Student Challenge

Graduate students: are you part of the sustainability solution? Win $10,000!

Do you have a sustainable, innovative solution for one of the many challenges our world faces? Submit your idea to the Dow Sustainability Innovation Student Challenge, hosted by the Sustainable Products and Solutions Program in the Haas Center for Responsible Business. Your world-changing solution could be worth big bucks! The top three entries will each receive $10,000, for a total of $30,000 in award money.

APPLICATIONS DUE: April 11, 2011
FINALISTS IDENTIFIED: April 22, 2011 (Earth Day)

Your entry can describe an innovative concept, device, product, process, or system.

Academic papers, abstracts, and other non-commercial works are also encouraged. However, the work

Contact: Shelley Brozenick <sbrozenick@berkeley.edu>

Special Catalysis Center Seminar
Wednesday, March 16, 2011
775A Tan Hall 1:30 PM

James E. “Ned” Jackson, Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

Building Block Reactions for the Biomass Refinery of the Future:
Aqueous Reductive Upgrading of Acids, Amides, Polyols, and Aromatics

As part of a longstanding collaborative project (NJ = Prof. Dennis Miller, Chem. Eng. and Chris Saffran, Biotech. Eng. & Forestry), work is underway in our labs at MSU to develop reactions needed for the “biomass refinery” of the future, including the partnership between chemical- and bio-catalytic approaches. Our focus—catalytic reductions (hydrogenation/hydrogenolysis, electrolysis) by which carbohydrates, organic acids, and related feedstocks can be converted to useful chemicals and monomer building blocks—will be described as illustrated below with the conversion of lactic acid to propylene glycol. Though begun with a practical aim, these efforts have uncovered a novel C11 activation, modest insights into catalytic mechanisms, and some hopeful approaches to the liquid fuels problem.

Glucose (from algal or cell-dose) → Lactic Acid (chiral monomer) → Propylene Glycol (commercial chemical >10^6 kg/year)

Contact: Shelley Brozenick <sbrozenick@berkeley.edu>
Molecular Design

What will you consider and why?

Feedstock + Reagents = Final properties

12 Principles of Green Chemistry

1. Prevent waste
2. Atom economy
3. Less hazardous chemical synthesis
4. Design safer chemicals
5. Safer solvents/reaction media
6. Energy efficiency
7. Use renewable feedstocks
8. Reduce derivatives
9. Catalysis
10. Design for end of life
11. Real-time process control
12. Inherently safer chemistry

How does this shape the interpretation or execution of the 12 principles?

Getting from A \( \rightarrow \) B

Practical Tools in Green Chemistry

“Green Chemistry is the molecular basis of sustainability”

Paul Anastas

Goals for this class:

• To think about better ways to do chemistry
• Better understand some of the 12 Principles
• Introduce practical metrics to determine ‘greenness’
• Understand why catalysis is an important and powerful synthetic concept
12 Principles of Green Chemistry

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary when possible and, when used, innocuous.
6. **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. **Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention.** Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.


![Figure 1.2: Green chemistry as a reduction process.](image)
Summary of GC Metrics

Green Chemistry Metrics
From Wikipedia, the free encyclopedia

Green chemistry metrics measures efficiency in a chemical process. Having made a Green Chemistry improvement in a chemical process, it is important to be able to quantify the change. By quantifying the improvement, there is a tangible element or benefit from the new technology introduced. This is likely to aid the communication of the work and promote fast facilitation from the investor to industry. For a non-chemist the most attractive method of quoting the improvement would be a decrease of $X$ per kilo of compound. This however is an oversimplification and does not allow a chemist to visualise the improvement made in terms of allowable for toxicity-based. For yield improvements and selectivity increase, simple percentages are suitable, but this simplistic approach may not always be appropriate. For example, when a highly pyrophoric reagent is replaced by a benign one, a numerical value is difficult to assign but the improvement is obvious, if all other factors are similar.

Numerous metrics have been formulated over time and their suitability discussed at great length.

The problem observed is that the more account and universally applicable the metric devised, the more complex and unintuitive it becomes. A good metric must be clearly defined, simple, measurable, objective rather than subjective and most ultimately drive the desired behavior.

Contents

• 1 Effective mass yield
• 2 Carbon efficiency
• 3 Atom economy
• 4 Reaction mass efficiency
• 5 Environmental (E) factor
• 6 Comparison of metrics
• 7 The E-factor
• 8 External links
• 9 References

• http://en.wikipedia.org/wiki/Green_Chemistry_Metrics
Traditional metrics in chemistry

• Yield (%)
  \[ \text{Yield} = \frac{\text{moles of product}}{\text{moles of limiting reagent}} \times 100 \]
• Purity (%)
• Reaction time (min, h)
• (Cost ($))

Common GC metrics

• E (Environmental) Factor (or E Value)
  – Useful industrial metric
• Atom Economy
• Atom Efficiency
• Reaction Mass Efficiency
• + others
**E Factor**

E Factor = \( \frac{\text{Total Waste (Kg)}}{\text{Product (Kg)}} \)

- Very useful metric for industry
- Important to define what ‘waste’ is
  - Organic waste
  - Aqueous waste
- The **smaller** the number, the better (0 - \( \infty \))

### Environmental acceptability (E)

\[
E = \frac{\text{Kg waste + unwanted byproducts}}{\text{Kg desired product(s)}}
\]

<table>
<thead>
<tr>
<th>Volume of production in tons per Year</th>
<th>E value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>( 10^8 ) - ( 10^5 )</td>
</tr>
<tr>
<td>commodity chemicals</td>
<td>( 10^4 ) - ( 10^8 )</td>
</tr>
<tr>
<td>special chemicals</td>
<td>( 10^2 ) - ( 10^4 )</td>
</tr>
<tr>
<td>drugs</td>
<td>( 10^1 ) - ( 10^4 )</td>
</tr>
</tbody>
</table>

More optimized processes
Higher complexity of synthesis
Atom Economy

- Molecular Weight = Relative Formula Mass, RFM: M_r
  The sum of the relative atomic masses of the atoms in the numbers shown in the formula of the compound
  e.g. M_r of H₂O = (2 x 1) + 16 = 18

For the reaction:

\[ A + C \rightarrow C \text{ (+ by-products)} \]

- % Atom Economy = \( \frac{100 \times M_r \text{ of Product } C}{M_r \text{ of } A + M_r \text{ of } B} \)

- Correlates how much of reactants end up in the product
- Simple!
- Doesn’t account for solvents
- Larger number is better (0-100%)

Example

Benzoic Oxidation

\[
\text{\begin{array}{c}
\text{Benzoic Oxidation} \\
\text{Formula weights:} \\
78 \quad 4 \times 32 = 144 \quad 98 \\
% \text{Atom Economy} = \frac{100 \times 98}{(78+144)} = \frac{100 \times 98}{222} = 44.1% \\
\end{array}}
\]

From: Lancaster, Green Chemistry
The Wittig Reaction

Reaction Mass Efficiency (RME)

Developed by GSK, RME takes into account atom economy, chemical yield and stoichiometry. The formula can take one of the two forms shown below:

- From a generic reaction where $A + B \rightarrow C$
  - $RME = \text{Molecular weight of product } C \times \text{yield m.w. } A + (\text{m.w. } B \times \text{molar ratio } B/A)$

- Or more simply:
  - $RME = \frac{\text{Mass of product } C \times 100}{\text{Mass of } A + \text{mass of } B}$

Like carbon efficiency, this measure shows the “clean-ness” of a reaction but not of a process, for example, neither metric takes into account waste produced. For example, these metrics could present a rearrangement as “very green” but they would fail to address any solvent, work-up and energy issues arising.
9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Why?

Stoichiometric Oxidation with Cr

Oxidation of diphenylmethanol to benzophenone

3 diphenyl methanol + 2CrO₃ + 3H₂SO₄\rightarrow 3 benzophenone + 2Cr₂(SO₄)₃ + 6H₂O

waste
Synthesis of Ethylene Oxide

• Stoichiometric

\[
\begin{align*}
\text{Step 1:} & \quad \text{H}_2\text{C} = \text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{HCl} + \text{HOCl} \\
\text{Step 2:} & \quad \text{H}_2\text{C} = \text{CH}_2 + \text{Cl}_2 + \text{Ca(OH)}_2 \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Scheme 6. The chlorohydrin process [25a,27].

Synthesis of Ethylene Oxide

• Catalytic

\[
\text{H}_2\text{C} = \text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Ag catalyst}, 10-30 \text{ atm}} \text{H}_2\text{C} = \text{CH}_2 + \text{O}_2
\]

• Selectivity for ethylene oxide, as with the traditional synthesis, is around 80%.
• All manufacture of ethylene oxide today is via the catalytic route.
Synthesis of Ethylene Oxide

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Utilised</th>
<th>Not utilised</th>
</tr>
</thead>
<tbody>
<tr>
<td>G_2H_4</td>
<td>28</td>
<td>G_2H_4</td>
</tr>
<tr>
<td>Cl_2</td>
<td>71</td>
<td>Cl_2</td>
</tr>
<tr>
<td>H_2O</td>
<td>18</td>
<td>H_2O</td>
</tr>
<tr>
<td>Ca(OH)_2</td>
<td>74.1</td>
<td>Ca(OH)_2</td>
</tr>
<tr>
<td>Total</td>
<td>Ethylene oxide</td>
<td>44</td>
</tr>
<tr>
<td>H_2O/Cl_2</td>
<td>147.1</td>
<td></td>
</tr>
</tbody>
</table>

% Atom economy = 44/191.1 x 100 = 23%

Scale of reactions

<table>
<thead>
<tr>
<th>Operation</th>
<th>Scale (million tonnes per year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid and poly(ethylene terephthalate)</td>
<td>9</td>
</tr>
<tr>
<td>Acetic acid and acetyl chemicals</td>
<td>7</td>
</tr>
<tr>
<td>Aldehydes and alcohols via hydroformylation</td>
<td>6</td>
</tr>
<tr>
<td>Adiponitrile</td>
<td>1</td>
</tr>
<tr>
<td>Detergent-range alkenes via SHOP</td>
<td>1</td>
</tr>
<tr>
<td>Total fine chemicals manufacture</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Olefin polymerization (60% uses Ziegler-Natta)</td>
<td>60</td>
</tr>
</tbody>
</table>

- 27% of US GNP and 90% of chemical industry involve products made using catalysts (food, fuels, polymers, textiles, pharma/agrochemicals, etc)
Introduction to catalysis

- A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved (unchanged at the end of the cycle)

- A catalyst does not influence the thermodynamics of a reaction – i.e. a kinetic effect

\[
A + B + [\text{CAT}] \xrightleftharpoons[k_{-1}]{k_1} C
\]

\[
K = \frac{k_1}{k_{-1}}
\]

- Important terms:
  - Selectivity
  - Turnover number
  - Turnover frequency
  - Catalyst phase: homogeneous or heterogeneous

General Scheme for Catalytic Activity

- Reactants bind to sites on the catalyst (open site on molecule (homogeneous) or surface (heterogeneous)
- Transformation occurs
- Reactants desorb
- Cycle repeats
Turnover Number

• The number of times the catalytic cycle operates before the catalyst ‘dies’

Figure 12.1 A schematic of the catalytic cycle for Acetic acid production via the Monsanto process.
Turnover Frequency (TOF)

• The number of times per second the catalytic cycle turns

• For most relevant industrial applications, the turnover frequency is in the range of $10^{-2} - 10^2$ s$^{-1}$ (enzymes $10^3 - 10^7$ s$^{-1}$).

Different types of catalysts

- enzyme (biocatalyst)
- zeolite (crystalline aluminosilicate)
- copper-zinc crystallites on silica
**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.

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**Nobel Prize in Chemistry 2005**

**Trio wins Nobel Prize for ‘green chemistry’**
Frenchman, 2 Americans develop environmentally friendly methods

Richard Schrock, Yves Chauvin and Robert Grubbs have won the Nobel Prize for chemistry for the development of the metathesis method in organic synthesis — an environmentally friendly process for making products ranging from baseball bats to biodiesel fuel.

Alkene Metathesis

\[ R\underset{\text{cat}}{\rightleftharpoons}R + \rightarrow R\underset{\text{cat}}{\rightleftharpoons}R \]

Schrock catalyst

Grubbs catalyst

Mechanism

\[
\begin{align*}
&M\rightleftharpoons R \\
&M\rightleftharpoons R \\
&H\quad H \\
&M\rightleftharpoons R \\
\end{align*}
\]
Ammomia Synthesis – The Haber Process

- The Haber process now produces 100 million tons of nitrogen fertilizer per year, mostly in the form of anhydrous ammonia, ammonium nitrate, and urea. 3–5% of world natural gas production is consumed in the Haber process (~1–2% of the world’s annual energy supply).

- Depending on the particular crop being grown, up to 200 pounds of ammonia per acre may be applied for each growing season.

- Responsible for sustaining one-third of the Earth’s population

- Ammonia is a widely used refrigerant in industrial refrigeration

- Nitric Acid production is the most important single use of ammonia — Made via oxidation to NO

- Hydrogen production using electrolysis of water powered by renewable energy is not yet competitive cost-wise with hydrogen from fossil fuels, such as natural gas, and so has been responsible for only 4% of current hydrogen production (almost all as a byproduct of the chloralkali process).
The Haber Process

\[ 3H_2 + N_2 \rightarrow 2NH_3 \]

- 400-500°C provides an acceptable yield of ammonia (10-20%) within an acceptable time period
- Very high pressure (~250 atm, ~351 kPa)
- Needs catalyst (porous iron, prepared by reducing magnetite, \( \text{Fe}_3\text{O}_4 \))
- Hydrogen required – made from methane by reaction with steam
- Nitrogen obtained by distillation of liquid air
Applications of oligomers and polymers from olefins

- Ethene and propene come directly from crude oil "crackers"
  - Primary petrochemical products, basic chemical feedstocks

- Dimerization rarely desired
  - Making butene very expensive

- Oligomers: surfactants, comonomers
  - High added value, but limited market

- Polymers: plastics, construction materials, foils and films
  - Very large market, bulk products
# Timetable and historical development of metallocene research

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1952</td>
<td>Development of the structure of metallocenes (ferrocene) by Fischer and Wilkinson</td>
</tr>
<tr>
<td>1955</td>
<td>Metallocene as component of Ziegler-Natta catalysts, low activity with common aluminium alkyls.</td>
</tr>
<tr>
<td>1973</td>
<td>Addition of small amount of water to increase the activity (Al:H₂O = 1:0.05 up to 1:0.3) (Reichert, Meyer and Breslow)</td>
</tr>
<tr>
<td>1975</td>
<td>Unusual increase in activity by adding water at the ratio Al:H₂O = 1:2 (Kaminsky, Sinn and Motweller)</td>
</tr>
<tr>
<td>1977</td>
<td>Using separately prepared methylaluminoxane (MAO) as cocatalyst for olefin polymerization. (Kaminsky and Sinn)</td>
</tr>
<tr>
<td>1982</td>
<td>Synthesis of ansa metallocenes with C₂ symmetry (Brintzinger)</td>
</tr>
<tr>
<td>1984</td>
<td>Polymerization of propylene using a rac/meso mixture of ansa titanocenes lead to partially isotactic polypropylene. (Ewen)</td>
</tr>
<tr>
<td>1984</td>
<td>Chiral ansa zirconocenes produce highly isotactic polypropylene (Kaminsky and Brintzinger)</td>
</tr>
</tbody>
</table>

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## Ziegler-Natta (Nobel Prize 1963)

- High density polyethene (HDPE)
  
  $$ \text{M}_{\text{cat}} $$

  High pressure free radical polymerization gives branched low molecular polyethene (LDPE)

- Stereocontrolled polymerization

  $$ \text{M}_{\text{cat}} $$
Important Types of PE

- **Highly crystalline polymer**
  - HDPE
  - Few short chain branches (SCB)

- **LDPE**
  - SCB: YES
  - LCB: YES
  - Cross-links amorphous polymer

- **LLDPE**
  - SCB: YES
  - Semi-crystalline

Ziegler-Natta Polymerization
Important Isomers of Polypropylene

- Isotactic polypropylene
- Syndiotactic polypropylene
- Atactic polypropylene

Metallocene Catalysts

- Group 4 (Ti, Zr, Hf) metallocene catalysts are considered to be the most versatile transition metal catalysts for olefin polymerization.
- Brintzinger and co-workers developed synthesis of the enantiomeric pure ansa-metallocene.
- Chiral ansa-metallocenes also catalyze:
  - Hydrogenations of C==C, C==O or C==N double bonds
  - Diels-Alder reactions
  - Epoxidations