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
Green (Sustainable) Chemistry

許拱北教授
成功大學化學系

中華民國102年5月30日15:00-17:00
成大唯農大樓許文龍講堂
(「永續發展講座」通識課程演講系列)

Outline

Background

Green Scale

Alternate Synthetic Processes

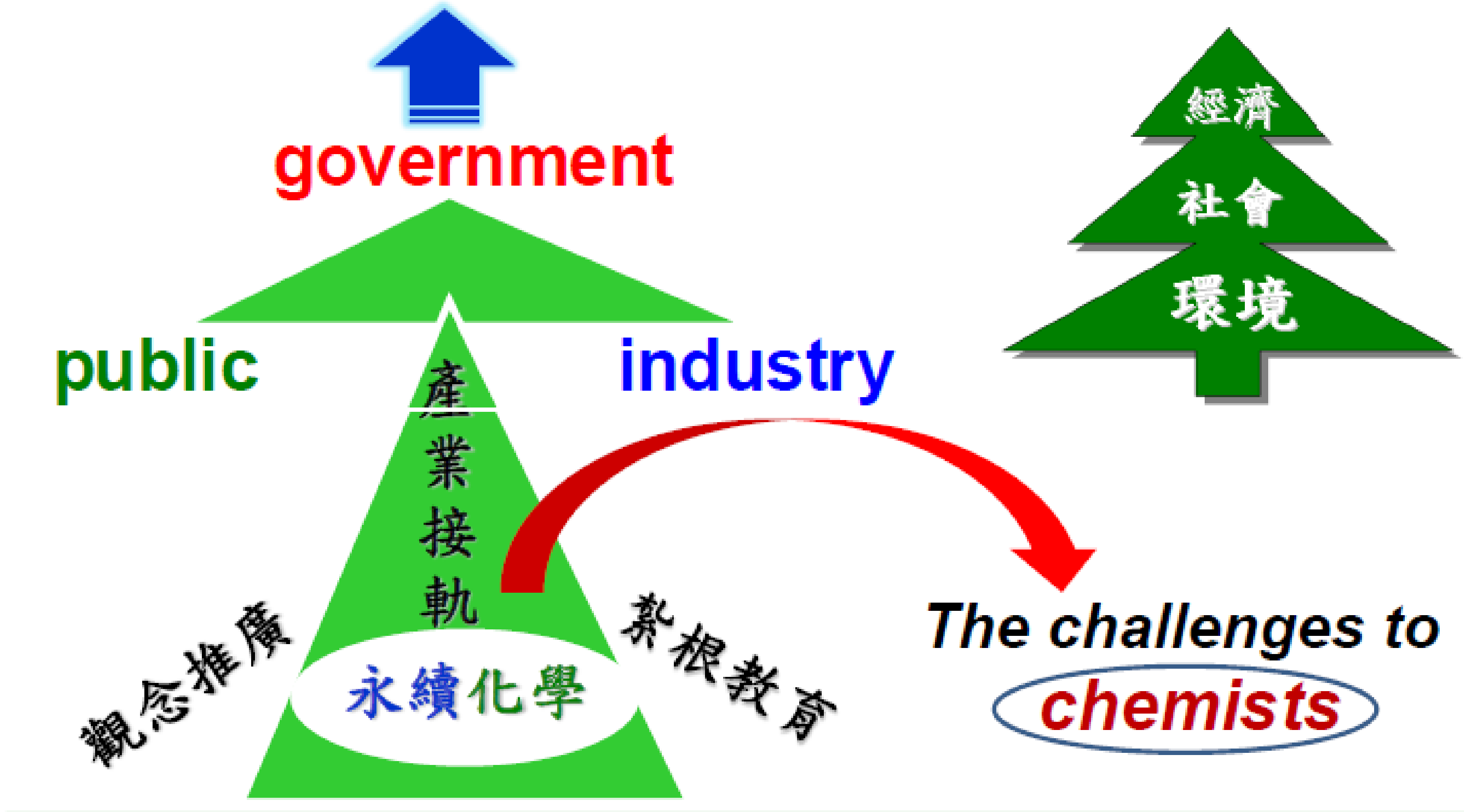
Green Awarded Processes

Think Green

Sustainable Development

"safeguarding human health and environment to allow for future generations to maintain the necessary resources to sustain life"

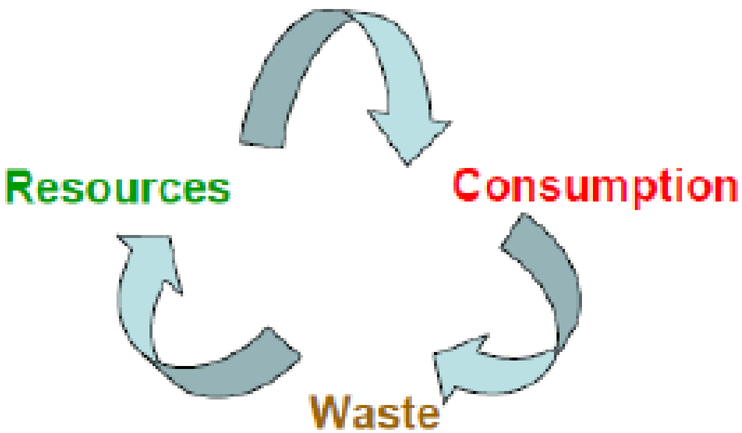
[永續發展：守護人類的健康和環境，讓子孫能持有永續其生命的必需資源。]



Nature vs Industrial Society

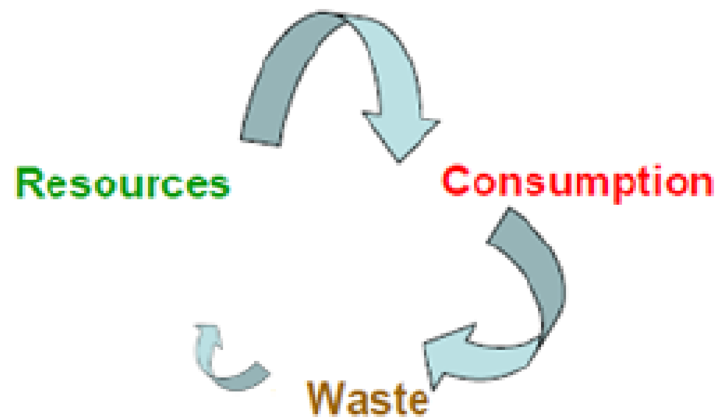
Nature

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

Benefits of the Chemical Industry

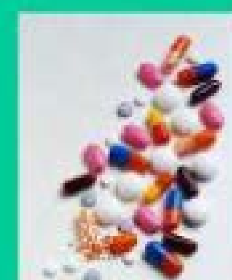
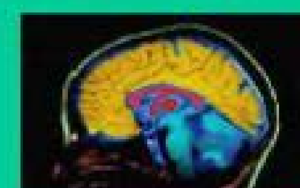






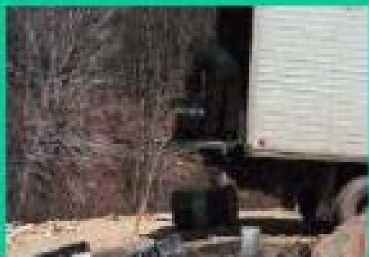




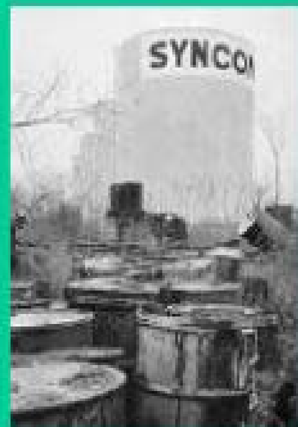




Green Chemistry at York

CHEMISTRY- A Dirty Word!



Waste Disposal



Disease

Pollution

Danger!

Depletion of natural resources

Toxic Emissions

Cancer

Land Fill

Accidents

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+

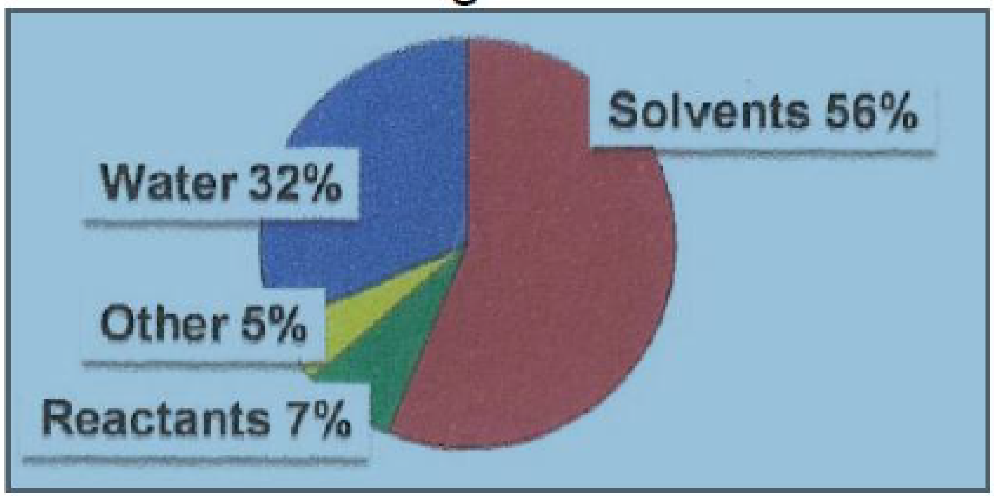
- Areas traditionally thought of as being dirty (oil refining & bulk chemical production) are relatively clean - they need to be since margins per Kg are low.
- Newer industries with higher profit margins and employing more complex chemistry produce much more waste relatively.

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 solv[illegible] are needed to make 1 kg of API. **E = 45**

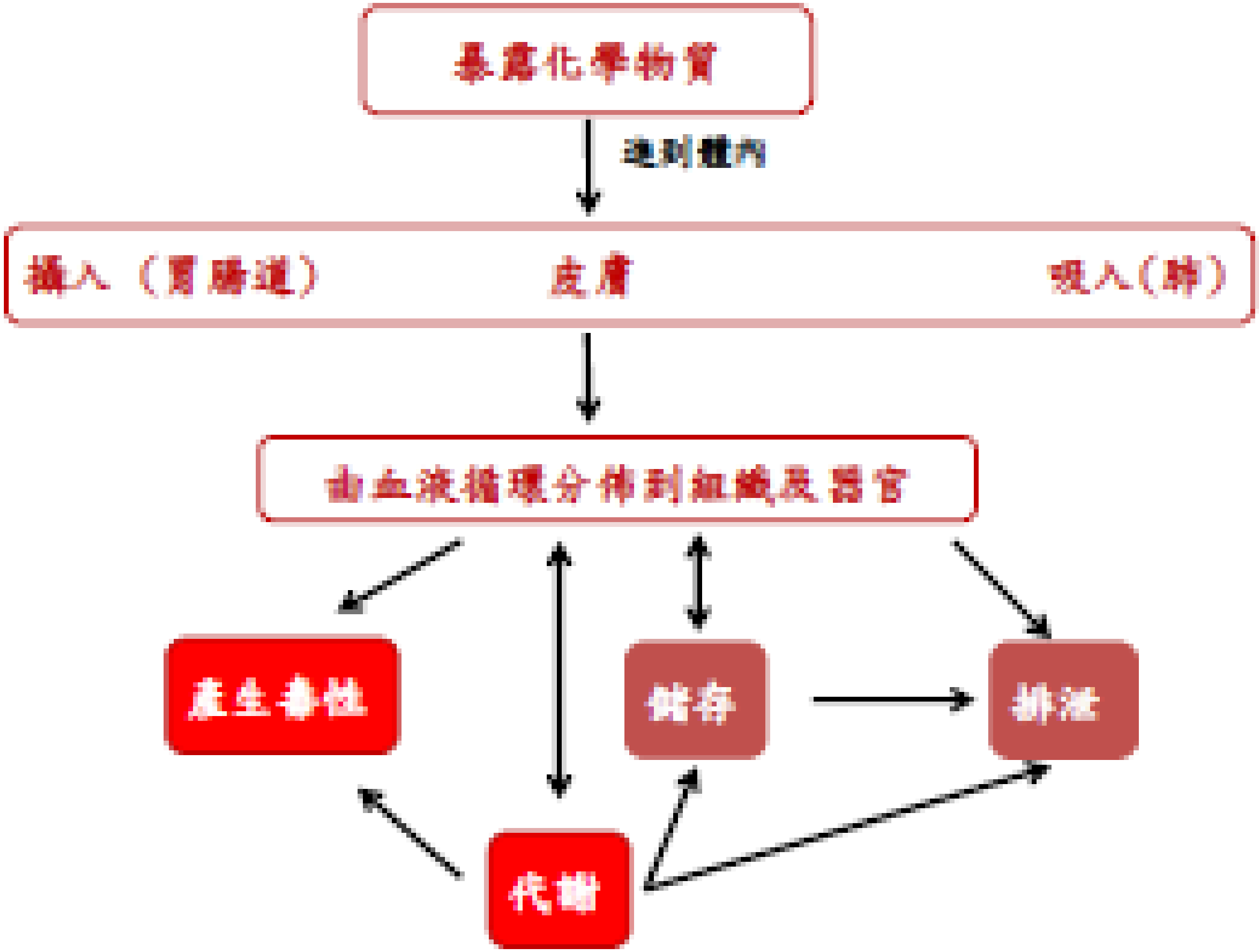
Solvent



Green Chem. **2011**, *13*, 854.
Org. Process Res. Dev. **2011**, *15*, 912.

- 溶劑是化學廢棄物的大宗，那些方向有助於改變現況?
- (I)傳統溶劑(藥品)的安全(綠色)考量:
- EHS, LCA, NFPA 704
- (II)傳統溶劑的減量(使用與回收)
- (III)無溶劑反應
- (IV)非傳統溶劑
- (V)尋找綠色溶劑的挑戰

無溶劑 > 水 > 超臨界溶劑 > 離子溶液 > 揮發性有機溶劑 (>為優於之意)


暴露化學物質
進到體內
攝入（胃腸道）
皮膚
吸入（肺）
由血液循環分佈到組織及器官
產生毒性
儲存
排泄
代謝

- Paracelsus提出 “沒有任何物質本身就是毒物，而是劑量使它變成毒物，劑量多寡決定它是毒物或良藥”

Paracelsus

Wiki

Table 1.4 Some solvent applications.

Application	*Description*
Solvent extraction	In hydrometallurgy to recover metals from ores
	In nuclear fuel reprocessing
	In waste water treatment
	To recover natural products from plants or from fermentation liquors
	In organic synthesis and analytical chemistry
	As a degreaser and cleaning agent
Analytical chemistry and electrochemistry	Eluant in analytical and preparative chromatography, and in other separation techniques
	Dissolving the electrolyte to permit current to flow between the electrodes, without being oxidized or reduced itself
	As an oxidant or a reductant
Organic chemistry	As a reaction medium and diluent
	In separations and purification
	As a dehydrator (also in materials chemistry)
Polymer and materials chemistry	As a dispersant
	As a plasticizer
	As a blowing agent to create porosity
	As a binder to achieve cohesiveness in composite materials
	Production of powders, coatings, films, *etc.*
	As a developer in photoresist materials
Household and others	Fuels and lubricants
	Paints, varnishes, adhesives, dyes, *etc.*
	Antifreeze
	Cleaning fluids
	As a humectant (hydrating material) and in emulsions within cosmetics and pharmaceuticals

Kerton, F. M. Alternative Solvents for Green Chemistry, RSC, 2009.

Chemical's EHS file

- An Environmental Health and Safety (EHS) tool has been developed to assess the direct environmental risks of a chemical compound. The EHS profile is calculated by considering for the environmental persistency, air hazard, and water hazard; for safety: release potential, fire/explosion risk, and irritation. Any compound is given a score for each of these factors, which are then summed to give an overall EHS profile.

Life Cycle Assessment (LCA)

- The gold standard for the quantification of greeness is the full LCA.
- The LCA seeks to assess the environmental impact of the production and use of a chemical product encompassing all stages of its life from the sourcing of its ingredients through its production, with the inclusion of all auxiliary substances used therein, to its transportation and use, and finally its eventual destination in the environment.

- Full life-cycle assessments
  - Chemists often do not know how the chemicals they use are made
  - Chemists often do not know how their chemistry affects the biosphere

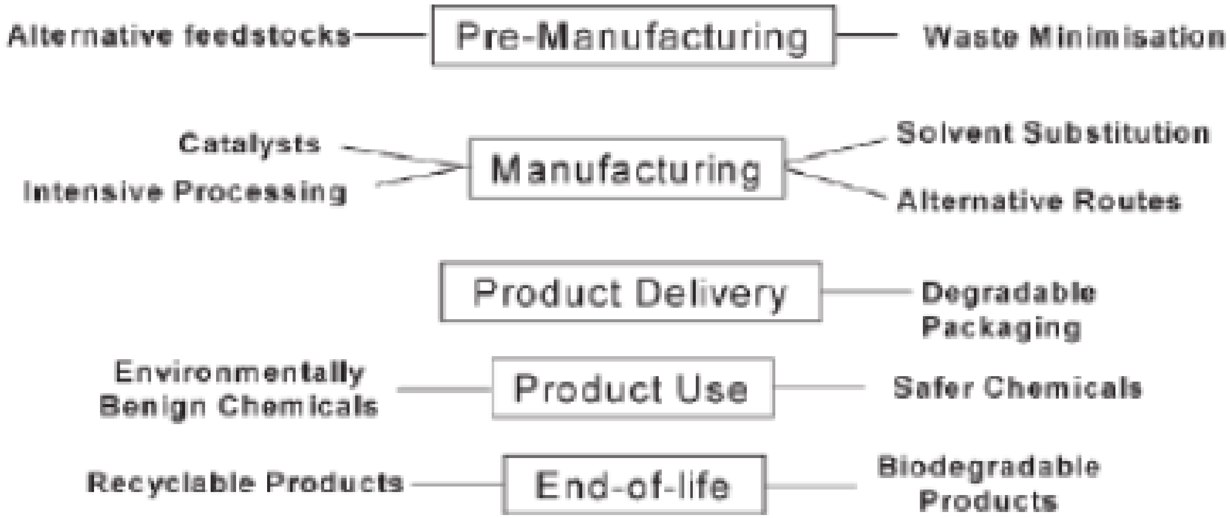
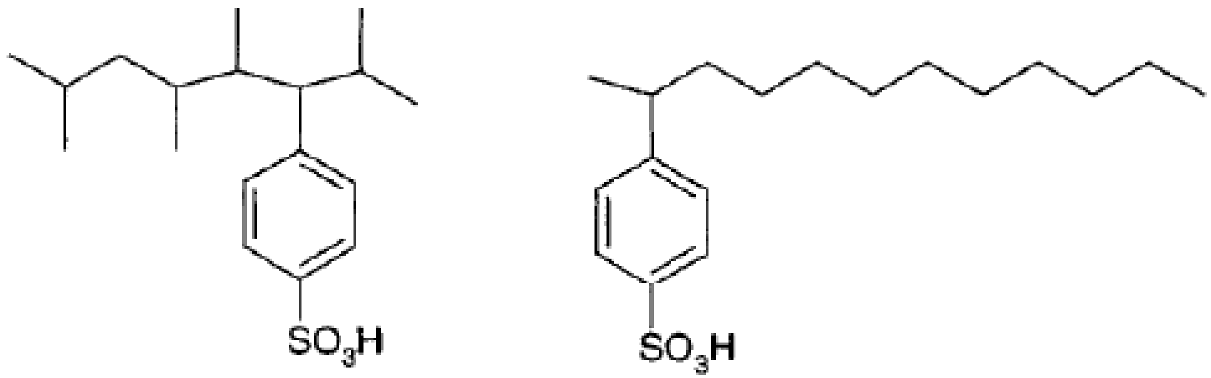


Fig. 3 Green chemistry applied from the cradle to the grave.

"Green Chemistry: Today (and Tomorrow)", J. H. Clark, *Green Chem.* 2006, 8, 17-21.

Long aliphatic chains degrade more readily than branched



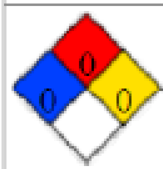
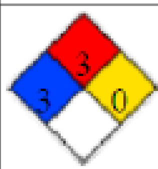
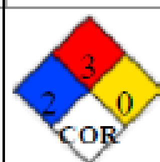
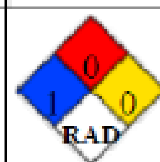
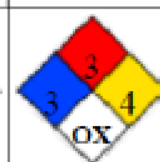
Low degradation rate High degradation rate

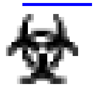
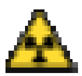
Scheme 2.7 *Structure/degradation relationship for alkylbenzene sulfonates*

From: Lancaster, M. "Green Chemistry: An Introductory Text", RSC, 2002, Chapter 2, p. 46.

Safety of Chemicals- NFPA 704

- **NFPA 704**是美國消防協會 (National Fire Protection Association) 制定的危險品緊急處理系統鑒別標準。它提供了一套簡單判斷化學品危害程度的系統，並將其用藍、紅、黃、白四色的警示菱形來表示。
- 警示菱形按顏色分為四部分：藍色表示健康危害性；紅色表示可燃性；黃色表示反應性；白色用於標記化學品的特殊危害性。前三部分根據危害程度被分為0、1、2、3、4，五個等級，用相應數字標識在顏色區域內。

水	甲醇	鉻酸鉀	三乙胺	乙酸鈾醯	三硝基苯酚
					

- **白色／特殊危害性**
- 警示菱形的白色區域可能有以下符號：
- W（有時被寫作W）：與水發生劇烈反應。如：鈣。
- OX（有時被寫作OXY）：氧化劑。如：高錳酸鉀。
- 以上兩個符號是NFPA 704標準中規定的符號，除此之外，化學品廠商有時還使用以下符號標記在白色區域：
- COR：腐蝕性。如：濃硫酸。
  - ACID：強酸。如：鹽酸。
  - ALK：強鹼。如：氫氧化鈉，氫氧化鈣。
- BIO或（）：生物危害性。如：溴化乙錠。
- RAD或：放射性。如：鈾。
- CRY 或 CRYO：低溫。如：液氮。

永續(綠色)化學大事紀

自Rachel Carson所著之『寂靜的春天』一書出版之後的1970年代引起「環保議題」的熱烈討論.

1972 聯合國環境委員會在瑞典Stockholm召開『人類與環境會議』.揭櫫了人類要和環境良性互動.並訂每年六月五為『世界環境日』.

1977 聯合國教科文組織(UNESCO)強調環境教育的倫理價值觀,成為永續發展的籃圖(Tbilisi宣言).

1980『世界自然保育方略(World Conservation Strategy)』一書出版.此書由聯合國環境計畫組織、世界保育聯盟和野生動物保育協會共同撰文.其目的為達成資源保護以供永續開發.

1986年美國國會通過了『應急規劃和社區知情權法案(Emergency Planning and Community Right-to-Know,或EPCRA)』.這是美國有害化學物質清除的超級基金(superfund)修正案之一.它授權給州及地方政府有被告知及取得有害化學物質之權利以及有權作出對化學有害物質應對方案.這啟發了民眾對有害化學物質的認識和落實了環境保護的意識.

1987 聯合國環境委員會(由挪威首相 Brundtland為召集人) 提出永續發展 Sustainable Development 的理念『我們共同的未來』(Our Common Future).強調『滿足這一代的需求,但不以下一代滿足他們自身需求的能力作為妥協 (Meeting the needs of the present generation without compromising the ability of future generations to meet their own needs)』.此宣言將人類福祉相關的因素列入考慮,打破了以往經濟發展(economic development)與環境保護(environmental protection)對立的局面,成為永續化學發展的策略和目標.

同年 我國行政院成立環境保護署推動自然環境保護,自然生態保育及合理運用資源等.

1990 美國訂定污染防治法案 (The Pollution Prevention Act),提倡「源頭減廢勝於管末處理」政策.

同年 美國環境保護署推行永續化學.

1991 Paul T. Anastas博士(時任職美國環境保護署Environmental Protection Agency, EPA) 首次提出『綠色化學(Green Chemistry Program)』一詞將永續化學口語化並定義為:『發明、設計和利用化學產品與化學製程,以減少或消除有害物質之使用與生產』.此名詞沿用至今.

1992『地球高峰會議』於巴西里約熱內盧召開,制定了里約宣言、二十一世紀議程、氣候變化綱要公約、生物多樣性公約及森林宣言等五項公約.
1995 美國成立『美國總統綠色化學挑戰獎 (The Presidential Green Chemistry Challenge Awards)』致力推行綠色化學.
1997 全球綠色化學運動先軀Joseph Breen創立美國綠色化學研究所(GCI)並出任第一屆所長.2001年合併入美國化學會(American Chemical Society).
1998 京都議定書.制定二氧化碳排放目標.由於只對已開發國家限制(中國、印度列開發中國家),以至有些工業大國(美國及澳大利亞)未簽署.
同年 Paul T. Anastas 博士和John C. Warner 博士合著"Green Chemistry: Theory and Practice" 一書由Oxford University Press出版.此書提出綠色化學的十二原則.成為落實綠色/永續化學之指標。
1999 英國皇家化學學會成立『綠色化學網』(The Green Chemistry Network)並出版綠色化學學誌(Green Chemistry, IF=6.32)).
2000 日本推動綠色和永續化學.
2001 國際純粹與應用化學組織(IUPAC)成立綠色化學委員會.
此後世界各國政府機關、學術界順應發展趨勢開始響應綠色/永續化學之研究,並著手推動與實行、設立研究組織、舉行研討會來致力推行綠色/永續化學.
我國國科會化學中心於2006年成立永續/綠色化學網路資源共享網(網址:http://gc.chem.sinica.edu.tw/).
各大學亦設立綠色化學課程.2010年成立綠色化學種子教師培訓工作坊,講師有趙奕姼、劉廣定、廖俊臣、周德璋、甘魯生五位.2012年有許拱北、蔡蘊明、陳月枝、沙晉康等老師加入.

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

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!!

Reduction of What?

Spirit of Green Chemistry

Risk = f(hazard x exposure)

Before

Now

Minimize risk by minimizing hazard

2020 Sustianability 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

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

Condensed Principles of Green Chemistry

P - Prevent wastes
R - Renewable materials
O - Omit derivatization steps
D - Degradable chemical products
U - Use safe synthetic methods
C - Catalytic reagents
T - Temperature, Pressure ambient
I - In-Process Monitoring
V - Very few auxiliary substances
E - E-factor, maximise feed in product
L - Low toxicity of chemical products
Y - Yes, it is safe

S. L. Y. Tang, R. L. Smith, and M. Poliakoff, Principles of green chemistry: PRODUCTIVELY, Green Chem., 2005, *7*, 761-762.

Green Chemistry is Cost Efficient

	環 境 思 維	經 濟 思 維
Atom Economy	*Minimal by-product formation* 減低環境負擔	*More from less – incorporate total value of materials* 降低成本
Conver-gency	*increased process efficiency* 減低環境負擔	*Higher efficiency – fewer operations* 降低成本
Reagent Optimi-zation	*Catalytic, low stoichiometry, recyclable reagents minimize usage,* 減低環境負擔	Higher efficiency - higher selectivities 降低成本
Solvent Reduction	*Less solvent waste,* 減低環境負擔	Higher throughput, less energy, 降低成本

Green Chemistry is Cost Efficient

	環境思維	經濟思維
Energy Reduction	*from power generation, transport, and use* 減低環境負擔	*reflects increased efficiency, shorter process, mild conditions* 降低成本
In-situ Analysis	*Reduced possibility for exposure or release to the environment*	*Real-time data increases throughput and process efficiency, fewer reworks* 降低成本
Safety	*Non-hazardous materials reduce risk of exposure, release, explosions and fires*	*Worker safety and reduced down time, Reduced time on special control measures.* 降低成本

Organic Process Research & Development, **2006**, *10*, 315.

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

Env. Sci. and Tech. **2003**, *37(5)*, 94A.

Principles of Green Engineering

I - Inherently non-hazardous and safe
M - Minimize material diversity
P - Prevention instead of treatment
R - Renewable material and energy inputs
O - Output-led design
V - Very simple
E - Efficient use of mass, energy, space & time
M - Meet the need
E - Easy to separate by design
N - Networks for exchange of local mass & energy
T - Test the life cycle of the design
S - Sustainability throughout product life cycle

S. Tang, R. Bourne, R. Smith and M. Poliakoff, The 24 Principles of Green Engineering and Green Chemistry: "IMPROVEMENTS PRODUCTIVELY", Green Chem., 2008, 10, 268–269.

The Twelve Principles of Green Engineering 化學工業12項原則

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

Inherent Rather Than Circumstantial 天然優於人工

Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.

Prevention Instead of Treatment 預防優於善後

It is better to prevent waste than to treat or clean up waste after it is formed.

Design for Separation 高瞻遠矚

Separation and purification operations should be designed to minimize energy consumption and materials use.

Maximize Efficiency 物(包括能及時間)盡其用

Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

Output-Pulled Versus Input-Pushed 順勢而為

Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.

Conserve Complexity 避免節外生枝

Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.

Durability Rather Than Immortality 耐用但不能不朽

Targeted durability, not immortality, should be a design goal.

Meet Need, Minimize Excess 樸實

Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.

Minimize Material Diversity 不能『鼫鼠五技而窮』

Material diversity in multicomponent products should be minimized to promote disassembly and value retention.

Integrate Material and Energy Flows 不能華而不實

Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.

Design for Commercial "Afterlife" 天生我材必有用

Products, processes, and systems should be designed for performance in a commercial "afterlife."

Renewable Rather Than Depleting 再生優於耗盡

Material and energy inputs should be renewable rather than depleting.

減少廢物(包括溶劑)　減低毒性(包括溶劑)　減少能量　減少災害

翻譯成工業界指標: 減少成本, 增加利潤

廢物之度量法

產率(yield): 目標產物的當量和化學反應式平衡之後應得的產物當量之比.

產率(Y) = 產物之實當量(或重量)/由化學反應式計得之當量(或重量)

原子經濟(atom economy): 產率值對化學反應之優劣可說是一目了然,但它卻沒說明目標產物在眾產物所佔之比.原子經濟之定義是目標產物中的原子在反應物所佔的份量.

原子經濟(AE) = 產物分子量/反應物分子量之和

原子效率(atom efficiency): 是同時考慮了上二項的結合體.

原子效率(AF) = AE x Y

有效質量產率(effective mass yield): 目標產物和所有反應物中有害物質之重量比.有害物質除了反應物及產物副產物外也包括所有參與的物質,如溶劑.

有效質量產率(EMY) = 產物的總量(公斤)/有害反應物的重量(公斤)

碳原子效率(carbon efficiency): 無論是有機物或藥物.碳原子是結構的要素.所以針對碳原子有一個度量,即碳原子效率.它是產物中之碳原子量和所有反應物中碳原子量總和之比.

碳原子效率(CE) = 產物中碳原子總重量/反應物中碳原子總重量

反應質量效率(reaction mass efficiency): 產物和留在溶液中的反應物重量之比.

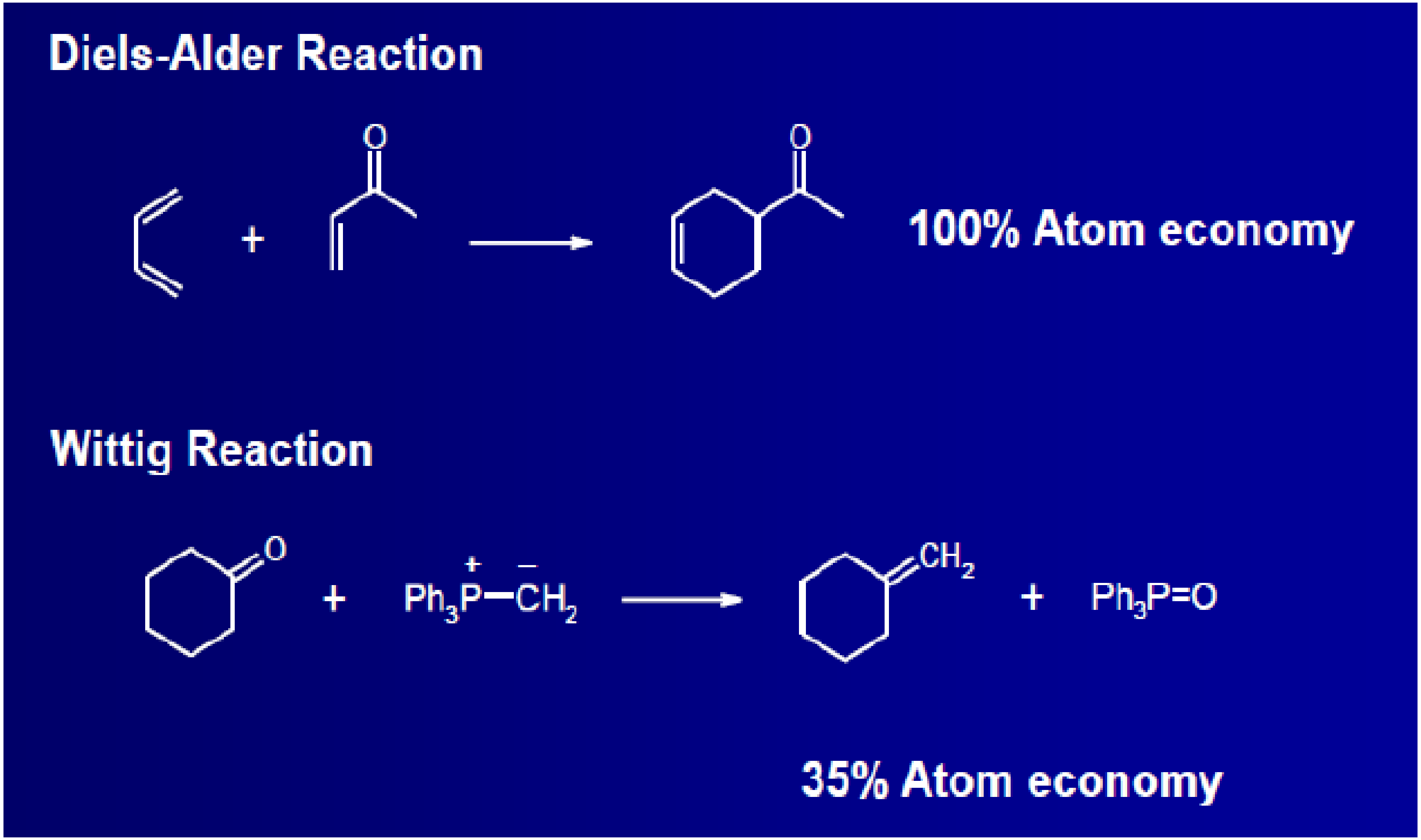
反應質量效率(RME) = 產物重量/未反應之反應物總和

(未完成反應物量等物反應物之總和x產率.)

環境因子(environmental factor): 反應後產物和反應中所有廢物之比.廢物包括了副產物及溶劑、催化劑、補助劑等.

環境因子(E) = 廢物的總量(公斤)/產物的重量(公斤)

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

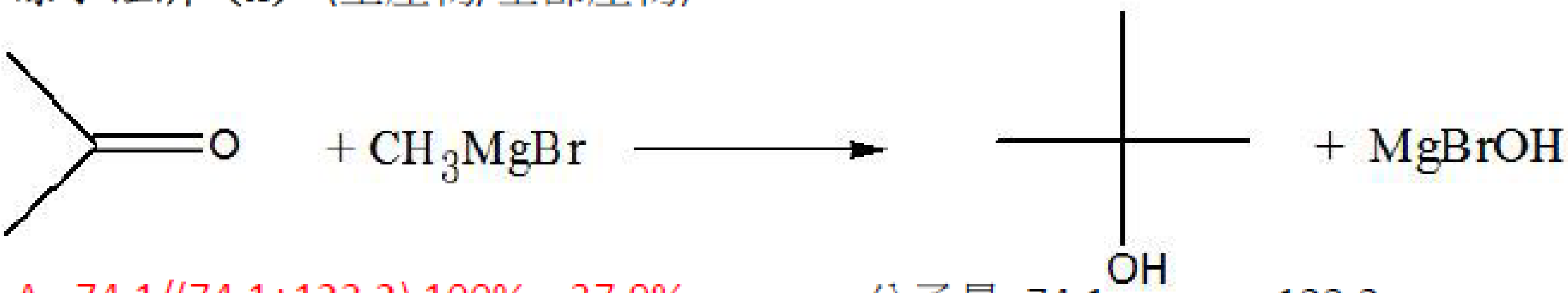


2. Atom economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

發揮最大的原子經濟: 設計合成使得終極產物含有最大部分的原始反應料. 而沒有甚麼浪費的原子. 即便有也是很少.

原子經濟 (A): (主產物/全部產物) x 100%

B. M.Trost, *Science, 254, 1471, 1991; Acc. Chem. Res. 35, 695, 2002.*



A =74.1/(74.1+123.2) 100% = 37.9%

分子量=74.1 123.2

原子經濟(atom economy) = 100%

<u>加成反應</u>: 例: 水加氧氣生產雙氧水.化學反應式為 $2H_2O + O_2 \rightarrow 2H_2O_2$

<u>重組反應</u>: 例: 氫原子轉移(hydride shift).化學反應式為

$CH_3CH(CH_3)CH{=}CH_2 \rightarrow CH_3CH{=}CHCH_2CH_3$

原子經濟 < 100%

<u>取代反應</u>: 例: 甲烷和氯氣作用產生氯化甲烷. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

欲得到的產物質量 = (12+3x1)+35.5 = 50.5; 反應物的總質量 = (12+4x1)+2x(35.5) = 87

原子經濟(%) = 100% x 50.5/87 = 58%

<u>分解反應</u>: 例: $Ca(OH)_2 \rightarrow CaO + H_2O$

欲得到的產物(CaO)質量 = 40.1+16 = 56.1; 反應物的總質量 = 40.1+2x(16+1) = 74.1

原子經濟(%) = 100% x 56.1/74.1 = 76%

其它反應的<u>化學通式</u>為 $aA + bB \rightarrow cC + dD$

若欲得到的產物是眾產物之一,照上列的計算可知原子經濟小於100%.

減少能量 (催化劑、非傳統方法)

耗能指數: 溫度 5 (反應溫度低於-20° C或高於280° C)

3 (反應溫度0 - -20° C或160 - 280° C)

2 (反應溫度0 - 10° C或90 - 160° C)

1 (反應溫度10 - 20° C或30 - 90° C)

0 (反應溫度20 - 30° C)

壓力

Step EE (Energy Efficiency) = $\frac{(f_T + |1\text{-}Pressure(atm)|) * time\ (hrs) * Weight * Heat\ Capacity\ (J/gm\cdot°K)}{Wt\ Desired\ Product}$

對環境友善指數(化合物的半生命期):

5 (以小時計); 4 (以天計); 3(以週計); 2(以月計); 1(以年計)

U.S. EPA BIOWIN program Expert Survey Biodegradation model

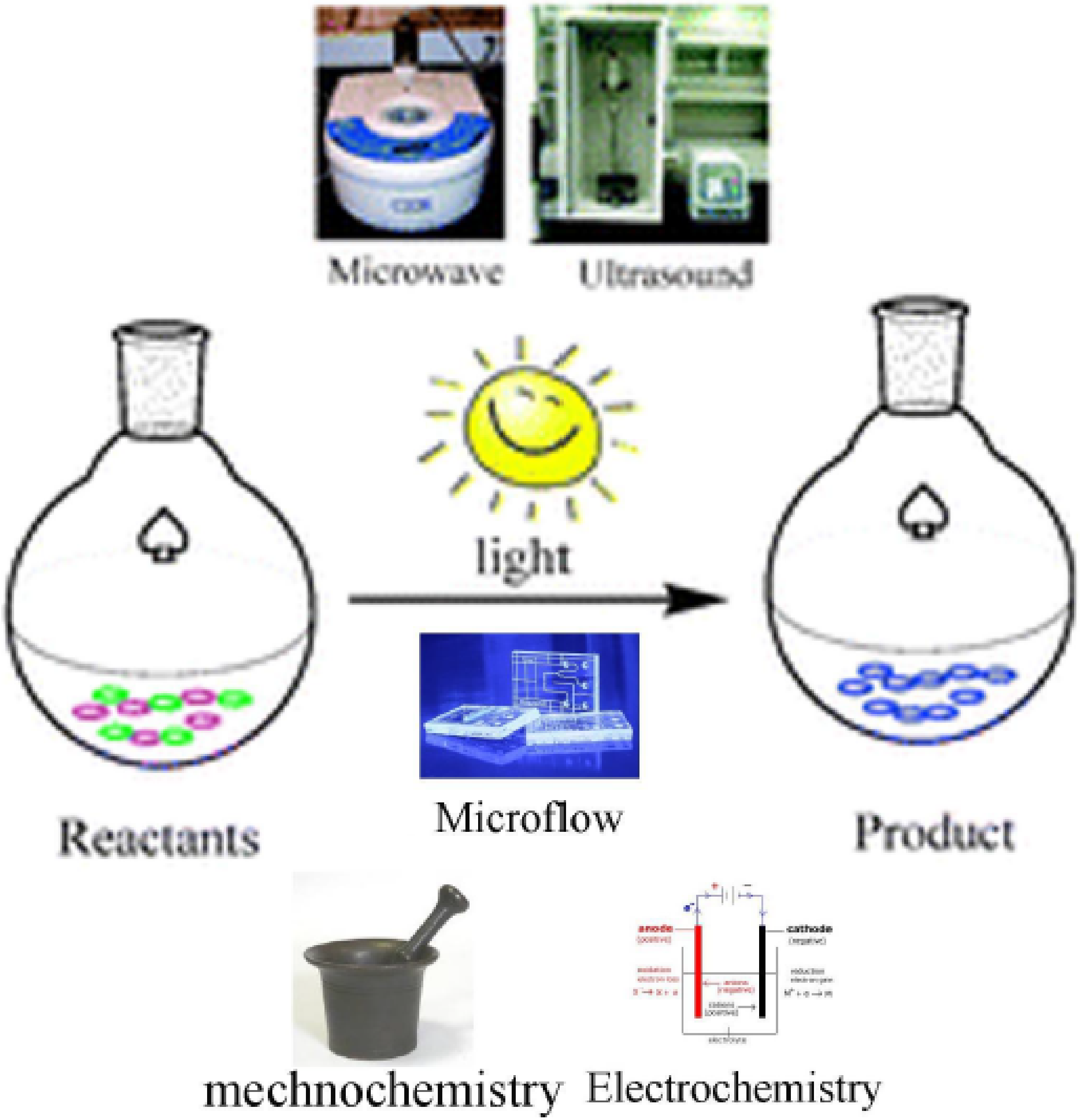
減少災害 (規章、法令、危險品取代、人為因素去除)

碳足跡(Carbon footprint)

碳足跡這名詞是由carbon footprint直譯而來.它的定義由直接和間接支持人類的活動所產生溫室氣體的總和.愈來愈多的証據顯示溫室氣體是造成氣溫上昇及氣候異常的元兇.常見的溫室氣體有二氧化碳、甲烷及臭氧.因人類活動產生二氧化碳遠比其它溫室氣體多得多.所以碳足跡就是產生二氧化碳的度量法.可依個人、家庭、社區、國家以及機器、生產線、工廠等為單位每年所產生之二氧化碳(噸)來計算.

下列之事項都能產生一公斤二氧化碳:
生產5 個塑膠袋.
生產2 只塑膠瓶.
操作電腦32 小時(功率60 瓦計).
開車6 公里.
乘公共交通工具12 公里.
乘飛機2.2 公里.

Alternative organic synthetic methods

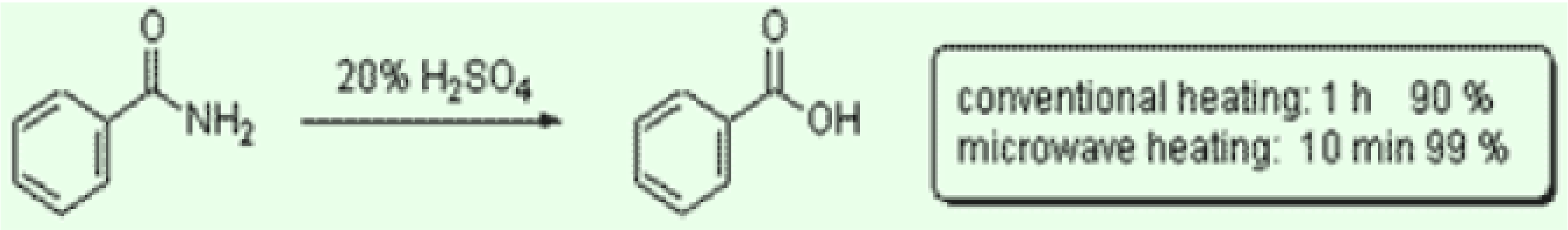


微波(Microwave)
極性或解離物質
微觀尺寸流動
(Microflow)
溶液
超音波化學
(Sonochemistry)
溶液
Mechanochemistry
固體
Electrochemistry
導電
Photochemistry
chromophore

S. K. Sharma, A. Chaudhary, and R. V. Singh, "GRAY CHEMISTRY VERSES GREEN CHEMISTRY: CHALLENGES AND OPPORTUNITIES, RASĀYAN JOURNAL OF CHEMISTRY (RJC), (2008), **1**, 68-92.

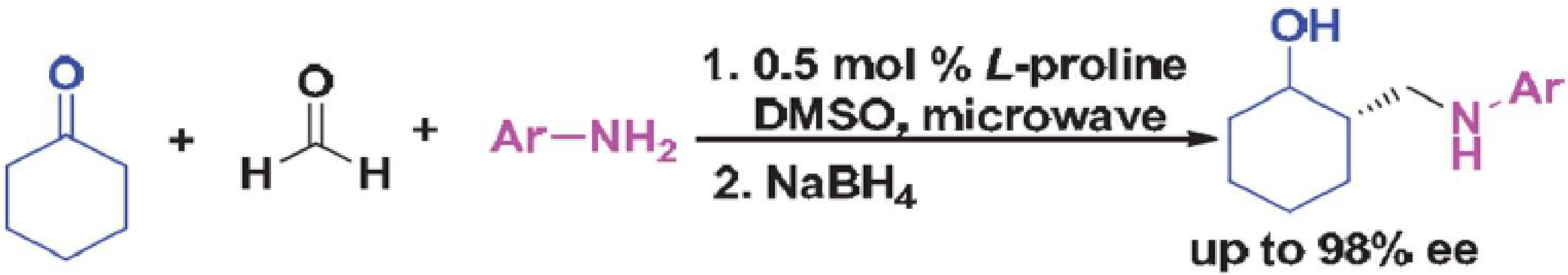
Advantages:

- Control of temperature and pressure
- Perform reactions impossible by conventional heating
- Dramatic reduction in reaction time (from days and hours to minutes).



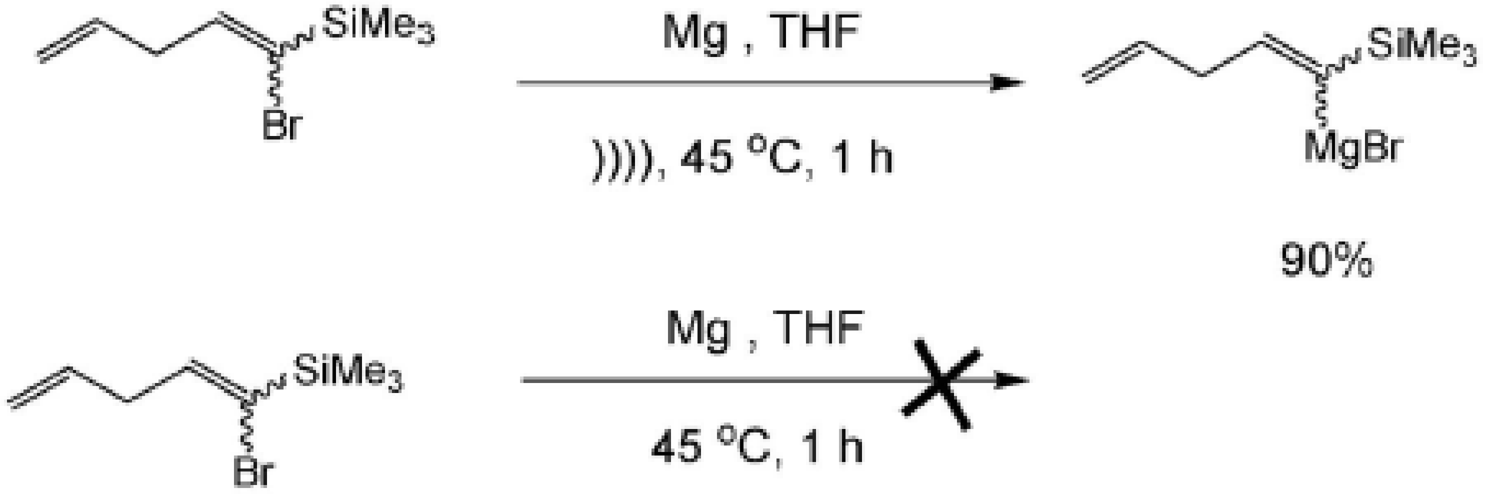
- Increase yields

Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L. and Rousell, J., Tetrahedron Letters, (1986) **27**, 279-282.

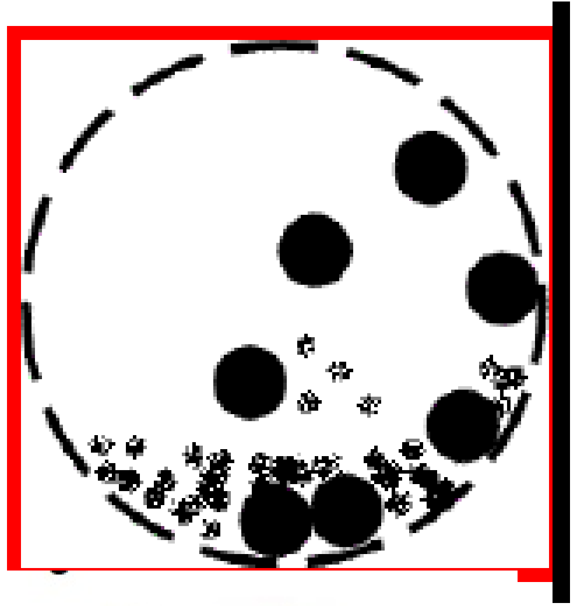


Mannich reactions: Synthesization of β-amino ketones via three-component condensation
B. Rodrıguez and C. Bolm, *J. Org. Chem.* **2006**, *71*, 2888-2891

- Reducation of side reactions
- Improve reproducibility



Scheme 55 Ultrasound-assisted synthesis of vinyl GR.




PM 100

Solvent-free Reactions

24 **25** **26**

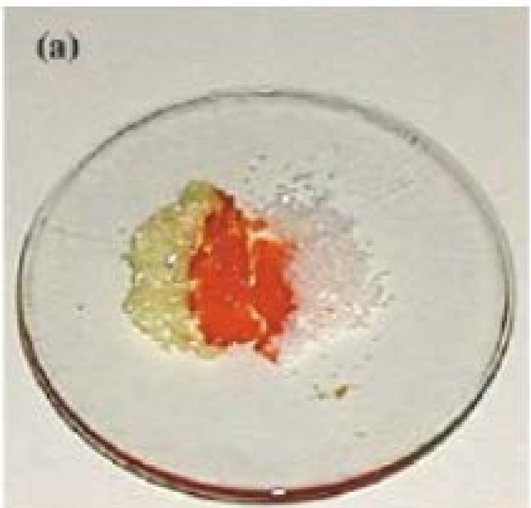
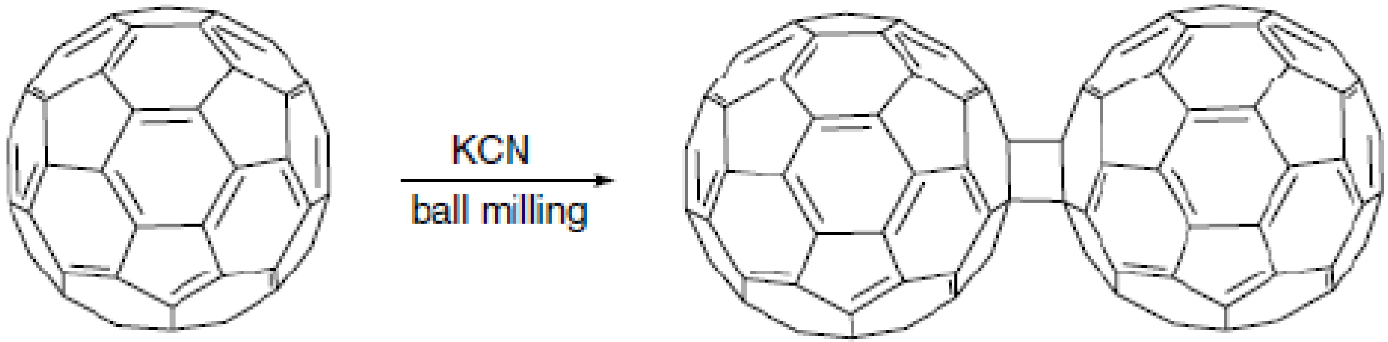
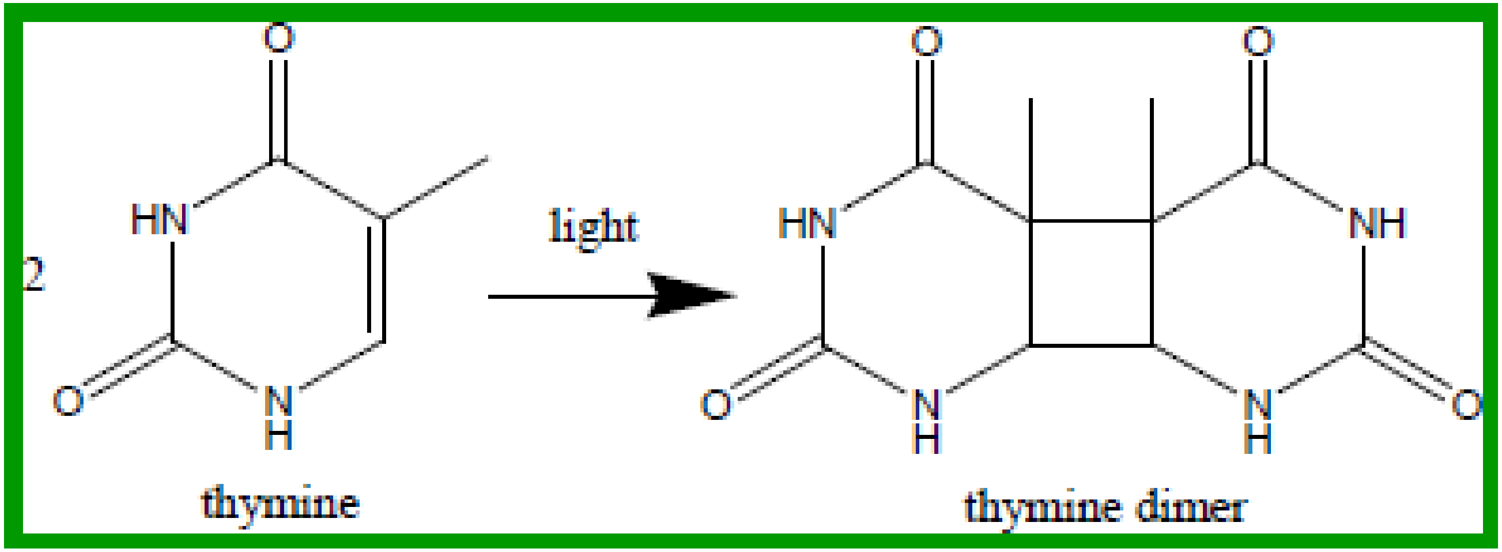


Fig. 7 Photographs of liquid phase formed upon mixing of *o*-vanillin and *p*-toluidine. (*a*) Pale yellow crystalline *o*-vanillin (left) and white crystalline *p*-toluidine (right) form an orange liquid phase upon contact

"Recent Advances in Solventless Organic Reactions: Towards Benign Synthesis with Remarkable Versatility"
G. W. V. Cave, C. L. Raston and J. L. Scotta, *Chem. Commun.*, **2001**, 21, 2159-2169.



Scheme 11.16 *Formation of a novel fullerene dimer under solvent-free ball milling conditions.*



2
O
HN
O
N
H
thymine
light
O
O
HN
NH
O
N
H
N
H
O
thymine dimer

US Presidential Green Chemistry Challenge Awards

Summary of hot key words in the past five years

• Catalysts	15
• Biomass and related	10
• Polymers	9
• Commodity chemicals	5
• Organic solvent & VOCs reduction	5
• Fuels	4
• Drugs and pesticides	4
• Paints	2
• Water	2
• Analysis	2

Supercritical carbon dioxide fluid, critical pressure (31.1 atm), temperature (73.8 C)
non-toxic, non-flammable, inexpensive, environmentally benign
solvating power similar to hexane and CCl_4. extraction decaffeinated coffee.

Replace perchloroethylene (perc) in dry clean
NoDryClean (http://www.nodryclean.com/carbon_dioxide_cleaning.htm)

Examples of catalytic reactions in supercritical fluids

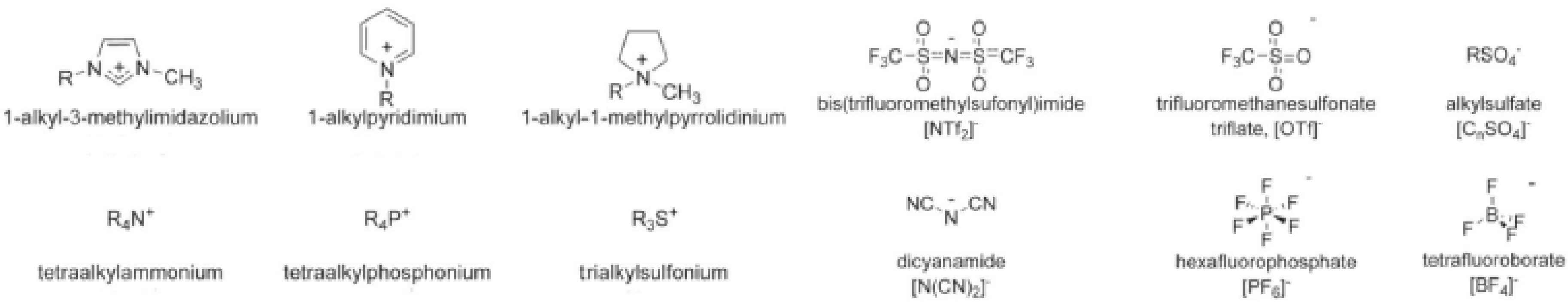
Type of reaction	Reaction	Catalyst	Reaction conditions	Effect
Alkylation	Isobutane + isobutene	H–Y (dealuminated)	Solvent: isobutane, $T = 50–140\,°C$, $P = 3–5\,MPa$	Increase activity, increase lifetime
Esterification	Oleicacid + methanol	Ion-exchange resins	Solvent: CO_2, $T = 40–60\,°C$, $P = 0.9–1.3\,MPa$	Increase activity
Hydrogenation	Fats and oil	Supported Pd	Solvent: propane, $T = 50–100\,°C$, $P = 7–12\,MPa$	Increase activity, increase selectivity
Isomerization	1-Hexene	Supported Pt	Solvent: CO_2 (cosolvent: pentane), $T = 250\,°C$, $P = 18\,MPa$	Increase activity, selectivity and lifetime
Oxidation	Toluene to benzaldehyde	Co/alumina	Solvent: CO_2, $T = 100–200\,°C$, $P = 8\,MPa$	Increase selectivity

A. Baiker, Chem. Rev. 99 (1999) 453.

Extracted d-limonene from orange peel. L.C. MacKenzie, et al., *Green Chem.*, ***2004, 6, 355-358.***

Ionic liquid

Cations   Anions



- air stable
- no measurable vapor pressure (non volatile)
- lack of flammability
- high conductivity
- high thermal and chemical stability for wide temperature range by fine tuning the variation of cations or anions
- recycling of ionic liquids for re-use was possible without decrease in yield--environmentally friendly

http://ilthermo.boulder.nist.gov/ILThermo/

Targets with high impact

- Fuels
- Polymers
- Paints
- Papers
- Drugs
- Pesticides
- Commodity chemicals

} With high demands worldwide (Drugs, Pesticides, Commodity chemicals)

Biocatalysis

Advantages:

- Highly efficient
- Aqueous phase
- Enantioselective
- Regioselective
- Chemoselective
- Mild conditions
  - low pH
  - low temperature
  - low pressure
- Fewer byproducts
- Simplified processing

Thayer, A. M. *C&EN* **2012**, *90*, 13

2010 Academic Award

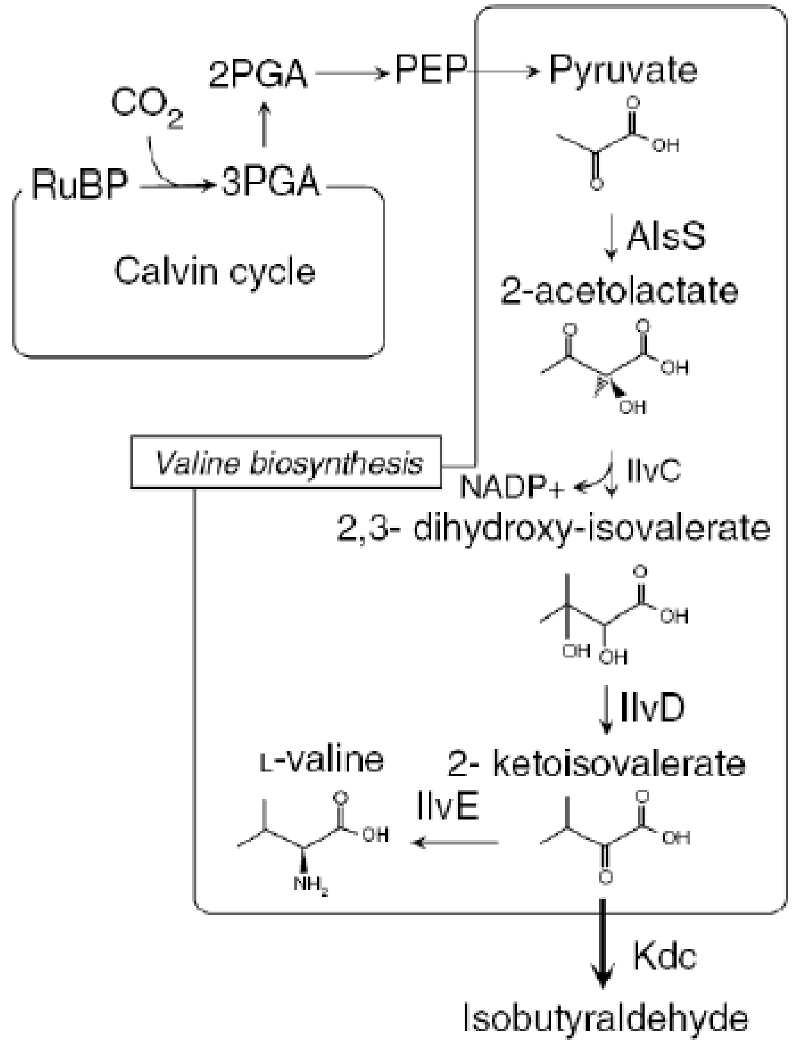
Prof. J. C. Liao
(UCLA and Easel Biotechnologies)

Biochemical recycling of CO_2 to higher alcohols

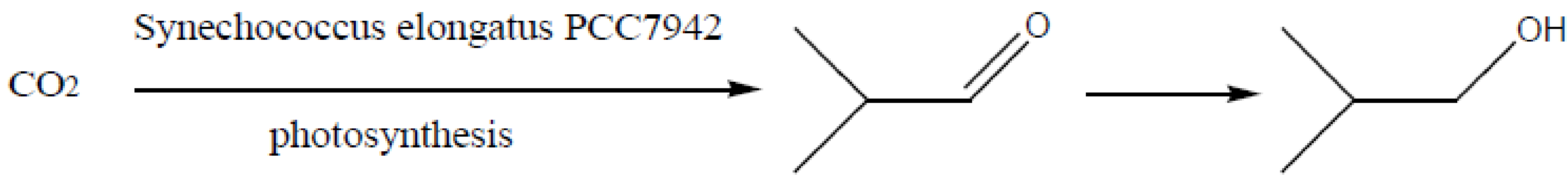
Nature Biotech. **2009**, *27*, 1177

genetically engineered *Synechococcus elongatus* PCC7942

60 billion gal higher alcohols = 8.3% total CO_2 emission in US/yr



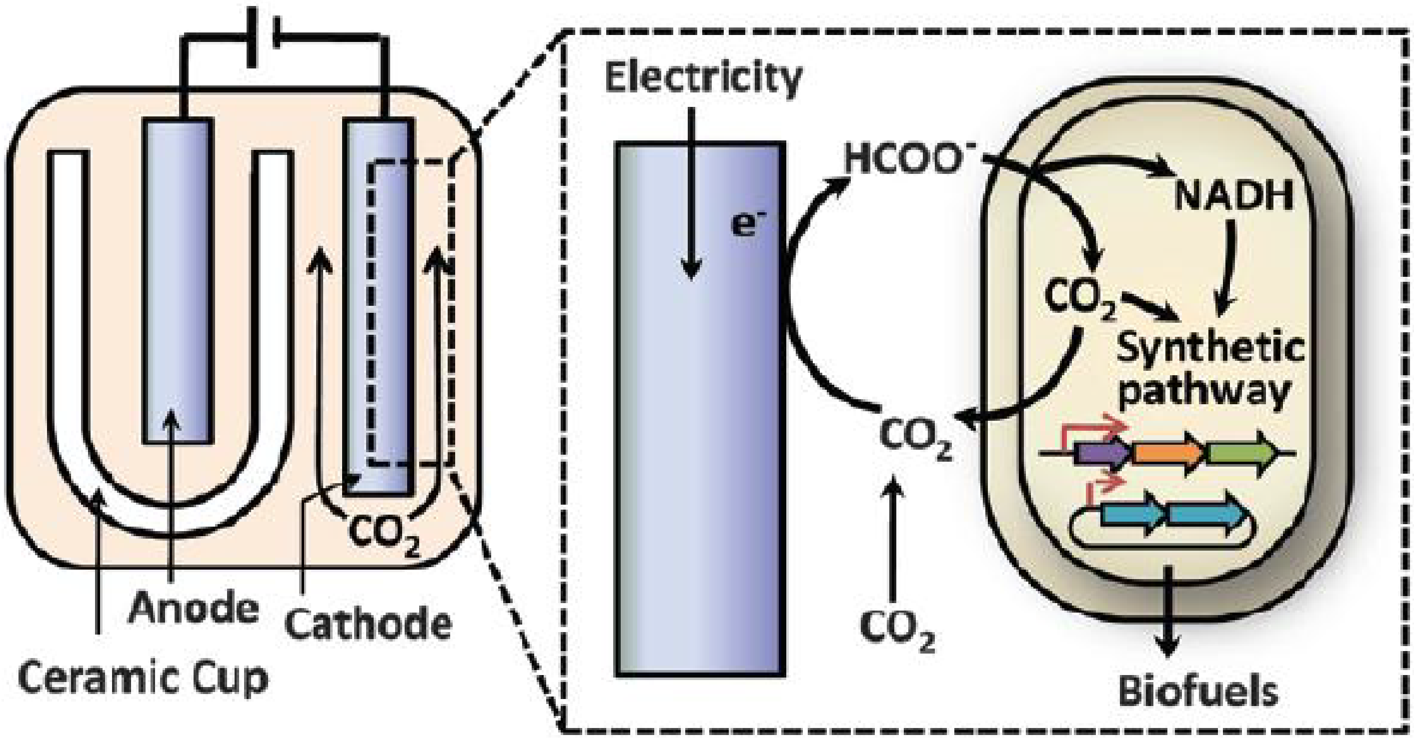
微生物行光合作用由葡萄糖生產異丁醛(isobutylaldehyde)



isobutyraldehyde isobutanol

Prof. J. C. Liao (UCLA and Easel Biotechnologies)

An integrated electromicrobial process to convert CO_2 to higher alcohols



Science **2012**, *335*, 1596

LS9, Inc.

Genetically engineered a variety of microorganisms to act like refineries

Engineered microorganisms

Fermentable sugars → alkanes, olefins, fatty alcohols, or fatty esters

- Eliminates benzene, sulfur, and the heavy metals found in petroleum-based diesel
- 85 percent decrease in greenhouse gas (GHG) emissions
- Competitive price

C&EN

Volume 90 Issue 38 | p. 16 | Concentrates
Issue Date: September 17, 2012

0 0
Email Print

LS9 Starts Up Florida Demonstration Plant

By Melody M. Bomgardner

Department: Business
Keywords: fatty acids, biobased chemicals, biofuels, LS9

Biobased chemicals and fuels firm LS9 has begun producing fatty alcohols from sugar at its first scale-up plant, in Okeechobee, Fla. The facility will be used to generate large commercial samples for testing and qualification by partners and prospective customers. The long-carbon-chain alcohols are used in surfactants for detergents and other applications. LS9 also plans to demonstrate its ability to produce diesel fuel and esters at the plant.

[+]Enlarge

LS9 makes fatty alcohols at this plant in Florida.

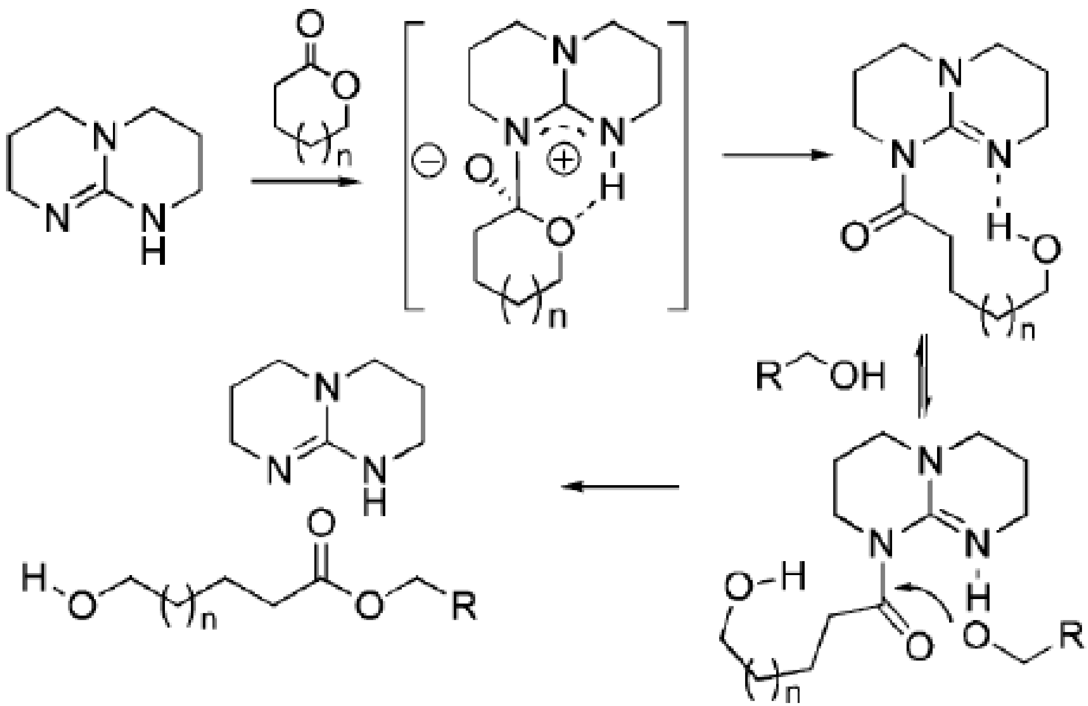
Credit: LS9

Organocatalysts

2012 Academic Award

Prof. R. M. Waymouth (Stanford), Dr. J. L. Hedrick (IBM)

Discovered metal-free catalysts that are highly active and able to make a wide variety of plastics



J. Am. Chem. Soc. **2006**, *128*, 4556

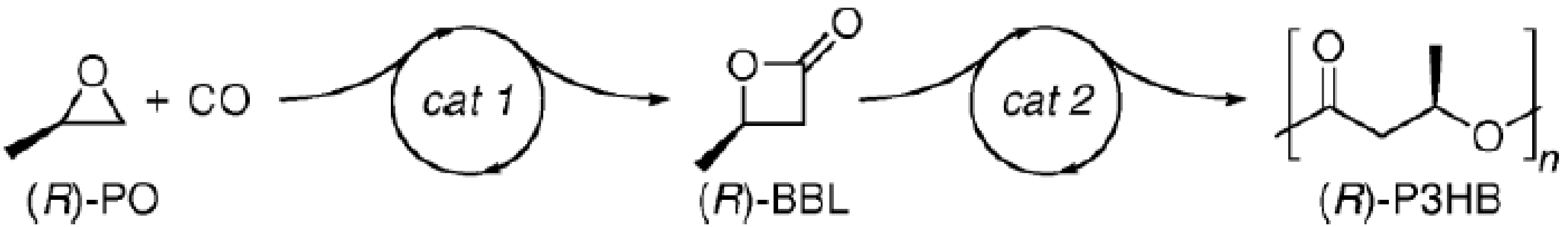
One-Pot Carbonylative Polymerization

2012 **US Presidential Green Chemistry Challenge Awards**

Academic Award

Prof. G. W. Coates (Cornell)

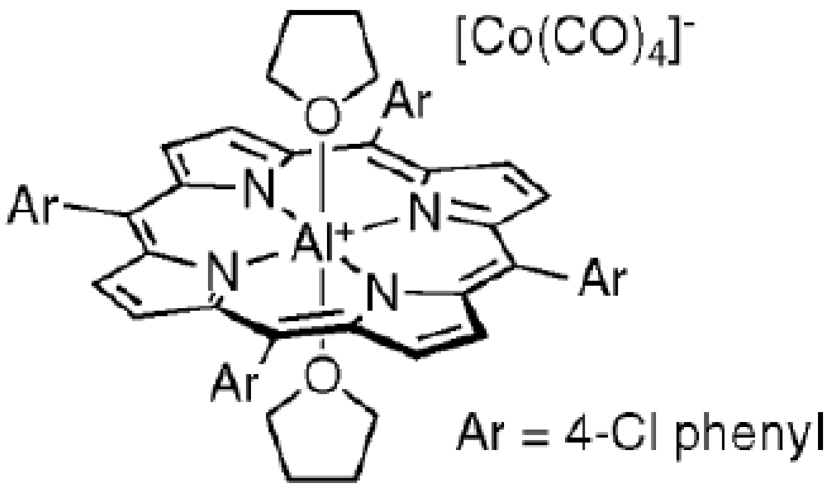
Developed catalysts that convert CO_2 and CO into polymers



J. Am. Chem. Soc. **2010**, *132*, 11412

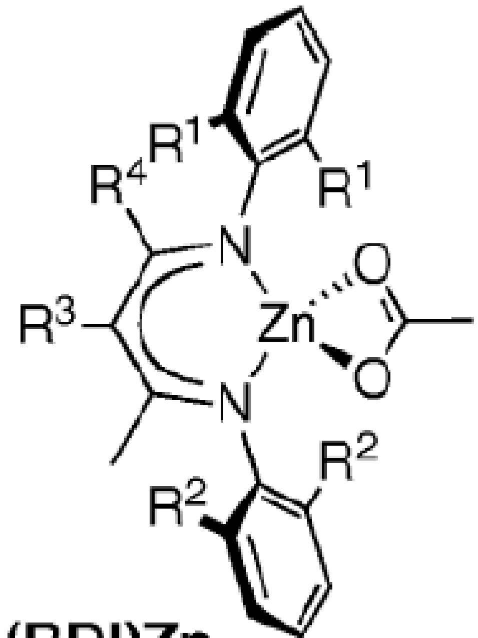
Carbonylation catalyst

0.05 mol %



Polymerization catalyst

0.5 mol %



(BDI)Zn

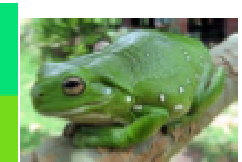
$R^1 = R^2 = {}^iPr$, $R^3 = H$, $R^4 = Me$

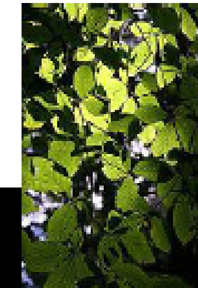
回顧:

What is green chemistry?
什麼是綠色(永續)化學?

- Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- 發明、設計化學產品及其製造過程不涉及或不產生有害物質的化學都可統稱為永續化學. 由於無害可以永續經營.
- Discovery and application of new chemistry/technology leading to prevention/reduction of environmental, health and safety impacts at source
- 探索並應用致使能防止/減少對環境、健康及安全衝擊之源頭的新化學及技術.

520-580 nm





綠色化學=永續化學

P. Tundo, P. Anastas, D. Black, J, Breen, T, Collins, S, Memoli, J, Miyamoto, M, Polyakoff, and W, Tumas, Synthetic pathways and processes in green chemistry. Introductory overview, *Pure and Applied Chemistry, 2000, 72, 1207-1208*

Think!

We do so much to prepare our children for the future, but are we doing enough to prepare the future for our children?

(Larry Chalfan, Zero Waste Alliance, 2001)

我們為了孩子的未來而費盡心力造就他們，但是否費足夠心力造就未來給孩子們嗎？

望子成龍、望女成鳳，但將來是否還有讓龍暢游的大海和供鳳翱翔的天空呢？

It is likely that we will have serious problems in next 20-30 years. Shall we do something now not only for our children, but also for ourselves?

綠色(永續)化學
人人有責

- 對於化學與化學相關的人員，須儘量遵照綠色化學原理與綠色工程原理，在化學(藥)品的設計與發明及製造的過程中不涉及或不產生有毒物質。
- 對於一般百姓普羅大眾，儘量以行動敦促化學與化學相關的人員，遵照綠色化學原理與綠色工程原理，製出化學(藥)品，否則拒絕或減少購買。

致謝

中國化學會與國科會化學中心的

綠色(永續)化學工作坊同仁

包括：

劉廣定教授、蔡蘊明教授、趙奕姼教授、甘魯生教授、周德璋教授、陳月枝教授與許拱北教授的資料

(http://gc.chem.sinica.edu.tw)