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]。

請先閱讀,共四頁.

綠色化學十二項原則

Paul Anastas and John Warner in Green Chemistry: Theory and Practice (Oxford University Press: New York, 1998).

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
避免廢料: 設計化學合成使之避免廢料, 不產生需處理或清理的廢料.

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設計較安全的化學劑和生成物: 設計完全有效而毒性很低或不具毒性的化學產物.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
設計危害性低的化學合成: 設計的合成是用對人類和環境的毒性都很低或不具毒性的反應物也產生同樣毒性很低或不具毒性的生成物.

綠色化學十二項原則

4. Use renewable feedstocks: Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

使用可再生的原料：使用可以再生，而非消耗性的原始物料和材質.再生性原料通常來自農作物或其它製作過程的廢料.而消耗性原料則來自石化燃料(石油.天然氣或煤)或是由採礦而得.

5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

使用觸媒而非化學當量的藥劑：利用觸媒反應將廢料減至最低量.觸媒僅需少量且可重複促成某一反應.觸媒比化學當量藥劑更為優先使用.因為後者常需用過量.且僅能使用一次.

綠色化學十二項原則

6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

避免化學衍生物：盡可能避免使用阻擋或保護群組或任何暫時的修飾. 衍生物須用更多的藥劑而且產生廢料.

7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.

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.

8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

使用較安全的溶劑和反應條件：避免使用溶劑、分離劑或其它輔助劑. 如果是必須時則使用無害的化學藥品.

綠色化學十二項原則

9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.

增加能源效率：盡可能在常溫常壓下進行化學反應.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

設計使用後能分解的化學藥劑和產物：設計使用後能分解為無害物的化學產物.以使它們不會在自然環境裡累積.

11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

瞬時分析已防污染：在合成過程中加入瞬時監管和控制.使副產物降至最低或不產生.

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

使發生意外的可能降到最低：設計化合物及它們的狀態(固態.液態,或氣態)以使發生化學意外的可能降到最低,包括爆炸、起火及波及周遭環境.

綠色/永續合成化學工作坊

中國化學會環境與化學委員會

國科會化學研究推動中心

綠色/永續化學原則與指標

甘魯生 博士

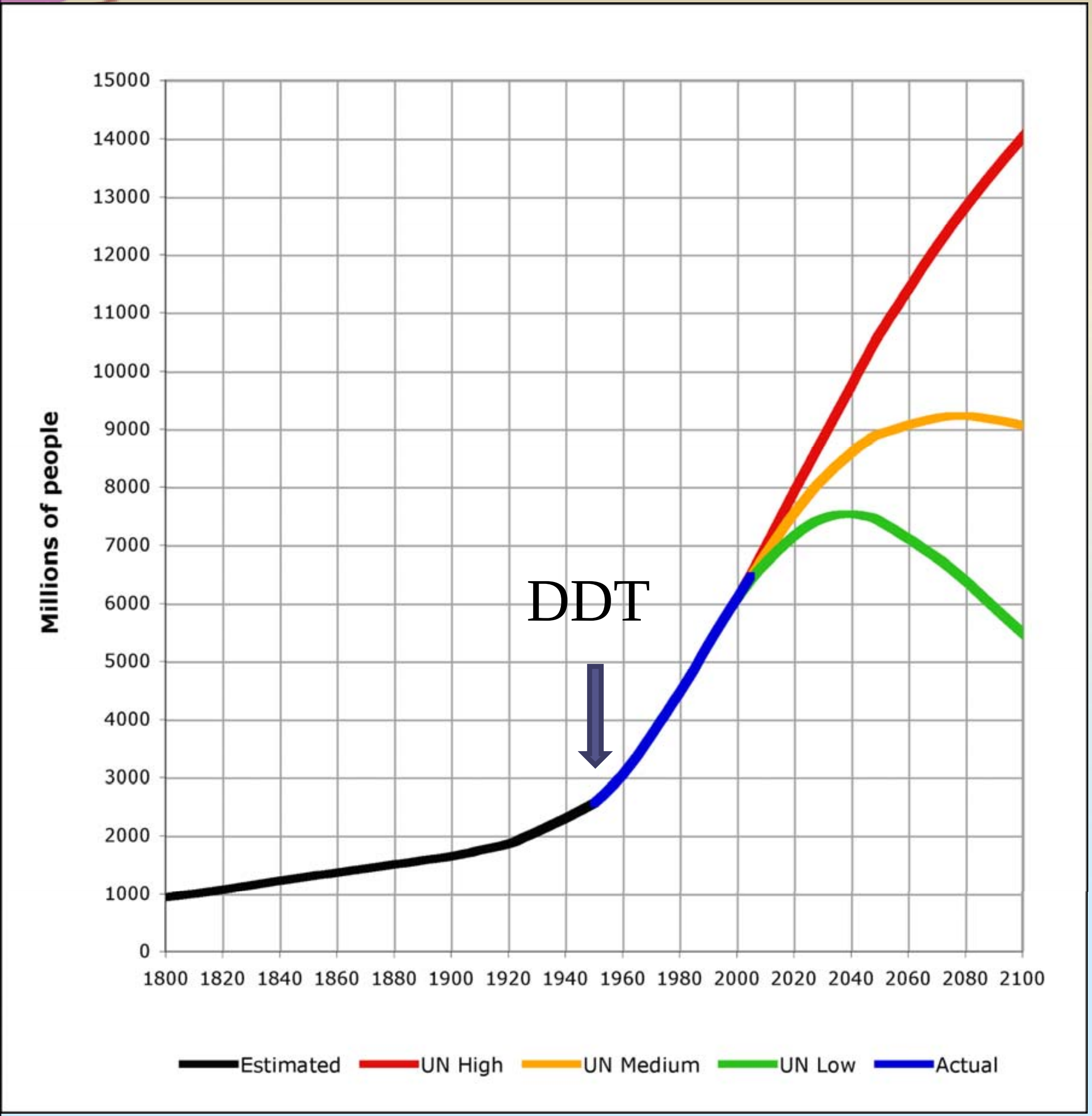
大同大學講座教授

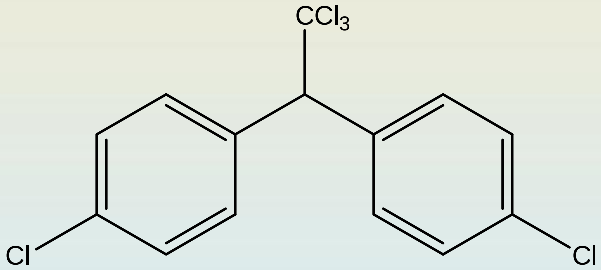
中央研究院合聘研究員

May 7, 2010

為什麼需要綠色化學?

化學改變了世界, 改善了人的衣、食、住、行, 給人們增添財富, 帶來幸福, 帶來了醫藥革命, 製造了大量化肥和農藥, 使農產品增產, 冶煉了各式各樣的合金、合成了塑膠、橡膠、纖維. 以這些為原料製成了汽車、飛機、高樓、電腦、化粧品等數不清的物品. 在這些生產過程中向自然界釋放大量的合成物質. 導至人類賴以生存的環境遭到嚴重的破壞. 綠色化學就是以好的化學替代壞的化學, 新的化學替代舊的化學.





dichloro**d**iphenyl**t**richloroethane

http://en.wikipedia.org/wiki/World_population

What is green chemistry? 什麼是綠色化學?

•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綠色化學. 由於無害可以永續經營, 亦稱之為永續化學.

•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.

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*

綠色化學十二項原則

Paul Anastas and John Warner in Green Chemistry: Theory and Practice (Oxford University Press: New York, 1998).

Dr. Joseph Breen

Dr. Paul T. Anastas

Dr. John C. Warner

The **Presidential Green Chemistry Challenge Awards Program** (EPA and GCI, USA) is an opportunity for individuals, groups, and organizations to compete for annual awards in recognition of innovations in cleaner, cheaper, smarter chemistry.

- Focus Area 1: An industry sponsor for a technology that uses greener synthetic pathways.
- Focus Area 2: An industry sponsor for a technology that uses greener reaction conditions.
- Focus Area 3: An industry sponsor for a technology that includes the design of greener chemicals.
- Small Business: A small business for a green chemistry technology in any of the three focus areas.
- Academic: An academic investigator for a technology in any of the three focus areas.

EXIT Disclaimer

Presidential Green Chemistry Challenge Awards

Since the program's inception in 1995, it has recognized 67 groundbreaking developments out of hundreds of applications. According to EPA statistics, these technologies combined will eliminate an estimated 193 million lb of hazardous chemicals and solvents, 21 billion gal of water, and 57 million lb of carbon dioxide from industrial processing in the U.S. this year *.

*till 2008.
Chem. & Eng. News (Sustainability special issue), August 18, 2008
http://pubs.acs.org/cen/coverstory/86/8633cover3.html

2001 Academic Award Professor Chao-Jun Li ,Tulane University
2000 Academic Award Professor Chi-Huey Wong, The Scripps Research Institute

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

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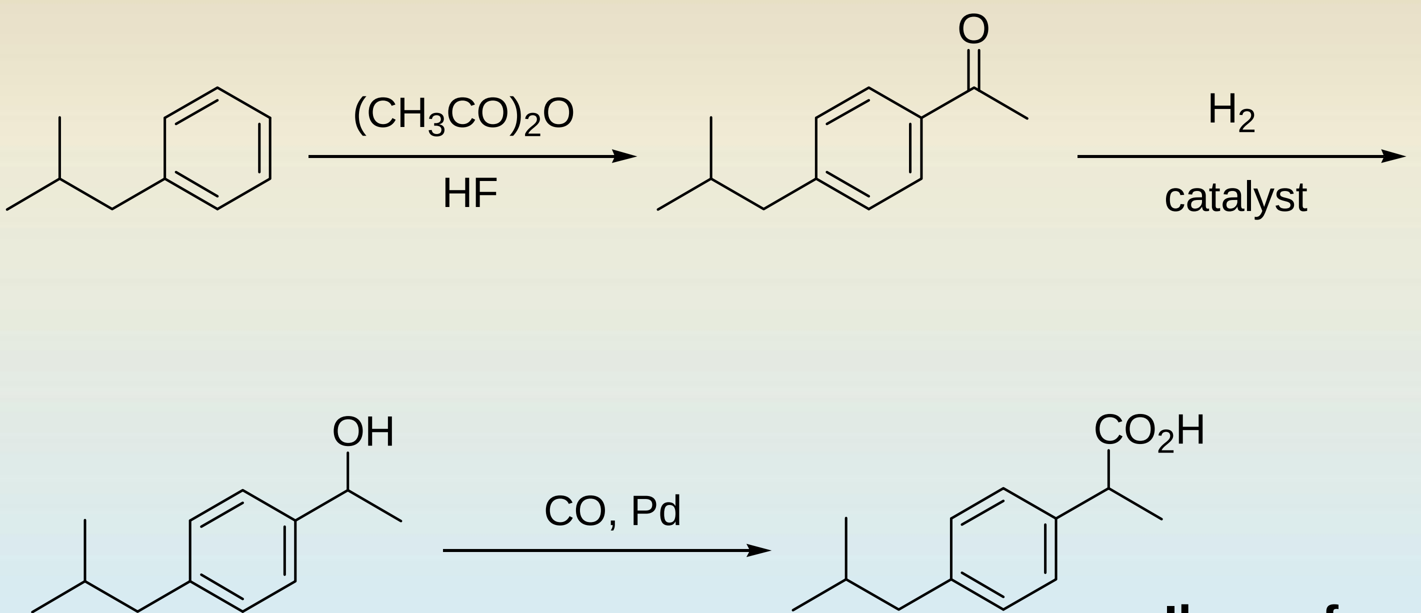
止痛藥(Advil, Motrin) Ibuprofen Boots Co. 之合成方法(U.S. Patent 3,385,886, 1960)

止痛藥(Advil, Motrin) Ibuprofen 之BHC Co 合成方法

(BHC = Boots + Hoechst Celanese Corporation http://www.answers.com/topic/hoechst-celanese-corporation)



Ibuprofen

6 ⟶ 3 步驟　　■效率 40 ⟶ 80%

- **1997 Greener Synthetic Pathways Award**

BHC Company (now BASF Corporation http://www.basf.com/group/corporate/en/)

Ibuprofen Process

- 綠色/永續化學網路資源共享網（http://gc.chem.sinica.edu.tw）

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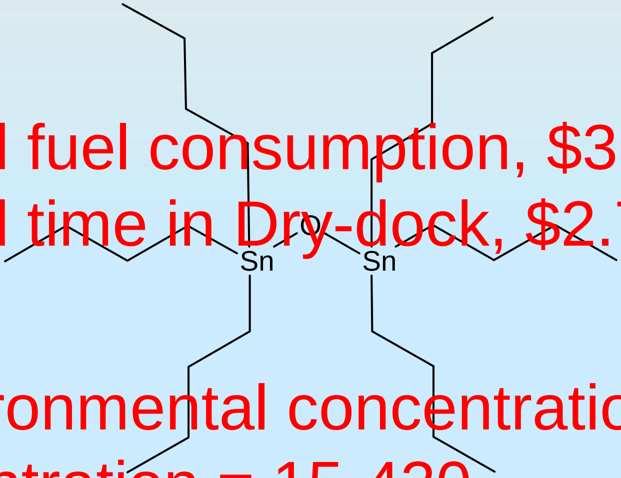
1996 Designing Greener Chemicals Award
Rohm and Haas Company
Inn

Ro ... ea
物 ... pla
sh ... 物
ap ... r in
Se ... ne
co
(貝 ... 外
年 ... 不
加二氧化碳的排放。)

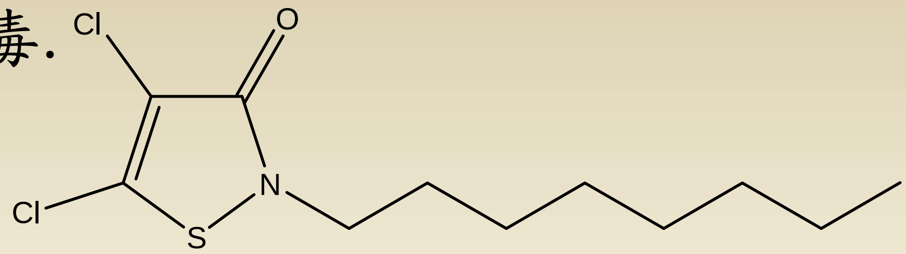
舊防污物質： tributyltin oxide
(三丁烷基錫氧化物)
半衰期大於6個月
對多種海洋生物有影響



Increased fuel consumption, $3 billion/year
Increased time in Dry-dock, $2.7 billion/year

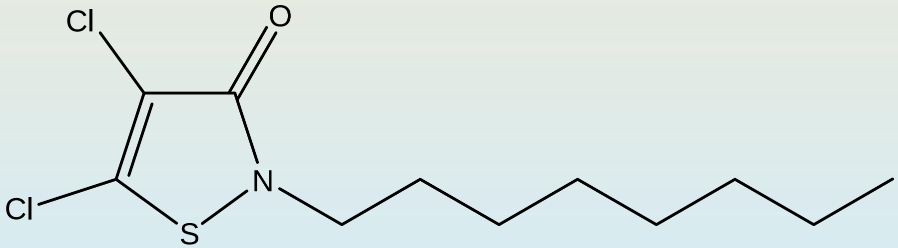
Risk Quotient = predicted environmental concentration / predicted no-effect environmental concentration = 15-430

Rohm and Haas公司篩檢了140多化合物之物, 找到4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine™ antifoulant). Sea-Nine和TBTO一樣對海洋的生物有劇毒.



半衰期小於一小時
降解為無毒物質

Sea-Nine 生物降解途徑



→ $C_8H_{17}NHC(O)CH_2COOH$

↓

$C_8H_{17}NHCOOH$ ← $C_8H_{17}NHC(O)COOH$ ← $C_8H_{17}NHC(O)CH_2CH_3$

Risk Quotient = 0.024-0.36 vs. TBTO 15-430

D. K. Larsen, I. Wagner, K. Gustavson, V. E. Forbes, T. Lund, Long-term effect of Sea-Nine on natural coastal phytoplankton communities assessed by pollution induced community tolerance, Aquatic Toxicology 62 (2003) 35/44

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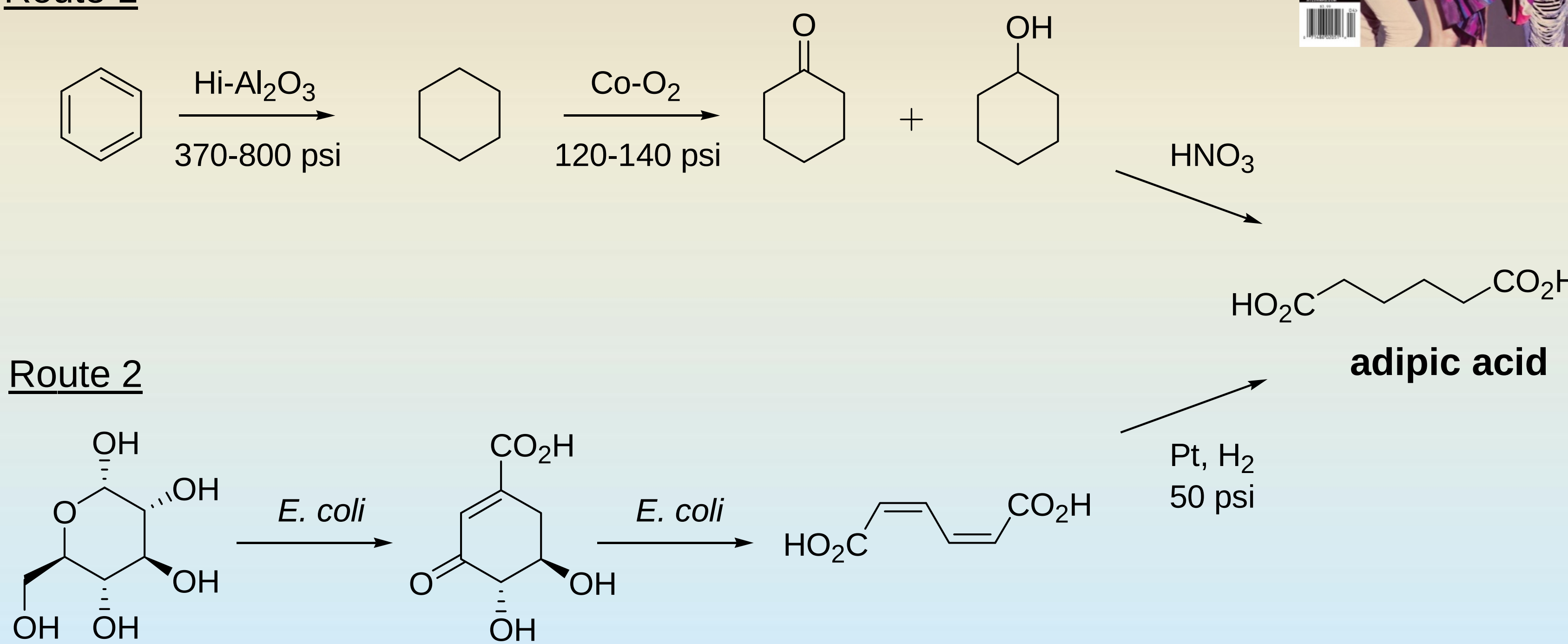
合成nylon的重要原料 – adipic acid

Route 1



■ Route 2 以葡萄糖代替苯，並減少使用高壓反應條件

Benzene-Free Synthesis of Adipic Acid, Wei Niu, K. M. Draths, and J. W. Frost, Biotechnol. Prog. 2002, 18, 201-211.

綠色/永續化學網路資源共享網（http://gc.chem.sinica.edu.tw）

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- Homogeneous catalysis
- Heterogeneous catalysis
- Organo-catalysis
- Bio-catalysis
- Photo-catalysis

Bio-catalysis

- Fast reaction due to correct catalyst orientation（加快反應）
- High degree of selectivity; possible for asymmetric synthesis（立體結構選擇性高）
- Water soluble（水溶, 可在水溶液進行）
- Naturally occurring; non-toxic, low hazard（自然發生, 毒性低）
- Energy-efficient reactions under moderate conditions of pH, temperature（反應溫和, 省能）
- Possibility for carrying out sequential one-pot synthesis（可進行一罐反應）

2009 **Academic Award**
Professor Krzysztof Matyjaszewski , Carnegie Mellon University
Atom Transfer Radical Polymerization: Low-impact Polymerization Using a Copper Catalyst and Environmentally Friendly Reducing Agents
2007 **Greener Reaction Conditions Award**
Headwaters Technology Innovation
Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology
2006 **Greener Reaction Conditions Award**
Codexis, Inc.
Directed Evolution of Three Biocatalysts to Produce the Key Chiral Building Block for Atorvastatin, the Active Ingredient in Lipitor®
2003 **Greener Synthetic Pathways Award**
Süd-Chemie Inc.
A Wastewater-Free Process for Synthesis of Solid Oxide Catalysts
2001 **Academic Award**
Professor Chao-Jun Li, Tulane University
Quasi-Nature Catalysis: Developing Transition Metal Catalysis in Air and Water
1999 **Greener Synthetic Pathways Award**
Lilly Research Laboratories
Practical Application of a Biocatalyst in Pharmaceutical Manufacturing
1998 **Academic Award**
Dr. Karen M. Draths and Professor John W. Frost
Michigan State University
Use of Microbes as Environmentally Benign Synthetic Catalysts
Presidential Green Chemistry Challenge, *http://www.epa.gov/gcc/pubs/pgcc/presgcc.html*

綠色化學十二項原則

6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

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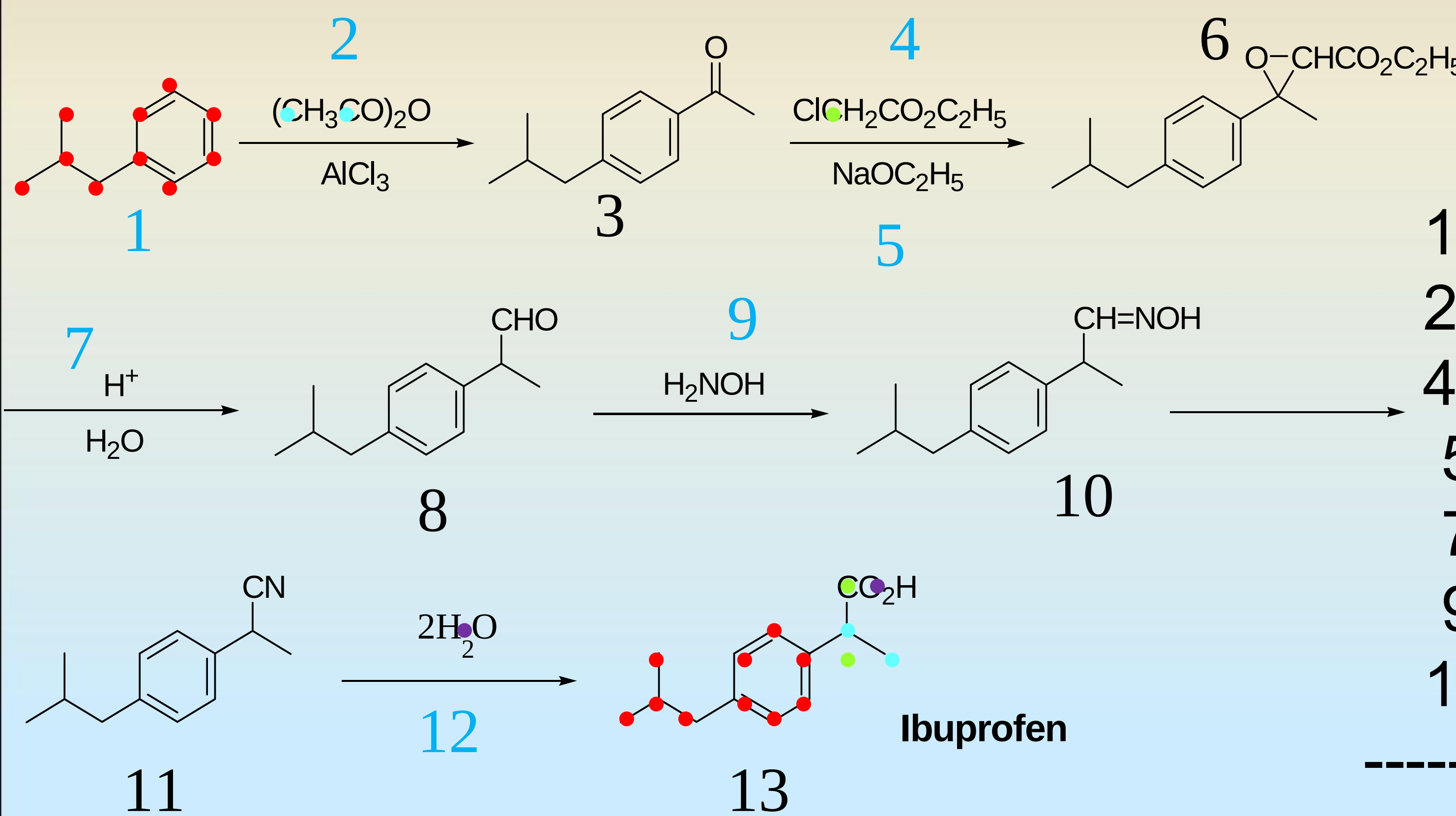
Atom Economy (原子經濟指標) =
m.w. of G x 100%/ Σ (m.w. A,B,D,F)
for a generic multi-stage reaction:

$A + B \rightarrow C \quad C + D \rightarrow E \quad E + F \rightarrow G$

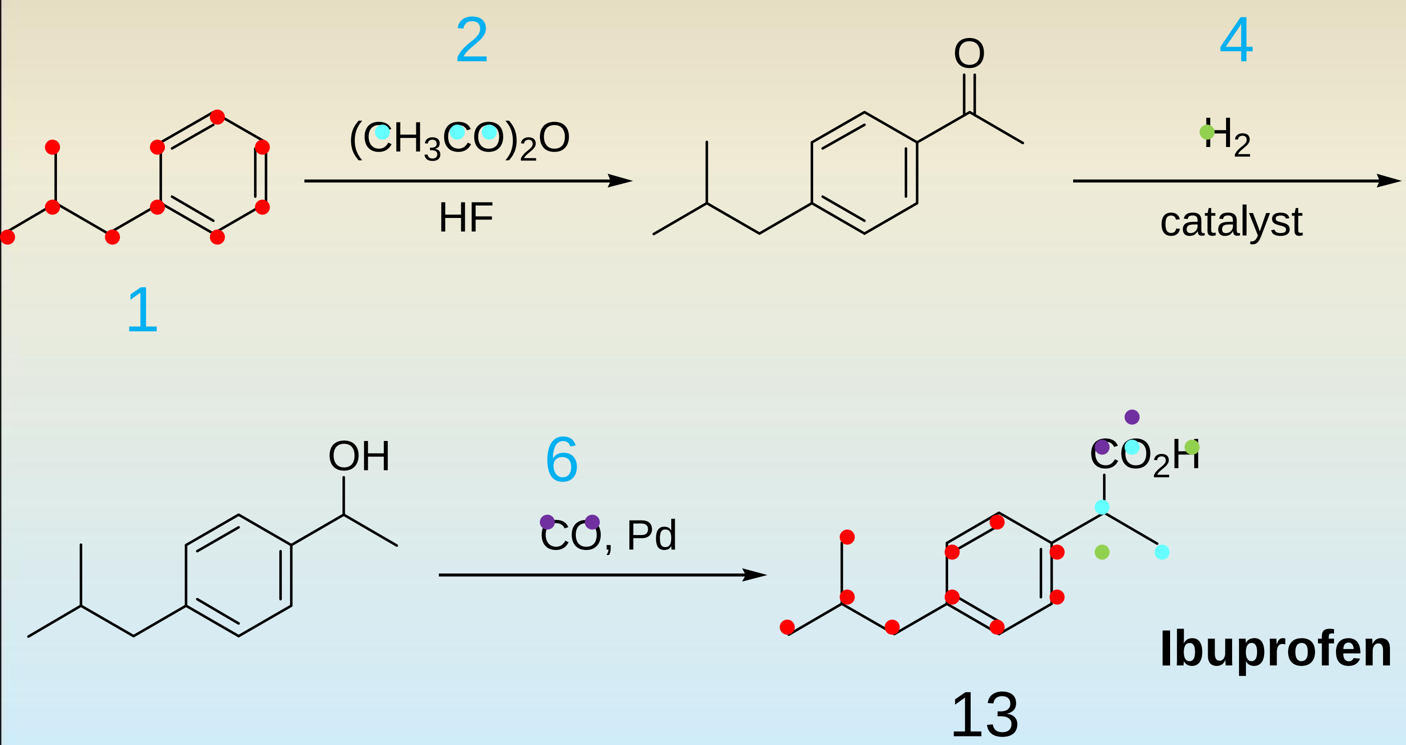
(Introduced by Barry Trost, Stanford University)



	m.Wt.	used
1	133	132
2	102	27
4	122.5	13
5	68	0
7	19	0
9	33	0
12	36	33
	514.5	206

A.E.=206/514.5=40%

BHC Co. Synthesis of Ibuprofen



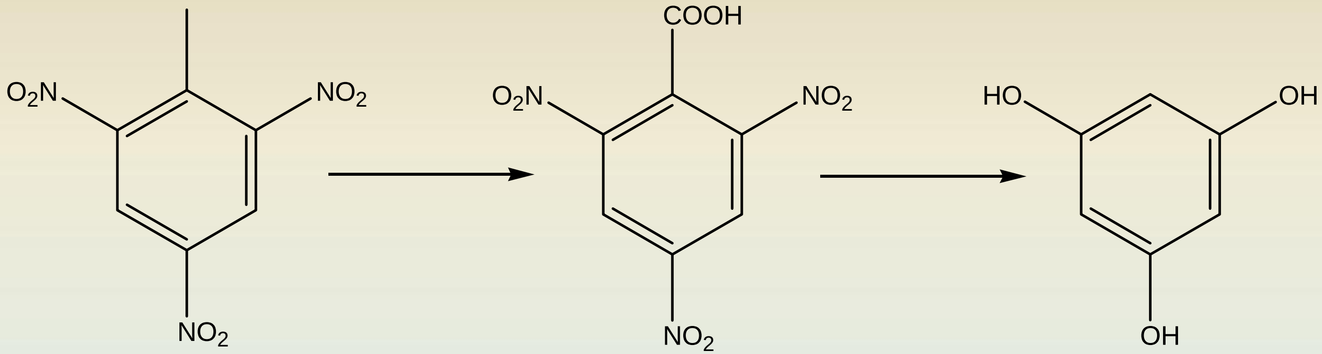
	m.Wt.	used
1	133	132
2	102	43
4	2	2
6	28	28
	266	206

A. E.=206/266=77%

Environmental (E) factor

E-Factor = Total Waste (kg) / Product (kg)　(廢料總量/產物總量)

The wastes of the synthesis of phloroglucinol (藤黃酚) from TNT.



TNT was oxidized by dichromate/sulfuric acid and then followed by Bechamp reduction with iron and hydrochloric acid to give phloroglucinol.

The wastes involved are $Cr_2(SO_4)_3$, NH_4Cl, $FeCl_2$, and $KHSO_4$.

40 kg wastes produced when 1 kg of phloroglucinol obtained.

E = 40 (However, the atom utilization is 5%.)

R. A. Sheldon, E Factors, green chemistry and catalysis: an odyssey, Chem. Commun., 2008, 3352-3365.

Environmental (E) factor

E-Factor = Total Waste (kg) / Product (kg)　(廢料總量/產物總量)

R. A. Sheldon, Chem. Commun., 2008, 3352-3365.

E-Factors across the chemical industry
(各類化學工業之 E-因子)

Industry Sector	Annual Production (ton)	E-Factor	Waste Produced (ton)
Oil Refining (煉油產品)	10^6-10^8	Ca. 0.1	10^5-10^7
Bulk Chemicals (大宗化學產品)	10^4-10^6	<1-5	10^4-5×10^6
Fine Chemicals (精細化學品)	10^2-10^4	5-50	5×10^2-5×10^5
Pharmaceuticals (藥)	10-10^3	25-100	2.5×10^2-10^5

廢棄物的代價

原料成本高
廢棄物處理帶來額外的開支

難以處理的公共關係
不利永續經營

健康的危害
環境的破壞

綠色化學十二項原則

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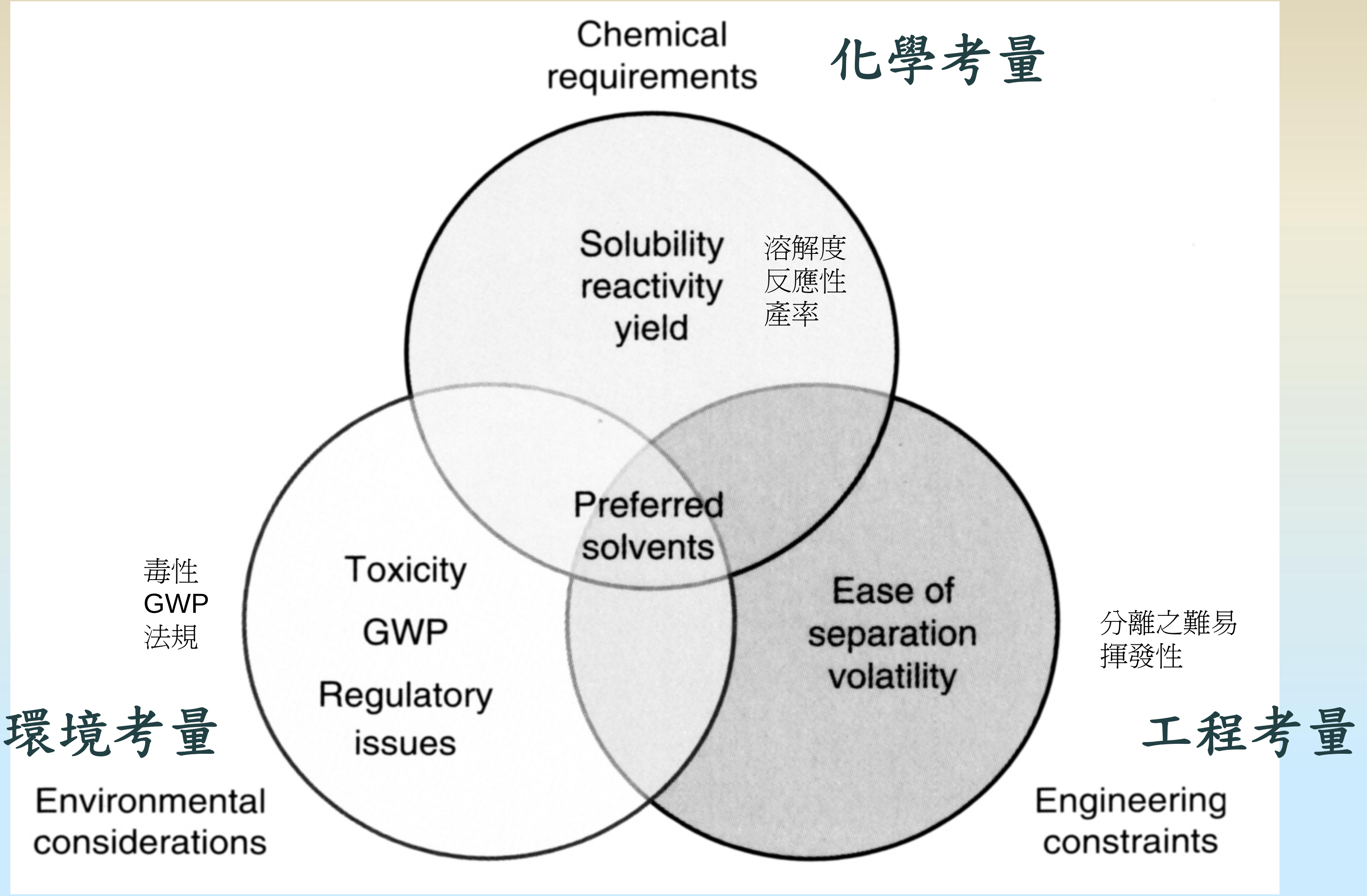
使用較安全的溶劑和反應條件：避免使用溶劑. 分離劑或其它輔助劑. 如果是必須時則使用無害的化學藥品.

Conceptual basis for preferable solvent selection
（選擇溶劑之考量）



Green Chemistry Metrics, p.22 (Blackwell, 2009)

Pfizer公司在藥物化學溶劑應用的規範

優先考慮	可用	不理想的
water	cyclohexane	pentane
acetone	heptanes	hexane
ethanol	toluene	di-isopropyl ether
2-propanol	methylcyclohexane	diethyl ether
1-propanol	methyl t-butyl ether	dichloromethane
ethyl acetate	isooctane	dichloroethane
isopropyl acetate	acetonitrile	chloroform
methanol	2-methylTHF	dimethyl formamide
methyl ethyl ketone	tetrahydrofuran	N-methylpyrrolidinone
1-butanol	xylenes	pyridine
t-butanol	dimethyl sulfoxide	~~dimethyl acetate~~
	acetic acid	dioxane
	ethylene glycol	dimethoxyethane
		benzene
		carbon tetrachloride

K. Alfonsi, *et al.*, *Green Chem*. **2008**, *10*, 31-36

Table 2 Solvent replacement table

Undesirable solvents	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or *N*-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine used as base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

K. Alfonsi, et al., Green Chem. ***2008****, 10, 31-36*

Searching for benign solvents (尋求無害溶劑)

Water (水)

Non-volatile solvents (ionic)
（非揮發性溶液）（離子）

Supercritical solvents
（超臨界溶劑）

Other benign solvents
（其他）

Solventless
（無溶劑）

Replace
（替代）

Volatile organic
and
hazardous
solvents
(揮發和有害溶劑)

Ionic solvents (離子溶劑)

2005 Academic Award, Professor Robin D. Rogers

The University of Alabama

A Platform Strategy Using Ionic Liquids to Dissolve and Process Cellulose for Advanced New Materials

Innovation and Benefits: Professor Rogers developed methods that allow cellulose from wood, cloth, or even paper to be chemically modified to make new biorenewable or biocompatible materials. His methods also allow cellulose to be mixed with other substances, such as dyes, or simply to be processed directly from solution into a formed shape. Together, these methods can potentially save resources, time, and energy.

1-butyl-3-methylimidazolium chloride ([C4mim]Cl),

氯化1-丁基-3-甲基咪唑鎓

recyclable

J. Am Chem Soc. 2002 May 8;124(18):4974-5.

以離子溶劑替代有機溶劑

1-butyl-3-methyl-4,5-dihydroimidazolinium iodide and 1-butyl-3-methyl-4,5-dihydroimidazolinium hexafluorophosphate 替代高極性有機溶劑如dimethyl formamide, 1,3-dimethyl-2-imidazolidinone, 和 dimethyl sulphoxide 高溫度下反應. 產率大多數能達九成以上.

Gok, Ozdemis, Cetinkaya, Chinese Journal of Catalysis, vol. 28, 489-491 (2007).

Supercritical Fluid（超臨界液體）

2002 Academic Award Professor Eric J. Beckman, University of Pittsburgh

Design of Non-Fluorous, Highly CO_2-Soluble Materials

Professor Beckman's simple heuristic model was demonstrated on three sets of materials: functional silicones; poly(ether-carbonates); and acetate-functional polyethers. Poly(ether-carbonates) were found to exhibit lower miscibility pressures in CO_2 than perfluoropolyethers, yet are biodegradable and 100 times less expensive to prepare. Other families of non-fluorous CO_2-philes will inevitably be discovered using this model, further broadening the applicability of CO_2 as a greener process solvent.

Presidential Green Chemistry Challenge, *http://www.epa.gov/gcc/pubs/pgcc/presgcc.html*

E. J. Beckman, et al., Design and evaluation of nonfluorous CO2-soluble oligomers and polymers. J Phys Chem B. 2009 Nov 12;113(45):14971-80.

Solventless synthesis (無溶劑合成)

2009 Greener Synthetic Pathways Award

Eastman Chemical Company

A Solvent-Free Biocatalytic Process for Cosmetic and Personal Care Ingredients

Innovation and Benefits: Esters are an important class of ingredients in cosmetics and personal care products. Usually, they are manufactured by harsh chemical methods that use strong acids and potentially hazardous solvents; these methods also require a great deal of energy. Eastman's new method uses immobilized enzymes to make esters, saving energy and avoiding both strong acids and organic solvents. This method is so gentle that Eastman can use delicate, natural raw materials to make esters never before available.

Old: esters are manufactured using strong acid catalysts at high temperatures, or require organic solvents.

Kodak: a variety of esters are synthesized via enzymatic (lipase) esterifications at mild temperatures.

綠色化學十二項原則

9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.

增加能源效率：盡可能在常溫常壓下進行化學反應.

Alternative energy source (其他能源)

- Photochemical reactions (光化學反應)
  - Specific bond targeted
  - Low reaction temperature/higher selectivity
- Microwave-assisted reactions (微波輔助反應)
  - Fast heating rate by rotation friction (10 ºC per second)
  - Target molecules with dipole
- Sonochemistry (超音波化學)
  - Generate local high pressure and temperature
- Electrochemical synthesis (電化學合成)
  - Often water-based
  - Usually mild operating conditions
  - Atom efficient – replacement of reagents by electrons

綠色化學十二項原則

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

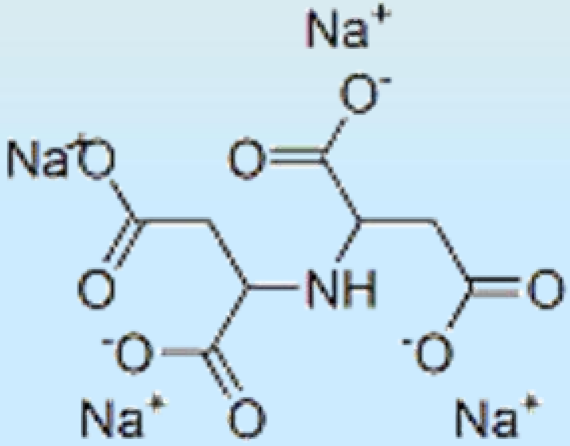
設計使用後能分解的化學藥劑和產物：設計使用後能分解為無害物的化學產物.以使它們不會在自然環境裡累積.

2001 **Greener Synthetic Pathways Award**

Bayer Corporation, Baypure™ CX (Sodium Iminodisuccinate)

An Environmentally Friendly and Readily Biodegradable Chelating Agent (可分解之鍵結劑)

Innovation and Benefits: Chelating agents are ingredients in a variety of products, such as detergents, fertilizers, and household and industrial cleaners. Most traditional chelating agents do not break down readily in the environment. Bayer Corporation and Bayer AG developed a waste-free, environmentally friendly manufacturing process for a new, biodegradable, nontoxic chelating agent. This new process eliminates the use of formaldehyde and hydrogen cyanide.



TETRASODIUM IMINIDISUCCINATE

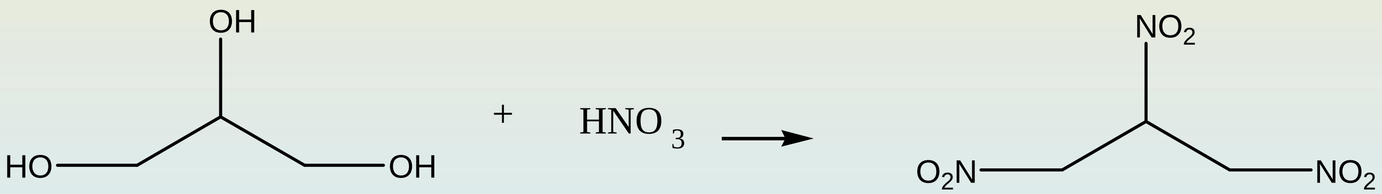
http://www.chemicalbook.com/ChemicalProductProperty_EN_CB6120799.htm

綠色化學十二項原則

11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

瞬時分析以防污染：在合成過程中加入瞬時監管和控制.使副產物降至最低或不產生.

例：Nitroglycerin 硝化甘油之合成



甘油加 1:1 濃硝酸及濃硫酸而成.

此反應產生大量之熱,要時時注意反應爐不能過熱.昔日工人坐在一枝腳的椅子上,只要一打瞌睡,人就會從椅子上跌下來.

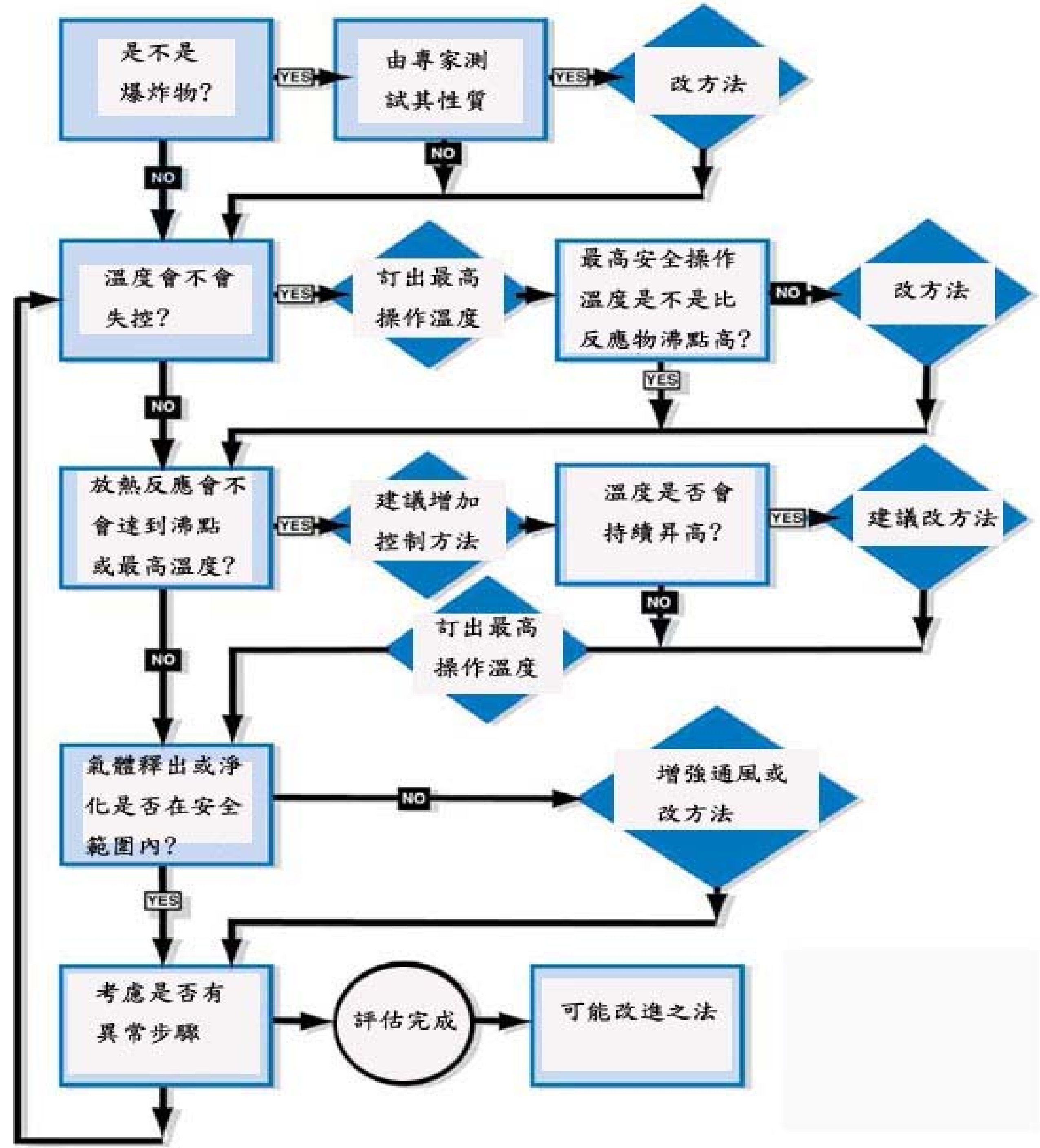
反應爐中裝太多東西是因為反應太慢.於是要改良鍋爐.

新的反應器如同一水的噴射器,酸從噴口噴出,產生的真空將甘油吸入,混合非常均勻,另外一個好處是可控制比例.

反應器裝一緊急洩氣閥,一打開真空被打破,就會停止供應甘油.

改變合成步驟：將攪拌式改為循環式,加快反應.

測驗流程



是不是爆炸物?
YES
由專家測試其性質
YES
改方法
NO
NO
溫度會不會失控?
YES
訂出最高操作溫度
最高安全操作溫度是不是比反應物沸點高?
NO
改方法
YES
NO
放熱反應會不會達到沸點或最高溫度?
YES
建議增加控制方法
溫度是否會持續昇高?
YES
建議改方法
NO
訂出最高操作溫度
NO
氣體釋出或淨化是否在安全範圍內?
NO
增強通風或改方法
YES
考慮是否有異常步驟
評估完成
可能改進之法

綠色化學十二項原則

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

使發生意外的可能降到最低：設計化合物及它們的狀態(固態.液態,或氣態)以使發生化學意外的可能降到最低,包括爆炸、起火及波及至周遭環境.

什麼是風險評估?

找出危害

評估甚麼人和如何會受到危害

作紀錄

向有關單位匯報

(防災止難, 人人有責)

重大的危害

火（不適當化合混合、意外點火、危險動作如燒焊、抽菸、外來的因素如撞擊、閃電、其他地方燒過來）

爆炸（火、撞擊、高壓氣體、不能控制放熱反應）

釋出有毒物質

釋出腐蝕物質

(作最壞的打算)

化學作業處理之管理作業指南及安全操作規範

改變及修飾規範

作業人員訓練

日常檢查及審核

緊急應變措施

工作環境之維護

(大都由人的疏忽而造成. 一定要照規章進行)

Designing and operating safe chemical reaction processes

Condensed Principles of Green Chemistry
（綠色化學十二原則再次審視）

P – Prevent wastes（防止廢料）
R – Renewable materials（用可再利用物質）
O – Omit derivatztation steps（省去衍生物步驟）
D – Degradable chemical products（化學物可自行分解）
U – Use safe synthetic methods（採用安全的合成法）
C – Catalytic reagents（利用催化物）
T – Temperature, Pressure ambient（在常溫、常壓下合成）
I – In–Process Monitoring（追踪合成過程）
V – Very few auxiliary substances（少用輔助物）
E – E-factor, maximize feed in product（常將E-因子瞭然於胸）
L – Low toxicity of chemical products（採用低毒化學物）
Y – Yes, it is safe（對, 就是要安全）

Twelve principles of green chemistry written in the form of a mnemonic: PRODUCTIVELY (12原則的英文字頭合起來成了英文 PRODUCTIVELY=有成果地）

S. L. Y. Tang, R. L. Smith, M. Poliakoff, Green Chem., 2005, 7, 761-762

Answers for quiz

1=p, 2=e, 3=u, 4=l, 5=v, 6=t, 7=r, 8=o, 9=c, 10=d, 11=I, 12=y

12 Principles of Green Engineering

1. Ensure that all materials and energy inputs and outputs are inherently non-hazardous.
2. Prevent waste rather than treat/clean up waste.
3. Separation and purification operations designed to minimize energy & materials use.
4. Products, processes, and systems designed to maximize mass, energy, space, and time efficiency.
5. Products, processes, and systems should be “output pulled” rather than “input pushed” through the use of energy and materials.
6. Recycle.
7. Targeted durability, not immortality, should be a design goal.
8. Design for unnecessary capacity or capability solutions should be considered a design flaw.
9. Material diversity in multi component products should by minimized to promote disassembly and value retention.
10. Design of products, processes and systems must include integration and interconnectivity with available energy and materials flows.
11. Products, processes & systems by designed for performance in commercial “afterlife”.
12. Material and energy inputs should be renewable rather than depleting.

P. T. Anastas and J. B. Zimmerman, Design through the 12 principles of green engineering. Environ Sci Technol. 2003 Mar 1;37(5):94A-101A.

如果我們不能創造發明有利的方法和環境,
至少可以減少

Waste (廢料)

Materials (用料)

Hazard (危害)

Risk (風險)

Energy (用能)

Environmental Impact (環境衝擊)

Cost (成本)

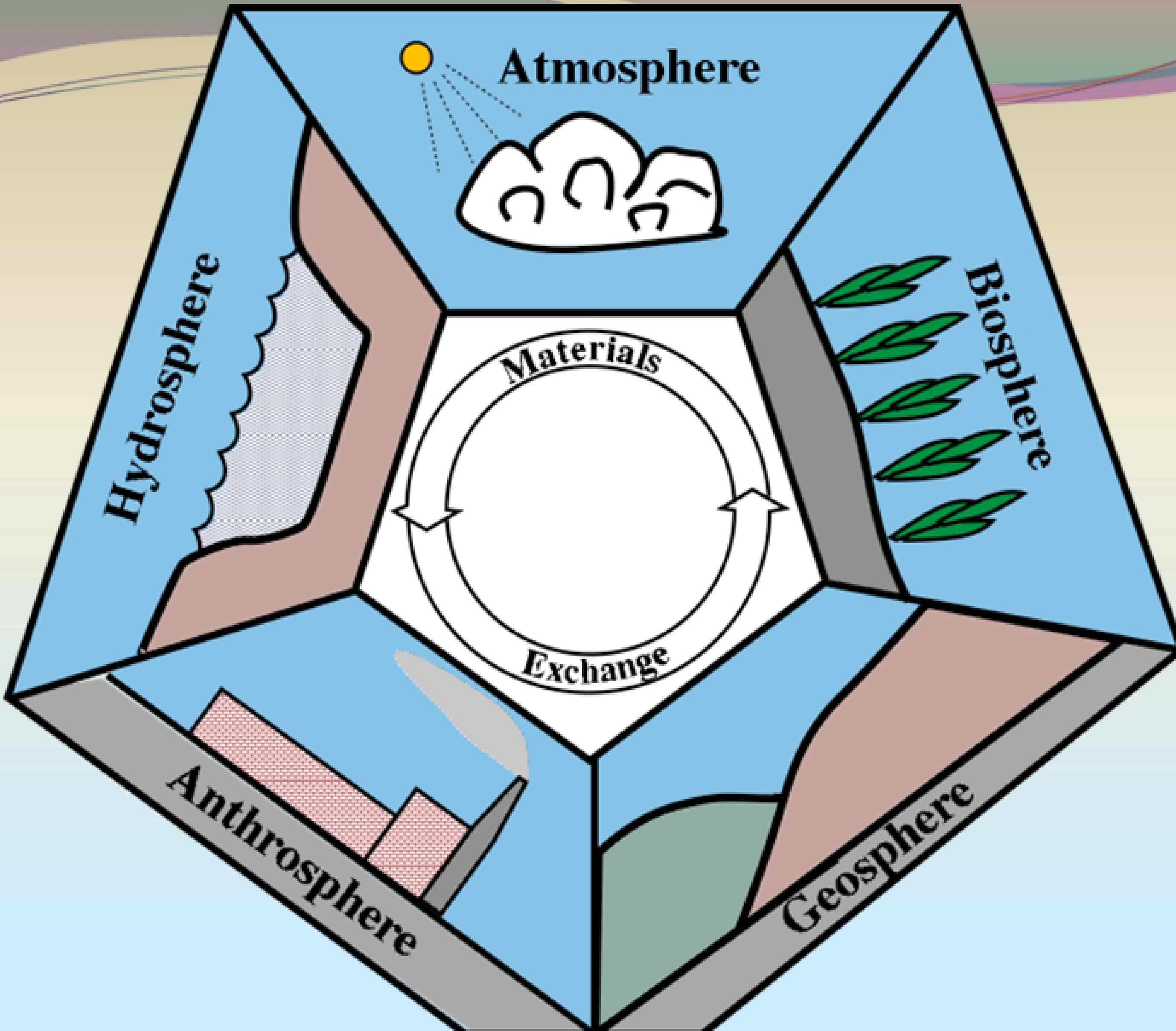
也符合綠色化學的精神

The chemical industry in the 21st century

(21世紀對化學工業及化學家的期望)

- Meeting social, environmental and economic responsibilities
(對社會、環境及經濟是責無旁貸)
- Maintaining a supply of innovative and viable chemical technology
(化學技術要日新又新、精益求精)
- Environmentally and socially responsible chemical manufacturing
(化學製造要對社會及環境負責)
- Teaching environmental awareness throughout the education process
(推廣教育, 喚醒大眾對環境保護的認知)

也是我們的機會



天、地、水、生物與人能和諧共處,生生不息,延綿萬世

S. E. Manahan, Green Chemistry and The Ten Commandments of Sustainability, ChemChar Research, Inc. (2005)

誌謝

劉廣定、趙奕姼、廖俊臣、周德璋諸位教授的指導與協助

主辦單位

中國化學會環境與化學委員會
（召集人吳丁凱）
國科會化學研究推動中心
（主任林英智）
義守大學
（吳裕文院長）
高雄師範大學
（徐永源主任）

贊助單位

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台橡股份有限公司
長春石油化學
東聯化學股份有限公司
中鼎工程股份有限公司

附錄

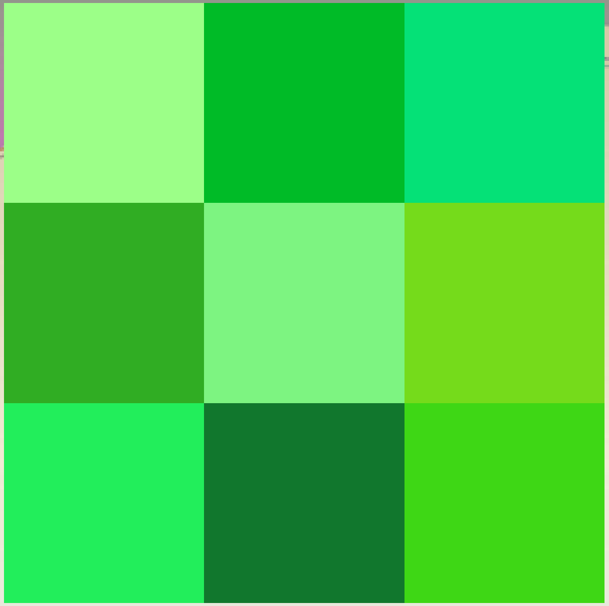
(請勿印製, no print, please)

附錄一：　漫談綠色

在科學上綠色是落在可見光的範圍內,波長在520-570奈米之間,換句話說發射在這範圍內的光是綠光,物質反射這段波長時則呈綠色.它不是三原色之一.藍色和黃色混合成綠色.比如說青蛙皮膚底層是藍色,表面是黃色,所以看到的青蛙是綠色.大自然界中有許多天然是綠色的,如植物葉綠素,所以植物葉子大都含有它,是綠色的.動物中兩棲類除上述之青蛙外也有許多是綠色的.昆蟲為了保護自己,模擬周遭的環境,也大多有綠色外皮.棲身在綠葉中來躲避天敵,傳延不息.礦石中也有許多綠色的,如翡翠有濃濃的深綠色(如祖母綠),得到人們的喜愛.人們將綠色溶入生活經驗之中就產生不同的代表及意義.比如說美國人稱錢為『綠背』(green back).因為一元美鈔的背面是綠色的.愛爾蘭人特別喜歡綠色,每年St. Patrick日(三月十七日)幾乎每人都要有綠色妝扮.最低程度也要打條綠色領帶上班.伊斯蘭教也特別崇拜綠色,認為天堂中充滿了翠綠.

綠色也有負面的意義,英國古老民俗中綠色代表巫術,妖術,邪惡,腐敗及毒性.所以百老匯上演之吸血鬼劇中 Drucala 的臉是綠色的.因此英國人迷信綠色不吉利,鮮有綠色之汽車或結婚禮服.塞爾提克人也迷信綠色衣服會招來不幸甚至死亡.我國人稱妻子有外遇的男人戴了『綠帽子』.不論中外都以『臉綠了』表示不健康或不舒服.

不過在多數人們心中綠色代表興旺及生生不息,所以許多國家(其中有歐洲國家,南美洲國家,尤其是非洲國家最多)國旗中有綠色.代表繁榮興盛,最甚者為Libya,她的國旗是一片綠布,完全沒有其他顏色或圖案.在人群結社(政治)方面有『綠黨』,『綠色和平組織』.它們的其宗旨為非暴力,愛護環境等.
化學製造之產品原則是符合人類生存之需求.比如說生產肥料及殺蟲劑可使糧食增產,使人類免於饑餓.製造抗生素及疫苗可以使人類免受病痛和延長壽命.但是製造這些有益的化學品同時也會產生不必要的副產物,嚴重污染了環境,妨碍了其他生物的生存,也妨碍了人類的生存.於是乎化學工業必須在其生產過程中減少有害排放物,走向永續經營.1990年美國通過「污染防制法案」:建立由源頭預防或降低污染之國家政策.由環境保護署提出「綠色化學」一詞,取其對環境友善而達到永續經營之意.
由於綠色之意義會因人、因時、因地、因信仰、因政治立場、因風俗習慣等而有不同的解釋.最鮮明的例子是我國股市價格下滑以綠色表示,但在美國卻是牛市的象徵.因此有些地區慣用綠色化學，餘則慣用永續化學，其來有自。



Green color wave length 520–570 nanometres

A frog

Leaves

Emerald

St. Patrick Day

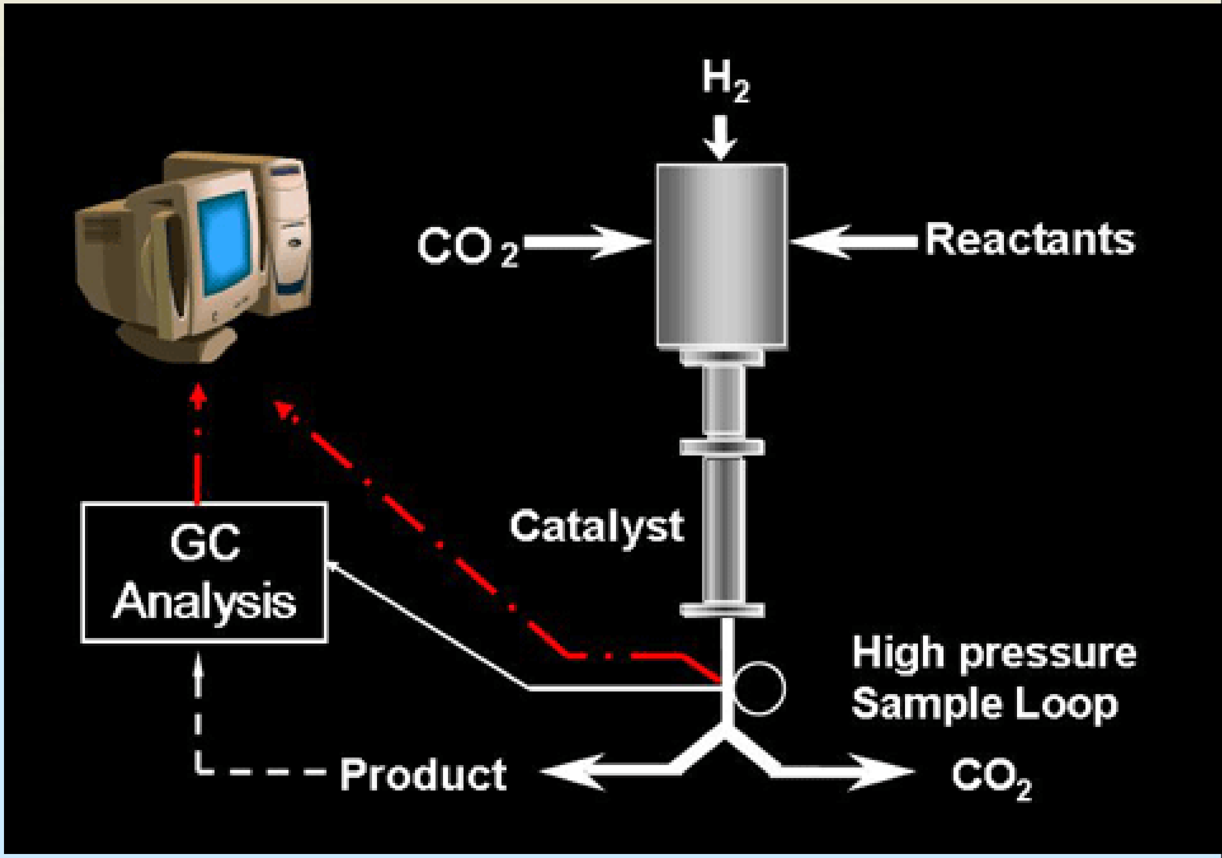
Libya flag

附錄二：超臨界二氧化碳設備

Continuous Reactions in Supercritical CO_2

With on-line analysis

Clean technology group,
Nottingham University, UK



The hydrogenation of isophorone yielded a product pure enough that down stream purification was unnecessary "Chemical Reactions in Supercritical Carbon Dioxide: From Laboratory to Commercial Plant" (P. Licence, M. Sokolova, S. K. Ross and M. Poliakoff) Green Chem. (2003) 5, 99–104.

Clean Technology Group , Univ. of Nottingham, UK

http://www.nottingham.ac.uk/supercritical/beta/hydrogenation.html

附錄三: 2007 Small Business Award on supercritical fluid

NovaSterilis Inc.

Environmentally Benign Medical Sterilization Using Supercritical Carbon Dioxide

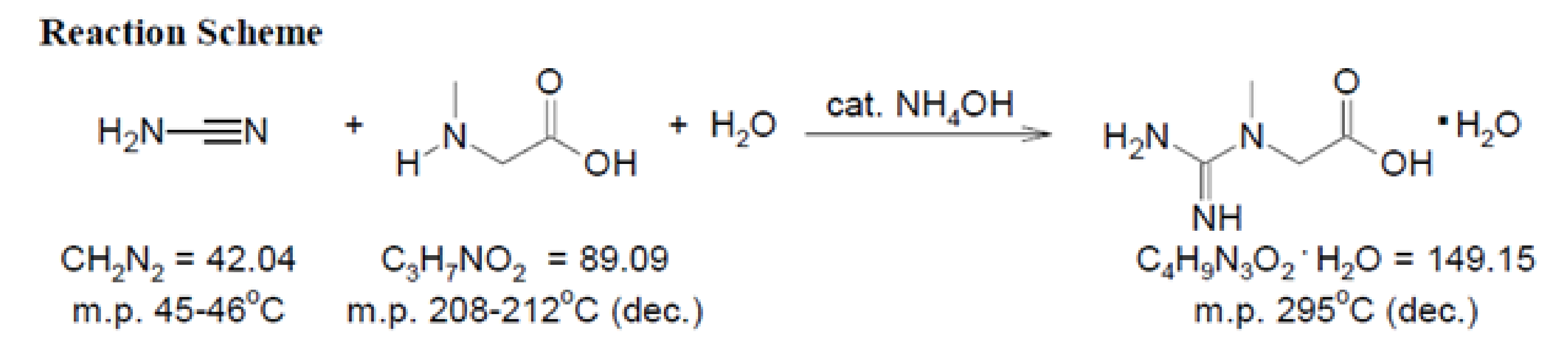
Innovation and Benefits: Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilization techniques use ethylene oxide or gamma radiation, which are toxic or have safety problems. NovaSterilis invented a technology that uses carbon dioxide and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Requires neither hazardous ethylene oxide nor gamma radiation.

Old: ethylene oxide and gamma radiation

NovaSterilis Inc.: supercritical CO_2 technology uses low temperature and cycles of moderate pressure along with a peroxide (peracetic acid) and small amounts of water.

附錄四:

例：以更安全的方法合成肌酸



Cyanamide 氨基化氰　　Sarcosine 肌氨酸　　Creatine monohydrate 肌酸單水結晶

肌酸係由氨基化氰與肌氨酸混合, 以氨水為催化劑合成. 不過以往的法是用過量(兩倍)氨基化氰及濃氨水(28-30%). 合成之肌酸單水化合物以兩倍的氯化鈉沉澱而出. 這反應的缺點其一是過多的氨基化氰會聚合成dicyanamide（  是一副產物. 其二是濃氨水不夠安全, 最後是產物中有氯化鈉. 品質不高.

同樣的反應可以更安全些, 首先是用1:1氨基化氰與肌氨酸, 不產生副產物. 其二是用稀氨水(家庭用氨水再稀釋5倍), 安全性大增. 其三是靜置24小時讓肌酸單水結晶沉澱, 不必用氯化鈉.

新反應程序符合了用綠色溶劑, 100% 原子經濟及溫和反應條件.

Lecher, C. S. *Synthesis of Creatine: A High School Procedure*, School of Mathematics and Sciences, Marian College, **2008**

附錄五:

Green Chemistry Metrics 綠色化學度量學

Effective Mass Yield (%) =
Mass of Products x 100 / Mass of Non-Benign Reagents

http://en.wikipedia.org/wiki/Green_Chemistry_Metrics

Carbon Efficiency (%) =
Amount of Carbon in Product x 100 / Total Carbon Present in Reactants

developed at GlaxoSmithKline (GSK).

Reaction Mass Efficiency =
Mass of product C x 100 / Mass of A
+ mass of B for a reaction of type A + B → C

developed by GSK.

Green Chemistry Metrics, Measuring and Monitoring Sustainable Processes, A. Lapkin and D. Constable, eds., Wiley 2008.