#### 聲明

本檔案之內容僅供下載者自我學習或推廣化學教育 之非營利目的使用。並請於使用時註明出處。例如 「本頁取材自〇〇〇教授演講內容」

# 談基礎有機化學教學內容

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# 化學教育

- 化學是基礎科學之一門,不但與其他科學學門密 切相關,而且不斷地快速發展。另有一些曾為人 視如老舊的知識觀念,經重新研發,又獲得了新 的生命力。當然也有一些新發明,很快就因始料 未及的缺點而遭修正或淘汰。因此在化學教育方 面,科學先進國家之基礎課程教材經常更新改進, 課程標準也常兼具時代性和前瞻性。本世紀以來 更趨於注重和其他學科的連貫性,包括了科學、 技術、工程與數學(STEM)的相關性。
- 教什麼比怎麼教重要,學什麼比怎麼學重要。

# 永續發展

- 聯合國世界環境與發展委員會(WCED)1987年正式宣布推動「永續發展(sustainable development)」,當時的定義是:「能滿足當代之所需但不損及後代滿足其所需之發展」稱為永續發展,是為世界之一主要新思潮。
- 1992年六月,聯合國首屆「環境與發展」會議,議定「廿一世紀待辦事項」(Agenda 21)40章。重新界定「永續發展」為「人類兼顧經濟成長、生態環境與社會責任三基柱的發展」,以及其發展原則。
- 2002年底聯合國決定依據二十一世紀待辦事項第36章,以2005-2014年為「永續發展教育的十年」。將永續發展觀念植入從幼稚園到成人的學校教育及社會教育。

### 聯合國17項永續發展目標(SDGs)

2016-2030

#### 17 Goals To Transform Our World

(Adopted by UN General Assembly, Sep. 25, 2015)

















<sup>&</sup>quot;Review of Targets for The Sustainable Development Goals: The Science Perspective" ICSU and ISSC, **2015** 

Matlin, et al., "Role of chemistry in inventing a sustainable future," Nature Chem. **2015**(Dec), 7, 941-943. (A commentary)

#### 野叟經驗談

- 曾在中央大學與吳春桂教授合作,設計過一些「零污染」之普通化學實驗(化學54卷4期63-66頁,1996年)。
- 2002年10月27日中國化學會年會發表過「大學階段永續化學實驗芻議」,建議經由實驗讓學生於學習化學原理、技術及功用外,更了解化學並不等於製造污染、破壞自然。而最終目標為賦予下一代正確之認識與觀念,能藉永續化學使化學永續發展、傳承。 Sustainable chemistry makes chemistry sustainable.
- 2002與2004臺大化學系選修課永續化學概論。
- 2003-2005 臺大農化系二年級有機化學(乙)。

# Implantation of the Principles of Green Chemistry in the Teaching of Sophomore Organic Chemistry

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(229th ACS National Meetings, Abstr. No. CHED 1334, Mar. 2005)

#### 兩個可行的教學理念

The future chemists should be taught to have sufficient knowledge in sustainable/green chemistry, and to think "sustainable/green" when dealing with real world problems.

Students in general would not catch the significance of a new concept unless it is mentioned repeatedly over the semester or the school year.

(Get personal experience through laboratory work)

#### 補充教材綱目

#### (A) Introduction to organic chemistry

The global carbon cycle and the disruption due to human activities.

The definition of sustainable development and sustainable/green chemistry.

**Key concepts** of sustainable chemistry, based on 12 principles by Anastas and Warner, and 12 more principles by Winterton.

#### Key concepts of sustainable/green chemistry

- Do our best to make "carbon cycle" sustainable.
- Prevent the waste rather than treat or clean up waste after it is formed.
- Economize on atoms by choosing synthetic methods which will maximize the incorporation of all or most of the reactant atoms into the desired product.
- Design processes to use nontoxic starting materials and solvents, and to minimize the potential for chemical accidents, including releases, explosions, and fires.
- Find ways to use renewable starting materials and catalytic reagents.
- Minimize the use of utilities (electricity, gas, water and steam).
- Avoid the use of auxiliary substances (solvents, separation agents, etc.) whenever possible.
- Invent chemical products which are environmentally benign, easily degradable, or recyclable.
- Carbon footprints and water footprints

#### (B) Introduction to organic reactions

Microwave and ultrasound methods as alternative means to promote reactions. (Alternative energy sources)

Supercritical fluid carbon dioxide, water as useful and "greener" reaction media than volatile organic solvents. (Alternative reaction media)

Solvent-free reactions.

#### (C) Principles of organic synthesis

In addition to those traditionally mentioned subjects, environmentally benign procedure and "atom economy" were emphasized. Examples of various reactions were given.

Students were asked to calculate **Experimental Atom Efficiency** (experimental atom economy × percentage yield) for the preparations they performed in laboratory.

(E-factor)

#### **Experimental atom economy & efficiency**

$$C_6H_{12}O \xrightarrow{85\% H_3PO_4} C_6H_{10} + H_2O$$

Cyclohexanol and phosphoric acid give cyclohexene and water on heating.

Reactants: cyclohexanol ( $C_6H_{12}O$ , 10.0 g, 0.1 mole); 85%  $H_3PO_4$  (5 mL: 7.15 g  $H_3PO_4$ , 0.073 mole; 1.26 g  $H_2O$ , 0.070 mole)

Desired product: cyclohexene ( $C_6H_{10}$ , 8.2 g, 0.1 mole in theory)

- Atom Economy = 8.2/10.0 = 82%
- Experimental atom economy = 8.2/18.4 = 44.6%
- average yield in a student laboratory, 30%
  - $\therefore$  Experimental atom efficiency = 44.6%  $\times$  30% = 13.4%

#### (D) Haloalkanes

The effects of many "useful" haloalkanes to global warming and ozone depletion.

Efforts to find environmentally benign substitute, such as aerosols, refrigerants (HFO-1234yf replaces R-134a) and solvents used in dry-cleaning, as opportunities for chemists.

#### (E) Oxidations

Principles of "green oxidations"

Use of H<sub>2</sub>O<sub>2</sub> with catalyst in oxidation, epoxidation, cleavage and dihydroxylation of C=C; "green synthesis" of adipic acid

Microwave-assisted oxidation with supported oxidizing agents Catalytic air oxidation of alcohols

#### (F) Diels-Alder reactions

Comparison of traditional reaction and microwave-assisted reaction (reaction of MVK with 2,3-dimethyl-1,3-butadiene)

Advantages of reaction in aqueous media, such as higher endoselectivity and faster rates (reaction of MVK with cyclopetadiene)

#### (G) Electrophilic aromatic substitutions

Friedel-Crafts acylation using no-chlorine catalysts (e. g., HF and  $Ac_2O$ )

Solvent-free nitration over zeolite H<sup>+</sup>beta

Microwave assisted bromination and nitration, comparison of ordinary synthesis and green synthesis

#### (H) Carbonyl compounds

Green oxidation for preparations.

Green reductions to alcohols.

Green Baeyer-Villiger oxidations.

"Grignard-like" reactions in aqueous media.

Microwave assisted condensation reactions, e.g., Knoevenagel reaction and formation of imines.

#### (I)Carboxylic acid derivatives

Use acetic trifluoroacetic anhydride to replace acetyl chloride

Microwave-assisted esterification

Greener route to ε-caprolactam

Polymers having both CO<sub>2</sub>-phobic and CO<sub>2</sub>-philic segments as new surfactants used for cleaning in supercritical fluid CO<sub>2</sub>

(Organic carbonates, Carbon capture and utilization)

#### (J) Biomolecules

The transformation of fats and oils to bio-diesels

Glucose as the starting material for environmentally benign synthesis using microbes

From aspartic acid to polyaspartate, a biodegradable polymer

(The use of glycerol, levulinic acid, succinic acid)

#### 討論與建議

- 約需10或12節課講授以上之教材 (教科書中哪些部分可以省略?)
- 發給學生補充讀物(中文?)增進了解
- 其他科目的配合
- 實驗教材改進
- 高年級宜有配合永續發展觀念的相關課程
- 必須據實和據理說明以免誤導學生

#### New solution to carbon pollution?

Science, (Jun. 10, 2016), 352, 1312-1314

220 tons of CO<sub>2</sub> be injected into layers of basalt rock between 400-800 m below the surface in Iceland, will be mineralized CaCO<sub>3</sub> in 2 years.

However, it requires 25 tons of water for 1 ton of CO<sub>2</sub>. Transportation and injection of CO<sub>2</sub> are costly.

#### Advantages and disadvantages of using water as a solvent

Advantages	Disadvantages
Nontoxic	Removing is energy intensive
Nonflammable	Contaminated waste streams may be difficult to treat and is highly cost
High specific heat capacity- exothermic reactions can be more easily controlled	High specific heat capacity- difficult to heat or cool rapidly

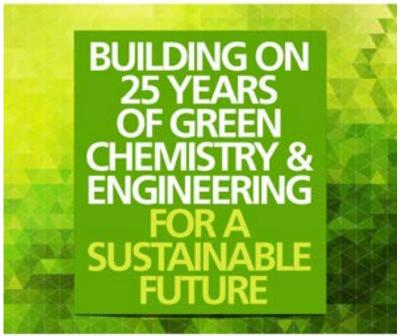
台積電去年用水3500萬噸,實驗工廠現回收工業用水每日24噸,每噸成本50元 (自來水每噸12元)。 [聯合報105年11月24日,A14版]

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#### Some recent literatures

- "Undergraduate Chemistry Education: A Workshop Summary," NAP Press,
   2014.
- ACS 2015 Guidelines for Undergraduate Professional Education in Chemistry, <a href="http://www.acs.org/content/dam/acsorg/about/governance/committees/training/2015-acs-guidelines-for-bachelorsdegree-programs.pdf">http://www.acs.org/content/dam/acsorg/about/governance/committees/training/2015-acs-guidelines-for-bachelorsdegree-programs.pdf</a>
- Lancaster, "Green Chemistry: An Introductory Text," 3rd Ed., RSC, 2016.
- Stefanidis and Stankiewicz (ed), "Alternative Energy Sources for Green Chemistry," RSC Green Chemistry series 47, 2016.
- "Sustainable Chemistry: Green Technologies for Clean Air & Safe Water,"
   C&EN Supplement, June 6, 2016 issue.
- Clean Techn. Environ. Policy, Vol. 18, No. 8, **2016**, a special Issue on "Mobilizing the Potentials towards Low Carbon Societies in Asia."
- ACS Sustainable Chem. Eng., Vol. 4, No. 11, **2016** a special issue for 25 Years of Green Chemistry and Engineering. Esp. the feature article by Haack and Hutchinson on "Green Chemistry Education: 25 Years Progresses and 25 years ahead" (pp 5889–5896).
- Winterton, Clean Techn. Environ. Policy (2016) **18**, 991-1001 [Green chemistry: Deliverance or distraction?]
- Matlin, et al., Nature Chem. (2016) **8**, 393-398 [One-world Chemistry and system thinking (a commentary)]





Isaac Newton is quoted as saying, "If I have seen further, it is by standing on the shoulders of giants." Clearly, the work of the past 25 years was produced by many intellectual giants. The next 25 years of innovations in Green Chemistry and Green Engineering will be produced by those standing on their shoulders while viewing a horizon not seen by the giants. (Anastas and Allen, p. 5820)

# 謝謝聆聽

# 敬請指教