versus amounts in inventory



Grocery stores use RFID to track sales and supplies of chilled food



# Principle 6

- Conserve complexity

*“embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition”*

- More focused on products than processes
- Less complicated products can more easily be recycled
- If a product is complex then it should be designed to be reused

## 6 example: PCs

- **IBM PC's used to be made with 15 different types of screws (unnecessary complexity)**
- **Replaced with 1 type of screw**
- **Easier to disassemble & recycle**
- **Why not reuse computers?**
  - make modular
  - replace processors, memory...
  - economics...



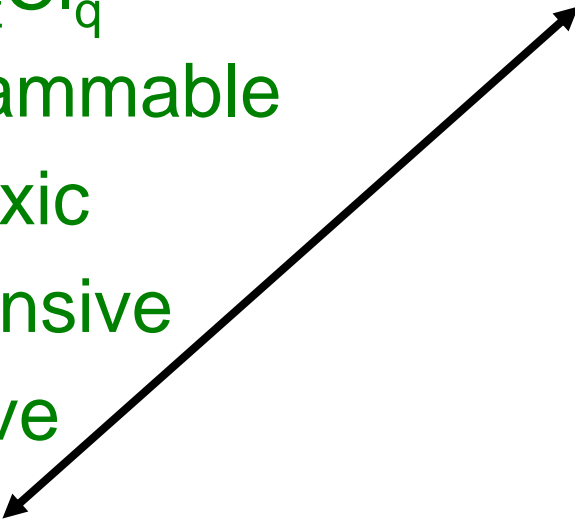
## Principle 7

- Durability rather than immortality;  
*“It is therefore necessary to design products with a targeted lifetime to avoid immortality of undesirable materials in the environment. However, this strategy must be balanced with the design of products that are durable enough to withstand anticipated operating conditions..”*

## Example: CFC's

- $C_xH_yF_zCl_q$
- Non-flammable
- Non-toxic
- Inexpensive
- Effective
- Stable

## Example: CFC's

- $C_xH_yF_zCl_q$
  - Non-flammable
  - Non-toxic
  - Inexpensive
  - Effective
  - Stable
- 
- Long-lived, migrate to upper atmosphere
  - UV-induced fragmentation in upper atmosphere leads to ozone depletion



## Principle 8

- Meet Need, Not Excess

*“design for unnecessary capacity or capability (e.g., “one size fits all”) solutions should be considered a design flaw”*

- Don't over design things; keep contingency factors low
- Extra size means wasted material and energy

## 8 example: whole industry overcapacity

- Global auto industry has 80 million vehicles/yr capacity for market of <60 million/yr  
(“Where Optimism Meets Overcapacity”, NYTimes, Oct. 1, 1997)
- U.S. 2002 plant utilization ~ 75% (Industry Week)

## Principle 9

- Minimize material diversity

*“options for final disposition are increased through upfront designs that minimize material diversity yet accomplish the needed functions”*

# Examples

- Automobile design: use single materials rather than alloys (metal and polymeric)
- Additives; create multi-functional additives rather than packages, incorporate additive functionality into polymeric backbone (dyes, flame retardants)
- Pigments; can pigments be switched “on” and “off”; can changes in pigment physical properties allow for variety of colors?

# Principle 10

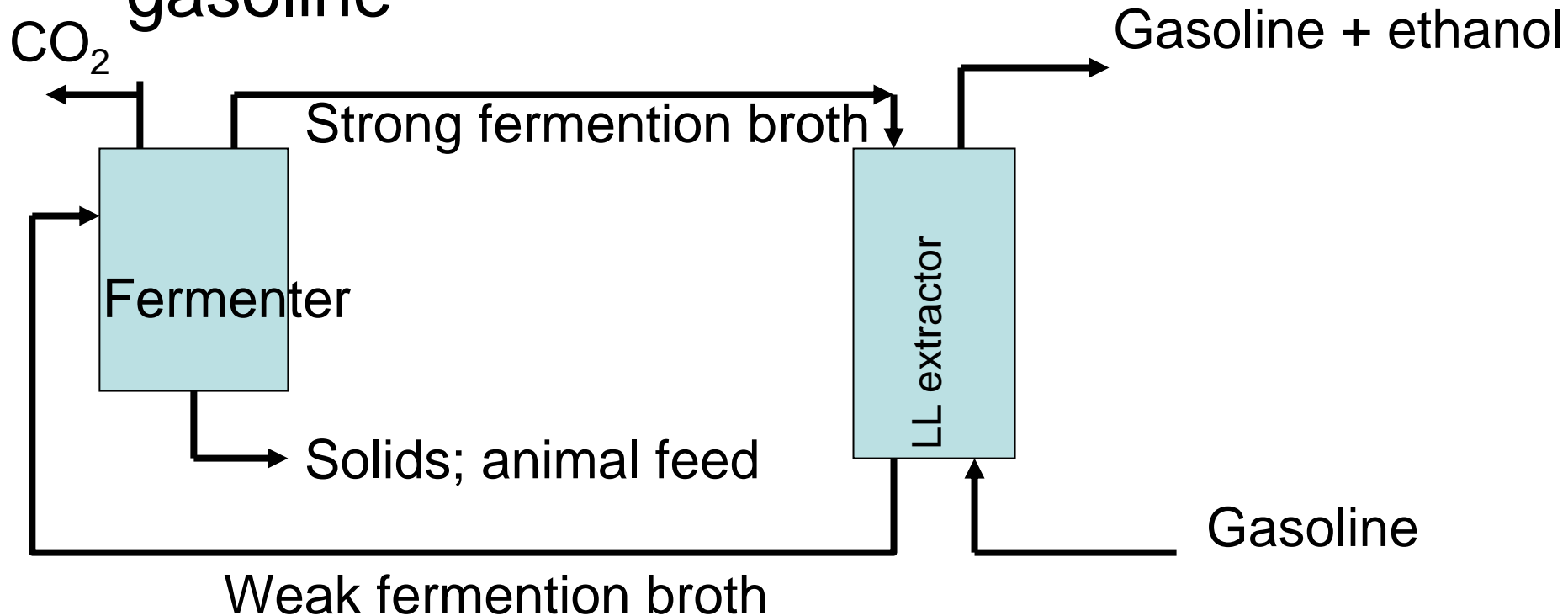
- Integrate Material and Energy Flows  
*“design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows”*
- Make use of what you’ve got available
- Heat integration (example 4)
- Mass integration (ethanol example)
- Large scale (Kalundborg industrial park)
- In process or on site

# 10 example: Ethanol for Gasoline

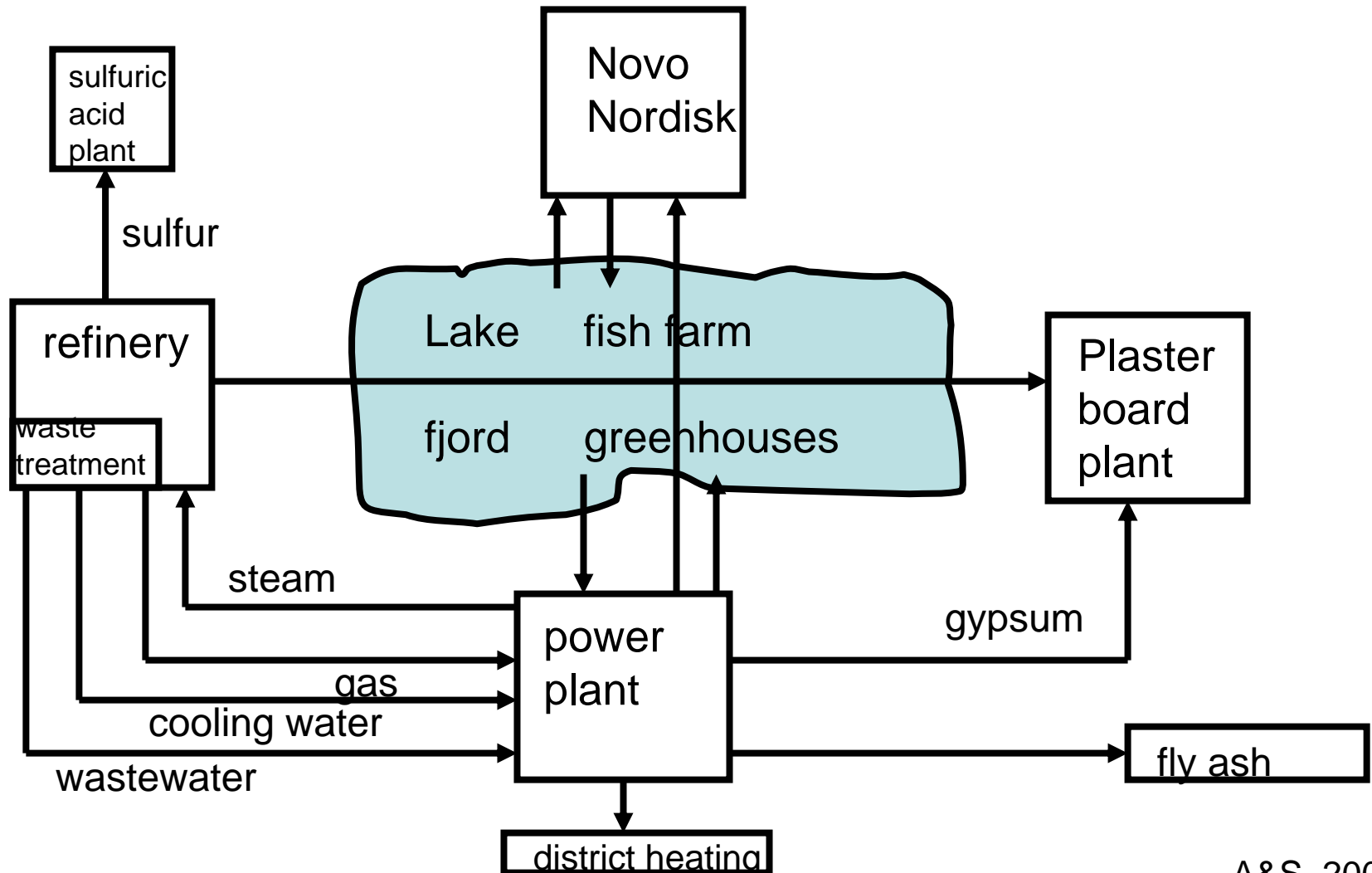
- Ethanol from fermentation of biomass
  - > ~15 wt% kills yeast
- distill ethanol; entrainer to break azeotrope
  - large energy use
  - benzene (carcinogen) common entrainer
- add purified ethanol to gasoline

# 10 example: Ethanol for Gasoline Alternative

- Direct contact of fermentation broth with gasoline



# 10 example: Kalundborg Industrial Park





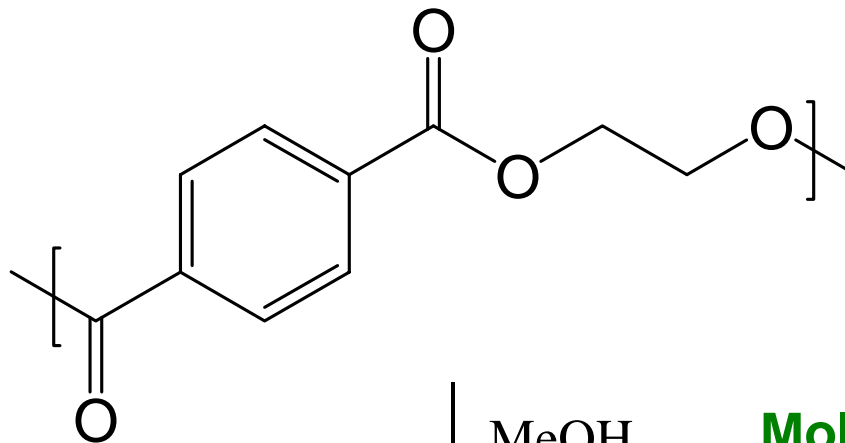
# Principle 11

- Design for commercial afterlife  
*“To reduce waste, components that remain functional and valuable can be recovered for reuse and/or reconfiguration”.*

# Examples

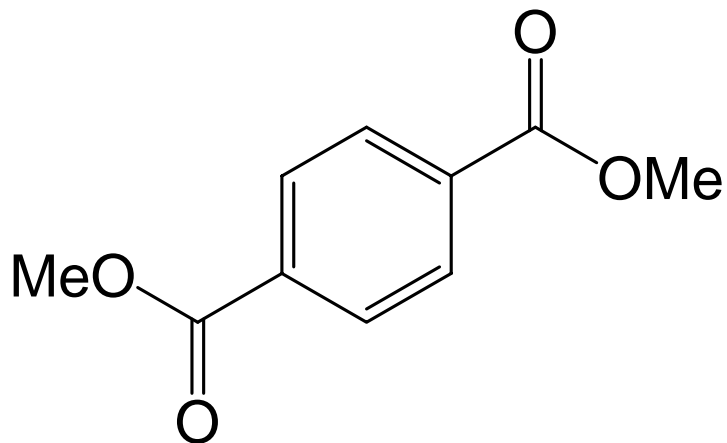
- Conversion of old factories to housing
- Disassembly of equipment for reuse of components
- Creation of “plastic lumber” from used polymeric packaging material (molecular reuse)

# Chemical Recycling Of PET

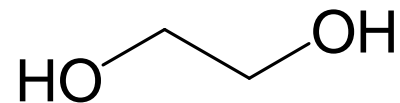


MeOH,  
Heat

**Molecule designed  
for disassembly**



+



**Used as antifreeze, etc**

**Purified, reused to make PET**

## Principle 12

- Renewable rather than depleting  
*“Material and energy inputs should be renewable rather than depleting”*
- Don't want to deplete our natural resources
- Need resources to be there for future generations
- Energy: solar, wind, hydroelectric, geothermal, biomass, hydrogen (fuel cells)

# References

- Allen and Rosselot, Pollution Prevention for Chemical Processes, 1997, John Wiley & Sons, Inc.
- Allen and Shonnard, Green Engineering, 2002, Prentice-Hall
- Seader and Henley, Separation Process Principles, 1998, John Wiley & Sons, Inc.
- Segars et al., ES&T, 2003, 37, 5269.

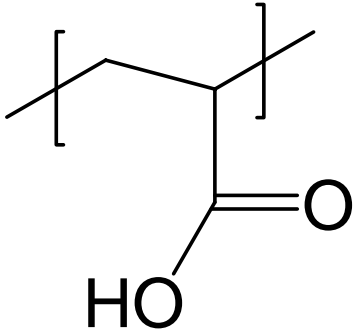
# GE: Defining the Principles

ECI, AIChE, ASME, SAE (2003)

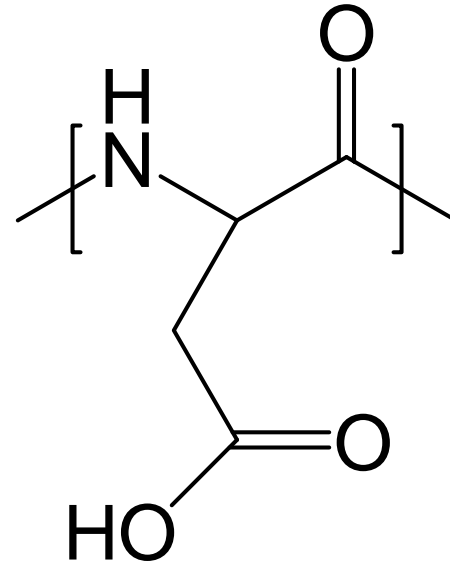
1. Engineer processes and products holistically, use **systems analysis**, and integrate environmental impact assessment tools
2. Conserve and improve natural **ecosystems** while protecting **human health** and well-being
3. Use **life-cycle** thinking in all engineering activities
4. Ensure that all material and energy inputs and outputs are as **inherently safe and benign** as possible
5. **Minimize depletion of natural resources**
6. Strive to **prevent waste**
7. Develop and apply engineering solutions, while being **cognizant of local geography, aspirations and cultures**
8. Create engineering solutions beyond current or dominant technologies; **improve, innovate and invent (technologies) to achieve sustainability**
9. Actively **engage communities and stake-holders** in development of engineering solutions

## Principle 4

- **Mass: use all your raw materials and concentration driving forces (10 example)**
- **Energy: heat integration**
- **Space: small cars**
- **Time: “just-in-time” manufacturing (operations research/scheduling)**
  - supply availability big issue



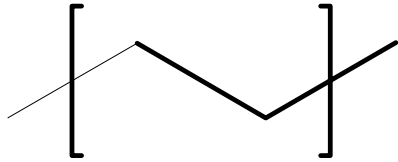
**Vs.**



**Polyacrylic acid,  
superabsorbent**

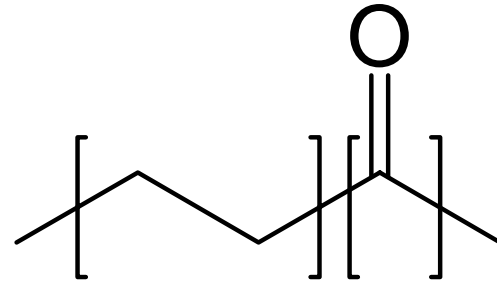
**Degradable analog,  
polyaspartic acid**





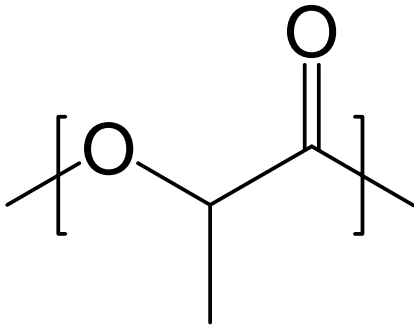
**Polyethylene, packaging**

**Vs.**



**Photodegradable analog**

**Vs.**



**Biodegradable analog**

**Differences in cost, density,  
and energy intensity**

# 12 Principles Applied to Redesigned Shaw Carpet Tiles

- 4.6 billion lb carpet to U.S. landfills annually
- Redesigned for recycle
  - Nylon 6 or Nylon 6,6 carpet
  - PVC plastisol backing replaced with branched LDPE
  - Can disassemble and recycle both nylon and backing
- 2003 Presidential Green Chemistry Challenge winner

- 1: Inherently nonhazardous
  - Replaced virgin calcium carbonate filler with coal fly ash
  - Replace PVC and phthalate plasticizer with (mostly) branched LDPE (metallocene catalyst important)
  - Less toxic flame retardant (not,  $\text{Sb}_2\text{O}_3$ , or proprietary aluminum trihydrate, what is it?)
- 2: Prevent waste
  - Recycle everything
  - Penalized by CPG under RCRA 6002 when introducing NEW recyclable material !!!

- 3: Minimize mass and energy use
  - Low energy mechanical separation and size reduction for recycle
  - Nylon sent for depolymerization (Honeywell)?
- 4: Efficiency
  - Extrusion coating requires less energy than radiant gas fusing (VOCs)
  - New tiles are 40% lighter (shipping!)
  - Telescoping boxes
- 5: Output pulled rather than input pushed
  - NA since replacement application

- 6: Embedded complexity is investment
  - Can't make out of one material due to performance
  - Separating and recycling next best thing
- 7: Durability, not immortality
  - These materials are immortal
  - OK because can recycle forever?
- 8: No unnecessary capacity
  - NA since replacement market
  - Problem if try to implement for regular carpet market

- 9: Minimize material diversity
  - Can't get this down due to performance criteria
  - Using same backing for multiple products is an example of this
- 10: Mass/energy integration
  - Cooling water in plant in closed loop
  - Recycling of polymers closes the loop
- 11: Design for commercial afterlife
  - Recycling so don't need to worry about afterlife
- 12: Renewable rather than depleting
  - Materials used are not renewable
  - Energy used is not renewable
  - ...but company has invested in a wind farm...