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]。

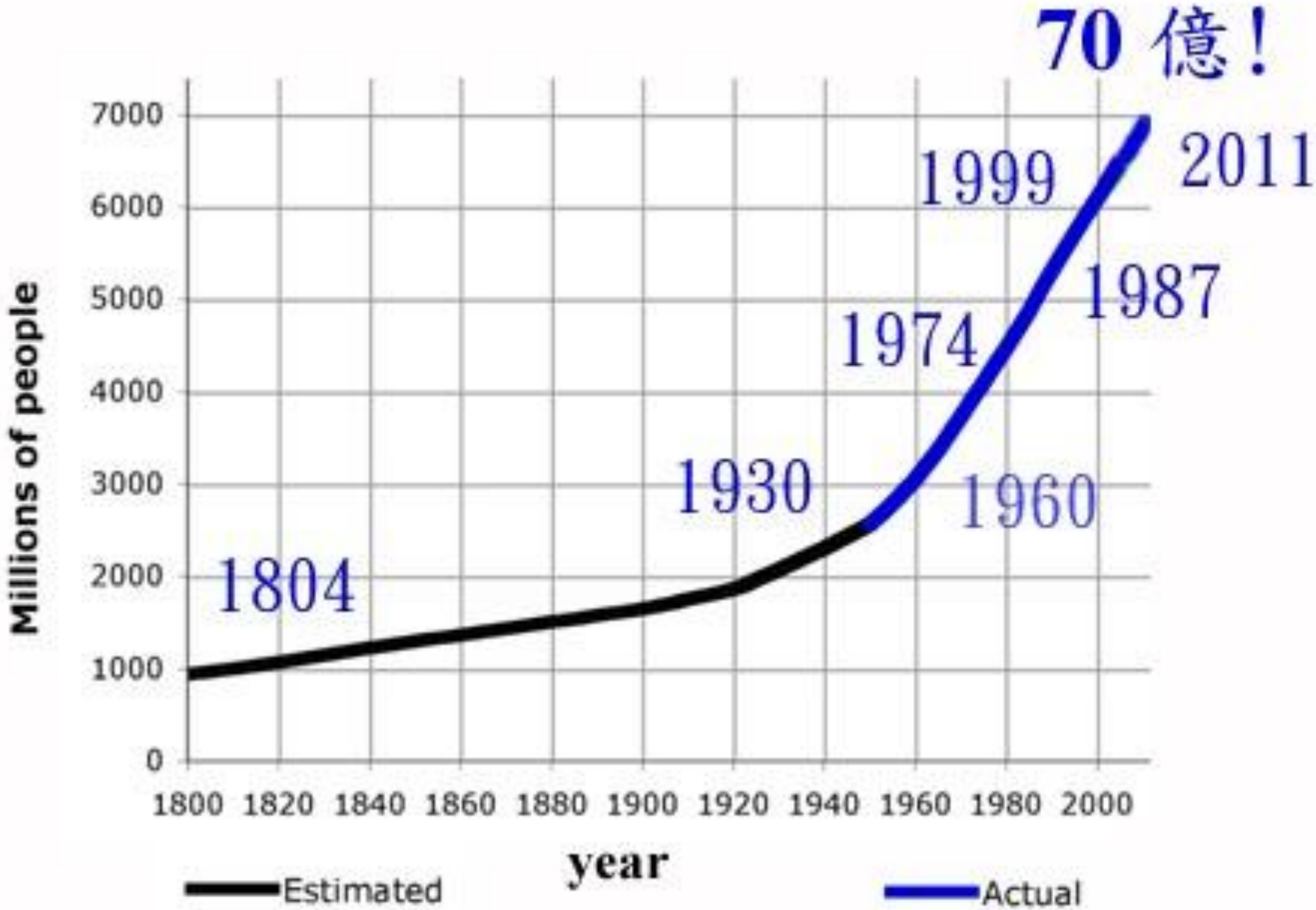
2012 綠色/永續合成化學工作坊
成功大學

綠色/永續化學：導言與原則/
綠色化學指標及度量法

9:45-10:10

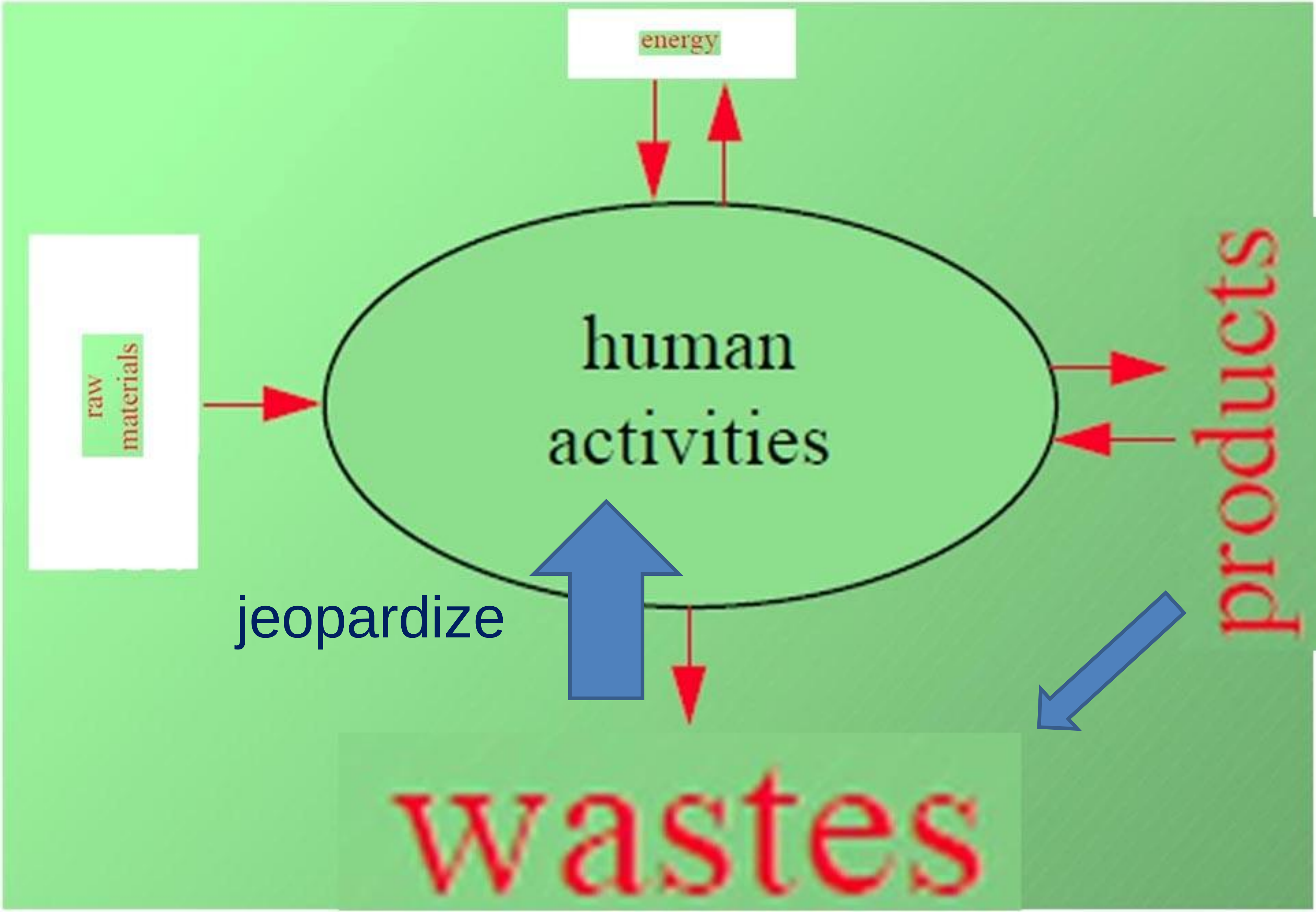
甘魯生
中央研究院化學研究所

People, people, people!



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

(呼應趙老師的論點)


energy
raw materials
human activities
products
jeopardize
wastes

綠色化學指標 (綠色化學十二原則)

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.

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.

減少衍生物: 儘可能減少或避免不需要的衍生反應(阻擋基、保護物/去保護物、物理/化學過程中之暫時修飾),因為此步驟需額外的試劑和產生廢料.

為分解而設計: 化學產物的設計應考慮到當它們的功能結束時會分解為無害的降解物而不會存留在環境中.

為用能效率而設計: 化學過程中能的需求應該被認定為對環境和經濟的衝擊縮為最小.如果可能,合成方法應該在常溫和常壓下進行.

催化作用: 儘可能使用有選擇能力之催化劑,且優先於使用化學當量的試劑.

低危險的化學合成: 無論在何地,只要實際可行,合成方法應設計成用的原料及製出的成品都無害於人類健康和環境,或是毒性很低.

設計更安全的化合物: 化學產品應設計成能在使它們的毒性縮到最小下實現達到所希望賦與的功能.

更安全的溶劑和輔助劑: 有關(化學合成)的輔助物質(即: 溶劑、分離劑等)儘可能不用,若用也要是無害的.

使用可再生的原料: 祇要技術和經濟可行時儘量用再生而非消耗的生物料和原料.

即時分析以防止污染: 發展出能即時和在線上監控和管理的分析方法,使在危險物質發生之前及時得到訊息,防止污染.

本質上更安全的化學以防止意外: 在化學反應中由一物質形成另一物質應該選擇能縮小化學意外的途徑,包括釋出(能)、爆炸及火災之可能性.

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

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.

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.

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)

接下頁

廢物之度量法 (接上頁)

Table 16.1 Current and aspirational E factors for industry segments.

Roger Sheldon 1992			Aspiration target	
Industry segment	E-factor		Industry segment	E-factor
Bulk chemicals	1–5	→	Bulk chemicals	Low
Fine chemicals	5–50		Fine chemicals	1–5
Pharmaceuticals[a]	25–>100		Pharmaceuticals[a]	5–>50

a) Refers to small molecule pharmaceutical drugs not biologics.

Green Chemistry in the *Pharmaceutical Industry, Wiley, 2010, Ch. 16*
DOI: 10.1002/9783527629688.ch16

接下頁

環境因子商(E-factor quotient, EQ)

EQ = S x E (公斤)

S(嚴重性因子) = 1 – 200, 依廢料之性質及多寡而定

Hazardous Waste to Land Disposal/Containment	10
Hazardous Waste to Incineration	4
Non-Hazardous Waste to Landfill	2
Waste Water (to Treatment Plant)	0.5

E: 0 (ideal), 0.4 (low), 6 (moderate), 50 (large), >200 (maximum)

Roger A. Sheldon, Chem & Ind., 7-Dec-1992, pg. 903
Roger A. Sheldon, Chem. Commun., 2008, 3352-3365

製程質量強度 (Process Mass Intensity, PMI)

A key, high-level metric for evaluating and benchmarking progress towards more sustainable manufacturing, has chosen by American Chemical Society Green Chemistry Institute's Pharmaceutical Roundtable.

PMI=total mass in a process or process step (kg)/mass of product (kg)

= E + 1

C. Jimenez-Gonzalez, C. S. Ponder, Q. B. Broxterman, and J. B. Manley, "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, 912–917. (dx.doi.org/10.1021/op200097d)

溶劑強度(solvent intensity, SI)

SI = 溶劑總量(公斤)/產物總量(公斤)

毒性度量

環境危險評估以環境中的預測濃度(**P**redicted **E**nvironmental **C**oncentration)和不傷害環境之預測濃度(**P**redicted **N**o **E**ffect **C**oncentration)之比為度量:

險商(risk quotient) = PEC/PNEC

(http://www.scienceinthebox.com/en_UK/safety/riskassenv_en.html)

評估方法

瞭解物理與化學性質; 估量在環境釋放的程度; 在環境中消長情形; 危險評估.(危險評估是要不斷的做)

(http://www.scienceinthebox.com/en_UK/safety/riskassenvapproach_en.html)

Finding a sufficient range of green solvents

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Toluene	Hexane(s)
Ethanol	Methylcyclohexane	Di-isopropyl ether
2-Propanol	TBME	Diethyl ether
1-Propanol	Isooctane	Dichloromethane
Heptane	Acetonitrile	Dichloroethane
Ethyl Acetate	2-MeTHF	Chloroform
Isopropyl acetate	THF	NMP
Methanol	Xylenes	DMF
MEK	DMSO	Pyridine
1-Butanol	Acetic Acid	DMAc
t-Butanol	Ethylene Glycol	Dioxane
		Dimethoxyethane
		Benzene
		Carbon Tetrachloride

Fig. 5 Solvent selection guide.[18]

Chem. Soc. Rev., 2012, **41**, 1437–1451 | 1441

recognizing whether a solvent is actually green,

finding an easily-removable polar aprotic solvent, and eliminating distillation.

P. G. Jessop, “Searching for green solvents”, Green Chem., 2011, **13**, 1391.

<u>減少能量</u>(催化劑、非傳統方法)

<u>耗能指數</u>: 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) = $\frac{(f_T + |1\text{-}Pressure(atm)|) * time\ (hrs) * Weight * Heat\ Capacity\ (J/gm\cdot{}^{\circ}K)}{Wt\ Desired\ Product}$

<u>對環境友善指數(化合物的半生命期)</u>:

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

<u>減少災害</u>(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.

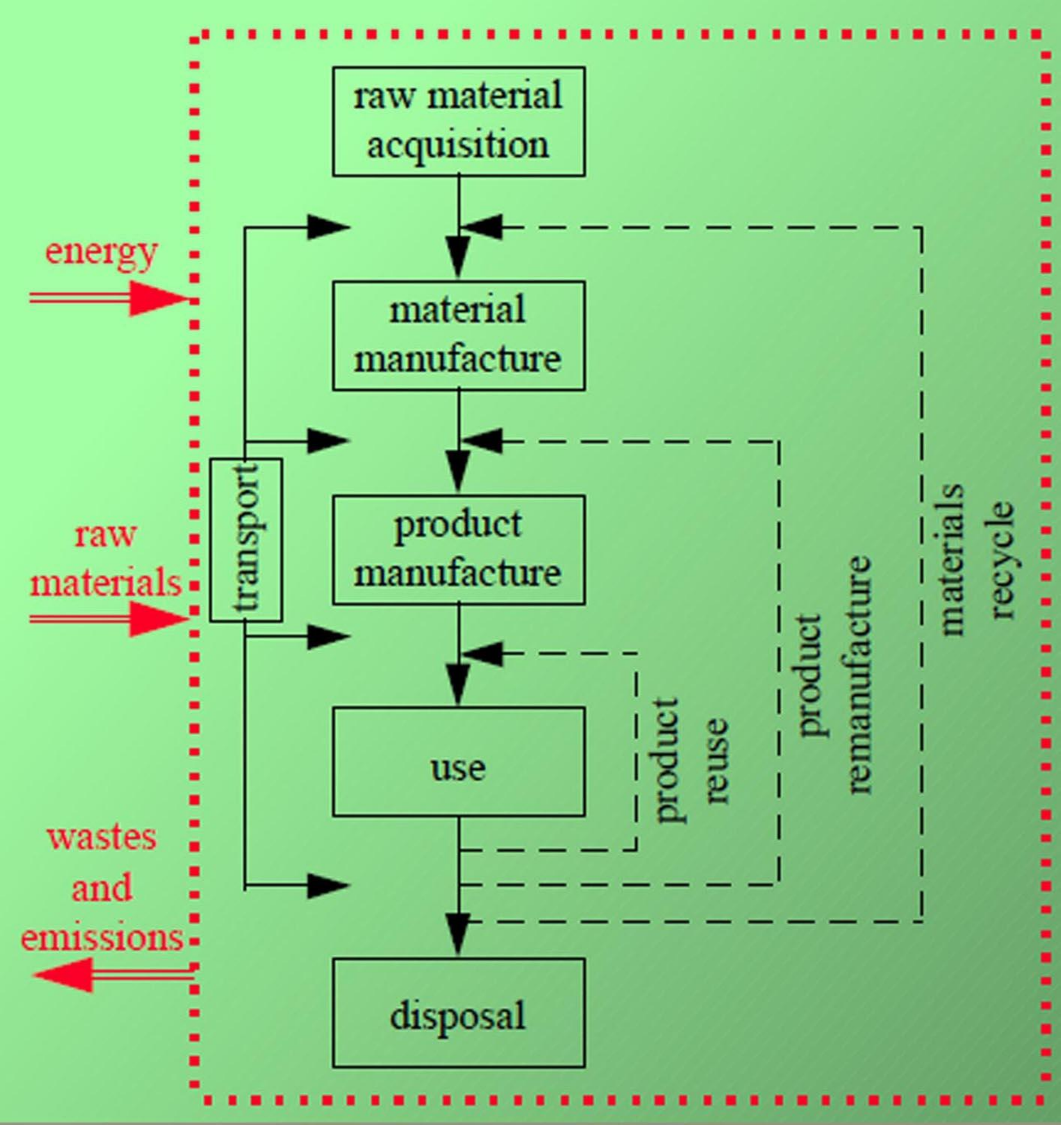
Life Cycle Analysis (LCA)

(Other names: Life Cycle Inventory (LCI), Life Cycle Assessment (LCA), Cradle to Grave Analysis, Eco-balancing, Dust-to-dust Energy Cost, and Material Flow Analysis.)

Definition:
LCA is a tool to access the potential environmental impacts of a product from the mining of the raw materials, used in its production and distribution, through to its use, possible re-use or recycling, and its eventual disposal.

Assessment items:
Global warming (greenhouse gases), acidification, smog, ozone layer depletion, eutrophication, ecotoxic and anthropotoxic pollutants, desertification, land use as well as depletion of minerals and fossil fuels.

Purposes:
Minimize the magnitude of pollution
Conserve non-renewable resources
Conserve ecological systems
Develop and utilize cleaner technologies
Maximize recycling of materials and waste
Apply the most appropriate pollution prevention and/or abatement techniques



Methods:
1. To determine the scope and boundaries of the assessment
2. To inventory the outputs that occur, such as products, byproducts, wastes and emissions, and the inputs, such as raw materials and energy, that are used during the life-cycle.
3. The output from a life cycle inventory is an extensive compilation of specific materials used and emitted.
4. To interpret the results of the impact assessment, suggesting improvements whenever possible.

Uncertainty in Results:
- assumptions made when choosing
- system boundaries and data sources
- use of regional or global data
- poor quality data
- unavailable data

Achievements:
- product development
- product improvement
- product comparison
- environmental labeling

Life cycle analysis Lesson 1
http://www.utexas.edu/research/ceer/esm282/dfe/LCAoverview.PDF
Kirsten Rosselot and David T. Allen
Life-Cycle Concepts, Product Stewardship and Green Engineering
http://www.utexas.edu/research/ceer/esm282/dfe/Chap13final.PDF
Life cycle analysis and assessment
http://www.gdrc.org/uem/lca/life-cycle.html

Summary

Resource efficiency: mass, energy, waste, atom economy
The environmental, health and safety profile of the materials used and the process.
Overall life cycle assessment: considerations such as the use of renewable feedstocks and impacts across the entire life cycle of a product or service.

CASE STUDIES

Swedish tomato ketchup
http://infohouse.p2ric.org/ref/37/36505.pdf
HP LaserJet cartridge
http://www.firstenvironment.com/html/lca_case_study-hewlett_packard.html
P&G kitchen products
http://www.scienceinthebox.com/en_UK/sustainability/casestudies_en.html
Western Australian grain products
http://www.tud.ttu.ee/material/piirimae/LCA/Case%20studies/LCA%20grain%20products.pdf
Thailand milled rice production
http://www.eurojournals.com/ejsr_30_2_02.pdf

GENERAL REFERENCES

•Green Chemistry themed issue, Guest editors Chao-Jun Li and Paul Anastas
Chemical Society Reviews (IF=28.76), 2012, **41**, Issue 4, Page 1405 to 1608.
http://pubs.rsc.org/en/Journals/JournalIssues/CS#!issueid=cs041004&type=current&issnprint=0306-0012

•P. J. Dunn, The importance of Green Chemistry in Process Research and Development, Chem. Soc. Rev., 2012, **41**, 1452–1461.

•C. Jimeʼnez-Gonzaʼ lez, D. J. C. Constable and C. S. Ponder, Evaluating the "Greenness" of chemical processes and products in the pharmaceutical industry—a green metrics primer, Chem. Soc. Rev., 2012, **41**, 1485–1498.

•R. A. Sheldon, Fundamentals of green chemistry: efficiency in reaction design, Chem. Soc. Rev., 2012, **41**, 1437–1451.

誰需要熟識綠色化學指標/度量法及Life cycle analysis?

教育工作者
合成化學工作者
智慧財產、技術轉移人員
工程師
化工業者
風險投資管理人
一般百姓 公職、商人、經濟學者、律師、醫護人員

謝謝大家