Alternative Solvents: Shades of Green

James H. Clark and Stewart J. Tavener, 2007

Which is the most efficient, environmentally sound, and cost effective?

Lauren Gunderson
Marian University
School of Mathematics and Science
Institute for Green and Sustainable Science
Indianapolis, IN

http://www.nrcm.org/green_chemistry.asp

Green Chemistry

- "The utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products." [1]
- Less or non-hazardous substitutes replace hazardous substances
- Focus on long-term environmental protection

[1] P. T. Anastas and J.C. Warner, "Greener Chemistry: Theory and Practice;" Oxford University Press: Oxford, 1998.

Solvents: Why are they used?

- Play critical roles in chemical processes
  - Dissolve reactants [1]
  - Speed up or slow down the reaction rate [2]
  - Act as a heat sink or heat transfer agent [2]
  - Prevent hot spots or run-away reactions [2]
  - Aid in the separation and purification of products [1]
  - Facilitate glassware cleaning [1]

[1] Doxsee, Kenneth M., and James E. Hutchison. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments.* United States of America: Brooks/Cole, 2004. Print.

[2] Lecher, Carl. CHE 305 Lecture Notes, Chapter 8, Part 3.

Typical Solvents

- Hydrocarbons: pentane, hexane, kerosene
  - Used for nonpolar compounds (greases, oils)
- Halogenated hydrocarbons: methylene chloride, chloroform, carbon tetrachloride, CFCs
  - Known for fast evaporation
- Aromatic hydrocarbons: benzene and its derivatives
- Alcohols: methanol, ethanol, propanol
- Ethers: diethyl ether, THF
- Dipolar aprotic solvents: acetone, DMSO, and other ketones

Doxsee, Kenneth M., and James E. Hutchison. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments.* United States of America: Brooks/Cole, 2004. Print.

And their hazards:

- “Over the previous decades, organic solvents had been associated with a series of environmental and health issues which lead to this scrutiny: benzene, carbon tetrachloride, and chloroform, three solvents which had been favourites amongst synthetic chemists, were removed from general use due to their toxic and carcinogenic effects; chlorofluorocarbons (CFCs) were outlawed because of their ozone-depleting effects, and volatile organic compounds (VOCs) were implicated in the production of photochemical smog.”

Clark, James H., and Steward J. Tavener. “Alternative Solvents: Shades of Green”. *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Methylene Chloride or Dichloromethane (CH2Cl2)

- Halogenated hydrocarbon
- “When unavoidable, dichloromethane appears to present the fewest hazards”
- Used as an effective reaction and recrys-tallization solvent in the extraction of several pharmaceutical compounds
- The active ingredient in paint removers including industrial and household use paint.
- Used as a chemical intermediate in the production of hydrofluorocarbon 32
- Painful or irritating if splashed into eyes or held in contact with skin
- Leads to the production of carboxyhemoglobin which causes health problems in itself

Doxsee, Kenneth M., and James E. Hutchison. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments.* United States of America: Brooks/Cole, 2004. Print.
http://www.hsia.org/backgrounders/dcm%20wp%202008.pdf

Ethanol

- An alcohol made from corn, barley, starchy crops, and other cellulose material.
- The solution made from the material is then fermented, distilled, and denatured.

http://www.youtube.com/watch?v=59R-NqykoXs&feature=player_embedded#at=32

Elemental Bromine

- Though not a solvent, it is typically used with volatile solvents and is volatile itself
- Corrosive
- Causes severe burns upon contact with skin
- Extremely irritating upon inhalation

McKenzie, L. C.; Huffman, L. M.; Hutchison, J. E. The Evolution of a Green Chemistry Laboratory Experiment: Greener Brominations of Stilbene. *J. Chem. E.* **2005**, 82, 306-310

Alternative Solvents

- Ionic Liquids – nonvolatile systems
- Supercritical CO_2
- Fluorous Solvents
- Water
- Solvent-free Chemistry – avoids problem completely

Easily recyclable (Supercritical CO_2, Fluorous Solvents)

Inorganic systems (Supercritical CO_2, Fluorous Solvents, Water)

Life Cycle Analysis

- Chemistry of the liquid phase
- Typically asked: “Which solvent?”
- Why don’t we ask “Do I need a solvent?”

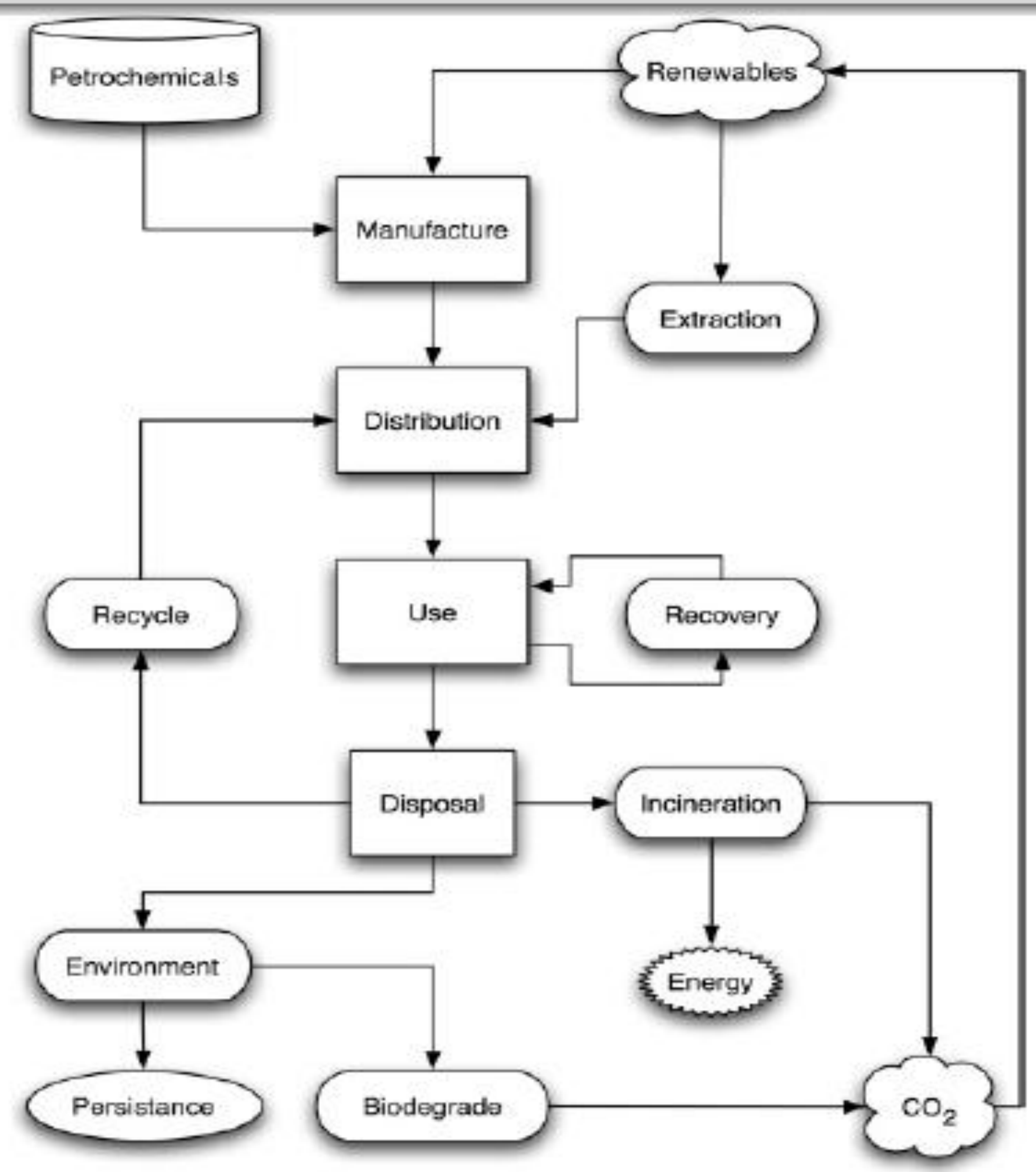

Figure 1. Life cycle flow chart for solvent usage. Primary life cycle stages are represented by rectangles.

Clark, James H., and Steward J. Tavener. "Alternative Solvents: Shades of Green". *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

- “The whole process must be considered, and the solvent (or lack thereof) is only one part of this jigsaw. The atom efficiency, energy use, demands on nonrenewable resources, and transport costs must al be taken into account.”

Clark, James H., and Steward J. Tavener. “Alternative Solvents: Shades of Green”. *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Manufacture

- Typically come from petrochemical feedstocks
  - Cracking and distillation of crude oil (simple or aromatic hydrocarbons)
  - More complex synthetic routes involving oxygen and halogens
- Effects on:
  - Fluorous and ionic liquids
  - CO2 and H2O
- Solvents don't always come from petrochemical resources

Distribution

- How does a solvent get from point A to point B?

“This is an aspect of the life cycle that may be forgotten, but with rising oil prices and concern about CO2 emissions, the impact of transporting chemicals is becoming increasing important, from both economic and environmental viewpoints.”

- Consider a solvent supplied locally
  - The benefits of green solvents decrease is long transportation is needed

Clark, James H., and Steward J. Tavener. “Alternative Solvents: Shades of Green”. *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Use

- Choosing an appropriate solvent reduces activation energy, lowers the temperature required to carry out the reaction, and reduces cooling requirements.
- All solvents have different properties
- For processing: viscosity, density, mp, bp, and volatility must be considered
- Safety issues: flash point, reactivity, and corrosiveness must also be considered

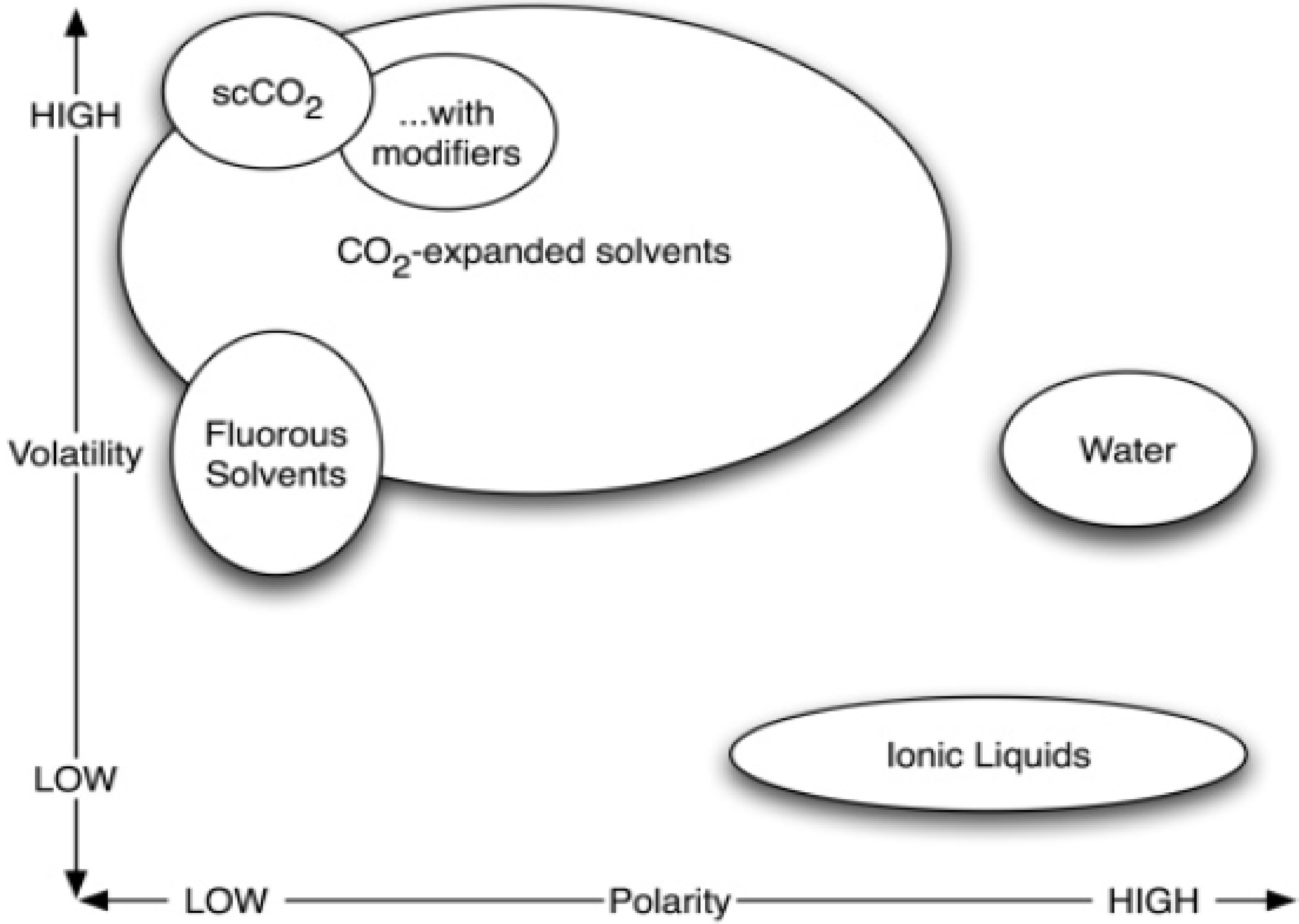

Figure 3. **Typical polarity and volatility characteristics of alternative reaction media.**

Clark, James H., and Steward J. Tavener. "Alternative Solvents: Shades of Green". *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Solvents in Experiments

- Using two different solvents in the same process can yield very different results.
- The success or failure of a particular solvent in an experiment can be analyzed by:
  - Theoretical yield
  - Percent yield
  - Atom economy
  - Experimental atom economy
  - Effective mass yield
  - Cost

Yield

- Theoretical yield: the amount of product that would be made if the experiment goes to completion. Found using stoichiometry
- Percent yield: the ratio of how much product was made compared to the expected quantity

$$\frac{\text{actual yield}}{\text{theoretical yield}} * 100\%$$

Atom Economy

- It is a method of expressing how efficiently a particular reaction makes use of reactant atoms
- Does not take yield into account
- The larger the percentage, the more reactants appear in the product, thus more efficient

$$\text{Atom economy} = (\text{MW}_{\text{desired product}} / \Sigma\, \text{MW}_{\text{reagents}}) \times 100\%$$

http://www.greener-industry.org.uk/pages/atom/1atom_yield.htm

Experimental Atom Economy

- Based upon atom economy analysis but is calculated using the actual masses of reagents and product in the reaction
- This measurement takes into account excess reagents
- Solvents are not considered in this measurement

Experimental Atom Economy =

$$(\text{mass}_{\text{product}} / \sum \text{mass}_{\text{reagents}}) \times 100\%$$

McKenzie, L. C.; Huffman, L. M.; Hutchison, J. E. The Evolution of a Green Chemistry Laboratory Experiment: Greener Brominations of Stilbene. *J. Chem. E.* **2005**, 82, 306-310

Effective Mass Yield

- Similar to experimental atom economy but takes into account relative toxicity
- Only hazardous components of the waste stream are included.

$$\text{Effective mass yield} = \left(\text{mass}_{\text{product}} / \sum \text{mass}_{\text{reagents and nonbenign solvents}}\right) \times 100\%$$

McKenzie, L. C.; Huffman, L. M.; Hutchison, J. E. The Evolution of a Green Chemistry Laboratory Experiment: Greener Brominations of Stilbene. *J. Chem. E.* **2005**, 82, 306-310

Disposal

- Reuse or recycle:
  - Life span of a solvent can increase with distillation, bisphasic separation, or another recovery method
- Eventually the life cycle does end
  - Volatile organic solvents are typically incinerated
  - If the solvent is impure, disposal difficulty increases

Applications

- Why should we turn to alternative solvents at all?
  - Avoid the environmental impact caused by accidental loss of VOCs through handling, use in the reaction, and separation after the reaction
  - Health and safety factors

“The ideal reaction solvent will have the right blend of solvation properties to maximize reaction routes but be unreactive in the system while enable facile postreaction separation and recycling, plus acceptable health and safety issues and cost”

Clark, James H., and Steward J. Tavener. “Alternative Solvents: Shades of Green”. *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Table 1. **Advantages and disadvantages for alternative solvents; score in parentheses is arbitrary grading on a scale of 1 (poor) to 5 (very good) in each category**

key solvent properties	ease of separation and reuse	health and safety	cost of use	cradle-to-grave environmental impact	arbitrary score (/25)
		Supercritical CO_2			
poor solvent for many compounds; may be improved with cosolvents or surfactants (1)	excellent: facile, efficient, and selective (5)	nontoxic; high-pressure reactors required (4)	energy cost is high; special reactors required; CO_2 is cheap and abundant (3)	sustainable and from multiple source; no significant end-of-life concerns (5)	18
		Ionic Liquids (ILs)			
enormously wide range of designer solvents for any reaction; always polar (4)	volatile products easily removed; others less so; reuse may be a problem if high purity is required (2)	very limited data available; some reported to be flammable/toxic (2)	expensive; but some lower-cost ILs will become available in time (2)	normally synthesised from petrochemicals, but sustainable ILs exist; synthesis may be wasteful and energy demanding; environmental fate not well understood (3)	13
		Fluorous Solvents			
limited to very nonpolar solutes; best used in biphasic systems (3)	readily forms biphases; may be distilled and reused (4)	bioaccumulative, greenhouse gases; perfluoroethers thought to be less problematic (2)	very expensive (1)	very resource demanding; may persist in environment (2)	12
		Water			
dissolves at least small quantities of many compounds; generally poor for nonpolar (3)	may be separated most organics; purification may be energy demanding (3)	non-toxic, non-flammable and safe to handle (5)	very low cost energy costs high (4)	sustainable and safe to the environment; may need purification (4)	19
		Solvents Based on/ Derived from Renewables			
wide range: ethers, esters, alcohols and acids are available (4)	may be distilled (4)	generally low toxicity (4)	mixed-cost will decrease with greater market volume (4)	sustainable resources biodegradable VOCs will cause problems (3)	19

Clark, James H., and Steward J. Tavener. "Alternative Solvents: Shades of Green". *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

Everyday Usage

- Hazardous solvents are found in household items such as paint, cleaners, and aerosol cans.
- Alternative solvents are much needed in home and personal care items because of the direct consumer exposure and because of the user's limited knowledge of the chemicals compared to a chemist leading to "greater accidental and uncontrolled loss of the solvent in use or storage"

http://www.nachi.org/dry-cleaner-commercial-inspection.htm

http://www.homefellas.com/blog/paint/paint-finishes.hf

http://www.greenlightoffice.com/office/stationery/819314615-lysol-disinfectant-aerosol-19fl-oz-clear.html

Clark, James H., and Steward J. Tavener. "Alternative Solvents: Shades of Green". *Organic Process Research and Development* 11.1 (2007): 149-155. Print.

"It is not realistic to envisage a complete replacement of VOCs in all applications; rather, we again need to put their well-publicized drawbacks into a life cycle context. In doing this we see a growing case for the use of VOCs derived from renewable resources."

Clark, James H., and Steward J. Tavener. "Alternative Solvents: Shades of Green". *Organic Process Research and Development* 11.1 (2007): 149-155. Print.