PRINCIPLES OF GREEN CHEMISTRY & ENGINEERING: APPLICATION OF THESE PRINCIPLES TO RESEARCH TEACHING AND INDUSTRY

Sudhakar G. Reddy, Ph.D.
Office of Campus Sustainability
The University of Michigan
Ann Arbor, MI 48109
redv@umich.edu

Green Chemistry and Sustainable Engineering 101 Workshop
November 03, 2015

WHAT IS GREEN CHEMISTRY?

- *"Green Chemistry is 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 ".*

- *It is Pollution prevention at Molecular Level.*

- *Very simply it is a fundamental building block in the efforts to create a Sustainable Economy.*

WHAT IS GREEN ENGINEERING?

- ***Green Engineering is the design, commercialization and use of processes and products that are feasible and economical while:***

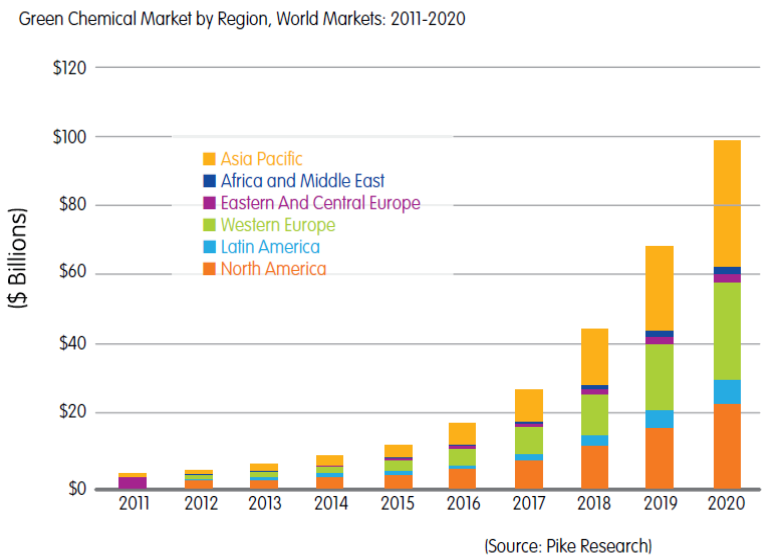
  -Reducing the generation of pollution at the source

  -Minimizing the risk to human health and the environment

- ***Very simply It is the design of a product or a process that has minimal impact on environment while creating sustainable economy.***

MEANS WHAT IN TERMS OF $$$s

- Global Chemical Industry from 4 t to 6 trillion by 2020
- Green chemistry market from ***3 b to 100+ billion by 2020!***
- Drivers:
  - GC & E principles
  - New Technologies
  - Waste minimization
  - Safer alternatives
  - Non-petroleum and renewable feed stocks



BACKGROUND

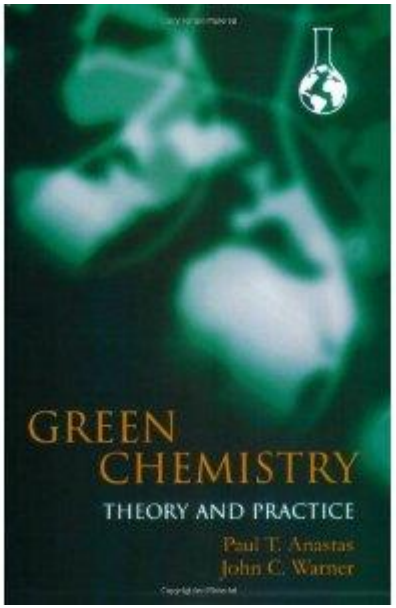
- **1993**: A white paper on “Chemistry for a Clean World” was published by the European Chemistry Council
- **1995:** Presidential Green Chemistry for Challenge Awards: Introduced in 1995 by President Clinton to encourage academic and industry sectors to incorporate sustainable chemistry.
- **1997**: Green Chemistry Institute was formed as a non-profit organization teamed up with ACS 2001.
- **1998:** John Warner and Paul Anastas published a book “Green Chemistry: Theory and Practice” defining 12 principles of green chemistry.
- **1999:** A dedicated journal on ***Green Chemistry*** launched by Royal Society of Chemistry.
- **2006:** Executive Directive on Green Chemistry singed by Michigan Governor Jennifer Granholm
- **2009:** President Barak Obama nominated Paul Anastas to lead US EPA’s Office of Research and Development.

12 PRINCLIPLES OF GC

Twelve Principles of Green Chemistry *

- **Prevention**
- **Atom Economy**
- **Less Hazardous Chemical Syntheses**
- **Designing Safer Chemicals**
- **Safer Solvents and Auxiliaries**
- **Design for Energy Efficiency**
- **Use of Renewable Feed stocks**
- **Reduce Derivatives**
- **Catalysis**
- **Design for Degradation**
- **Real-time analysis for Pollution Prevention**
- **Inherently Safer Chemistry for Accident Prevention**

**** Anastas, P. T.; Warner, J. C.; Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press***

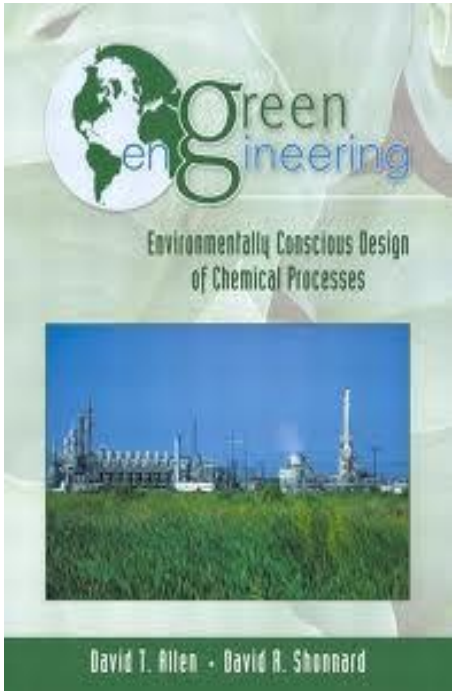


12 PRINCLIPLES OF GE

Twelve Principles of Green Engineering *

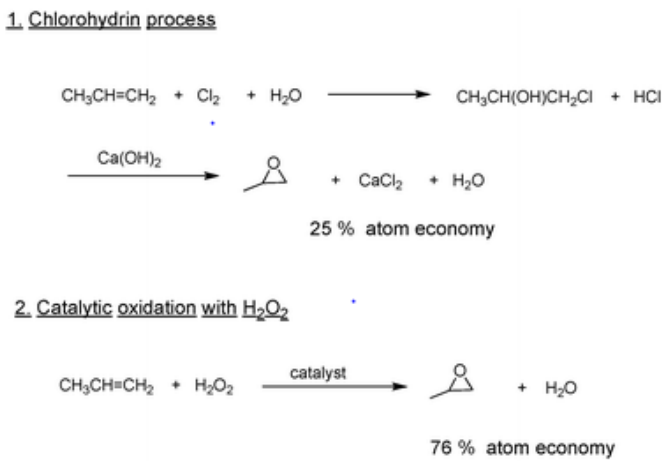
- **Inherent Rather Than Circumstantial**
- **Prevention Instead of Treatment**
- **Design for Separation**
- **Maximize Efficiency**
- **Output-Pulled Versus Input-Pushed**
- **Conserve Complexity**
- **Durability Rather Than Immortality**
- **Meet Need, Minimize Excess**
- **Minimize Material Diversity**
- **Integrate Material and Energy Flows**
- **Design for Commercial "Afterlife"**
- **Renewable Rather Than Depleting**

- ***Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", Env. Sci. and Tech., 37, 5, 94A-101A, 2003.***



12 PRINCIPLES OF GC (1-2)

1. **Prevention**: *Prevent waste than to treat or cleanup.*
2. **Atom Efficiency**: *Design the reaction to get a product to utilize all atoms used.*



Another classic example to mention is the green synthesis of Ibuprofen by Pfizer here in this building…..won Presidential Green Chemistry Award!

12 PRINCIPLES OF GC (3-4)

3. **Less Hazardous Chemicals**: *Design synthetic methods to employ materials that carry little or no toxicity to humans and environment.*

Reduction of Aldehydes to Alcohols:

(R2CHO)4B- Na+ ⟹ 4 RCH(OH)R' + NaH2BO3

Sodium borohydride is a milder reducing agent than lithium aluminum hydride. LiAlH4 reacts violently with water and the reaction must be done anhydrous. Reactions with NaBH4 can be done in water or alcohol**.**

4. **Safer Chemicals**: *Search for safer chemicals that are degradable and has less impact on the environment.*

12 PRINCIPLES OF GC (5-6)

5. **Safer Solvents**: *Search for safer benign solvents that can be recycled and has less impact on the environment.*

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Diisopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	t-Butylmethyl Ether	Dichloromethane
Ethyl Acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-Me Tetrahydrofuran	N-Methylpyrrolidinon
Methyl Ethyl Ketone	Tetrahydrofuran	Dimethyl Formamide
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl Sulfoxide	Dimethyl Acetamide
	Acetic Acid	Dioxane
	Ethylene Glycol	Dimethoxyethane

6. **Energy Efficiency:** *Design synthetic methods that utilize less or no energy. Room temp. and Atm. Pressure reactions/Sonication/Microwave.*

12 PRINCIPLES OF GC (7-8)

7. **Renewable Feedstocks:** *A raw material or feedstock should be renewable rather than depleting that is economically practicable.*

   Dupont came up with a new method to produce 1,3-propanediol, a key ingredient of Sorona polymer. Genetically engineered microprobe converts glucose to the desired 1,3-propanediol.

   A Presidential Green Chemistry Challenge Award winning technology!

8. **Reduce Derivatives:** *Minimize unnecessary derivatization (blocking groups) as they require additional reagents and generate waste.*

12 PRINCIPLES OF GC (9-10)

9. **Use of Catalysts:** *Employ catalysts that promote reactions and can be regenerated.*

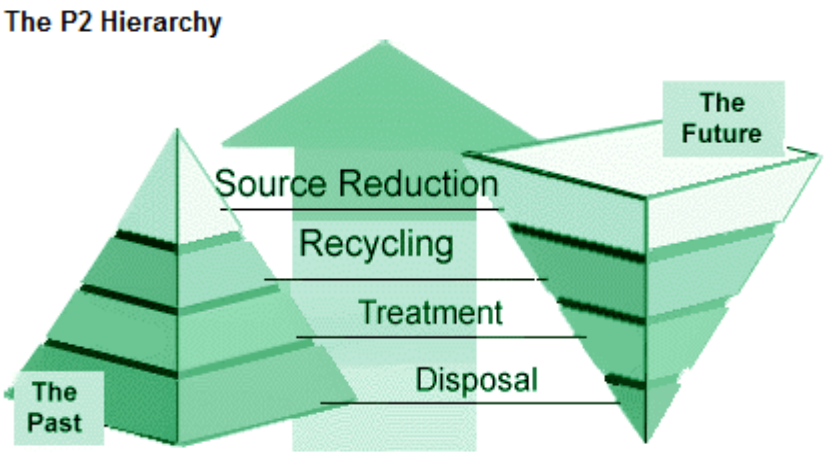
   Genetically engineered E. Coli converts glucose to cis,cis-muconic acid that accumulates extra-cellularly, is then hydrogenated to obtain adipic acid. Adipic acid is produced in excess of 1.9 billion kg annually and used in the manufacture of nylon 66.

   A Presidential Green Chemistry Challenge Award winning technology!

10. **Design for Degradation:** *Final chemical products and by-products should be designed to break down to benign fragments at the end of their function.*

12 PRINCIPLES OF GC (11-12)

11.Pollution Prevention: *Develop methodologies to control the formation of hazardous substances.*



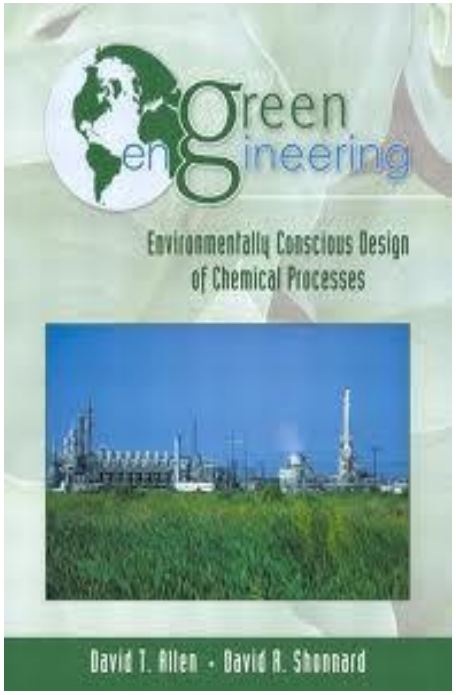
12.Accident Prevention: *Design the chemical processes to minimize the potential for accidents, releases, explosions and fires thereby increasing safety in the laboratory.*

12 PRINCLIPLES OF GE

Twelve Principles of Green Engineering *

- **Inherent Rather Than Circumstantial**
- **Prevention Instead of Treatment**
- **Design for Separation**
- **Maximize Efficiency**
- **Output-Pulled Versus Input-Pushed**
- **Conserve Complexity**
- **Durability Rather Than Immortality**
- **Meet Need, Minimize Excess**
- **Minimize Material Diversity**
- **Integrate Material and Energy Flows**
- **Design for Commercial "Afterlife"**
- **Renewable Rather Than Depleting**

- ***Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", Env. Sci. and Tech., 37, 5, 94A-101A, 2003.***



12 PRINCIPLES OF GE (1-3)

1. Inherent Rather Than Circumstantial: *Designers need to strive to ensure that all materials and energy inputs are as inherently nonhazardous as possible.*

2. Prevention Instead of Treatment: *It is better to prevent waste than to treat or clean up after it is formed.*

Power generation Fossil Fuel Vs. Fusion

3. Design for Separation: *Separation and purification should be designed to minimize energy consumption and material use.*

Separation/purification Vs. Polymers can used to control the solubility of substrates, ligands and catalysts for separation.

12 PRINCIPLES OF GE (4-6)

4. Maximize Efficiency: *Products, processes and systems should be designed to maximize mass, energy, space and time efficiency.*

5. Output-Pulled Vs. Input-Pushed : *Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.*

Concept of Le Chatelier's principle: Minimize the amount of resources consumed to transform inputs into the desired outputs.

6. Conserve Complexity: *Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse and beneficial disposition.*

12 PRINCIPLES OF GE (7-9)

7. Durability Rather Than Immortality: *Targeted durability, not immortality, should be a design goal.*

Single use disposable diapers: Replace non bio-degradable plastic with Eco-silver ware (PLA, starch and water)

8. Meet Need, Minimize Excess: *Design for unnecessary capacity or capability (e.g. one size fits all) solutions should be considered a design flaw.*

9. Minimize Material Diversity : *Material diversity is multicomponent products should be minimized to promote disassembly and value retention.*

Mono-material design strategy in auto industry: Easy disassembling

12 PRINCIPLES OF GE (10-12)

10. Integrate Material and Energy Flows: *Design products, processes, and systems must include integration and interconnectivity with available energy and material flows.*

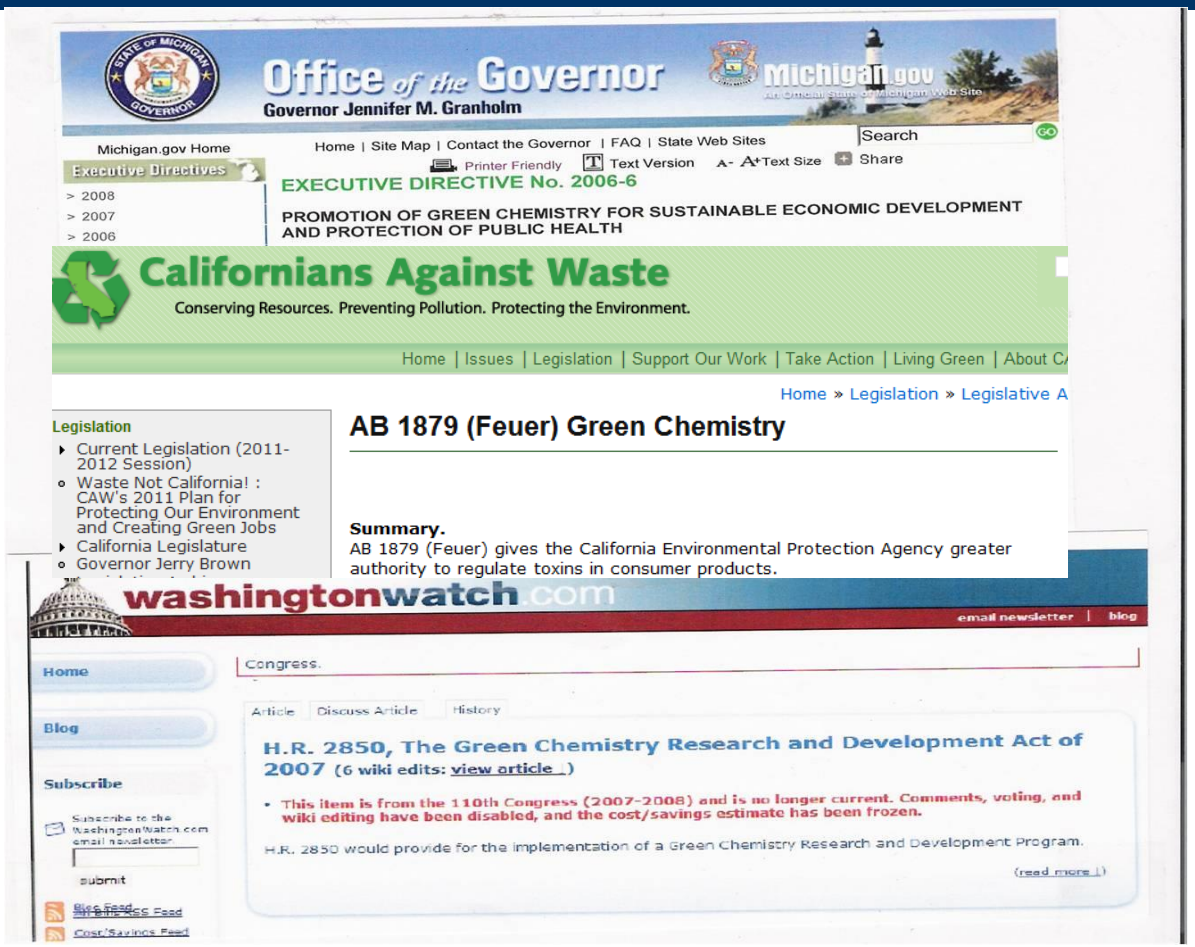
Regenerative Braking Systems in Hybrid vehicles: Heat generated is fed back into the battery and stored as energy to propel the car.

11. Design for Commercial "Afterlife": *Products, processes, and systems should be designed for performance in a commercial 'afterlife". Cell phones/Laptops*

12. Renewable Rather Than Depleting: *Material and energy inputs should be renewable rather than depleting.*

Biomass feed stocks, bio-based plastics, waste water treatment with natural eco-systems

GREEN CHEMISTRY AT STATE AND US LEGISLATIVE FRONTS



GREEN CHEMISTRY

WORLDWIDE:

USA, Australia, China, Germany, India, Italy, the Netherlands, Spain, and the United Kingdom, to mention a few.

USA:

Michigan, California, Minnesota, Oregon and few other states

UNIVERSITIES/COLLEGES:

50+ universities and colleges have adapted green curriculum into their teaching in some form or the other

REAL WORLD EXAMPLES

- Laundry is going Green! (P&G): Done at room temperature with less water.

REAL WORLD EXAMPLES

- Ozone laundry
  - O2+O = O3
  - Short lived species
  - Cleans and disinfects
  - Increases life of clothes
  - 80% less natural gas
  - 50% less energy
  - 25% less chemicals
  - Ideal for hotels and hospitals

REAL WORLD EXAMPLES

- By Green Works in support with Sierra Club and USEPA (Biodegradable and No NH3)

Design for the Environment
U.S. EPA
Recognized for Safer Chemistry

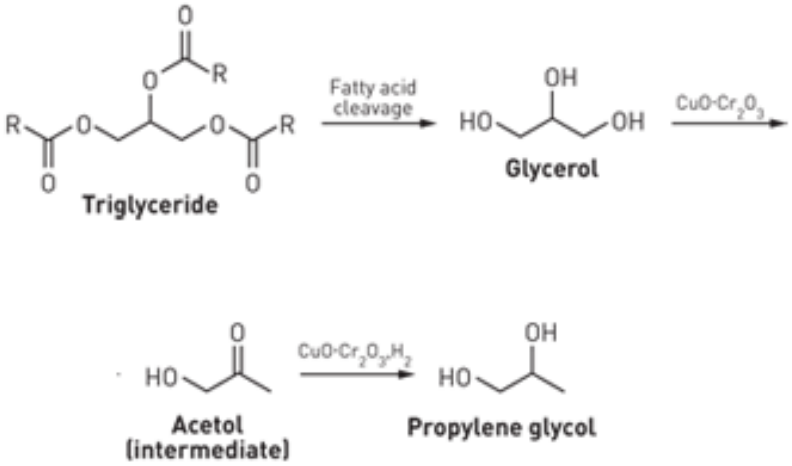
REAL WORLD EXAMPLES

- Compostable Silverware (PLA, starch, Plant material)

ecoware
biodegradables

REAL WORLD EXAMPLES

- Biodiesel bi-product Glycerol converted into propylene glycol. Propylene glycol is used to make Sorona polymer.



REAL WORLD EXAMPLES

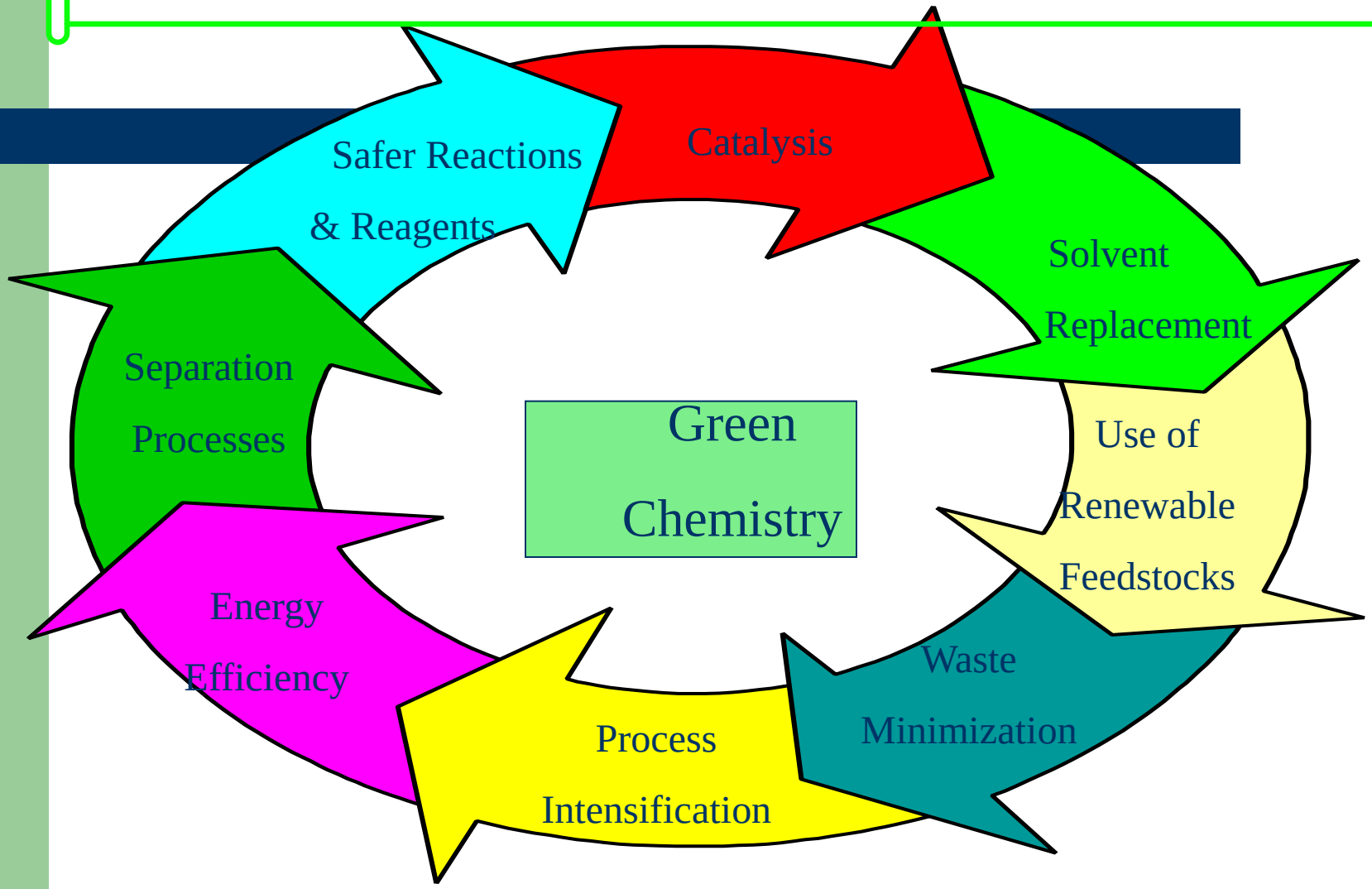
- **Greening the Carpet World:**
- Dupont and Mohawk Industries produce Green carpets from Sorona, a polymer made from 1,3-propanediol.
- This SmartStrand carpets contain 37% renewable content by Weight.
- According to a survey, 65% of respondents are willing to pay more for the products that use renewable resources.
- Another survey showed that 86% of women preferred these Green products compared with 74% men.

ACHIEVE GREEN CHEMISTRY

THROUGH

- **Research**
- **Knowledge**
- **Awareness**
- **Support**
- **Common Sense**
- **Teaching**
- **COMMITMENT**

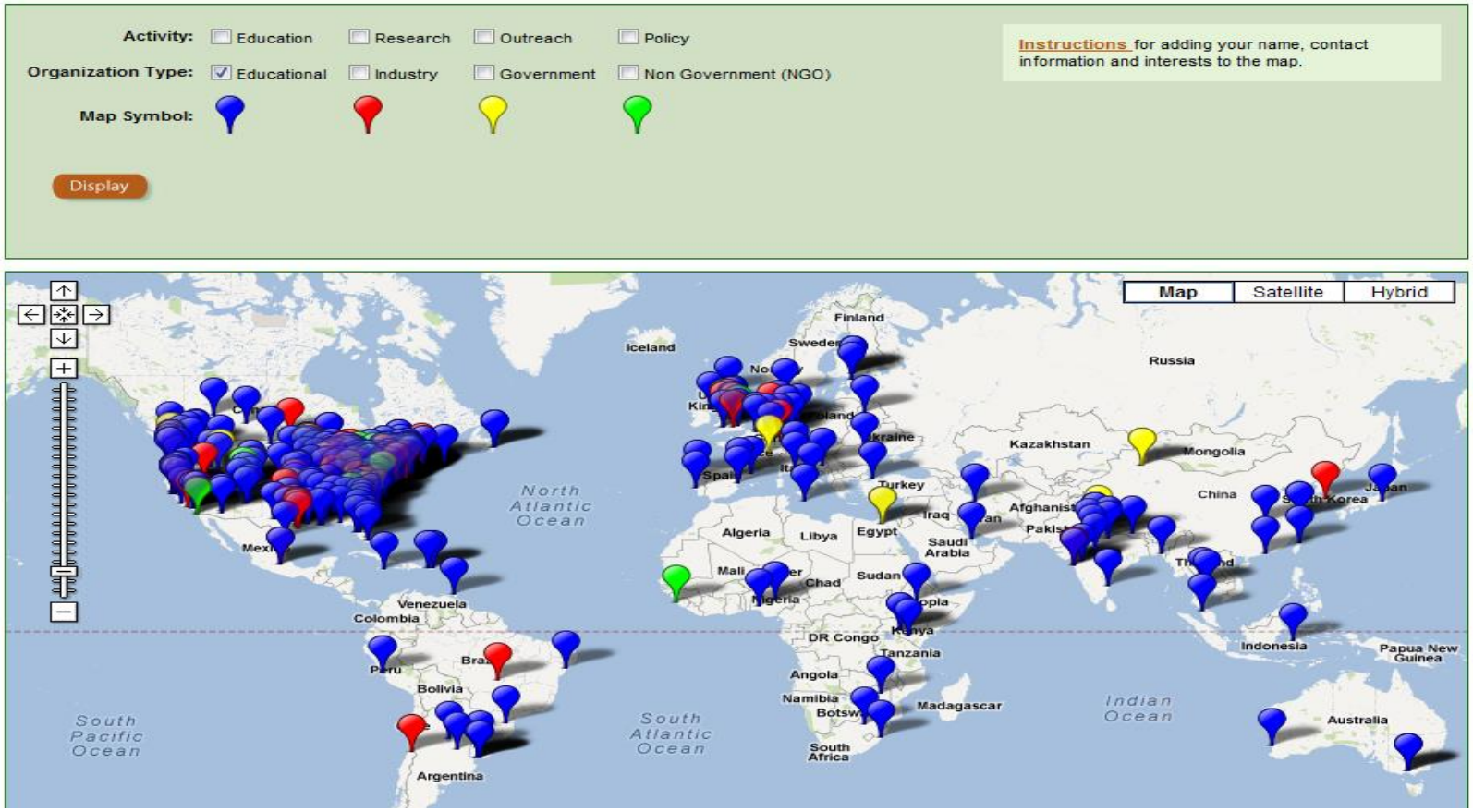
GREEN CHEMISTRY IN SHORT…….



BENEFITS OF GREEN CHEMISTRY

- Waste Minimization
- Pollution Prevention
- Energy Conservation
- Increasing Health & Safety
- Less impact on the Environment
- Investment into the Future
- Sustainable Growth = Economic Growth

GREEN CHEMISTRY (Google Map)



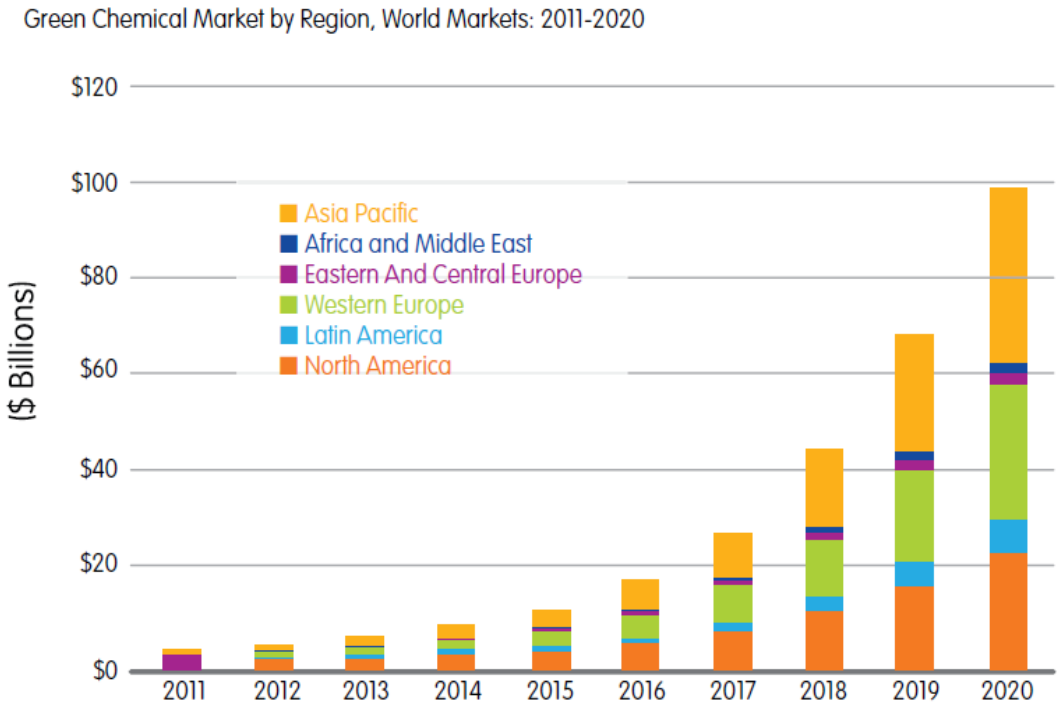
EIGHT WORLD RENOWNED GREEN CHEMISTRY INSTITUTIONS

1. American Chemical Society: *Implementing GC Principles*
2. University of Massachusetts: *First Ph.D. in GC*
3. US Environmental Protection Agency: *PP Act of 1990*
4. Warner Babcock Institute for Green Chemistry: *Novel Innovative GC Solutions for Industry*
5. University of York, UK: *Leads GC Center for Excellence*
6. University of Nottingham, UK: *Spreading Innovation in GC*
7. McGill University, UK: *World-leading Institution in GC*
8. Environmental Protection Encouragement Agency: *Founded by Michael Braungart promoting GC*

EIGHT IMPACTS OF GREEN CHEMISTRY IN MOVING WORLD'S ECONOMY TO 99 b.

1. Better Manufacturing Capacity
2. Improved E-factor
3. Lower Energy and Water Consumption
4. Hazardous Waste Minimization
5. Savings on Waste Disposal
6. Lower Material Procurement Costs
7. Lower Inventory Costs
8. Fewer Environment, health and Safety Overheads

GC & E DRIVING THE ECONOMY



(Source: Pike Research)

GREEN CHEMISTRY RESOURCES

Greener Education Materials for Chemists (GEMS)

http://greenchem.uoregon.edu/gems.html

Green Chemistry Education Network (GCEdNet)

http://cmetim.ning.com/

ACS Green Chemistry Institute

http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_TRANSITIONMAIN&node_id=830&use_sec=false&sec_url_var=region1&__uuid=241e0d8a-4c20-4ca9-8ee2-01c82e9de278

Green Chemical Alternatives

http://ehs.mit.edu/site/content/green-chemical-alternatives-purchasing-wizard

Green Screen for Safer Chemicals – Clean Production Action

http://www.cleanproduction.org/Greenscreen.php

Presidential Green Chemistry Challenge Awards

http://www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html

GREEN CHEMISTRY RESOURCES

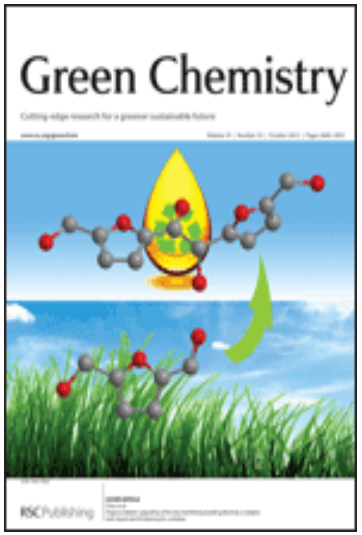
JOURNALS:

Green Chemistry

Journal of Chemical Education

Green Chemistry Letters and Reviews

ACS Sustainable Chemistry & Engineering



CONFERENCES:

Annual conferences at national and international level

Annual Michigan Green Chemistry conference

WEB RESOURCES:

https://migreenchemistry.org/toolbox/directory/?doing_wp_cron=1382469908.6189360618591308593750

GREEN CHEMISTRY RESOURCES

MICHIGAN:

DEQ Green Chemistry
http://www.michigan.gov/deq/0,1607,7-135-3585_49005---,00.html

Green Chemistry Clearing House
http://migreenchemistry.org/

Ecology Center
http://www.ecocenter.org/greening-chemistry

MI Green Chemistry Round Table
http://www.michigan.gov/deq/0,4561,7-135-3585_49005-185068--,00.html

GREEN CHEMISTRY & ENGINEERING MAKES SENSE!

THANK YOU