Chemicals and petroleum industries account for 50% of industrial energy usage.

~1/4 of the energy used is consumed in distillation and drying processes.

7. Use of Renewable Feedstocks
Biomaterials [Carbohydrates, Proteins, Lipids]
Highly Functionalized Molecules

Petroleum Products [Hydrocarbons]

Singly Functionalized Compounds [Olefins, Alkylchlorides]

Highly Functionalized Molecules

Polymers from Renewable Resources: Polyhydroxyalkanoates (PHAs)

- Fermentation of glucose in the presence of bacteria and propanoic acid (product contains 5-20% polyhydroxyvalerate)
- Similar to polypropene and polyethene
- Biodegradable (credit card)

![Chemical structure of a polyhydroxyalkanoate polymer](image)
Polymers from Renewable Resources: Poly(lactic acid)

Beverages find a natural R with NatureWorks® PLA packaging. Beverages are worldwide with containers and labels made from NatureWorks PLA. Showcase your brand while allowing consumers to see and taste your product. Even more refreshing is consumer reaction to the NatureWorks brand story. Market research clearly shows that consumers believe that beverages packaged in containers made from nature are fresher and more wholesome. Performance and the environmental attributes of bottles and labels made from PLA can provide you with a strong point of differentiation.

http://www.natureworksllc.com/corporate/nw_pack_home.asp

Raw Materials from Renewable Resources: The BioFine Process

- Paper mill sludge
- Agricultural residues, Waste wood
- Municipal solid waste and waste paper
- Levulinic acid

Green Chemistry Challenge Award
1999 Small Business Award
Levulinic acid as a platform chemical

- Conversion of waste biomass to levulinic acid
  - paper mill sludge, municipal solid waste,
  - unrecyclable waste paper, agricultural residues

8. Reduce Derivatives
Protecting Groups

2 synthetic steps are added each time one is used
Overall yield and atom economy will decrease

“Protecting groups are used because there is no direct way to solve the problem without them.”

9. Catalysis
Different types of catalysts

- Enzyme (biocatalyst)
- Copper-zinc crystallites on silica
- Zeolite (crystalline aluminosilicate)
- L-proline (organocatalyst)
- (R,R)-DPAMPH-RH (organometallic complex)

Heterogeneous vs Homogenous

<table>
<thead>
<tr>
<th>Heterogeneous</th>
<th>Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Readily separated ✔</td>
<td>Difficult to separate ✗</td>
</tr>
<tr>
<td>Readily recycled / regenerated ✔</td>
<td>Difficult to recover ✗</td>
</tr>
<tr>
<td>Long-lived ✔</td>
<td>Short service life ✗</td>
</tr>
<tr>
<td>Cheap ✔</td>
<td>Expensive ✗</td>
</tr>
<tr>
<td>Lower rates (diffusion limited) ✗</td>
<td>Very high rates ✔</td>
</tr>
<tr>
<td>Sensitive to poisons ✗</td>
<td>Robust to poisons ✔</td>
</tr>
<tr>
<td>Lower selectivity ✗</td>
<td>Highly selective ✔</td>
</tr>
<tr>
<td>High energy process ✗</td>
<td>Mild conditions ✔</td>
</tr>
<tr>
<td>Poor mechanistic understanding ✗</td>
<td>Mechanisms often known ✔</td>
</tr>
</tbody>
</table>

Ultimate goal: to combine the fast rates and high selectivities of homogeneous catalysts with the ease of recovery/recycle of heterogeneous catalysts.
10. Design for Degradation

Early examples
- Sulfonated detergents
  - Alkylbenzene sulfonates – 1950’s & 60’s
  - Foam in sewage plants, rivers and streams
  - Persistence was due to long alkyl chain
  - Introduction of alkene group into the chain increased degradation
- Chlorofluorocarbons (CFCs)
  - Do not break down, persist in atmosphere and contribute to destruction of ozone layer
- DDT
  - Bioaccumulate and cause thinning of egg shells
Degradation of Polymers: Polylactic Acid

- Manufactured from renewable resources
  - Corn or wheat; agricultural waste in future
- Uses 20-50% fewer fossil fuels than conventional plastics
- PLA products can be recycled or composted

Cargill Dow

11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Inherently Safer Chemistry for Accident Prevention

Tragedy in Bhopal, India - 1984

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate (MIC) were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

Chemists try to avoid things that explode, light on fire, are air-sensitive, etc.

In the “real world” when these things happen, lives are lost.
Minimize hazard

- Catalytically synthesize methylisocyanate to reduce risk of exposure
  - eliminates use of phosgene

Manzer, DuPont
Maleic anhydride may be prepared using two routes:

**Oxidation of benzene:**

\[
\text{C}_6\text{H}_6 + \frac{9}{2}\text{O}_2 \rightarrow \text{C}_4\text{H}_4\text{O}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

The benzene oxidation route typically occurs in 65% yield and produces 35 g non-benign waste for every 100 g benzene used, while the but-1-ene route only gives yields of 55%, and produces 45 g waste per 100 g but-1-ene.

(a) Assuming that each reaction is performed in the gas phase only, and that no additional chemicals are required, calculate (i) the atom economy and (ii) the effective mass yield of both reactions. You should assume that O\(_2\), CO\(_2\) and H\(_2\)O are benign chemicals.

(b) Which route would you recommend to industry? Outline the factors which might influence your decision.

### Case study

<table>
<thead>
<tr>
<th>Route</th>
<th>Reactants RMM</th>
<th>Desires Product RMM</th>
<th>Atom Economy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene Oxidation</td>
<td>78 + (4.5 x 32) = 222</td>
<td>98</td>
<td>44%</td>
</tr>
<tr>
<td>But-1-ene Oxidation</td>
<td>56 + (3 x 32) = 152</td>
<td>98</td>
<td>64%</td>
</tr>
</tbody>
</table>
There are several ways of tackling this question - this is one way...

**Benzene Oxidation**

100 g benzene (1.28 mol) would give 81.5 g maleic anhydride (0.83 mol, 65%).

\[
\text{EMY} = \frac{\text{mass of maleic anhydride}}{\text{mass of non-benign reagents}} \times 100\% = \left(\frac{81.5}{100}\right) \times 100\% = 81.5\%
\]

**But-1-ene Oxidation**

100 g but-1-ene (1.79 mol) would give 96.3 g maleic anhydride (0.98 mol, 55%).

\[
\text{EMY} = \frac{\text{mass of maleic anhydride}}{\text{mass of non-benign reagents}} \times 100\% = \left(\frac{96.3}{100}\right) \times 100\% = 96.3\%
\]

The butene oxidation route would appear to be slightly greener (higher atom economy and a higher effective mass yield). It also avoids the use of the toxic reagent benzene (we would therefore expect its wastestream to be less hazardous). However, the percentage yield is higher for the benzene oxidation route.

However, without a full life cycle analysis (which would take into account the environmental impact of producing both benzene and butene) a definitive answer is clearly not possible.

**Recommendation**

Recommendation: Butene route is possibly better - but only if raw material costs are acceptable.
Boots synthesis of Ibuprofen

- AcOH, HCl, Al waste
- HCl
- AcOH

All three steps are catalytic
99% conversion
96% selectivity
Less waste generated

Hoechst synthesis of Ibuprofen

All three steps are catalytic
99% conversion
96% selectivity
Less waste generated