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。[如本頁取材自〇〇〇教授演講內容]。

綠色/永續化學簡介

中央研究院化學所

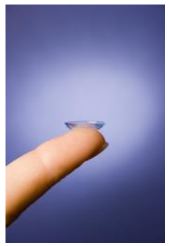
趙奕姼

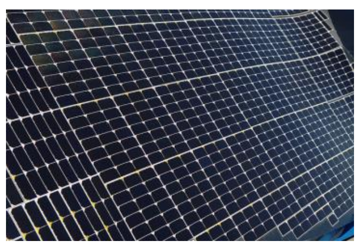
2013/11/23/暨南大學/中國化學年會/綠色暨永續化學講習會

為什麼需要綠色化學或是永續化學?

--The Reality

化學--現代社會的支柱





化學工業延長壽命增進生活品質

Life Expectancy

- 1900 --- 47 歲
- 1990 --- 75 歲

化學工業帶來工作機會

歐洲　雇用一百二十萬人

美國　雇用八十萬人

台灣

製造業分為四大產業；分別為金屬機械、資訊電子、化學工業與民生工業

- 2000年生產產值比例依序為24.68%、37.39%、22.84%(1.92兆)與15.09%
- 2008年生產產值比例依序為27.96%、31.94%、30.36%(3.03兆)與9.75%
- 2012年生產產值比例依序為26.08%、32.74%、31.34%(3.13兆)與9.85%

資訊電子與化學工業近年來分佔第一、二位，且差距變小

人活得長了
生活品質變高了
大環境的變化?

污染、碳循環與氮循環失衡、金屬資源面臨匱乏、廢棄物累積、因更多的人口需要更多的資源...

人類未來五十年面對的問題
(R. Smalley)

- Energy
- Water
- Food
- Environment
- Poverty
- Terrorism & War
- Disease
- Education
- Democracy
- Population

➢ 至少一半需要化學解決

-- by Richard Smalley (2003)

http://cnst.rice.edu/content.aspx?id=246

聯合國永續發展會議Rio+20
討論之七大議題

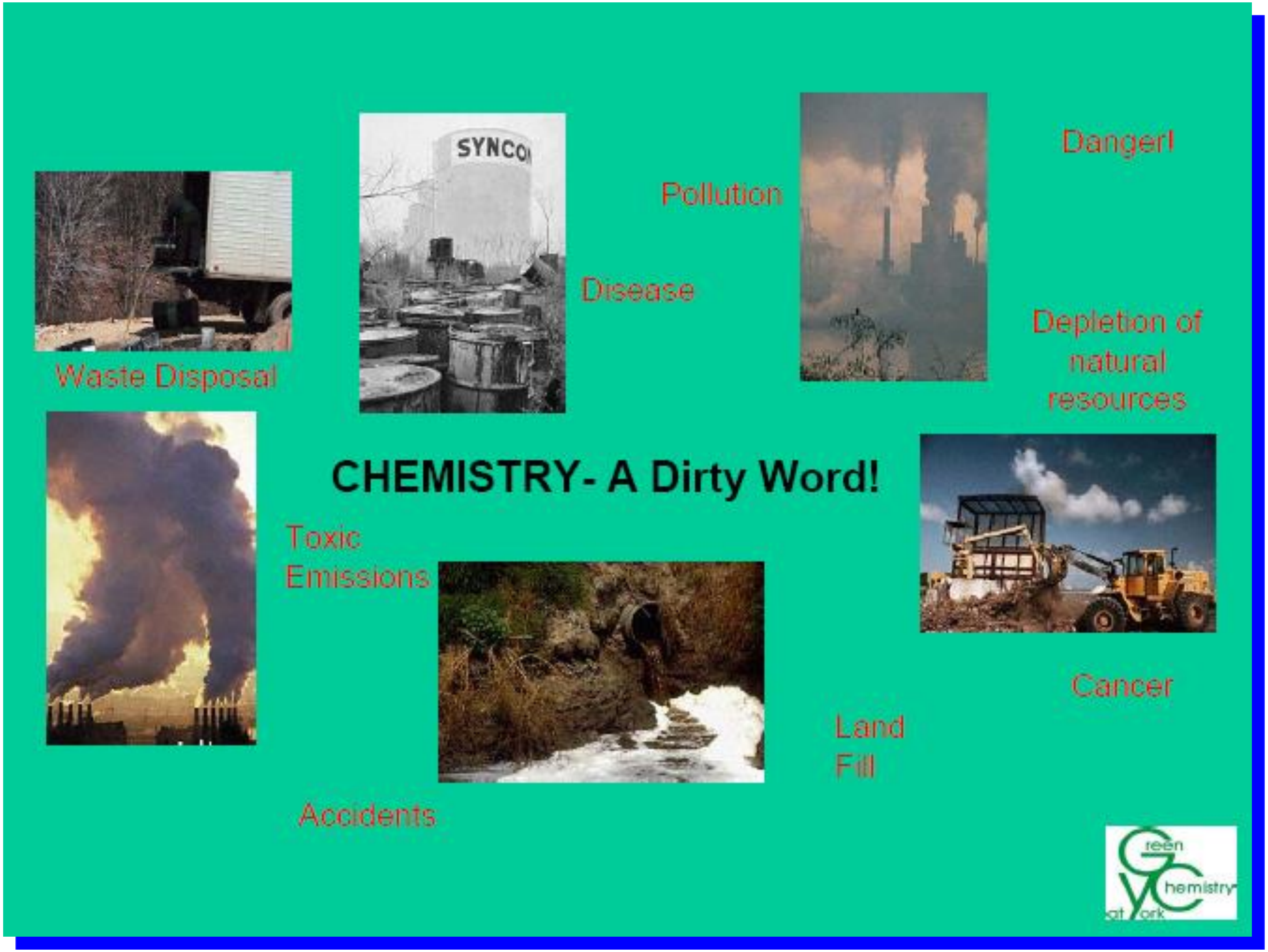
- Jobs
- Energy
- Cities
- Food
- Water
- Oceans
- Disasters

➢ 皆需化學一起使力

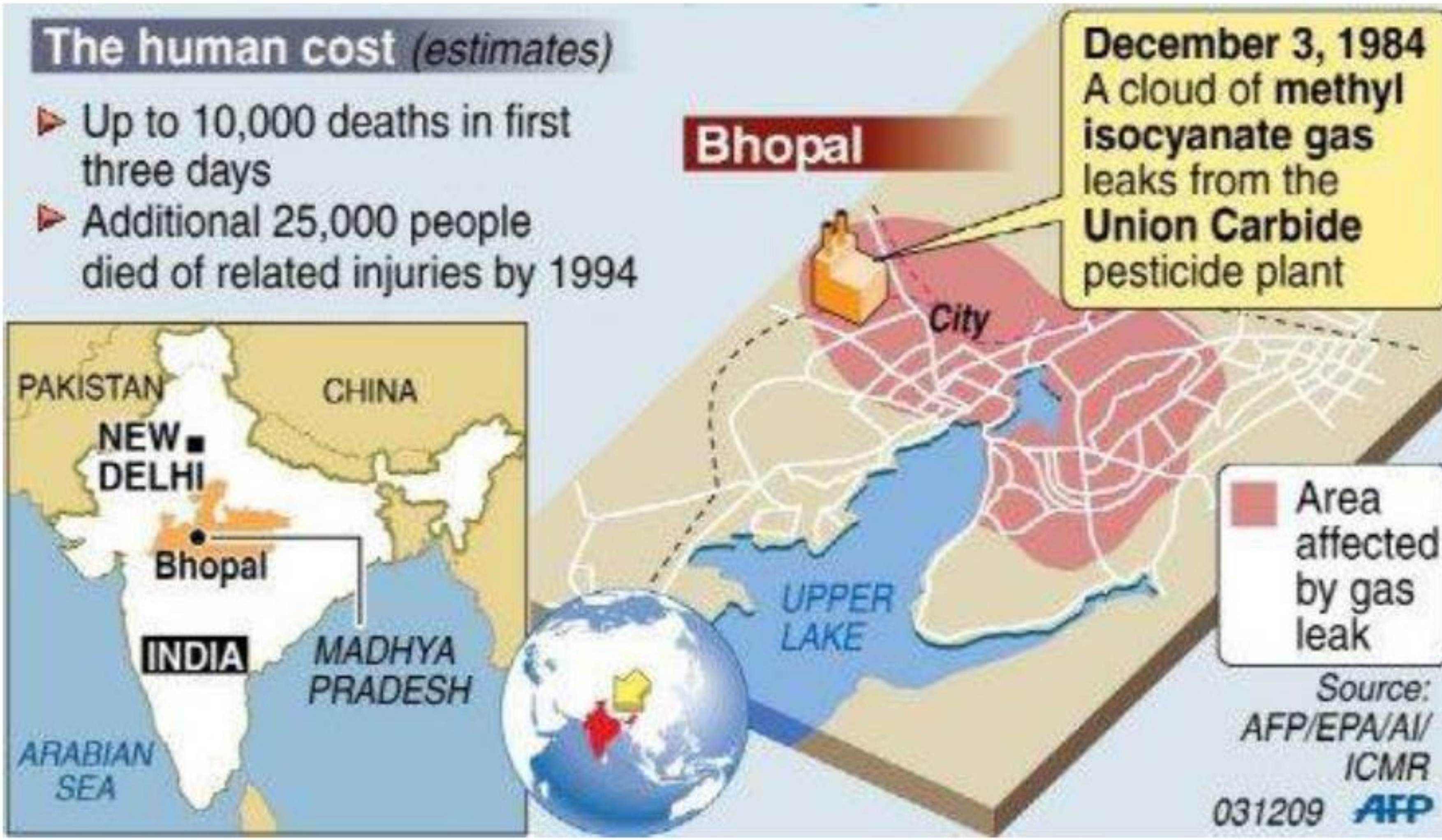
-- Rio+20 United Nations Conference on Sustainable Development

http://www.uncsd2012.org/7issues.html

化學—天災之外的恐懼來源



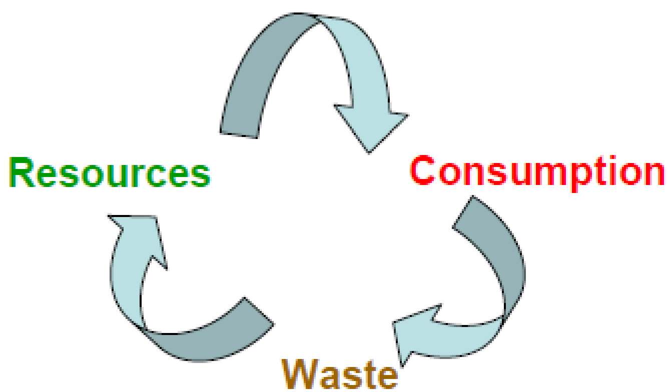
Bhopal (India) disaster 1984



Nature vs Industrial Society

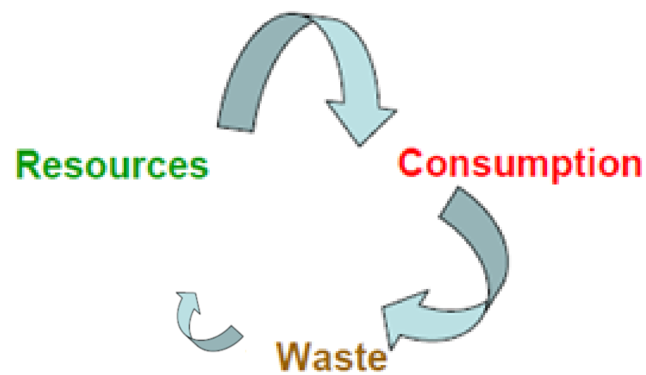
Nature

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

ACS Chemistry for Life

ACS Green Chemistry Institute®

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)

Slide Courtesy Dr. Bob Peoples

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+

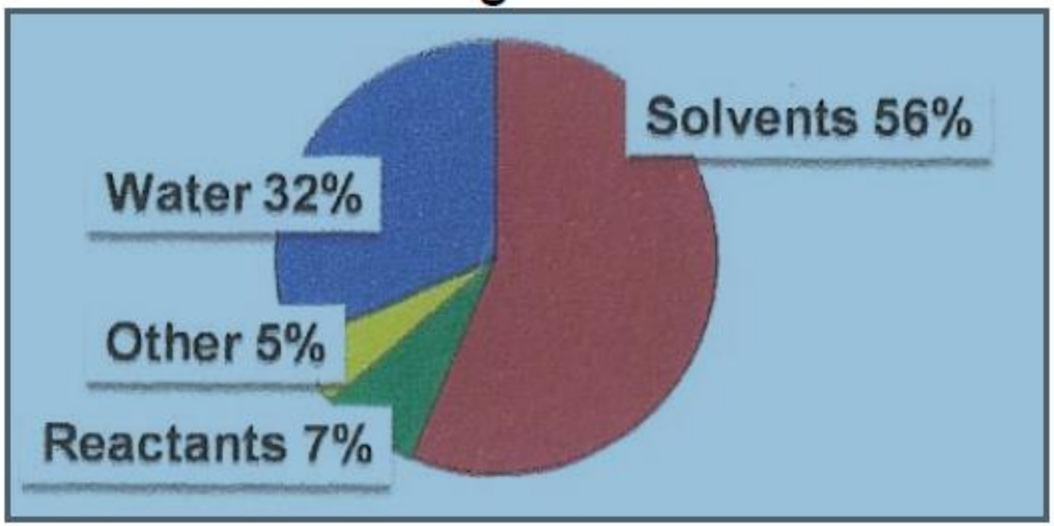
- Areas traditionally thought of as being dirty (oil refining & bulk chemical production) are relatively clean - they need to be since margins per Kg are low.
- Newer industries with higher profit margins and employing more complex chemistry produce much more waste relatively.

Chemtech **1994**, *24*, 38-47

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.

什麼是綠色化學?跟傳統的化學有什麼不同?

--Definition and Spirit

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=mrSy6RKOge8

Hazardous?

- Toxicity
- Flammability
- Explosion potential
- Environmental persistence

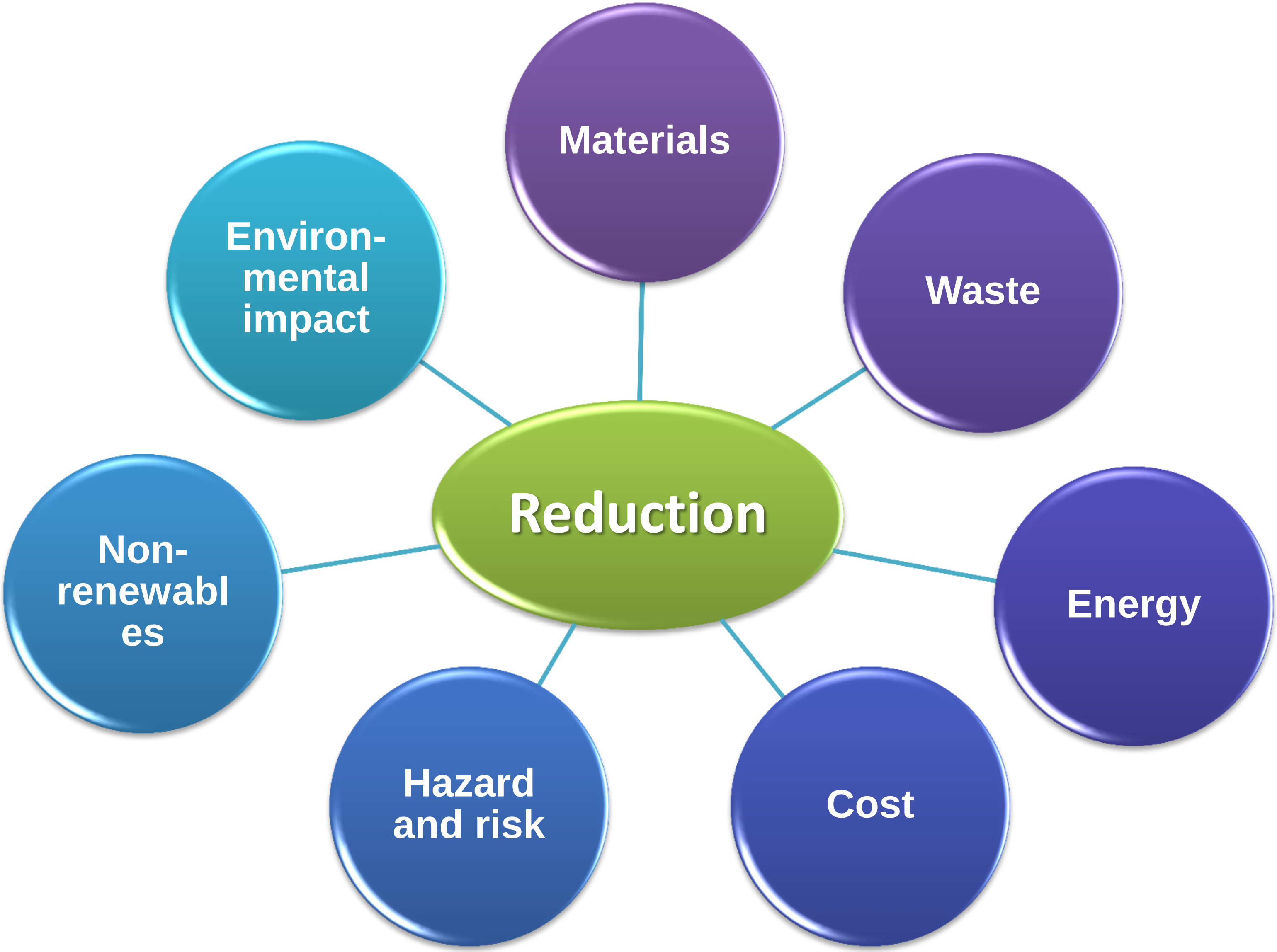
Spirit of Green Chemistry

*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)

Before

Now

Minimize risk by minimizing hazard

Green/Environmental/Sustainable Chemistry不同之處?

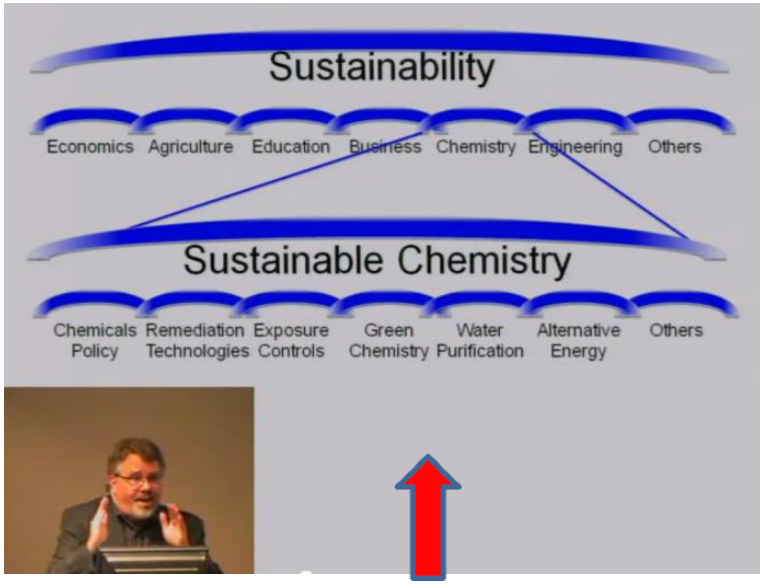
- **Environmental Chemistry**: study chemical events in the environment
- **Green Chemistry**: reduction of materials, waste, energy, cost, hazard and risk, non-renewables, environmental impact. (Eco-friendly chemistry!)

~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

- **Green Chemistry** and **Sustainable Chemistry** are used interchangeably by some, but not all.
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

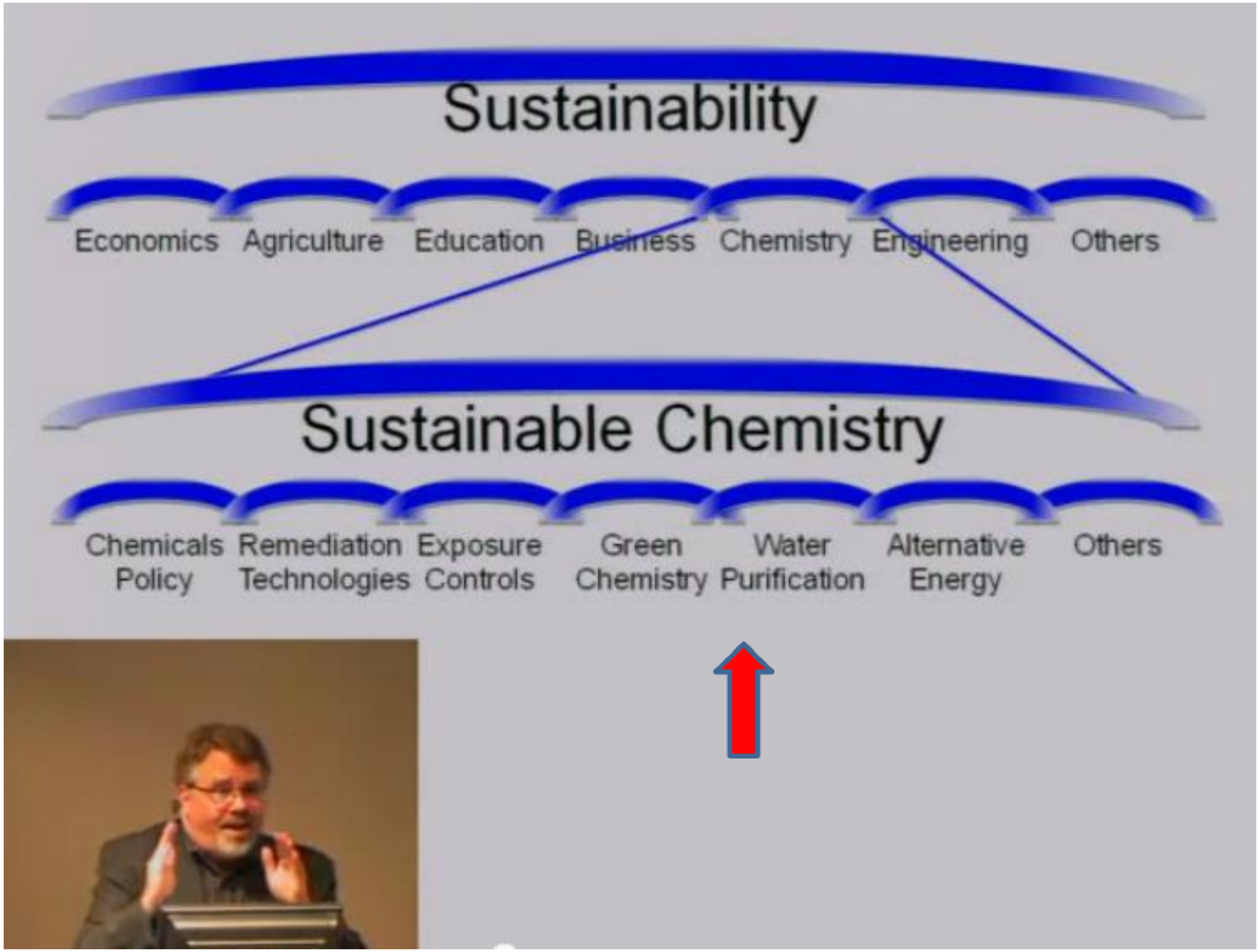
Warner's View on Green and Sustainable Chemistry

- **Sustainable Chemistry**: help to solve sustainability problems, with green chemistry as an important sub-field.



http://www.youtube.com/user/citrisuc#p/c/3/mrSy6RKOge8

Warner's View on Green and Sustainable Chemistry



http://www.youtube.com/user/citrisuc#p/c/3/mrSy6RKOge8

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**"

有具體的想法/作法嗎?

--The Twelve Principles and Metrics

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

Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.

12 Principles of Green Chemistry Demonstrated with Real Cases

See lecture notes
[Green Chemistry: Principles and Practice]

Beginners' must read for 12 principles

by Mary Kirchhoff, Ph.D.,
American Chemical Society Education Division
Given in 2012 ACS Summer School on Green Chemistry and Sustainable Energy

http://portal.acs.org/portal/PublicWebSite/greenchemistry/education/summerschool/CNBP_030373

如何衡量不同的化學反應?

--The Metrics

Metrics

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

$$\textbf{E-factor} = \frac{\text{mass of waste}}{\text{mass of product}}$$

✓ $$\textbf{Process Mass Intensity} = \frac{\text{mass of all materials in}}{\text{mass of product}}$$

$$\text{Solvent Intensity} = \frac{\text{mass of all solvent } (- H_2O)}{\text{mass of product}}$$

$$\text{Renewables Intensity} = \frac{\text{mass of all renewables used}}{\text{mass of product}}$$

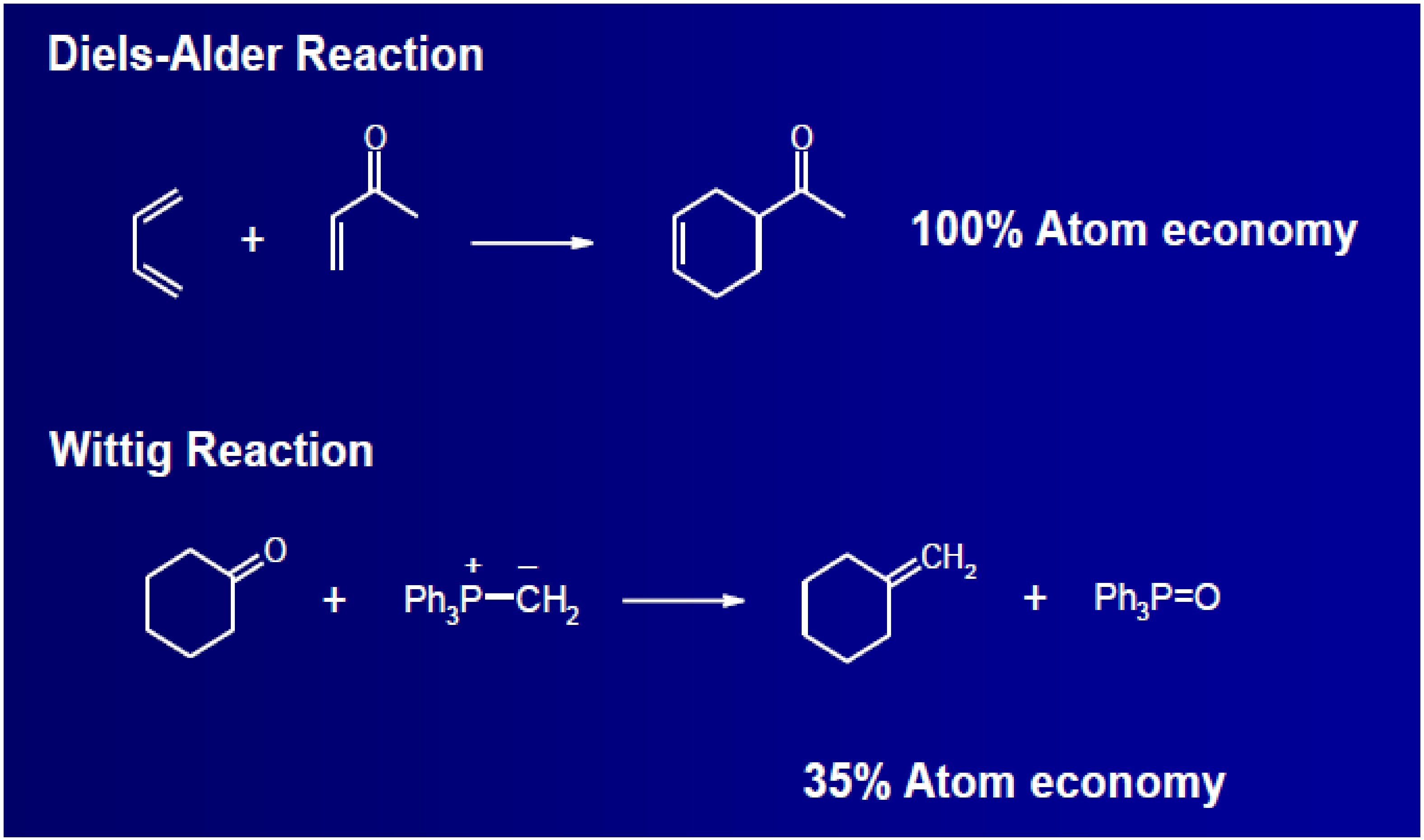
c.f. $$\textbf{Yield} = \frac{\text{quantity of actual product}}{\text{quantity of predicted product}} \times 100\%$$

and more…

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

Chem. Soc. Rev. **2012**, *41*, 1485

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



The amount of ***all reactants*** *is concerned! Different from* ***yield****!!*

Atom Economy

Atom economic reactions	Atom un-economic reactions
• Rearrangement	• Substitution
• Addition	• Elimination
• Diels-Alder	• Wittig
• Other concerted reactions	• Grignard

Green Chemistry: An Introductory Text, RSC, 2002.

✓ **Process Mass Intensity** = $\frac{\text{mass of all materials in}}{\text{mass of product}}$

"materials in"

||

reactants

reagents

catalysts

solvents (for reaction and purification)

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

假想有一化學反應如下

$$\underset{5\ \mathrm{g}}{\mathrm{A}} + \underset{5\ \mathrm{g}}{\mathrm{B}} \xrightarrow[\text{Solvent 14 g}]{\text{Catalyst 1 g}} \underset{3\ \mathrm{g}}{\mathrm{C}} + \underset{4\ \mathrm{g}}{\mathrm{D}} + \underset{3\ \mathrm{g}}{\mathrm{E}} \xrightarrow[\text{純化過程用到的物質總重30 g}]{\text{Purification}} \underset{4\ \mathrm{g}}{\mathrm{D}}$$

Yield = ?

Atom Economy = ?

Process Mass Intensity = ?

以上三種指標是否帶來不同的改進的動機?

Metrics

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

E-factor = $\frac{\text{mass of waste}}{\text{mass of product}}$

✓ **Process Ma**… = …ls in / …uct

Solvent Inte… = …solvent (- H_2O) / mass of product

溫度?毒性?
更多metrics見甘魯生老師2012年講義『綠色化學指標』

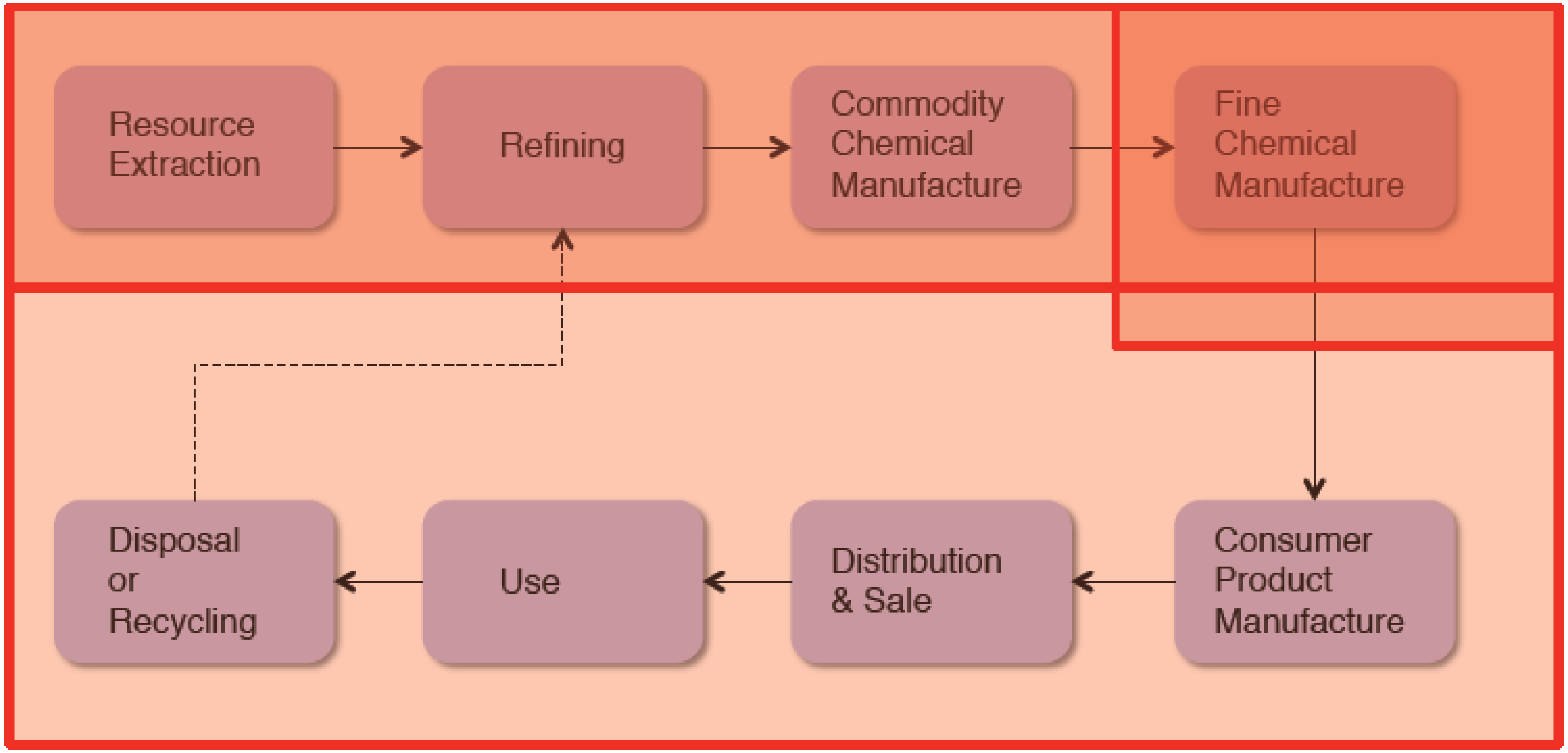
Renewables Intensity = $\frac{\text{mass of all renewables used}}{\text{mass of product}}$

c.f. **yield =** $\frac{\text{quantity of actual product}}{\text{quantity of predicted product}}$

and more…

Chem. Soc. Rev., 2012, **41**, 1485

Life Cycle Assessment (LCA)



Slide courtesy Dr. Philip Jessop

至今Green Chemistry是否有貢獻?

--Industrial Cases

--Pharmaceutical roundtable

The Magnitude of What Can be Accomplished

Presidential Green Chemistry Challenge Award

-- *C&EN* 2013, Volume 91, Issue 36, pp. 75-79

Collectively, the **88** award-winning **technologies**

- Eliminated the use of **825 million lb of hazardous chemicals and solvents**
- Saved **21 billion gal of water**
- Prevented release of nearly **3,600 metric tons of carbon dioxide**

What Can Be Accomplished Economically

51% E-Factor Reduction → **>65% Cost Reduction**

CP 1.0

Step	Yield	E-Factor
1	73%	93
2	81%	66
3	92%	11
4	82%	61
Total	45%	*231*

CP 2.0

Step	Yield	E-Factor
1	68%	30
2	92%	22
3	86%	23
4	87%	33
5	96%	24
Total	45%	*132*

CP 2.1

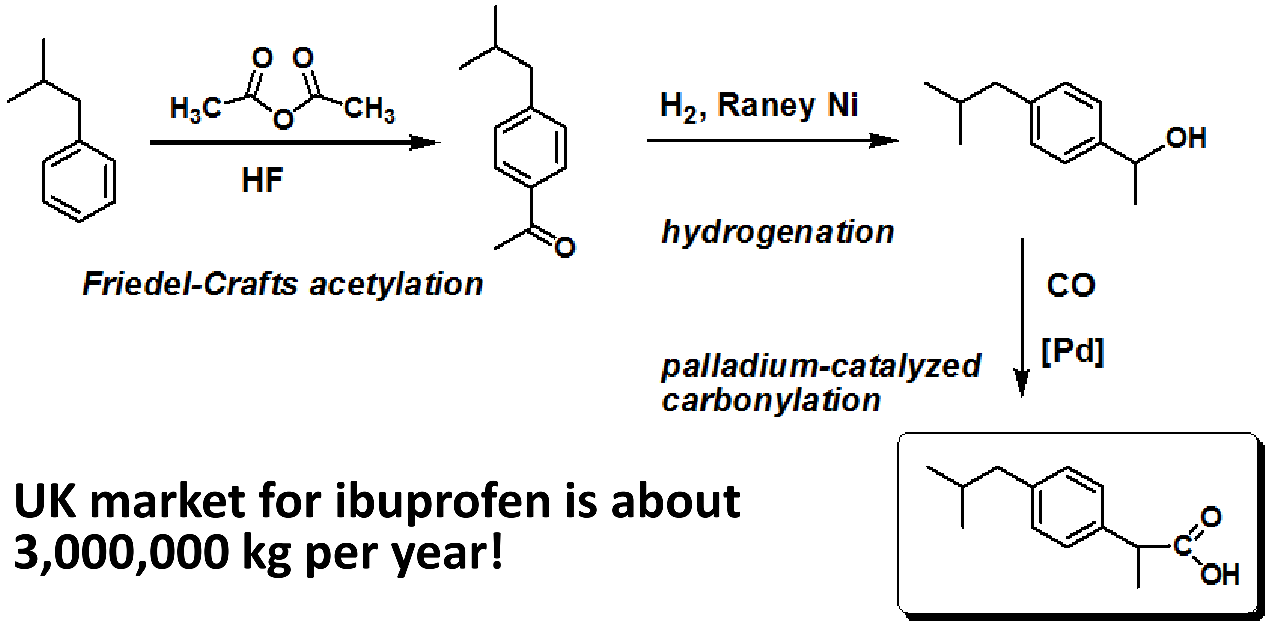
Step	Yield	E-Factor
1	98%	17
2	89%	21
3	86%	23
4	87%	30
5	95%	23
Total	62%	*114*

Figure 4. Example correlation between E-factor and cost reduction.

Org. Process Res. Rev. **2013**, *17*, 1099.

Success

Green Synthesis of Ibuprofen



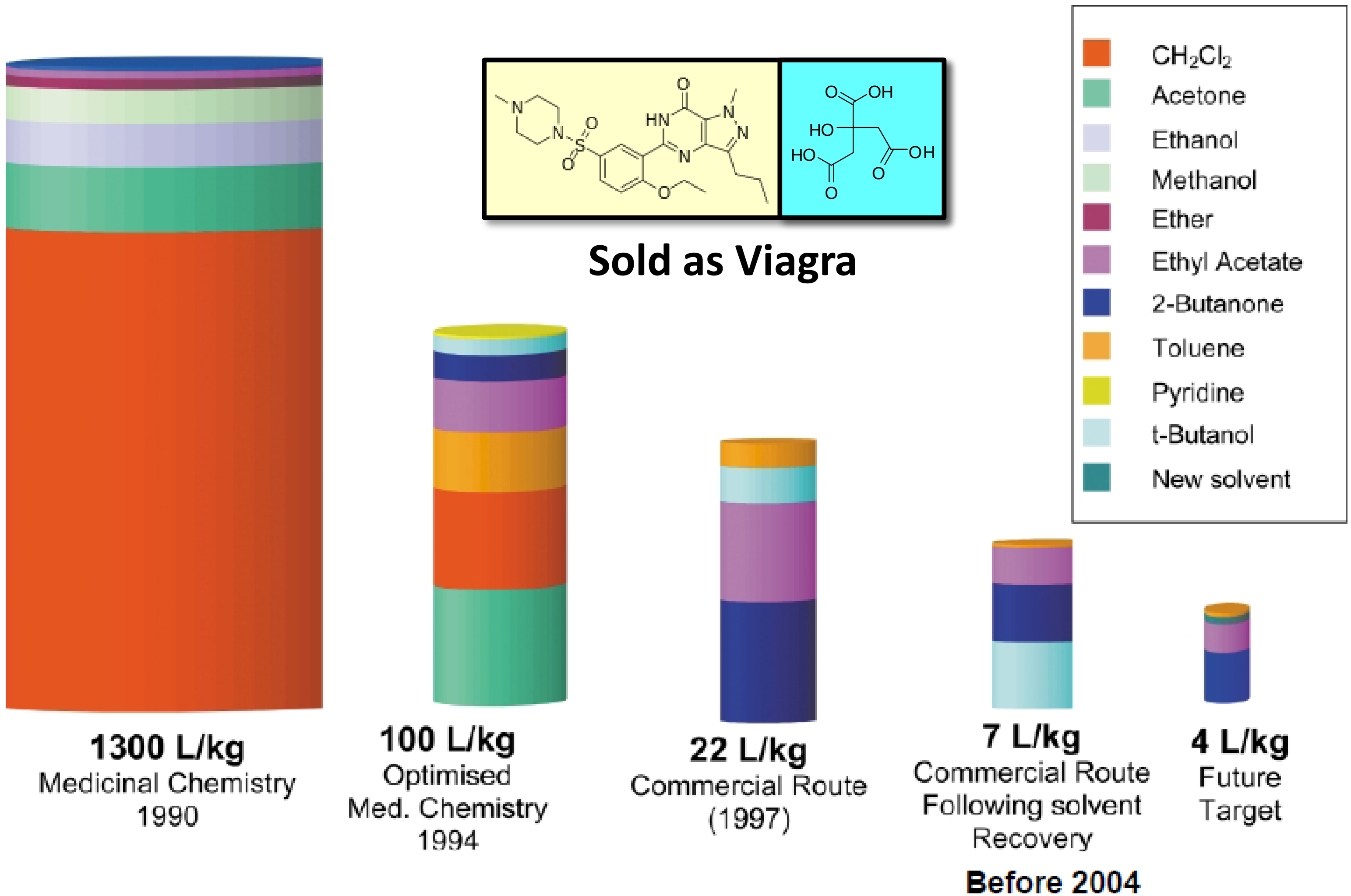
UK market for ibuprofen is about 3,000,000 kg per year!

- Greater overall yield; **3** steps vs. **6** steps
- Greater atom economy (**80%** atom economy vs. < **40%** atom utilization)
- Fewer auxiliary substances (products and solvents separation agents)
- **Less waste:** greater atom economy, catalytic vs. stoichiometric reagents, recovery of byproducts and reagents, recycling, and reuse, lower disposal costs.

(USA) Presidential Green Chemistry Challenge Awards

Greener Synthetic Pathways Award in 1997

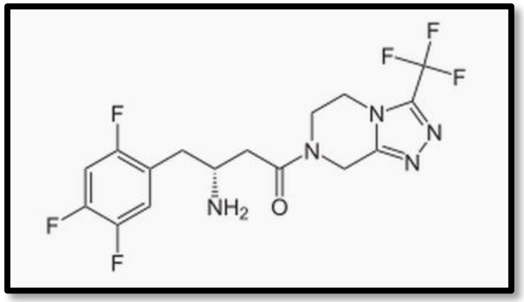
The Sildenafil Citrate Process: Reduction of Solvent Usage



2003 CRTSTAL Faraday Award

Green Chem. **2004**, *6*, 43; *Org. Proc. Res. Dev*. **2005**, *9*, 88.

Green Synthesis of Sitagliptin: Biocatalysis



Active ingredient in Januvia
for treating of type 2 diabetes

- Enzymatic process affording chiral amine
- Eliminate the use of a rare metal catalyst
- Remove the use of high pressure condition
- Increase yield
- **Less waste:** compared to original catalytic synthesis, the enzymatic process creates **99.8 kg less waste for each kg** of sitagliptin produced.

Presidential Green Chemistry Challenge Award
Greener Reaction Conditions Award in 2010
Science **2010**, *329*, 305.

ACS Chemistry for Life™

ACS Green Chemistry Institute®

ACS GCI Pharmaceutical Roundtable

gsk GlaxoSmithKline

Pfizer

MERCK

Roche

AstraZeneca

Lilly

NOVARTIS caring and curing

ACS Green Chemistry Institute

Abbott A Promise for Life

CODEXIS®

DSM BRIGHT SCIENCE. BRIGHTER LIVING.

AMGEN

Boehringer Ingelheim

SANOFI

Lonza

DR.REDDY'S

Bristol-Myers Squibb

Johnson & Johnson

Slide Courtesy Dr. Rich Williams

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

Slide Courtesy Dr. Rich Williams

ACS Chemistry for Life™

ACS Green Chemistry Institute®

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.

ACS Green Chemistry Institute® PHARMACEUTICAL ROUNDTABLE

Slide Courtesy Dr. Rich Williams

Green Chemistry的挑戰?

Challenges

Alternative feedstocks

- Move from petroleum to renewable or biologically derived sources
  - Petroleum chemistry => need oxidation chemistry
  - Sugar => need reduction chemistry
- CO_2 => need new catalysts

Alternative solvents

- No solvent (neat solution; grinding)
- Supercritical CO_2, 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

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

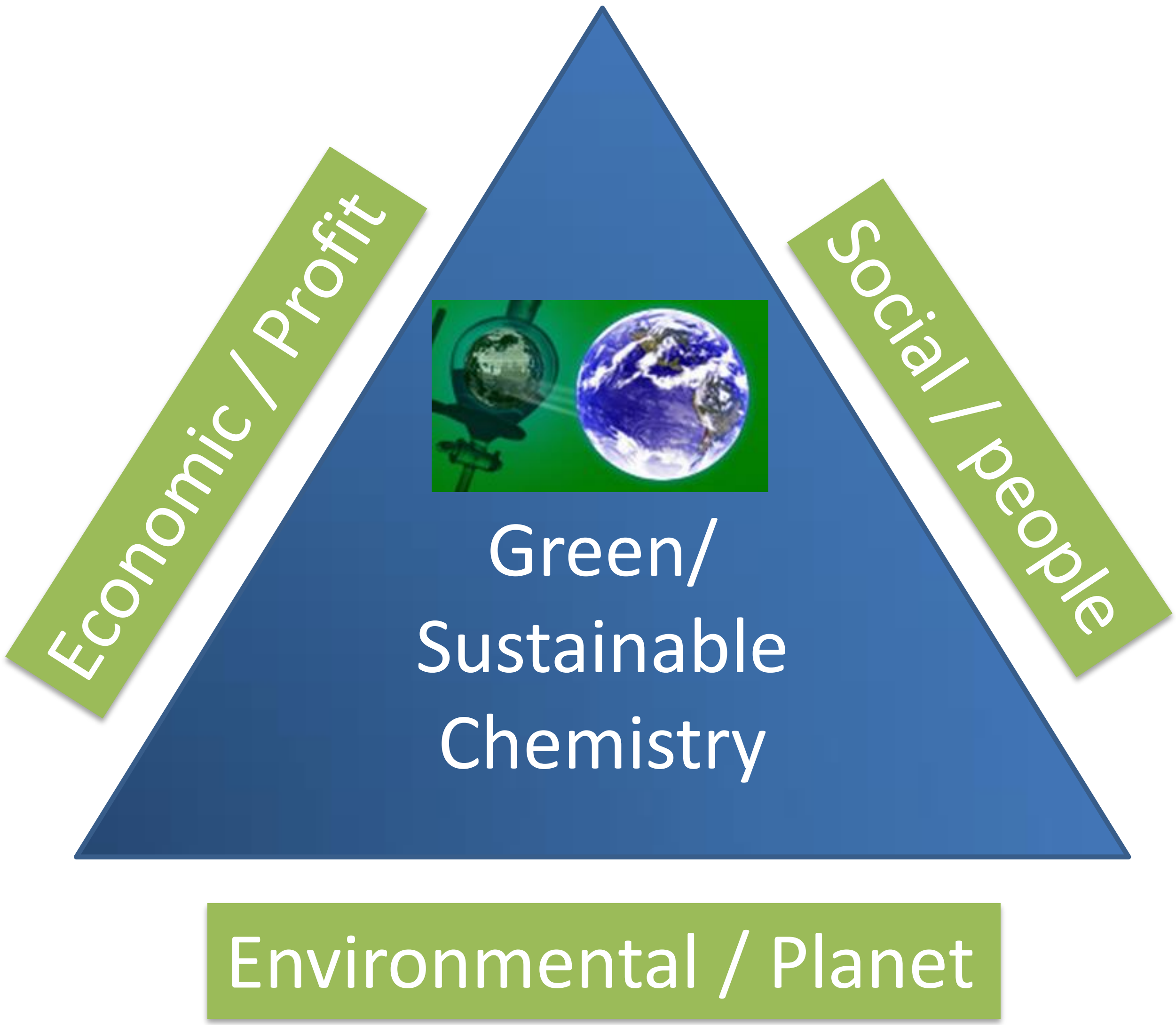
“Green Toxicology” in Book: *Green Techniques for Organic Synthesis and Medicinal Chemistry* (ISBN-10: 0470711515)

“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.

Green Chemistry的未來前景

Chemistry and Sustainability



能源、水、食物、環境、
疾病、資源短缺等問題，
可以不用化學解決嗎?

如何避免一邊解決問題
一邊製造問題?

Industry

Green Chemistry:

- Market opportunity grows from $2.8 billion in 2011 to $98.5 billion by 2020.
- Cost saving reaches $65.5 billion by 2020.

Reports from Pike Research

Funding Agency

美國國家科學基金會(NSF) 2013宣佈 ”Sustainable Chemistry, Engineering and Materials (SusChEM) Awards”: $49 million in 101 groups of scientists

SusChEM: aims to support the discovery of new science and engineering that will provide humanity with a safe, stable and sustainable supply of chemicals and materials sufficient to meet future global demand.

Academia

Impact factor (IF)	Green Chemistry	ChemSusChem
2000	2.111	
2002	2.547	
2004	3.503	
2006	4.192	
2008	4.746	
2010	5.472	6.325
2012	6.828	7.475

跳進綠色化學或永續化學之前可以做些什麼？

- 留意綠色化學的趨勢
- 留意化學中關鍵之課題或技術
- 把握機會學習或教授綠色化學
- 瀏覽綠色化學相關之網站、期刊與書本
- 參加綠色化學相關之會議
- 留意自身實驗中所用試劑的特性。
在可能的情況下 Make a “greener choice”
- 其他…?

從多讀多聽開始!

學習有機無機物化分析
事實上也不知道會對自己有什麼影響
時間到了就會開花結果....

(見附錄二“訊息來源推薦”)

Conclusion

Green Chemistry…

"It's more **effective**,
it's more **efficient**,
it's more **elegant**,
it's simply **better chemistry**"

by Paul Anastas

Conclusion

" Today, most students who want to change the world end up being activists. How many 18-year-olds who care about the planet say, 'I'm going to go be a chemist'? But now they can go to the lab and invent something that can save the world. "

by John Warner

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)*

What can we learn from the people…

- Step out the comfort zone (John Warner)
- Forget you're a "nobody" (Martin Mulvihill)
- Promote green chemistry to eliminate the term (Paul Anastas)

Thank you

ichao@chem.sinica.edu.tw

Acknowledgement

- 劉廣定教授、甘魯生教授、蔡蘊明教授、魏國佐教授
- 國科會化學研究推動中心、中國化學會
- 暨南大學、中央研究院
- 陳秋雲小姐

重點回顧

- 什麼是綠色化學或是永續化學?
- 為什麼需要綠色化學或是永續化學?
- 綠色化學有具體的想法與作法嗎?
- 綠色化學至今是否有貢獻?
- 綠色化學面臨的挑戰?
- 綠色化學的前景?
- 我可以做什麼?

附錄一
綠色化學十二原則全文

- **Prevention**
  It’s better to prevent waste than to treat or clean up waste afterwards.
- **Atom Economy**
  Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.
- **Less Hazardous Chemical Syntheses**
  Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.
- **Designing Safer Chemicals**
  Design chemical products to affect their desired function while minimizing their toxicity.
- **Safer Solvents and Auxiliaries**
  Minimize the use of auxiliary substances wherever possible make them innocuous when used.

http://www.epa.gov/sciencematters/june2011/principles.htm

- **Design for Energy Efficiency**
  Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.
- **Use of Renewable Feedstocks**
  Use renewable raw material or feedstock rather whenever practicable.
- **Reduce Derivatives**
  Minimize or avoid unnecessary derivatization if possible, which requires additional reagents and generate waste.
- **Catalysis**
  Catalytic reagents are superior to stoichiometric reagents.
- **Design for Degradation**
  Design chemical products so they break down into innocuous products that do not persist in the environment.
- **Real-time Analysis for Pollution Prevention**
  Develop analytical methodologies needed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- **Inherently Safer Chemistry for Accident Prevention** Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

附錄二

綠色化學訊息來源 推薦

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; 2012 IF = 6.828)**
- **Green Chemistry Letters and Reviews (Taylor & Francis; 2007)**
- **ChemSusChem (Wiley; 2008; 2012 IF = 7.475)**
- **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