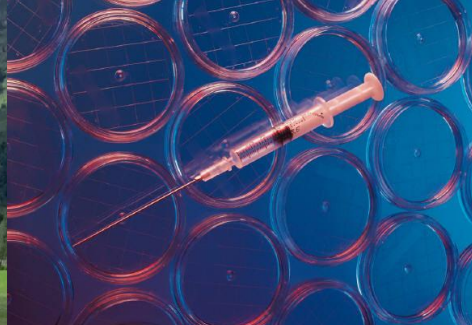

聲明

本檔案之內容僅供下載人自學或推廣化學教育之非營利目的使用。並請於使用時註明出處。

[如本頁取材自○○○教授演講內容]。



綠色/永續化學： 導言與原則

中央研究院化學所

趙奕妤

Nature vs Industrial Society

Nature
a cycle



Industrial Society
the natural cycle disrupted



Human are depleting resources and making wastes much faster than nature can take the wastes and convert them back into resources

Question 1

How many pounds of stuff does it take to make a 5 laptop computer? (Hint: think about mining, transport, manufacturing, packaging, etc.)

- a) 50
- b) 500
- c) 20,000
- d) 12,500



Ref: "Confessions of a Radical Industrialist," page 9 (adjusted for 5 lb)

Question 2

What is the thermodynamic efficiency of the economy of the United States?

- a) 10%
- b) 5.5%
- c) 2.5%
- d) 22%



The National Academy of Engineering estimates the thermodynamic efficiency of the American economy is $\sim 2.5\%$.

Ref: "Confessions of a Radical Industrialist," page 73



Slide Courtesy Dr. Bob Peoples

Question 3

How many trees does it take to produce the Sunday edition of the NY Times?

- a) 10,000
- b) 5,000
- c) 45,000
- d) 70,000



Question 6

For every kg of product produced, on average about how much waste is produced?

- a) <1 kg
- b) 5-10 kg
- c) 25 kg
- d) 25-100 kg
- e) >100 kg

Nancy Paul-008s



Benefits of the Chemical Industry





Waste Disposal



Disease

Pollution



Danger!

Depletion of natural resources

CHEMISTRY- A Dirty Word!



Toxic Emissions



Accidents



Land Fill

Cancer

Waste and the Chemical Industry

- Where dose it come from?

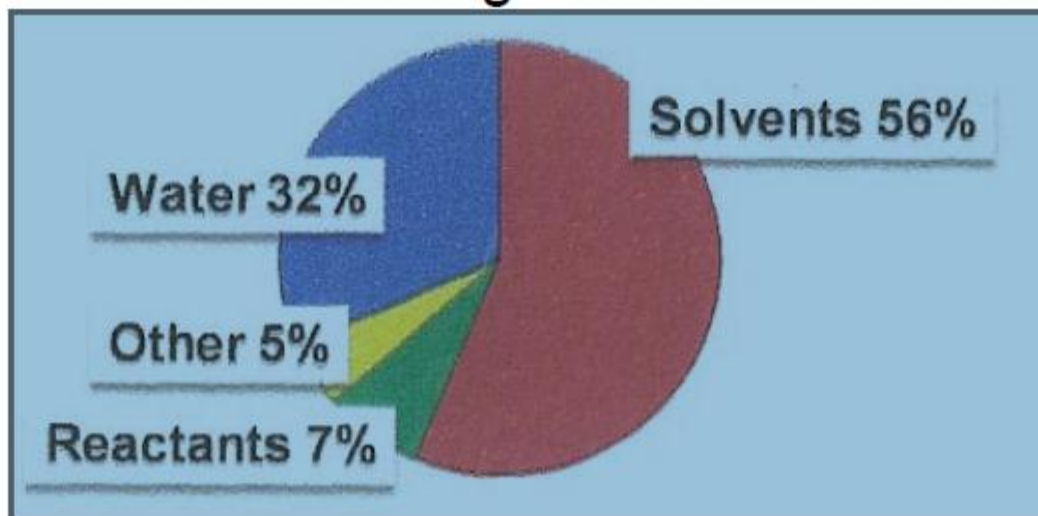
Industry Segment	TONNAGE	RATIO Kg Byproducts / Kg Product
Oil Refining	$10^6 - 10^8$	<0.1
Bulk Chemicals	$10^4 - 10^6$	1 - 5
Fine Chemicals	$10^2 - 10^4$	5 - 50
Pharmaceuticals	$10 - 10^3$	25 - 100+

- Areas traditionally thought of as being dirty (oil refining & bulk chemical production) are relatively clean - they need to be since margins per Kg are low.
- Newer industries with higher profit margins and employing more complex chemistry produce much more waste relatively.

Environmental impact of manufacturing processes of active pharmaceutical Ingredients

A 2007 study showed the median amount of materials used to make 1 kg of API was 46 kg, in which 56% of the mass used was solvent. That is, 22 kg of solvent are needed to make 1 kg of API. **E = 45**

Solvent



Green Chem. **2011**, 13, 854.

Org. Process Res. Dev. **2011**, 15, 912.

Brief History of Green Chemistry

- 1991** The phrase "Green Chemistry" invented by the chemist **Paul Anastas** of US Environmental Protection Agency (EPA)
- 1992** United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro. Agenda 21 was adopted.
- 1995** On President Bill Clinton's initiative, EPA started to give a yearly "the **U.S. Presidential Green Chemistry Challenge Award**"
- 1997** "The **Green Chemistry Institute**" is formed by Joe Breen in the United States (became part of ACS operations since 2001)
- 1998** Paul Anastas and **John C. Warner** published the book "Green Chemistry: Theory and Practice" (the book includes "**The Twelve Principles of Green Chemistry**")
- 1999** The Royal Society of Chemistry formed "The Green Chemistry Network" and started the journal "**Green Chemistry**"

Definition of Green Chemistry

*The design of products and processes that reduce or eliminate the use and generation of **hazardous** substances*

Fathers of Green Chemistry : Paul Anastas and John C. Warner



C&E News October 4, 2010

[Warner's talk at the Berkeley Green Chemistry Center
http://www.youtube.com/watch?NR=1&v=mrSy6RK0ge8](http://www.youtube.com/watch?NR=1&v=mrSy6RK0ge8)

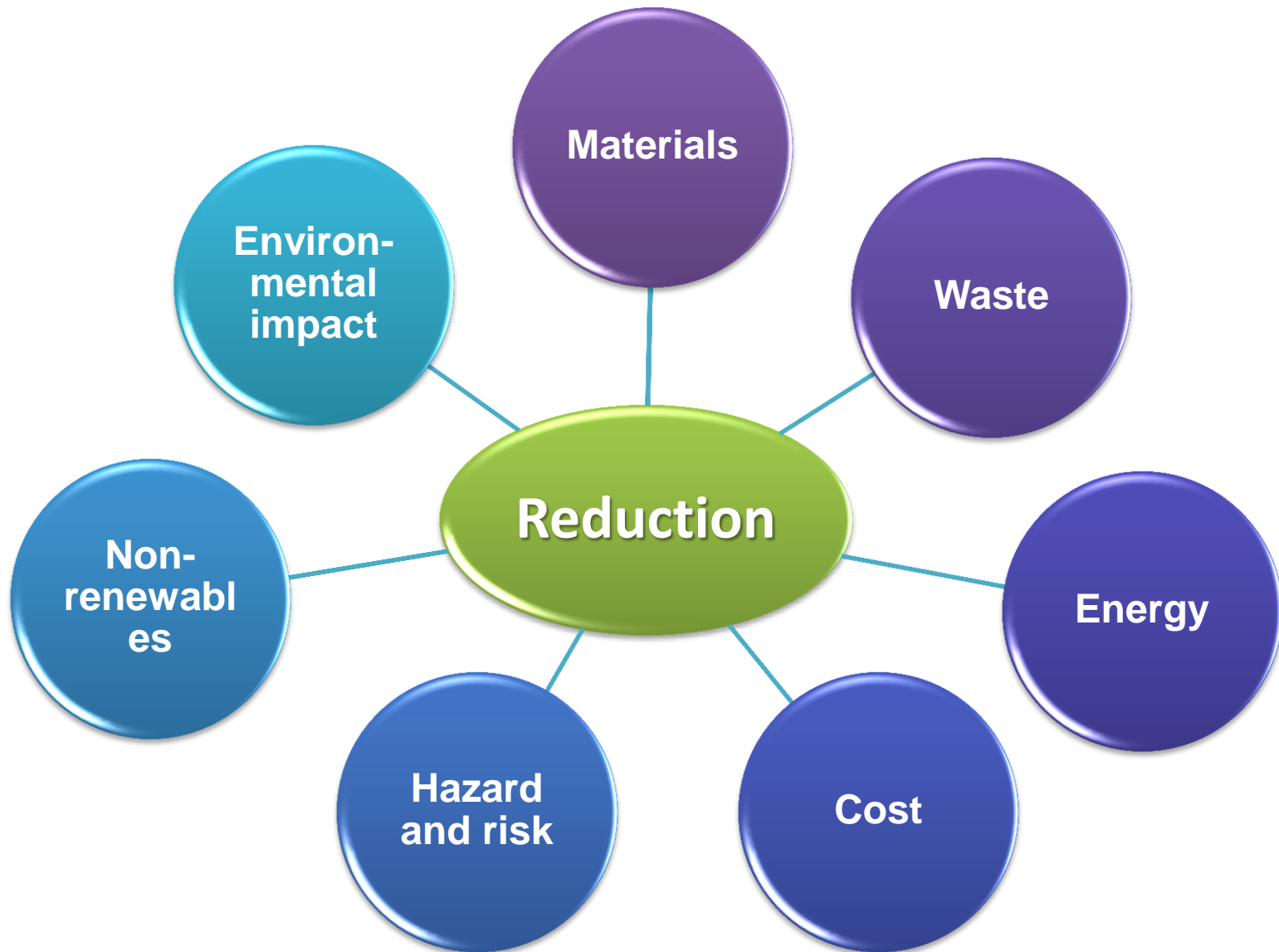
Spirit of Green Chemistry

*The design of products and processes that reduce or eliminate the use and generation of **hazardous** substances*

- **Prevention!**
- **Reduction!**
- **Increase efficiency**
- **Holistic thinking**
- **Smart chemistry!!**

- Not just looking for new energy materials
- Not equivalent to environmental chemistry

Reduction of What?



Spirit of Green Chemistry

Risk = f(hazard x exposure)



Now



Before

Minimize risk by minimizing hazard

2020 Sustainability Goals

Zero Waste: eliminate the concept of waste in product, process, materials and energy

Zero Toxic Substances: eliminate substances known or suspected to be harmful to human health or the health of biological systems

100% Closed Loop Processes: take 100% responsibility for our products at all stages of our product and process lifecycle

Sustainable Growth and Profitability: create an economy the planet is capable of sustaining indefinitely

(Zero Waste Alliance, 2001)

How to realize the goals?

12 Principles of Green Chemistry

1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
7. Use renewable feedstocks
8. Avoid chemical derivatives
9. Use catalysts, not stoichiometric reagents
10. Design chemicals and products that degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

12 Principles of Green Chemistry Demonstrated with Real Cases

See lecture notes

[Green Chemistry: Principles and Practice](#)

by Mary Kirchhoff, Ph.D.,

American Chemical Society Education Division

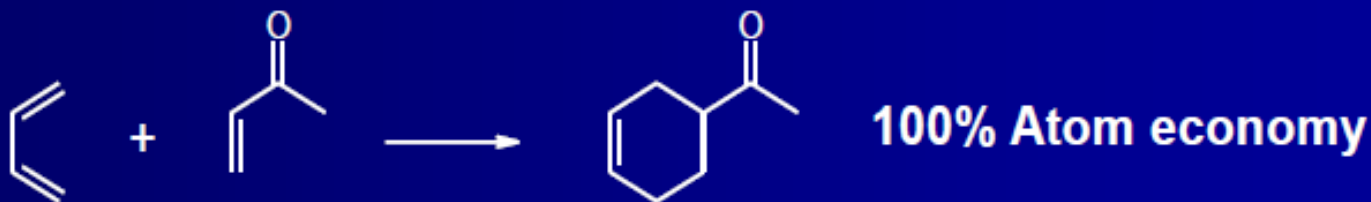
Given in 2012 ACS Summer School on Green Chemistry
and Sustainable Energy

**Beginners' must read for
12 principles**

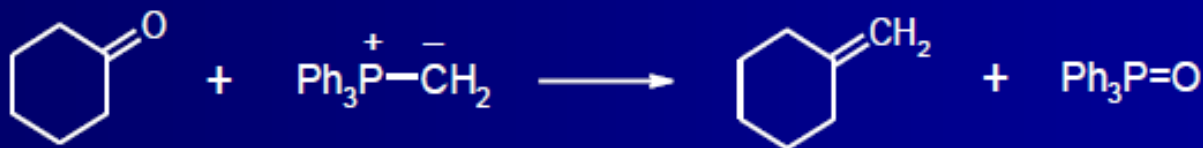
[http://portal.acs.org/portal/PublicWebSite/
greenchemistry/education/summerschool/CNBP_030373](http://portal.acs.org/portal/PublicWebSite/greenchemistry/education/summerschool/CNBP_030373)

$$\text{Atom Economy} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all reactants}} \times 100\%$$

Diels-Alder Reaction



Wittig Reaction



*The amount of **INPUT** is concerned! Different from **yield**!!*

Many more metrics developed... (見甘魯生老師講義)

12 Principles of Green Engineering

1. Inherent Rather Than Circumstantial
2. Prevention Instead of Treatment
3. Design for Separation
4. Maximize Efficiency
5. Output-Pulled Versus Input-Pushed
6. Conserve Complexity
7. Durability Rather Than Immortality
8. Meet Need, Minimize Excess
9. Minimize Material Diversity
10. Integrate Material and Energy Flows
11. Design for Commercial “Afterlife”
12. Renewable Rather Than Depleting

Academic and Industrial Endeavors



New Courses

TOPICS in GREEN CHEMISTRY & DESIGN

A series of three 1-unit interdisciplinary seminar courses

Take just one... or all three

Three New Graduate Seminars Announced

BCGC faculty and staff have created three new green chemistry modules for the Spring 2012 semester.

Advancing Green Chemistry

"The future belongs to those who give the next generation reason for hope." - Pierre Teilhard de Chardin

The University of California, Berkeley Center for Green Chemistry (BCGC) is advancing green chemistry through research, teaching and engagement in the interdisciplinary areas of: New Chemistries, Health and Environment, Policy and Law, and Business and Economics. Investigators in chemistry, the environmental health sciences, public policy, business, and law are developing new science and scholarship that is placing green chemistry, alongside carbon-neutral technologies, as a cornerstone of environmentally sustainable development and the green economy.

Announcements

- [Cradle to Cradle Products Innovation Institute is looking for two fall interns](#)
- [The application period for the 2013 Switzer Environmental Fellowships is now open](#)
- [Now Hiring: Green Labs Research Associates](#)
- [Join us for a conversation with Philip Campbell, Editor in Chief of Nature](#)
- [Read The First Articles from ACS Sustainable Chemistry & Engineering](#)
- [Green Chemistry Innovation in the Chemical Industry: Venturing and Start Ups](#)

Pfizer Green Chemistry Initiative

- Site-based green chemistry teams, first in Groton, CT: 2001
 - ✓ Members: Across disciplines & divisions
 - ✓ Results-oriented, senior management support
- Activities:
 - ✓ Annual Green Chemistry Award - establish recognition of principles of green chemistry, prominently acknowledge performance
 - ✓ Brought leading green chemists for seminars
 - ✓ Sponsored onsite workshops
 - ✓ Prepared award nomination packages – won US PGCC Award
 - ✓ Created a solvent selection guide
 - ✓ Published scientific papers highlighting benefits and achievements
 - ✓ Reduced or eliminated the use of some hazardous solvents
 - ✓ Contributed to lab and manufacturing process improvements
 - ✓ Community outreach

**Importance
of Culture!**

The Principles Workshop – Key Learning Objectives



Day one

- Sustainability matters to the Chemical Industry
- Introduction to the Principles of Sustainable Chemistry and Engineering
- Introduction to “Tox 101 for R&D”
- Overview of Life Cycle Thinking (“Holistic Design”)
- Industrial case study: Glycerin to Epichlorohydrin, is it more sustainable?
- Overnight – homework!



Day two

- Group breakout and debrief: Glycerin to Epichlorohydrin
- Wrap-Up: End of Life Considerations, The Future

ACS GCI Pharmaceutical Roundtable



Developing Tools

- **Process Mass Intensity (PMI) - done**

$$\text{Process mass intensity} = \frac{\text{quantity of raw materials input (kg)}}{\text{quantity of bulk API out (kg)}}$$

- **Solvent Selection Guide - done**
- **Reagent Selection Guide - ongoing**
- **Greener Reaction Mechanisms - ongoing**



The Power of Collaboration!

**AND
COMMUNICATION!!**

**“a group – even of ‘competitors’ –
can accomplish what no one member could
do alone.”**

T. Tierney, Harvard Business Review, July-August 2011, 38.



The Magnitude of What Can be Accomplished

Presidential Green Chemistry Challenge Award Winners (all sectors). Results through 2011 (16 years of results)*:

- ❑ 199 million pounds of hazardous chemicals and solvents eliminated each year
 - ✓ Enough to fill almost 900 railroad tank cars - - a train nearly 11 miles long
- ❑ 21 billion gallons of water saved each year
 - ✓ Amount used by 820,000 people annually
- ❑ 57 million pounds of carbon dioxide releases to air eliminated each year
 - ✓ Equal to taking 6,000 automobiles off the road

* Source: US EPA, Green Chemistry Program, Fact Sheet EPA744F11001, June 2011.

Challenges

Alternative feedstocks

- Move from petroleum to renewable or biologically derived sources
 - Petroleum chemistry => need oxidation chemistry
 - Sugar => need reduction chemistry
- CO₂ => need new catalysts

Alternative solvents

- No solvent (neat solution; grinding)
- Supercritical CO₂, ionic liquid...

Alternative synthetic pathways

- New catalysts (with more abundant metal)
- Move to biocatalysts (no toxic metals; intrinsically safer)
- Research into reuse and recycling catalysts still in infancy

<http://www.sciencemag.org/cgi/content/full/297/5582/807>

Challenges

Education

Lack of toxicology training

When to use what metrics

Address the problems of waste, toxicity, energy consumption altogether, rather than individually.

Challenges (cont.)

“Teaching Green” *C&EN* **2012** (Oct. 1), *90* (40), 64.

“Green Toxicology” in Book: *Green Techniques for Organic Synthesis and Medicinal Chemistry* (ISBN-10: 0470711515)

“Using the Right Green Yardstick: Why Process Mass Intensity Is Used in the Pharmaceutical Industry To Drive More Sustainable Processes” *Org. Process Res. Dev.* **2011**, *15*, 912.

“Barriers to the Implementation of Green Chemistry in the United States” *Environ. Sci. Technol.* **2012**, *46*, 10892.

Resources

Websites

- GreenChemWeb (<http://www.greenchem.org>)
- RSC list for reviews in Green Chemistry published in 3 journals since 2011.
<http://blogs.rsc.org/gc/2012/02/08/reviews-in-green-chemistry-a-cross-journal-collection>

On-Line Learning

- ACS course: **Toxicology for Chemists**
- Free ACS webinar: **Green Chemistry Series**
- Free video course: Carnegie Mellon Univ. The Institute for Green Science
 - **Introduction to Green Chemistry**
(<http://igs.chem.cmu.edu/>)

Resources

Lecture Notes

- ACS Summer School on Green Chemistry and Sustainable Energy
- 綠色/永續化學工作坊
<http://gc.chem.sinica.edu.tw/workshop/notes.php>

Organizations

- ACS Green Chemistry Institute
 - The Nexus Newsletter
 - ACS GCI Industrial Roundtables
 - [ACS GCI Pharmaceutical Roundtable](#)
 - [ACS GCI Formulator's Roundtable](#)
 - [ACS GCI Chemical Manufacturer's Roundtable](#)
- Warner-Babcock Institute for Green Chemistry
- SusChem
 - Strategic Research Agenda /Implementation Action Plan
- GreenCenter Canada

Resources

Journals

- **Green Chemistry (RSC; launched 1999)**
- **Green Chemistry Letters and Reviews (Taylor & Francis; 2007)**
- **ChemSusChem (Wiley; 2008)**
- **ACS Sustainable Chemistry and Engineering (ACS; 2013)**
- **Clean Technologies and Environmental Policy (Springer; 2002)**
- **Energy and Environmental Science (RSC; 2008)**
- **Green and Sustainable Chemistry (open access)**
- **Green Processing and Synthesis (De Gruyter; 2012)**

News

- ACS C&EN Green Chemistry Collection
<http://cen.acs.org/collections/greenchem.html>

Resources

Presidential Green Chemistry Challenge Awards

(USA EPA 1996)

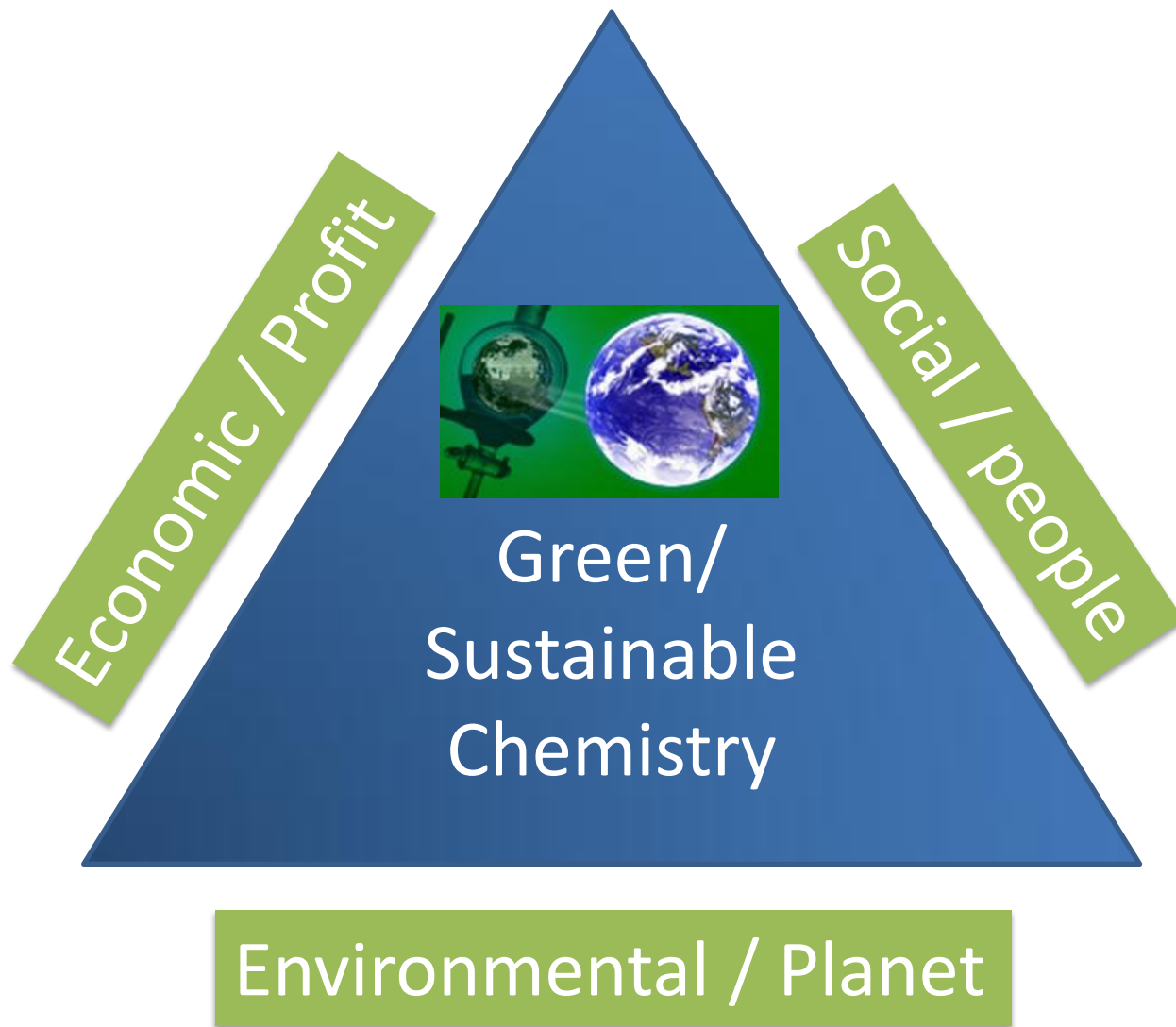
Greener **Synthetic Pathways** Award
Greener **Reaction Conditions** Award
Designing **Greener Chemicals** Award
Small Business Award
Academic Award

The European Sustainable Chemistry Award

(EuCheMS 2010)

Alternative **Synthetic Pathways**
Alternative **Feedstocks**
Alternative **Reactor Design and Reaction Condition**
Design and Use of **Less Hazardous Chemicals** and
Chemical Products

Chemistry and Sustainability



Conclusion

“It’s more **effective**,
it’s more **efficient**,
it’s more **elegant**,
it’s simply **better chemistry**,”



-- Paul Anastas

唯有永續化學
能使化學永續

-- 劉廣定教授

What can we learn from the history of Green Chemistry...

When facing complex and emergent issues

- Identify the missing pieces needed to solve the problems (*e.g., Warner pointed out chemists' problem of lacking knowledge in toxicity*)
- Work collaboratively even with competitors to construct the missing pieces (*e.g., pharmaceutical companies made joint efforts*)