

綠色/永續化學通訊
**Green/Sustainable
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國科會化學中心



Green / Sustainable Chemical Communication

Preface

For past couple years, everyone in Taiwan more or less should feel the abruptly abnormal change of our environment due to the impact of global warming. From academic point of view, what we should do and how we can do to turn the earth back to the original status is to educate our next generation to think and to do the right thing on earth. Consequently, education of green/sustainable concept is highly important to our young students.

This edition of Green/Sustainable Chemical Communication (GSCC) denotes the invaluable information in the fields of education, chemical engineering, industry, chemistry and biochemistry related to new invention and development of sustainable solutions which may be helpful for us to protect and improve our environment in the near future.

We are indebted to two experts Kwang-Ting Liu (劉廣定) and Lou-sing Kan (甘魯生) who sincerely wrote and collected the information at several stages for their helpful and invaluable suggestions on how to construct a practicable communication.

I also wish to gratefully acknowledge two photographers, YiChi Jao and Steven Zan, who provided us a series of pictures about the nature and green world taken in many countries in Europe.

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Academia Sinica
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RESOURCE SHARING

永續化學的教育(Education in sustainable/green chemistry)

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化學是與全球永續發展所遭遇之難題關係最密切的學科。2002 年底聯合國依據 1992 年所提出「二十一世紀待辦事項」(Agenda 21)的第 36 項，決定以 2005-2014 年為「永續發展教育的十年 (Decade of Education for Sustainable Development)」。

強調「觀念上永續發展教育遠超過環境教育」，希望經由「教育」普遍灌輸正確「永續發展」的觀念及知識於人心，以求順利達成「永續」之目標。世界許多國家紛紛投入，積極推行。較新版教科書已多為配合，如 *Chemistry for Changing Times* (J. W. Hill and D. K. Kolb 著)第 11 版(2007)每章都有永續化學的專題介紹。但在台灣，與永續發展相關的化學教育一向不受重視。大學裡開有關課程的不多，而教育部新訂民國 99 年實施的「高中化學課綱」中，「永續發展」竟只有「基礎化學(2)」列了約一節課！為免學生知識與觀念過於落後，失去將來的競爭能力，本期「資源共享」增加「永續化學的教育」一欄，將 2008 年起國外及大陸刊物中編者認為有用的資料，提供化學界從事教育工作的同仁充實教材和改進實驗之參考。

(1) 新資源：

In September SusChem, the European technology platform for sustainable chemistry, launched an online database of European education activities in sustainable chemistry. The resource aims to:

- provide concise information on existing and planned activities (publications, websites, workshops, lectures *etc*) and courses (from secondary school to PhD level) in sustainable chemistry;
- support the development of new secondary school and university courses by disseminating best practice; and
- promote new collaborative activities and provide information about sources of funding.

You can search the database by educational level, *eg* secondary school, bachelor,

master *etc*, and by the type of educational activity. The database currently covers the UK, Belgium, Finland, France, Germany Ireland, Italy, the Netherlands and Spain, but the aim is to extend coverage to all EU countries. Users are invited to submit materials and details of useful resources to the database by contacting the website (e-mail: learning@suschem.org). (取材自 *Education in Chemistry*, November, 2008)

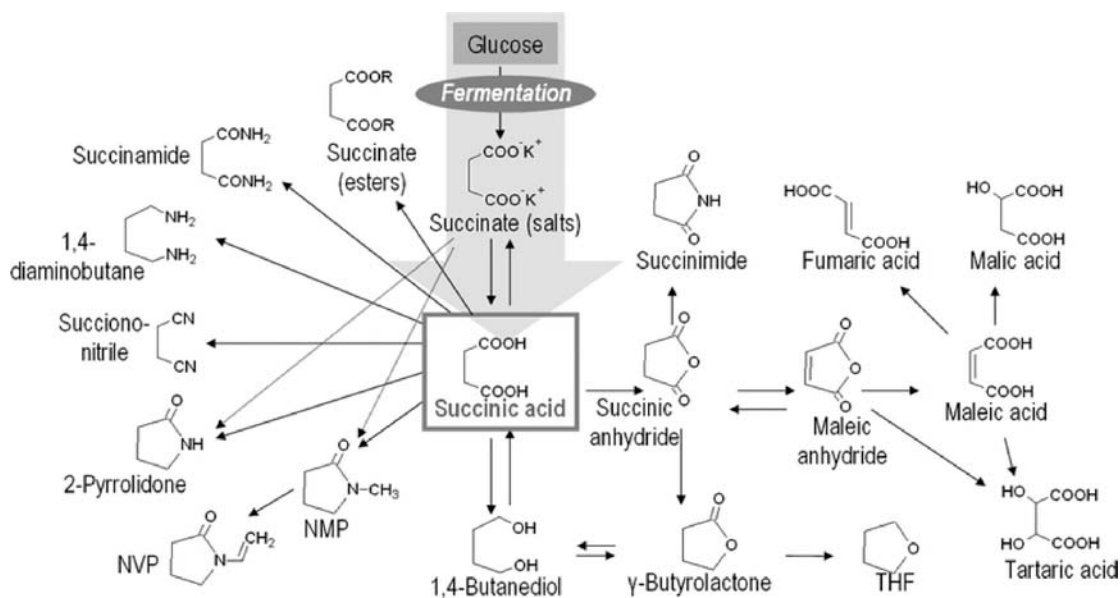
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(2) 講課參考資料:

Succinic acid from renewable resources as a C4 building-block chemical—a review of the catalytic possibilities in aqueous media

Aqueous hydrogenation of bio-based succinic acid has been reported for the production of value added chemicals, *e.g.* 1,4-butanediol, tetrahydrofuran, γ -butyrolactone, 2-pyrrolidone or *N*-methyl-2-pyrrolidone. A variety of heterogeneous metallic catalysts, active under quite severe conditions have previously been studied, whereas research into organometallic complexes is thus far limited to solvent reactions or to aqueous reactions producing succinic acid.

Clara Delhomme et al., *Green Chem.*, 2009, 11, 13-26.



Solvents from nature

In this perspective, a personal journey from solvent to solvent is presented to demonstrate how environmentally friendly solvents can be part of the solution of various chemical challenges. Solvents are important components of Nature to provide one or more liquid phases for chemical reactions and processes. While some



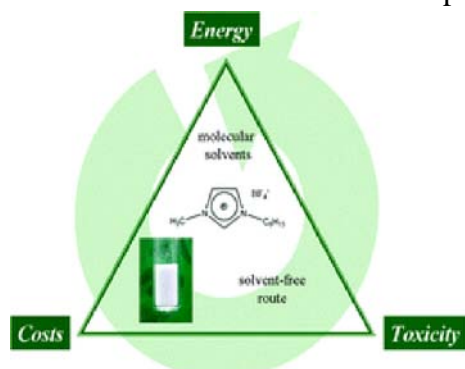
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solvents are available from Nature even in large quantities, most of the solvents are man-made. Historically, solvents were developed and/or selected to help the chemical or physical objectives of the user(s) only. With the increasing importance of local and global health and environmental issues, including the introduction of green chemistry and the molecular approach for pollution prevention, the potential impacts of solvents became important selection tools. One of the key principles of green chemistry is the elimination of solvents in chemical processes or the replacement of hazardous solvents with environmentally benign solvents. The development of solvent-free alternative processes is the best solution, especially when either one of the substrates or the product is a liquid and can be used as the solvent of the reaction. However, if solvents are crucial to a process we should select from solvents that will have no or limited impact on health and the environment.

István T. Horváth et al., *Green Chem.*, **2008**, *10*, 1024-1028.

Evaluating the greenness of alternative reaction media

The solvent performances and ecological (dis)advantages of different solvent systems for the Diels–Alder reaction of cyclopentadiene and methyl acrylate were investigated. Promising solvent alternatives, especially $[\text{C}_6\text{MIM}][\text{BF}_4]$ (1-hexyl-3-methylimidazolium tetrafluoroborate), citric acid/*N,N'*-dimethyl urea as well as a solvent-free alternative were compared to the conventional solvent systems methanol,



cyclohexane, acetone and methanol/water. By means of the ECO (Ecological and Economic Optimisation) method these solvent alternatives were evaluated already during an R&D (Research and Development) stage in a holistic approach. This method is a screening tool that

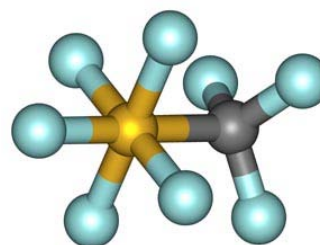
employs a Simplified Life Cycle Assessment (SLCA) approach in combination with an optimisation procedure. All life cycle stages from the production of reactants, solvents *etc.*, synthesis and workup, recycling and disposal are considered within this methodology. With the help of the ECO method, some significant environmental issues depending on the solvent selection are compared in order to make a contribution to the assessment of the greenness of chemical processes and products during R&D.

Denise Reinhardt et al., *Green Chem.*, **2008**, *10*, 1170 – 1181.

CF₃SF₅ - a 'super' greenhouse gas

Trifluoromethyl sulfur pentafluoride - a byproduct of the electronics industry - has been named a 'super' greenhouse gas by physical chemists. But what evidence do they have that makes this molecule a potential threat to the environment?

Richard Tuckett, *Education in Chemistry*, **2008**, *1*, 17-21.



From waxes to riches



Supercritical carbon dioxide can be used to remove valuable chemicals, including waxes, from plants, the most widely available and cheap source of biomass in the world.

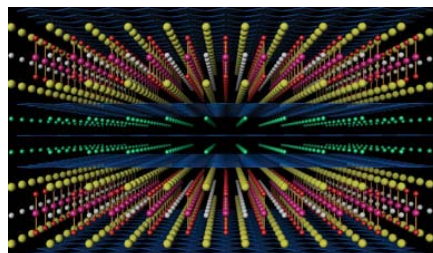
James Clark and Fabien Deswarte, *Education in Chemistry*, **2008**, *3*, 76-79.

Resistance is useless

Chemistry holds the key to commercialisation of high-temperature superconductors that could revolutionise electrical power supply.

In Short:

(a) The underlying mechanisms of high-temperature superconductivity must be unravelled before it can be commercially exploited.



(b) Multidisciplinary collaboration will be essential in the search for new classes of higher-T_c materials.

(c) Commercial breakthroughs are imminent and prototypes are already successfully operating in the electric grid.

J. McEntee, *Chem. World*, **2008**, 2, 42-44 and 46-47.

Sustainable fashion and textiles

Synthetic fibres are back in fashion after an ecological makeover.

In Short:

(a) A new generation of 'greener' synthetic fibres are entering the textiles market

(b) The fibres are based on polymers derived from plants rather than petrochemicals

(c) Class (Creativity, Lifestyle and Sustainable Synergy) is one project that brings manufacturers of these textiles together with the designers who use them.

M. Burke, *Chem. World*, **2008**, 3, 58-61.



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Sustainable water: chemical science priorities

This report highlights the key role of the chemical sciences in driving future developments in water management, nationally and internationally.

The report encompasses the entire hydrological cycle with an emphasis on human



activity, particularly:

(a) Managing domestic, industrial and agricultural water use

(b) Contamination

(c) Climate change.

The report summarises the current situation and recommends future developments. It presents sound

scientific evidence to support its key recommendations.

(<http://www.rsc.org/ScienceAndTechnology/Policy/Documents/water.asp>)(available on Nov. 1, 2007)

Sustainability education and the ACS committee on environmental improvement

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The Committee on Environmental Improvement (CEI) is a governance committee appointed jointly by the ACS Council and the Board of Directors. Environmental sustainability has been a long term focus of this committee in terms of writing policy statements to inform U.S. Congressional action as well as providing outreach to the general public. The Education subcommittee of CEI is working on several complementary sustainability projects including informing chemistry departments about energy efficient fume hood management and working with textbook authors to incorporate sustainability throughout their educational materials.

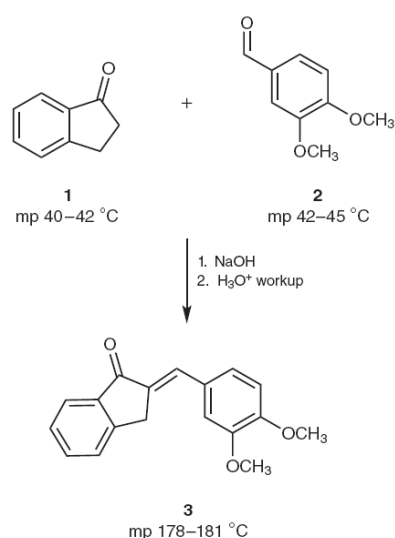
Laura E. Pence, *J. Chem. Educ.* **2008**, 85, 1608.

(3) 學生實驗參考資料:

(Journal of Chemical Education 中所載各篇皆另附補充材料)

Greener solutions for the organic chemistry teaching lab: exploring the advantages of alternative reaction media

A major approach for implementing green chemistry is the discovery and development of synthetic strategies that reduce the quantity of solvent needed, eliminate it altogether, or rely on new reaction media. An increasing number of examples have demonstrated that greener reaction solvents or media can enhance performance as well as reduce hazard. Here we describe four experiments designed for the undergraduate organic chemistry laboratory that illustrate both enhanced performance and a greener approach: (i) a solventless aldol condensation that involves the reaction of two solid reagents, (ii) a solvent-free, room



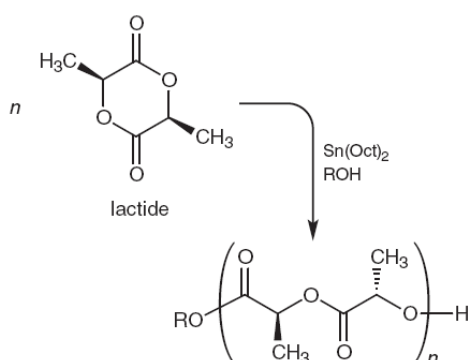
Scheme 1. The aldol condensation reaction of 1-indanone, **1**, and 3,4-dimethoxybenzaldehyde, **2**. Although the reaction could yield both diastereomers, only the one shown is obtained (*8a*).

temperature Diels–Alder reaction followed by an intramolecular nucleophilic acyl substitution, (iii) a Diels–Alder reaction in water, and (iv) a Diels–Alder reaction in polyethylene glycol (PEG) that may be conducted using microwave heating. The alternative solvents or reaction media used in these experiments not only reduce the use of hazardous and volatile organic solvents but also enhance the transformations by increasing the rate of reaction or facilitating recovery of the product. These thoroughly tested laboratory experiments are convenient, inexpensive, and rapid, thereby providing an opportunity to introduce green chemistry into educational settings easily.

Lallie C. McKenzie et al., *J. Chem. Educ.* **2009**, *86*, 488–493.

Ring-opening polymerization of lactide to form a biodegradable polymer

In this laboratory activity for introductory organic chemistry, students carry out the tin(II) bis(2-ethylhexanoate)/benzyl alcohol mediated ring-opening polymerization of lactide to form the biodegradable polymer polylactide (PLA). As the mechanism of the polymerization is analogous to that of a transesterification reaction, the experiment can be used to demonstrate reactions of carboxylic acid derivatives. The polymerization can be successfully carried out using standard teaching laboratory



Scheme 1. PLA formed by the chain growth ring-opening polymerization of lactide.

(non-Schlenk) conditions. Analysis of polymer stereochemistry by ^1H NMR and a discussion of the effect of monomer stereochemistry on the stereochemistry of the polymer are included in the experiment. The effect of adventitious water on the rate of the polymerization and the number-average molecular weight, M_n of the resulting polymer are

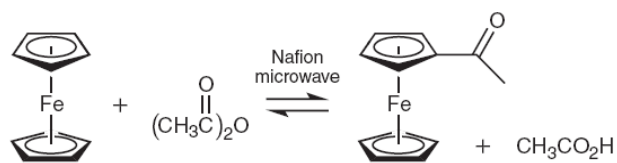
discussed in the Supplemental Material.

Jennifer L. Robert et al., *J. Chem. Educ.* **2008**, *85*, 258–260.

Acylation of ferrocene: a greener approach

The acylation of ferrocene is a common reaction used in organic laboratories to demonstrate Friedel–Crafts acylation and the purification of compounds using column

chromatography. This article describes an acylation of ferrocene experiment that is more eco-friendly than the conventional acylation experiment. The traditional experiment was modified by replacing mineral acid with a polymeric acid catalyst and by using microwave heating instead of conventional heating.

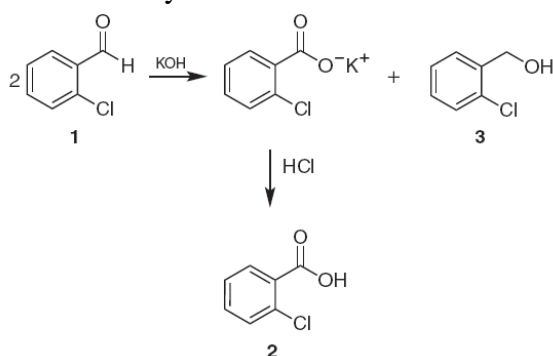


Scheme 1. Nafion catalyzed acylation reaction of ferrocene.

Kurt R. Birdwhistell et al., *J. Chem. Educ.* **2008**, *85*, 261-262.

A facile solvent-free cannizzaro reaction. An instructional model for introductory organic chemistry laboratory

Liquid 2-chlorobenzaldehyde was converted, by grinding with potassium hydroxide pellets, into equimolar quantities of solid 2-chlorobenzoic acid and solid 2-chlorobenzyl alcohol in a Cannizzaro reaction. TLC, IR, and NMR experiments,



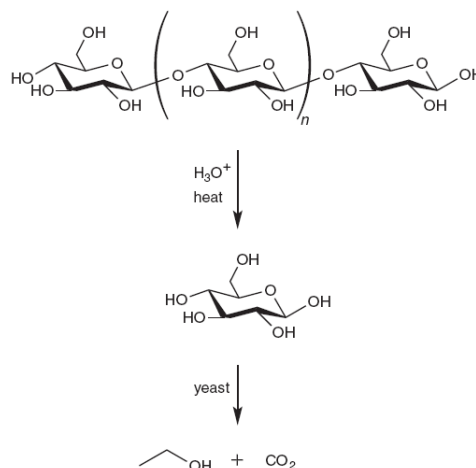
Scheme 1. The solvent-free Cannizzaro reaction of 2-chlorobenzaldehyde, **1**, gives 2-chlorobenzoic acid, **2**, and 2-chlorobenzyl alcohol, **3**.

using authentic samples for comparison, confirmed the identity and purity of the two products. Guided-inquiry pedagogy was employed as an instructional model for teaching this green chemistry laboratory to undergraduates who were responsible for partially designing their experiment.

Sonthe Phonchaiya et al., *J. Chem. Educ.* **2009**, *86*, 85-86.

Converting municipal waste into automobile fuel: ethanol from newspaper

Waste newspaper is pulped with acid and its cellulose is hydrolyzed. The resulting glucose syrup is fermented with yeast and distilled to give ethanol. The experiment highlights the potential of applied chemistry to confront problems of economic importance, that is, the effective utilization of biomass to



Scheme 1. The hydrolysis of cellulose to glucose and the fermentation of glucose into ethanol.

reduce dependence on non-renewable petroleum. In the course of this laboratory exercise students are introduced to carbohydrate chemistry and the use of fermentation in organic synthesis. They also gain practical experience in microdistillation, vacuum filtration, and thin-layer chromatography. It is most appropriate for students of the advanced organic chemistry laboratory.

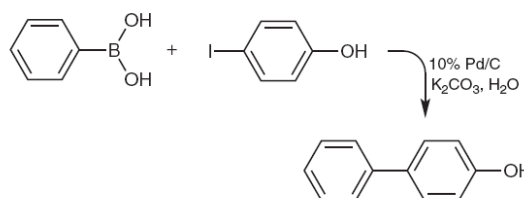
Mark Mascall et al., *J. Chem. Educ.* **2008**, *85*, 546-548.

"Greening up" the Suzuki reaction

This article describes the rapid, green synthesis of a biaryl compound (4-phenylphenol) via a Pd(0)-catalyzed Suzuki cross-coupling reaction in water. Mild reaction conditions and operational simplicity makes this experiment especially amenable to both mid- and upper-level undergraduates. The methodology exposes students to purely aqueous microscale organic reactivity and showcases topical research in the milieu of an industrially applicable process.



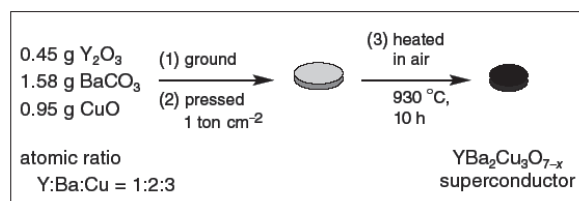
Scheme I. A traditional Suzuki reaction.



Scheme II. Suzuki synthesis of 4-phenylphenol in water.

Evangelos Aktoudianakis et al., *J. Chem. Educ.* **2008**, *85*, 555-557.

A simplified synthetic experiment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor for first-year chemistry laboratory



Scheme I. Synthesis of Y-123 superconductor.

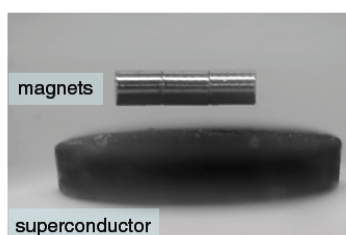


Figure 1. The levitation of three magnets over a Y-123 superconductor immersed in liquid nitrogen.

In this study, a simplified synthetic experiment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y-123) superconductor was devised for first-year chemistry laboratory to demonstrate high temperature superconductor and the Meissner effect. The traditional synthetic methods of Y-123 superconductor need repeated grinding and heating in oxygen at high temperature, which are often tedious and time-consuming. In

this experiment, a stoichiometric reduced quantity of starting materials was heated in air in a computer-controlled box furnace after grinding and pressing. The black pellet obtained exhibited superconductivity that levitated a magnet to about 4 mm height in liquid nitrogen to demonstrate the Meissner effect. The synthesis of the superconductors can be easily finished in 3-hour laboratory class, and the Meissner effect was tested in the following week. This simplified synthetic experiment of Y-123 superconductor reduces the chemical amount, takes less energy as well as less preparation time, and was successfully carried out by first-year students.

Jui-Lin She et al., *J. Chem. Educ.* **2008**, *85*, 825-826.

Teaching sustainable development concepts in the laboratory: a solid-liquid extraction experiment

One of the principles of sustainable development is to replace chemicals traditionally derived from oil with alternative, renewable materials. For example, phenol and phenol derivatives currently used in the manufacture of wood adhesives can be replaced (at least in part) by biopolymers extracted from biomass. In this work, pine bark (a renewable resource containing easily extractable, reactive phenols) is employed as a substrate for solid-liquid extraction with dilute NaOH solutions. The kinetics of polyphenol extraction is followed spectrophotometrically. In order to convert absorbance data into concentrations, the extracted polyphenols can be measured gravimetrically for selected samples. The experimental data are interpreted by equations involving two or three regression parameters. Additional aspects illustrating the "biomass refinery" concept applied to pine bark are discussed.

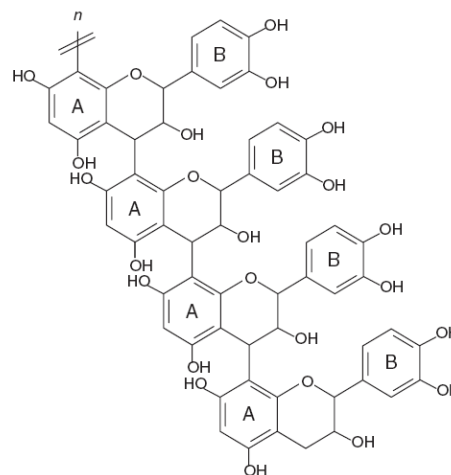


Figure 1. Structure of pine bark polyflavonoids.

Juan Carlos Parajó et al., *J. Chem. Educ.* **2008**, *85*, 972-975.

The discovery-oriented approach to organic chemistry. 7. Rearrangement of trans-stilbene oxide with bismuth trifluoromethanesulfonate and other metal triflates. A microscale green organic chemistry laboratory experiment

Although green chemistry principles are increasingly stressed in the undergraduate curriculum, there are only a few lab experiments wherein the toxicity of reagents is

Table 1. Rearrangement of *trans*-Stilbene Oxide Using Metal Triflates as Catalysts

Catalyst	Solvent	Major Product
Bi(OTf) ₃ ·xH ₂ O	CH ₂ Cl ₂	2
Bi(OTf) ₃ ·xH ₂ O	CDCl ₃	2
Bi(OTf) ₃ ·xH ₂ O	CH ₃ CN	NR
Bi(OTf) ₃ ·xH ₂ O	Diethyl ether	2
Bi(OTf) ₃ ·xH ₂ O	THF	2
Bi(OTf) ₃ ·xH ₂ O	Toluene	2
In(OTf) ₃	CH ₂ Cl ₂	2
KOTf	CH ₂ Cl ₂	NR
La(OTf) ₃	CH ₂ Cl ₂	NR
La(OTf) ₃	CH ₂ Cl ₂	NR

NOTE: OTf is trifluoromethanesulfonate, CF₃SO₃⁻.

taken into consideration in the design of the experiment. We report a microscale green organic chemistry laboratory experiment that illustrates the utility of metal triflates, especially bismuth triflate as a Lewis acid catalyst. Bismuth compounds are especially attractive for use as catalysts in organic synthesis because of their remarkably low toxicity, low cost, and ease of handling.

James E. Christensen et al., *J. Chem. Educ.* **2008**, *85*, 1274-1275.

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A green, guided-inquiry based electrophilic aromatic substitution for the organic chemistry laboratory

We developed an alternative electrophilic aromatic substitution reaction for the organic chemistry teaching laboratory. The experiment is an electrophilic iodination reaction of salicylamide, a popular analgesic, using environmentally friendly reagents—sodium iodide and household bleach. Further, we designed the lab as a guided-inquiry experiment, asking the students first to predict the orientation of the substitution reaction. After synthesizing the product, the students are asked to determine its structure using FT-IR spectroscopy. The choice of this method of characterization was intentional because of the utility of infrared spectroscopy in determining substitution patterns on aromatic rings and also because it requires students to analyze the fingerprint region of the spectrum. Given that most classroom instruction on IR focuses on functional group determination, we believe this is an added benefit to this experiment.

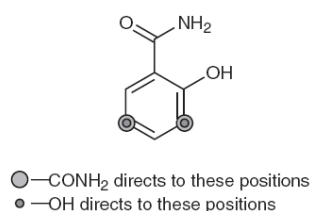
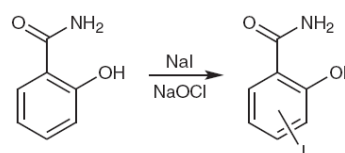


Figure 1. EAS directing effects of the substituents on salicylamide.



Scheme 1. Iodination of salicylamide.

Eric Eby et al., *J. Chem. Educ.* **2008**, 85, 1426-1428.

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剖析師生對綠色化學的認知偏差

在綠色化學思想逐漸普及的同時，發現許多學生和教師對"綠色化學"和"綠色化學實驗"的認知存在偏差。學生錯誤地認為"綠色化學"就是任何時候都禁止排放任何廢物的化學；教師錯誤地認為：實施綠色化學實驗教學時，不能向教室或實驗室泄漏一丁點廢氣，致使學生的嗅覺等感官體驗被剝奪，造成他們對事物的感知不完整。

楊廣斌，賀宏；浙江麗水市麗水中學，浙江麗水市第二高級中學；化學教育，*Chinese Journal of Chemical Education*，編輯部郵箱 **2008** 年 04 期 58-60 頁。

化學實驗中的綠色化技術

綠色化技術是新課程化學實驗倡導的實驗技術之一，但是使用現有的儀器使化學實驗技術綠色化顯得力不從心。為此，我們研制了一些裝置，並從實驗前的準備、實驗的實施和實驗產物的處理 3 個階段對化學實驗綠色化技術進行了探索，為開展綠色化學實驗和改進實驗儀器提供了思路。

張慶云；長江師範學院化學及環境科學系；化學教育，*Chinese Journal of Chemical Education*，編輯部郵箱 **2008** 年 04 期 61-62 頁。

四川省農村中學綠色化學教育現狀調查

通過對四川省部分農村中學師生綠色化學理念、綠色化學行為和綠色化學價值觀 3 個方面的調查與分析，反映出農村中學學生綠色化學意識普遍不強，綠色化學教育匱乏，加強農村中學綠色化學教育勢在必行。

夏開國，帥常文，鮑正榮；四川廣元蒼溪中學校，西華師範大學化學化工學院；化學教育，*Chinese Journal of Chemical Education*，編輯部郵箱 **2008** 年 07 期 56-58 頁。



RESEARCH BREAKTHROUGHS

The integration of green chemistry into future biorefineries

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The use of biorefineries for the production of chemicals as well as materials and energy products is key to ensuring a sustainable future for the chemical and allied industries. Through the integration of green chemistry into biorefineries, and the use of low environmental impact technologies, we can establish future supply chains for genuinely green and sustainable chemical products. The first step in these future biorefineries should be the benign extraction of surface chemicals; here the use of greener solvents, such as supercritical carbon dioxide and bioethanol, should be considered. The residues will

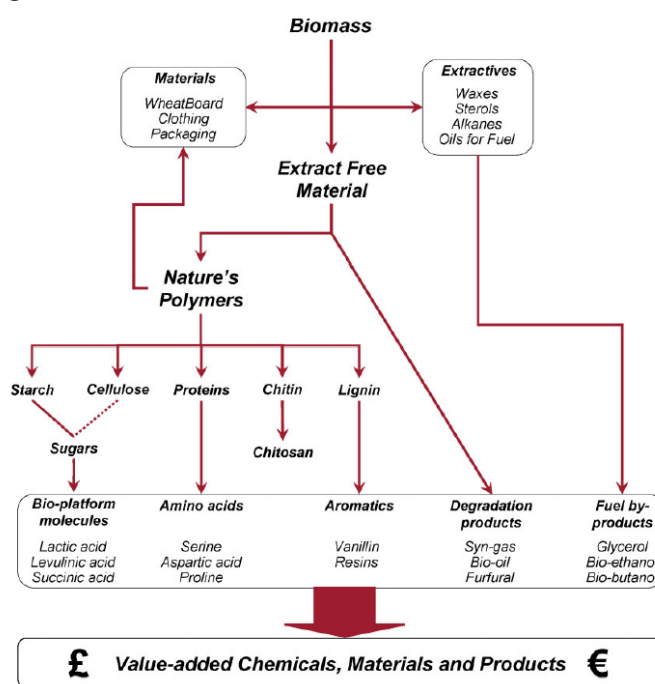


Figure 1. Simplistic idealized biorefinery flowchart.

often be rich in lignocellulosics and the effective separation of the cellulose is a major challenge which may, in the future, be assisted by greener solvents, such as ionic liquids. Lignin is nature's major source of aromatics; we need new ways to produce small aromatic building blocks from lignin in order to satisfy the enormous and diverse industrial demand for aromatics. Fermentation can be used to convert biomass into a wide range of bioplatfrom chemicals in addition to ethanol. Their green chemical conversion to higher value chemicals is as important as their efficient production; here clean technologies such as catalysis - notably biocatalysis and heterogeneous catalysis - the use of benign solvents, and energy efficient reactors are essential. Thermochemical processes for the conversion of biomass, such as the production of pyrolysis oil, will also play an important role in future biorefineries and

here again green chemistry methods should be used to go to higher value downstream chemicals.

James H. Clark et al., *Biofuels, Bioprod. Bioref.* **2009**, 3, 72–90.

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Biofuels, Bioprod. Bioref. **2009**, 3, 72–90.

精煉通常和化石燃料(石油、煤及天然氣)聯在一起. 因為吾人目前日常生活食衣住行育樂所需之用品都和化石燃料有關. 然而化石燃料有一天會用罄. 這是人類永續發展的一大威脅. 而且當供應開始減少而需求增高的時候價格會上揚. 這正是我們面臨的情況.

生物質是取代石化原料選擇之一. 所以下一步工業將以生物質為原料. 有別於化石燃料, 以生物概念. 比如說不同, 此外也和時也不能全年的儲藏庫的建生物質的物性合我們的需要理想的生物質排除對環境有的利用和產



工業有許多新的同生物質的產量季節息息相關. 有不斷的供應. 大型立是必須的. 改變和成份使它們符也是重要的考量. 精煉是在過程中害及有毒化合物生、原料要有永續

性的特質、產品要能自然分解. 凡此種種都是綠色化學的概念. 因此綠色化學是無法避免要整合到將來生物質精煉之中.

本篇也將所有可以由生物質中精煉出的原料作了一個回顧. 其實這部份才是此論文的重點, 也佔了大部份篇幅. 有『可抽取化合物的分離』、『木質纖維素』、『自然聚合物的改良』、『發酵產品』及『燃料生物質精煉的副產化合物』等章節. 相互獨立. 讀者可全讀或選讀有興趣的部分.

總之, 地球上的生物質是非常豐富的. 其中一小部份就足以供應我們的需要. 要發展出永續性, 無害性並兼有經濟性的綠色化學製造過程是科學家面臨的挑戰.

Green decomposition of organic dyes using octahedral molecular sieve manganese oxide catalysts

The catalytic degradation of organic dye (methylene blue, MB) has been studied using green oxidation methods (tertiary-butyl hydrogen peroxide, TBHP, as the oxidant with several doped mixed-valent and regular manganese oxide catalysts in water) at room and higher temperatures. These catalysts belong to a class of porous manganese oxides known as octahedral molecular sieves (OMS). The most active catalysts were those of Mo^{6+} - and V^{5+} -doped OMS. Rates of reaction were found to be first-order

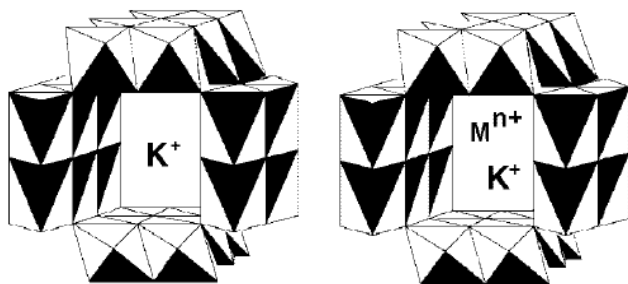


Figure 1. Structures of K-OMS-2 and doped K-OMS-2 catalysts.

with respect to the dye. TBHP has been found to enhance the MB decomposition, whereas H_2O_2 does not. Reactions were studied at pH 3.

The optimum pH for these reactions was pH 3.

Dye-decomposing activity was proportional to the amount of catalyst used, and a significant increase in catalytic activity was observed with increasing temperature. X-ray diffraction (XRD), energy dispersive spectroscopy (EDX), and thermogravimetric analysis (TGA) studies showed that no changes in the catalyst structure occurred after the dye-degradation reaction. The products as analyzed by electrospray ionization mass spectrometry (ESI-MS) showed that MB was successively decomposed through different intermediate species.

Thamayanthy Sriskandakumar et al., *J. Phys. Chem. A*, **2009**, *113*, 1523–1530.

The twelve principles of green chemistry

In this, the centenary year of the Industrial and Engineering Chemistry Division, we present a dozen short essays, one for each of the 12 principles of green chemistry. These principles were first articulated in 1998 as a set of tools to help the design scientist to anticipate downstream issues at the earliest stage of an R&D effort. Recognizing that most materials scientists lack the formal training necessary to deal with issues related to human health, the environment, and regulatory implications, the twelve principles serve to provide a path forward in designing products and processes that would be less environmentally damaging while maintaining or enhancing product performance and economic cost. Designing processes to minimize environmental impact has become, in recent years, essential to industrial and engineering chemistry, and is likely to shape the field for the next 100 years.

Philip G. Jessop et al., *ACS Symposium Series* **2009**, *1000* (Innovations in Industrial and Engineering Chemistry), 401-436.

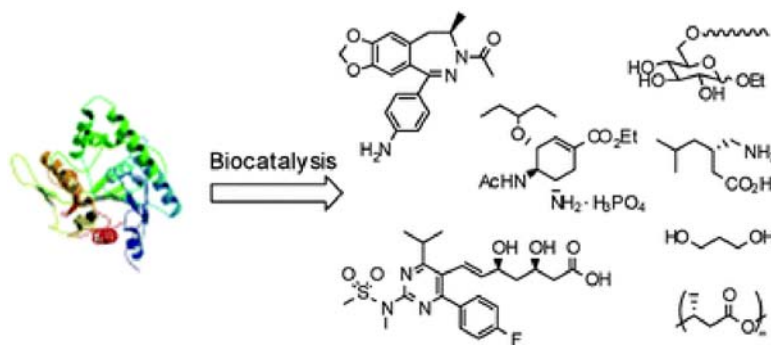
Recent applications of biocatalysis in developing green chemistry for chemical synthesis at the industrial scale

Application of the twelve principles of green chemistry can deliver higher efficiency and reduce the environmental burden during chemical synthesis. As a result of recent

advances in genomics, proteomics and pathway engineering, biocatalysis is emerging as one of the greenest technologies. Enzymes are highly efficient with excellent

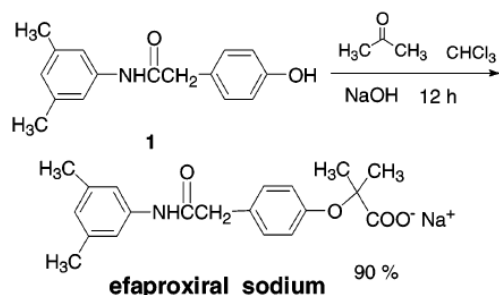
regioselectivity and stereoselectivity. By conducting reactions in water under ambient reaction conditions, both the use of organic solvents and energy input are minimized.

Ningqing Ran et al., *Green Chemistry* **2008**, *10*, 361-372.



Green synthesis applicable for industrial-scale preparation of efaproxiral sodium

Scheme 6. Direct Obtaining of Efaproxiral Sodium through O-Alkylation Reaction



In this article we proposed a novel procedure for the synthesis of efaproxiral sodium, including two reaction steps, condensation, and O-alkylation. In the condensation step, a convenient method was adopted to eliminate the use of solvents, i.e., 4-hydroxyphenylacetic acid and

3,5-dimethylaniline were heated at 15080 °C for 3–5 h, and the reaction was successfully carried out. The yield of anilide in 4-hydroxyphenylacetic acid was 90–93%. In the O-alkylation step, the old circuitous process was avoided, and high-quality sodium salt was directly obtained with a yield of 90%. The final product of efaproxiral sodium was crystallized in water, yielding a new crystalline form containing a unique X-ray powder diffraction pattern with only one peak of $3.7^\circ \pm 0.2^\circ$ in 2θ . The quality of the final product is high with a content of 99.51% according to high-performance liquid chromatographic detection. The present study provided a new environmentally friendly procedure for the preparation of efaproxiral sodium with high yield, low cost, and a short reaction pathway.

Hongchang Shi et al., *Industrial & Engineering Chemistry Research* **2008**, *47*, 2861-2866.

Synthesis of an environmentally friendly water network system.

Water network synthesis (WNS) contributes to cost redn. and water resources conservation by reducing water consumption. A math. optimization model was developed to synthesize an environmentally friendly water network system (WNS) by minimizing environmental impacts of a WNS. Life cycle assessment was integrated into the objective function of the model to evaluate the environmental effect scores (EES) of principal contributors to the environmental impacts of a WNS and optimize trade-offs among their EES. Mass balances were formulated from the superstructure model; constraints were formulated to account for actual situations in industrial facilities. A case study demonstrated the effect of the objective function on configuration and environmental performance of a WNS; it also validated the math. optimization model. This model can be used to design the environment of WNS in a sustainable development context.

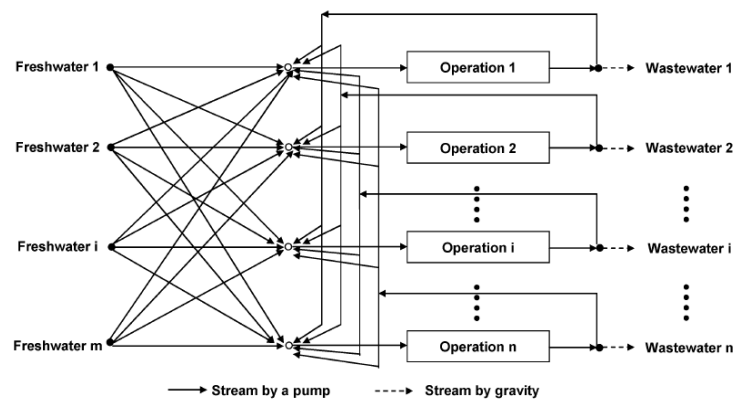
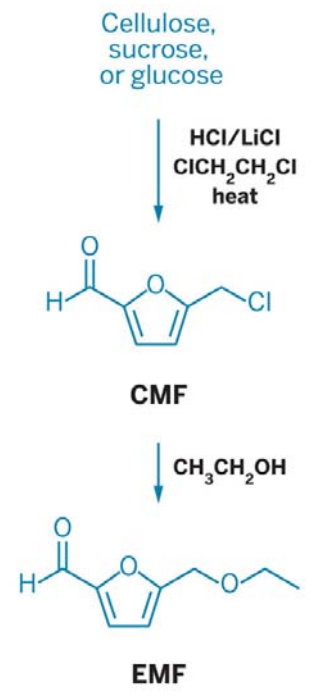


Figure 1. Generalized superstructure model used to generate a WNS.

Seong-Rin Lim et al., *Industrial & Engineering Chemistry Research* **2008**, *47*, 1988-1994.

Direct, high-yield conversion of cellulose into biofuel

A streamlined chemical method that permits easier, direct conversion of purified cellulose into a biofuel has been devised by researchers at the University of California, Davis (*Angew. Chem. Int. Ed.*, DOI: [10.1002/anie.200801594](https://doi.org/10.1002/anie.200801594)). The process transforms cellulose into 5-(chloromethyl)-furfural (CMF) and then into 5-(ethoxymethyl)-furfural (EMF), which is a promising alternative fuel. Ethanol, currently the most widely produced biofuel, is made via a fermentation process that is relatively slow and expensive and requires simple sugars from food crops as a feedstock. To use



nonfood cellulose as a fuel source, a conversion method that can efficiently and cost-effectively break down cellulose on a large scale is necessary. Other researchers have converted biomass-derived sugars into furan-based compounds that are potentially useful as biofuels. But UC Davis' [Mark Mascal](#) and Edward B. Nikitin advanced this process by eliminating a separate step to break down cellulose. The researchers use a solution of HCl and LiCl to digest pure cellulose, continuously extracting the reaction with dichloromethane to obtain CMF along with minor furan products in 85% yield. This intermediate mixture is treated with ethanol to produce EMF. Mascal and Nikitin say the process works equally well when starting with sucrose, glucose, or even tough lignocellulosic biomass such as cotton, straw, and wood.

Mark Mascal et al., *Angew. Chem. Int. Ed.* **2008**, *47*,7924-7926. (*Chemical & Engineering News* **2008**, *86*, pp. 37-38)

Production of polyhydroxybutyrate in switchgrass, a value-added co-product in an important lignocellulosic biomass crop

SCIENTISTS at Cambridge, Mass.-based [Metabolix](#) have genetically engineered switchgrass to produce significant amounts of a biodegradable polyester within the plant's cell walls (*Plant Biotechnol. J.* **2008**, *6*, 663). The ability to coproduce a bioplastic along with a biofuel derived from the plant's cellulose boosts the prospects for using switchgrass and other nonfood crops as renewable feedstocks for biorefineries that one day are expected to economically produce fuels and chemicals. Some bacteria naturally make polyhydroxyalkanoates (PHAs) for energy storage, much in the way animals use fat. Metabolix has previously optimized this process by



incorporating a series of genes from PHA-producing bacteria into other microbes. The genes express enzymes that convert sugars or oils into PHAs via a multistep process within the bacterial cells. Metabolix has partnered with [Archer Daniels Midland](#) through a joint venture called Telles for fermentation production of Mirel brand biodegradable PHAs for use in fibers, films, and molded goods.

Now, a Metabolix research team led by Kristi D. Snell has rewired the genetic sequence of switchgrass to enable production of polyhydroxybutyrate. The polymer accumulates in beadlike granules inside chloroplasts of the plant's cells, primarily in leaves but also in stalks. In greenhouse studies, the engineered plants produced leaves with PHA content up to

3.7% dry weight. The company projects that polymer levels will need to hit 5.0 to 7.5% dry weight for commercial production to be viable.

Switchgrass PHA could be used directly as a polymer, or it could be depolymerized to form hydroxy acids for use as chemical feedstocks. Residual plant material could be burned to produce electricity, or the cellulose could be converted into liquid fuels.

The paper "represents a very good research result," says Michigan State University's [Mariam B. Sticklen](#), an expert in genetically modified biomass crops. Sticklen stresses that coproducing bioplastics in plants is not new, but because of patent licensing the early efforts have primarily been of academic interest and have yet to pan out commercially. The Metabolix development is promising, she says, but due to regulatory hurdles it could still be years before bioplastics from engineered plants are commercially available.

Kristi D. Snell et al., *Plant Biotechnology Journal* **2008**, 6, 663–678. (*Chemical & Engineering News* **2008**, 86, 13)



NEWS DIGEST

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Greening the Farm

Safer and environmentally friendlier pesticides and agricultural practices gain traction on U.S. farms

AD HOC efforts by an impressive array of federal and state agencies, farmer alliances, chemical companies, and nonprofit advocacy groups are dramatically shifting the way pesticides are made and used. As a result, pesticide use in the U.S. has dropped. Data from the Environmental Protection Agency



show that conventional pesticide use, which includes agricultural and home and garden applications, peaked at 1.46 billion lb in 1979 and fell to 1.23 billion lb in 2001, the last year for which comprehensive data are available. Since then, pesticide use in the U.S. appears to have remained flat, according to limited government data and market research reports.

The drop in pesticide use is due to a host of factors, including better pesticides that not only are more selective and applied at lower rates, but also have lower inherent toxicity and thus a lower impact on human health and the environment. Another factor is the set of farming strategies called integrated pest management (IPM), which relies on the life cycles of pests and crops to control pests economically and withholds use of pesticides until potential damage reaches a certain threshold.

A third factor is organic farming, which shuns synthetic pesticides altogether. But when organic farmers need help, they can turn to approved nonsynthetic pesticides and so-called biopesticides, which have emerged as a viable alternative pest-control agent for safety- and environment-conscious farmers and consumers.

Stephen K. Ritter, *Chemical & Engineering News* **2009**, 87, 13-20.



CONFERENCE INFORMATION

1. 5th International Conference on Renewable Resources & Biorefineries Ghent, Belgium, June 10-12, 2009 (<http://www.rrbconference.com/>)

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2. 2nd International Congress on Green Process Engineering, GPE 2009 Venice, Italy, June 14-17, 2009 (<http://www.gpe-epic2009.org/>)



3. 13th Annual Green Chemistry & Engineering Conference College Park, MD, USA, June 23-25, 2009 (www.acs.org/greenchemistry)



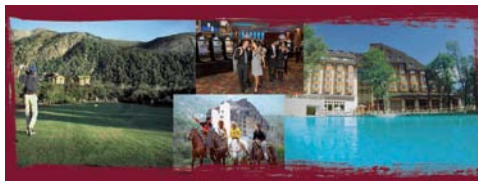
13th Annual Green Chemistry & Engineering Conference

4. Green Pharma Summit: The Ritz-Carlton, 10 Avenue of the Arts, Philadelphia, PA, United States of America July 20-21 2009 (<http://www.iirusa.com/greenpharma/venue-information.xml>)



5. 8th Green Chemistry Conference: Universidad de Zaragoza, Paraninfo, Building Paraninfo, Zaragoza, Spain, September 9-11 2009 (<http://8gcc.unizar.es/index.html>)

6. AAIC 21st Annual Meeting: 2009 International Conference: The Next Generation of Industrial Crops, Processes, and Products, Termas de Chillán, Chillán, Chile, November 14-19th, 2009 (http://www.aaic.org/2009_meeting.htm).



7. 3rd International IUPAC Conference on Green Chemistry, August 15-19, 2010, Ottawa Westin Hotel, Ottawa, Canada (<http://www.icgc2010.ca/>)



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Cover picture:

冰島的高山上有永凍層冰帽。下雨或下雪會堆積在冰帽上，愈堆愈高愈重，夏天冰的外層會慢慢融化，慢慢往下滑，從山頂滑到海邊，要幾百萬年之類的，就是冰河。以往這個冰河可以延伸到海邊，現在因為全球暖化，到離海岸 200 公尺左右就完全溶化完了，變成河流 (abstract from Steven Zan)。