Chemistry:

A Description of Metrics with Applications in Academia and Industry

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Outline

- Metrics Past and Present
- Formulas and Uses of Different Metrics
- Application of Metrics in Academia
- Application of Metrics in Industry
- Conclusions

The 12 Principles of Green Chemistry

- **1. Prevention**
  It is better to prevent waste than to treat or clean up waste after it has been created.
- **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 Syntheses**
  Wherever practicable, synthetic methods 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 affect their desired function while minimizing their toxicity.
- **5. Safer Solvents and Auxiliaries**
  The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- **6. Design for Energy Efficiency**
  Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

(*Anastas and Warner, 1998*)

The 12 Principles of Green Chemistry

- **7. Use of Renewable Feedstocks**
  A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- **8. Reduce Derivatives**
  Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- **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 break down into innocuous degradation products and do not persist in the environment.
- **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**
  Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

(*Anastas and Warner, 1998*)

Introduction to Metrics

- Metrics: "a combining form with the meaning ***'the science of measuring'*** that specified by the initial element: *biometrics; econometrics*" -Webster
- What have we used historically in academia?
- Guidelines for creating Greener metrics:
  - 12 Principles of Green Chemistry
- Each metric is unique
- Methods for analyzing metrics:
  - Tried and Failed
    - Numeric combinations on a scale from 1 to 10
    - Assigning red, yellow, green status
  - Useful
    - Comparing processes

Examples of Common Metrics

Melting Point

Percent (%) Yield

Examples of Common Metrics

- E-Factor
  - Solvent Minimization
- Atom Economy
- Atom Efficiency
- Effective Mass Yield
- Carbon Efficiency
- Reaction Mass Efficiency
- Other Issues not addressed by these metrics:
  - Energy concerns (Process – interior and exterior)
  - Renewable Feedstocks (starting materials)
  - Reaction Types
    - Catalysts vs. stoichiometric reagents
    - Safety
  - Life Cycle Analysis
  - Environmental Quotient

E-Factor

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

- Depends on one's definition of 'waste'
  - Include:
    - Process use only
    - Or chemicals needed for scrubbing
- Very useful metric for industry
- E-factor can be split into different sub-categories:
  - Organic waste
  - Aqueous waste
- The **smaller** the number, the closer to zero waste being produced
  - (0-∞)

Atom Economy

$$\%\text{ Atom Economy} = 100 \text{ X } \frac{\text{m.w. of Product C}}{\text{m.w. of A + m.w. of B}}$$

A + B → C + by-products

- Defined: 'a calculation of how much of the reactants remain in the final product' (Constable *et al.*)
- Simple calculation
- Does not account for solvents, reagents, reaction yield, and reactant molar excess
- The **larger** the number, the higher the percent of all reactants appearing in the product
  - (0-100%)

Atom Efficiency

Atom Efficiency = %Yield X Atom Economy

- Importance:
  - Could be used to replace Yield and Atom economy
  - Example: Atom economy could be 100% and yield 5% making this a not very green reaction
- The closer to **100%**, the greener the process
  - (0-100%)

Effective Mass Yield

$$\text{Eff. Mass Yield (\%)} = 100 \text{ X } \frac{\text{Product (Kg)}}{\text{Hazardous reagents (Kg)}}$$

- Defined: 'the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis' (Hudlicky *et al.*)
- What is benign? Who decides?
- This metric Ignores RME
  - There are no benign solvents accounted for. What would happen if benign solvents combined with non-benign solvents in-situ to form non-benign?
- Like atom economy, a **larger** percent (number) is better
  - (0-100%)

Carbon Efficiency

$$\%\text{ Carbon Efficiency} = 100 \text{ X } \frac{\text{Mass of Carbon in Product}}{\text{Mass of Carbon in Reactants}}$$

$$\text{CE} = 100 \text{ X } \frac{\text{(\# of moles of Product) X (\# of Carbons in Product)}}{\text{(moles A x Carbons in A) + (moles B x Carbons in B)}}$$

A + B → C

- Defined: 'the percentage of carbon in the reactants that remain in the final product' (Constable *et al.*)
- Takes into account: yield and stoichiometry
- Importance: directly related to greenhouse gases
- **Larger** number is better
  - (0-100%)

Reaction Mass Efficiency

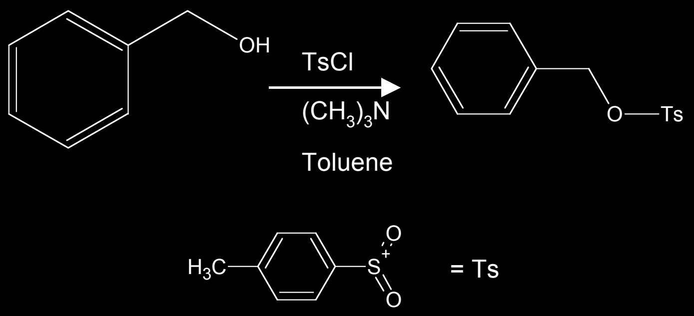
$$\text{RME} = 100\ \text{X}\ \frac{\text{Mass of product C (Kg)}}{\text{Mass of A (Kg) + Mass of B (Kg)}}$$

$$\text{Try this!} = \text{yield X}\ \frac{\text{m.w. of product C}}{\text{m.w. of A + (m.w. of B x molar ratio B/A)}}$$

A + B → C

- Defined: 'the percentage of the mass of the reactants that remain in the product' (Constable *et al.*)
- Takes into account: atom economy, yield, reactant stoichiometry
- **Larger** number is better
  - (0-100%)

Example of Calculating Metrics



An example demonstrated by Constable *et al.*

From the Journal of Green Chemistry, 2002, 4, 521-7

Example Process

%Yield: 90%

Reactant	**Benzyl alcohol**	**10.81 g**	**0.10 mol**	**FW 108.1**
Reactant	**Tosyl Chloride**	**21.9 g**	**0.115 mol**	**FW 190.65**
Solvent	**Toluene**	**500 g**		
Auxiliary	**Triethylamine**	**15 g**		**FW 101**
Product	**Sulfonate ester**	**23.6 g**	**0.09 mol**	**FW 262.29**

E-Factor = [(10.81 + 21.9 + 500+ 15) – 23.6] / 23.6 = 22.2 Kg waste / 1 Kg Prod

Atom Economy = 262.29 / (108.1 + 190.65 + 101) X 100 = 65.8%

Atom Efficiency = 90% x 65.8% = 59.2%

Carbon Efficiency = (0.09 x 14)/((0.1 x 7) + (0.115 x 7)) X 100 = 83.7%

Reaction Mass Efficiency = 23.6/(10.81 + 21.9) X 100 = 70.9%

Constable et al. & Curzons et al.

Academia

- The *development* of green chemists through using metrics in undergraduate course study
- Green procedures should:
  - Be able to demonstrate the same types of reactions being taught
- Metrics can be used in and outside of the lab:
  - learning how to calculate the different metrics
  - then applying them by comparing metrics of one procedure to a previously used procedure
- Case study analysis:
  - Calculating metrics of a simple process in organic chemistry to see where improvements could be made

Industry

- Education of Chemists:
  - The basics of green chemistry
    - through workshops or guidelines
  - Then apply the principles in even the earliest stages of process development
- GC metrics are a versatile tool that can clearly demonstrate:
  - the changes and improvements made throughout the journey of development
    - to analyze and track these changes
  - compare and contrast different processes or pathways that have the same end goal
  - show cost analysis

Tables and Graphs

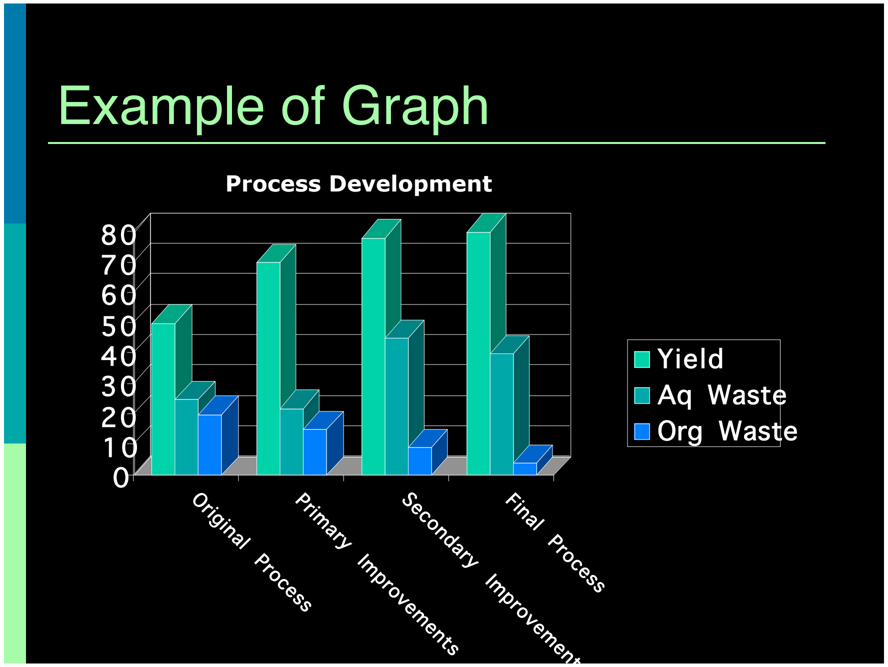
- Tables:
  - comparing different processes
  - tracking process development
- Graphs:
  - demonstrate the life of a process, cradle to grave

Example of Table in Academia

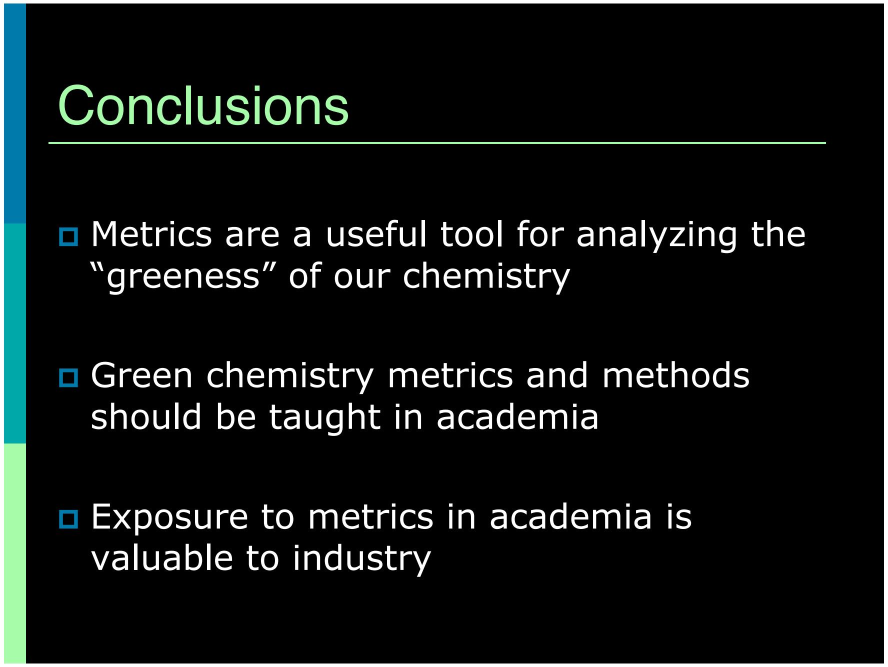
Metric	**Process #1**	**Process #2**
Melting Point		
% Yield		
# of Steps		
# of Catalysts		
# of Solvents		
▪ Organic vs. Aqueous Solvents		
Process Hazards		
Renewable Starting Materials ($)		
E-Factor		
Atom Economy, Atom Efficiency		
Effective Mass Yield		
Carbon Efficiency		
Reaction Mass Efficiency		

Example of Table in Industry

Metric	**Process #1**	**Process #2**
Melting Point		
% Yield		
# of Steps		
# of Catalysts		
# of Solvents		
▪ Organic vs. Aqueous Solvents		
E-F: Organic Waste per Kg product		
E-F: Aqueous Waste per Kg product		
Process Hazards		
Renewable Starting Materials		
Cost per Kg of Product		
Atom Economy, Atom Efficiency		
Effective Mass Yield, Carbon Efficiency		
Reaction Mass Efficiency		

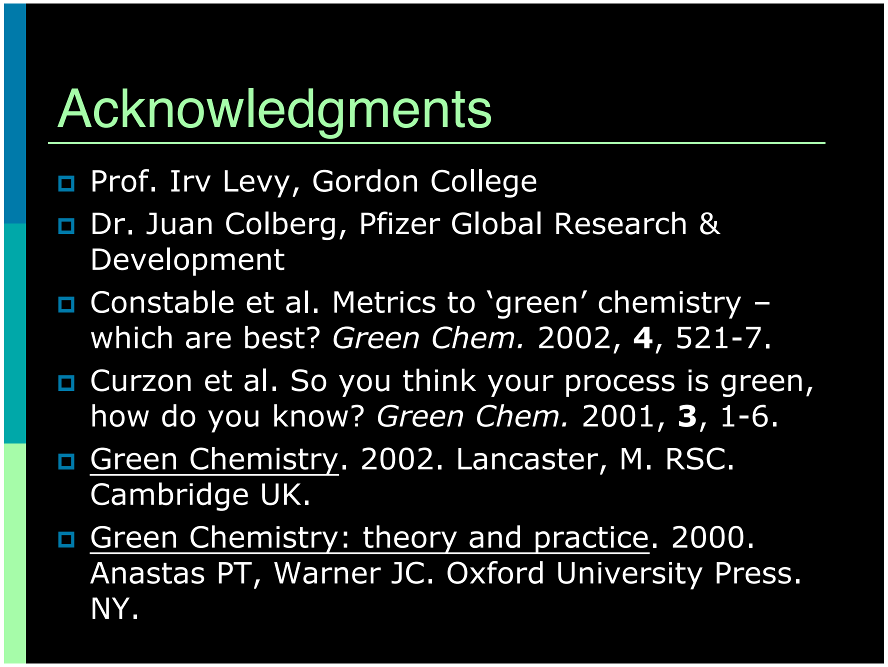


Example of Graph



Conclusions

- Metrics are a useful tool for analyzing the "greeness" of our chemistry
- Green chemistry metrics and methods should be taught in academia
- Exposure to metrics in academia is valuable to industry



Acknowledgments

- Prof. Irv Levy, Gordon College
- Dr. Juan Colberg, Pfizer Global Research & Development
- Constable et al. Metrics to 'green' chemistry – which are best? *Green Chem.* 2002, **4**, 521-7.
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