Green & Sustainable Chemical Communication
綠色與永續化學通訊
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引言

今年美國總統綠色化學挑戰獎（Presidential Green Chemistry Challenge Awards）的各獎項得主已於十月間公佈，項目有 Greener Synthetic Pathways、Greener Reaction Conditions、Designing Greener Chemicals、Small Business、Academic 等。根據 C&EN 的報導（C&EN 2014, Volume 92, Issue 42, p. 32），從 1996 年至今的得獎技術，已為地球減少了八億磅有害化學物質的使用，省下兩百億加侖的水，並避免了近八十億磅的二氧化碳排放。今年的學術獎得獎人為美國 University of Wisconsin-Madison 的 Shannon S. Stahl 教授，他的實驗室發展出可於室溫與空氣下操作，以一價銅 Cu/TEMPO（TEMPO = 2,2,6,6-tetramethyl-1-piperidinyl-N-oxyl）與隨手可得的氧氣為催化主體的氧化反應，將醇類轉化為醛類。傳統的氧化試劑常伴隨反應選擇性不佳，與產生有害廢棄物的問題。獲獎之催化劑反應選擇性好、副產物少、安全性高，除了有學術上的價值，已得到藥廠的青睞。在其他的獎項方面，從混和無氟界面活性劑與糖而製得的泡沫滅火劑、更潔淨的量子點（quantum dot）製程，到應用生物科技來得到油品，可看出化學家旺盛的創造力是造福社會的關鍵。編輯黃鴻裕細心地為今年的得獎內容整理了許多連結，讓相關訊息伸指可及，感謝他的主動與用心。

在環境日益惡化的今日，創造對環境友善的化學製程與技術是眾人的渴望，將部份廢棄物變為資源亦蔚為風潮。在今年六月的第十八屆 Annual Green Chemistry & Engineering Conference（GC&E）中，就有《From Waste to Wealth》的系列演講，而美國化學學會的 ACS Webinar 也規劃過這樣的主題，由英國 York University 化學系的四位學者描述他們為了從食物與電子廢棄物取出有用的化合物與元素所做的創新（From Waste to Wealth Using Green Chemistry https://www.youtube.com/watch?v=gZaKnQisdQI）。在外國人眼裡，台灣在塑膠回收與再利用方面相當先進，因此在八月四日出版的 C&EN 雜誌，有一篇〈Taiwan

Resets To Green〉的報導，此篇的連結，提供於本期通訊中（見 p. 9）。

美國化學學會之下的 Green Chemistry Institute（GCI）是負責推動綠色化學的組織。GCI 與美西的 Western Sustainability and Pollution Prevention Network 合作，將綠色化學的十二原則，每一項都以一支長約二十分鐘的影片進行介紹，有興趣的同行可以多加利用（見 p. 23）。最後，本年度 11/22－23 在工研院舉行的化學年會有三項與綠色化學相關的活動，期待大家的參與。此三項活動分別為：

1. **11/22** 中午的**午餐討論會**：淡江陳幹男教授、工研院沈永清研究員、前美國艾克森美孚（ExxonMobil）石油公司石化上中游研發與智慧財產管理主持人區迪頤博士將以他們的經驗與看到的趨勢作為引言，促發大家的討論。
2. **11/22** 下午的**綠色/永續化學講習會**：中研院甘魯生研究員、中興李進發教授、工研院杜子邦研究員、台大梁文傑教授將以他們蒐集到的資訊，簡報綠色化學十二原則、綠色耦聯反應、綠色溶劑、化學安全的進展。
3. **11/23** 上午的**綠色化學教育的推展與實踐討論會**：清華凌永健教授、靜宜梁偉明教授、中研院趙奕姼研究員、東華宋秉明教授引言，讓我們一起來討論如何將綠色化學教育在教育體系中生根。其中自 2010 年開始舉辦的綠色/永續化學講習會（之前稱工作坊），講師們精心準備的講義可由以下網站連結，歡迎舊雨新知造訪。http://gc.chem.sinica.edu.tw/workshop/notes.php

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Webinar

Planting the Seeds for Sustainable Chemistry

What can be done to incorporate green chemistry in to all parts of the industry? Join us to learn about the Network of Early-Career Sustainable Scientist and Engineers (NESSE) and how they are working to build a community of confident and able early-career sustainable scientists. These professionals are connecting across disciplines, sharing knowledge and resources, forging collaborations, and finding solutions towards making research and its outcomes greener and more sustainable.

http://www.acs.org/content/dam/acsorg/events/slides/2014-09-04-planting-the-seeds-of-sustainable-chemistry.pdf

Salvaging Carbon Dioxide: Finding Value Beyond the Smokestack

Thursday, December 4, 2014 @ 2-3pm ET

Carbon dioxide doesn’t need to be a dirty word. Join Sam Rushing from Advanced Cryogenics as he explores some of the commercial applications that can exist for recaptured CO_2, including industrial cleaning, fumigation and supercritical extraction. He will also examine the growing market for these services.

http://www.acs.org/content/acs/en/events/upcoming-acs-webinars/green-carbon.html

Conferences

2014 Michigan Green Chemistry and Engineering Conference

"Cultivating Next Generation Solutions"

November 11-12, 2014

East Lansing, Michigan, USA

http://www.michigan.gov/deq/0,4561,7-135-3585_49005-329144--,00.html

8th International Algae Congress

December 2-3, 2014

Florence, Italy

http://www.algaecongress.com/page/3789

3rd Conference on Carbon Dioxide as Feedstock for Chemistry and Polymers

December 2-3 , 2014

Essen, Germany

http://www.co2-chemistry.eu/

Green Polymer Chemistry 2015

March 18-19, 2015

Cologne, Germany

http://www.amiplastics.com/events/event?Code=C637#4585

International Symposium on Green Chemistry

May 3-7, 2015

La Rochelle, France

http://www.isgc2015.com/

19th Annual Green Chemistry & Engineering Conference

July 14-16, 2015

North Bethesda, Maryland, USA

http://www.gcande.org/

Award

The 2014 Winners of the Presidential Green Chemistry Challenge Awards

Brief summary

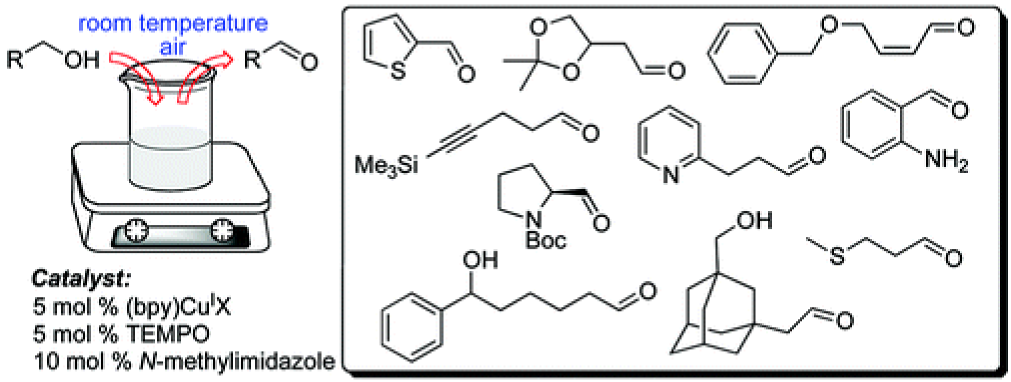
http://blog.epa.gov/epaconnect/2014/10/who-are-this-years-innovators-tackling-climate-change-and-promoting-energy-efficiency/

http://www2.epa.gov/green-chemistry/presidential-green-chemistry-challenge-winners

For Academic

Professor Shannon S. Stahl of the University of Wisconsin-Madison

Aerobic Oxidation Methods for Pharmaceutical Synthesis



Practical Aerobic Oxidations of Alcohols and Amines with Homogeneous Copper/TEMPO and Related Catalyst Systems

Ryland, B. L.; Stahl, S. S. *Angew. Chem. Int. Ed*. **2014**, *53*, 8824-8838.

DOI: 10.1002/anie.201403110

Highly Practical Copper(I)/TEMPO Catalyst System for Chemoselective Aerobic Oxidation of Primary Alcohols

Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc*. **2011**, *133*, 16901-16910.

DOI: 10.1021/ja206230h

http://cen.acs.org/articles/92/i42/Academic-Award.html

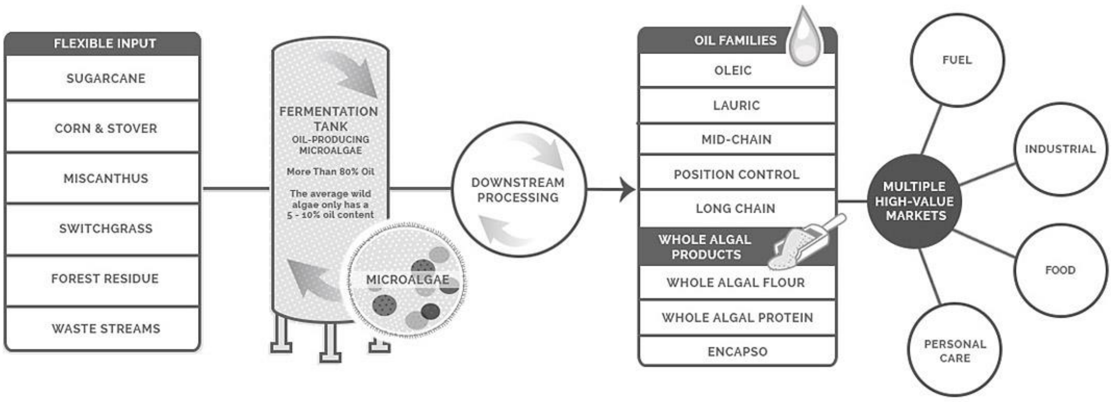
http://www2.epa.gov/green-chemistry/2014-academic-award

http://stahl.chem.wisc.edu/research

For Greener Synthetic Pathways

Solazyme, Inc.

Tailored Oils Produced from Microalgal Fermentation



http://cen.acs.org/articles/92/i42/Greener-Synthetic-Pathways-AWARD.htm

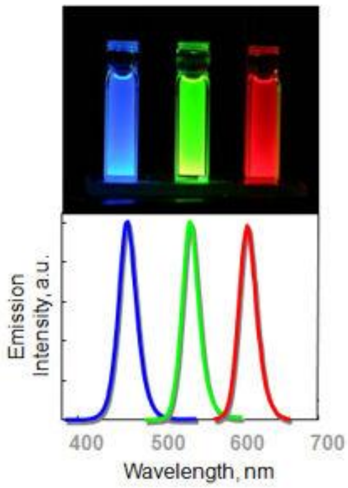
http://www2.epa.gov/green-chemistry/2014-greener-synthetic-pathways-award

http://solazyme.com/innovation/?lang=en

For Greener Reaction Conditions

QD Vision, Inc.

Greener Quantum Dot Synthesis for Energy Efficient Display and Lighting Products



http://cen.acs.org/articles/92/i42/Greener-Reaction-Conditions-Award.html

http://www2.epa.gov/green-chemistry/2014-greener-reaction-conditions-award

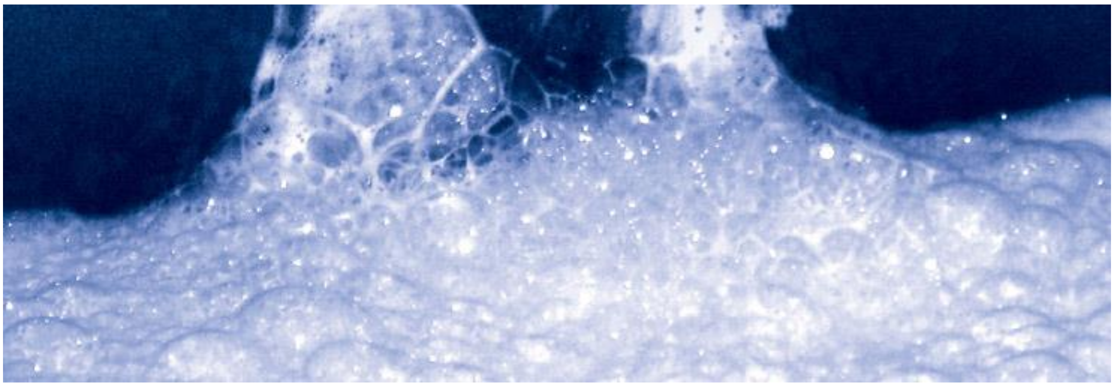
http://www.qdvision.com/content1652

http://coloriq.com/

For Designing Greener Chemicals

The Solberg Company

RE-HEALINGTM Foam Concentrates–Effective Halogen-Free Firefighting



http://cen.acs.org/articles/92/i42/Designing-Greener-Chemicals-Award.html

http://www2.epa.gov/green-chemistry/2014-designing-greener-chemicals-award

http://www.solbergfoam.com/Foam-Concentrates/RE-HEALING-Foam.aspx

For Small Business

Amyris

Farnesane: a Breakthrough Renewable Hydrocarbon for Use as Diesel and Jet Fuel

http://cen.acs.org/articles/92/i42/Small-Business-Award.html

http://www2.epa.gov/green-chemistry/2014-small-business-award

http://www.amyris.com/Products/173/Fuels

News

Climate Change

ACS Select on Ocean Acidification: Causes, Consequences and Cures

Environmental Science & Technology publishes leading research in the area of ocean acidification. This ACS Select brings together authors developing sensor technology and measuring the effects on organisms. These advance our understanding of the ocean acidification process.

http://pubs.acs.org/page/esthag/select/ocean_acidification.html

Stratospheric Ozone Layer on the Mend—But Another Problem Has Arisen

Climate Change: United Nations report details impacts of the Montreal protocol, the treaty that led to change as well as new greenhouse gases

http://cen.acs.org/articles/92/web/2014/09/Stratospheric-Ozone-Layer-MendAnother-Problem.html

Methane's Role in Climate Change

Whether natural gas is a savior or destroyer of climate depends on how much is leaking into the atmosphere

https://cen.acs.org/articles/92/i27/Methanes-Role-Climate-Change.html

What Do Chinese Dumplings Have to Do With Global Warming?

http://www.nytimes.com/2014/07/27/magazine/what-do-chinese-dumplings-have-to-do-with-global-warming.html

Capture and Conversion of CO_2

Lowering the Cost of Carbon Capture

ACS Meeting News: Phase-changing ionic-liquid-based material could reduce the energy needed to trap CO_2

http://cen.acs.org/articles/92/web/2014/08/ACS-Meeting-News-Lowering-Cost.html

Copper Foam Turns CO_2 into Useful Chemicals

Scientists at Brown University's Center for Capture and Conversion of CO_2 have discovered that copper foam could provide a new way of converting excess CO_2 into

useful industrial chemicals, including formic acid.
https://news.brown.edu/articles/2014/08/copper

New Chemical Feedstocks: Abundant Innovation

A review of some of the talks present at the GC&E Conference from the session, "Abundant Innovation: Pathways to new chemical feedstocks from CO_2 and natural gas"
https://communities.acs.org/community/science/sustainability/green-chemistry-nexus-blog/blog/2014/07/23/new-chemical-feedstocks-abundant-innvoation

Alternative Energy

Organic Photocatalyst Helps Split Water

Catalysis: Graphitic carbon nitride looks promising as a catalyst to harness sunlight to produce hydrogen fuel from water
http://cen.acs.org/articles/92/web/2014/09/Organic-Photocatalyst-Helps-Split-Water.html

Perovskites Take Lead in Solar Hydrogen Race

Highly efficient solar cells and catalysts made from cheap, common materials use sunlight to split water.
http://www.sciencemag.org/content/345/6204/1566.full

Researchers Design a High-Power Paper Battery that Bends

Materials: Flexible batteries made from cellulose and carbon nanotubes require fewer components and could power portable electronics
http://cen.acs.org/articles/92/web/2014/10/Researchers-Design-High-Power-Paper.html

Leaves Inspire Photon Energy Upconversion Material

Materials Science: A cellulose-based material protects light-sensitive dye molecules from oxygen damage and could help boost the efficiency of some solar cells
http://cen.acs.org/articles/92/web/2014/08/Leaves-Inspire-Photon-Energy-Upconversion.html

Bumping up Ethanol Yields

Biotechnology: Simple alterations in fermentations could boost yeast productivity
http://cen.acs.org/articles/92/web/2014/10/Bumping-Ethanol-Yields.html

Synthesis

Organic Synthesis: The Robo-chemist

The race is on to build a machine that can synthesize any organic compound. It could transform chemistry.

http://www.nature.com/news/organic-synthesis-the-robo-chemist-1.15661

Scripps Research Institute Chemists Uncover Powerful New Click Chemistry Reactivity

Chemists led by Nobel laureate K. Barry Sharpless have used his click chemistry to uncover unprecedented, powerful reactivity for making new drugs, diagnostics, plastics, smart materials and many other products.

http://www.scripps.edu/news/press/2014/20140813sharpless.html

Green Boost for C–C Bond-Forming Reaction

Researchers expand aqueous organometallic chemistry by conducting a Barbier-Grignard-type direct arylation of carbonyls in water.

http://cen.acs.org/articles/92/i26/Green-Boost-CC-Bond-Forming.html

More on Microwaves

Additional experiments help chemists better elucidate the thermal effects of microwaves in heating chemical reactions.

http://cen.acs.org/articles/92/i32/Microwaves.html

Catalyst

Inorganic Nanowire Photocatalyst Turns Methane into Benzene

Shining light on gallium nitride nanowires overcomes the C–H activation energy barrier under mild conditions.

http://cen.acs.org/articles/92/i22/Inorganic-Nanowire-Photocatalyst-Turns-Methane.html

‘Green’ Route to Chromanols

Organic Chemistry: Organocatalysis creates tocopherol’s chiral core.

http://cen.acs.org/articles/92/i29/GreenRoute-Chromanols.html

Seeing the Green Side of Innovation

Green Chemistry & Engineering Conference focuses on translating use-inspired basic research into sustainable products.

- Green Chemistry Gets a Boost from Open Innovation Platforms
  Launch program and White House "maker" project provide opportunities for chemical innovation.
- Green Business Plan Competition Fosters Innovation
  Conference event encourages research, development, and marketing of industrially relevant green products and processes.
- Natural Biocide Offers an Alternative for Fracking
  Bacteria-derived lipopeptide could help manage bacterial fouling of oil and gas wells.
- Sigma-Aldrich Develops Green Cross-Coupling Reaction Kits
  Off-the-shelf kits allow single organic synthesis reactions to be performed in water for research and in teaching labs.
- EMD Millipore Makes Progress in Biopharma Plastics Recycling
  Company develops take-back program to reduce amount of plastics used in biopharmaceutical production that ends up in landfills.

http://cen.acs.org/articles/92/i26/Seeing-Green-Side-Innovation.html#4

Analysis and Diagnosis

Handheld Analyzer Provides Lab-Like Capabilities for Only $25

A mobile electrochemical detector called uMED can test for a variety of molecular-level health or environmental indicators and then use any cell phone on any cellular network to transmit results for remote analysis and diagnosis.
https://cen.acs.org/articles/92/i32/Handheld-Analyzer-Provides-Lab-Like.html

Recycle

Taiwan Resets to Green

Once heavily polluted, island reinvents itself as a leader in green practices and recycled materials
http://cen.acs.org/articles/92/i31/Taiwan-Resets-Green.html

E-Waste

The Geography of the Global Electronic Waste ('e-waste') Burden

As local and national governments struggle to deal with ever-growing piles of

electronic waste (or "e-waste"), scientists are now refining the picture of just how much there is and where it really ends up. Published in the ACS journal, their study found that nearly a quarter of e-waste that developed countries discard floods into just seven developing countries — with major potential health risks for the people who live there.
https://communities.acs.org/community/science/sustainability/green-chemistry-nexus-blog/blog/2014/08/04/the-geography-of-the-global-electronic-waste-e-waste-burden

Toxicity

Fracking Wastewater Could Encourage Formation of Toxic Compounds during Drinking Water Disinfection

Environmental Chemistry: Laboratory experiments suggest that bromide and iodide in wastewater may contribute to formation of halogenated disinfection by-products.
http://cen.acs.org/articles/92/web/2014/09/Fracking-Wastewater-Encourage-Formation-Toxic.html

Oil Dispersant Compound Persists for Years After Gulf Spill

Environmental Toxicology: Traces of dispersants applied in the Deepwater Horizon spill remain months later in deep-sea coral communities and years later on coastlines.
http://cen.acs.org/articles/92/web/2014/07/Oil-Dispersant-Compound-Persists-Years.html

Formaldehyde is a Human Carcinogen, US National Research Council Says

Toxicology: Report affirms National Toxicology Program’s classification of compound
http://cen.acs.org/articles/92/i33/Formaldehyde-Human-Carcinogen-National-Research.html

Sunscreens Release Hydrogen Peroxide into Seawater

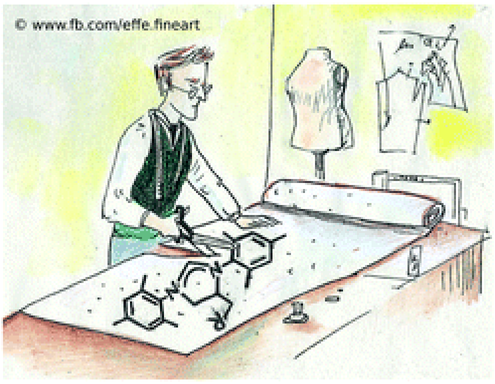
Emerging Contaminants: New study finds that titanium dioxide nanoparticles in sunscreens could produce enough hydrogen peroxide in coastal waters to stress algae
http://cen.acs.org/articles/92/web/2014/08/Sunscreens-Release-Hydrogen-Peroxide-Seawater.html

Reviews and Papers

Catalyst

Towards "Cleaner" Olefin Metathesis: Tailoring the NHC Ligand of Second Generation Ruthenium Catalysts to Afford Auxiliary Traits

Green Chem., **2014**, *16*, 4474-4492. **DOI**: 10.1039/C4GC00705K

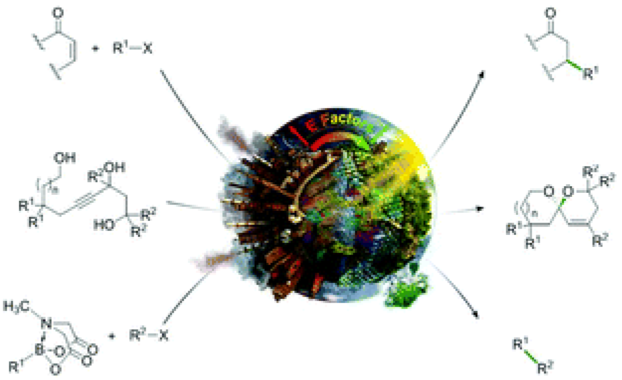


The increasing use of olefin metathesis in practical syntheses led to a greater demand for tailored catalysts that offer not only high reactivity and stability in the presence of impurities, but also improved handling characteristics, such as custom solubility profiles, simpler post-reaction workup and easier removal of ruthenium residues from the products. Due to mechanistic considerations, the most appropriate way to create such compounds is to decorate known catalysts with utility related tags placed in nonlabile ligands. This critical review summarizes how the NHC ligand can be modified to confer novel auxiliary traits and examines the practical consequences of these modifications.

Solvent

Transitioning Organic Synthesis from Organic Solvents to Water. What's Your E Factor?

Green Chem., **2014**, *16*, 3660-3679. **DOI**: 10.1039/C4GC00503A



Traditional organic chemistry, and organic synthesis in particular, relies heavily on organic solvents, as most reactions involve organic substrates and catalysts that tend to be water-insoluble. Unfortunately, organic solvents make up most of the organic waste created by the chemical enterprise, whether from academic, industrial, or governmental labs. One alternative to organic solvents follows the lead of Nature: water. To circumvent the solubility issues, newly engineered "designer" surfactants offer an opportunity to efficiently enable many of the commonly used transition metal-catalyzed and related reactions in organic synthesis to be run in water, and usually at ambient temperatures. This review focuses on recent progress in this area, where such amphiphiles spontaneously self-aggregate in water. The resulting micellar arrays serve as nanoreactors, obviating organic solvents as the reaction medium, while maximizing environmental benefits.

Ionic Liquid Solutions as Extractive Solvents for Value-added Compounds from Biomass

Green Chem., **2014**, Advance Article **DOI**: 10.1039/C4GC00236A

In the past few years, the number of studies regarding the application of ionic liquids (ILs) as alternative solvents to extract value-added compounds from biomass has been growing. Based on an extended compilation and analysis of the data hitherto reported, the main objective of this review is to provide an overview on the use of ILs and their mixtures with molecular solvents for the extraction of value-added compounds present in natural sources. The ILs (or IL solutions) investigated as solvents for the extraction of natural compounds, such as alkaloids, flavonoids, terpenoids, lipids, among others, are outlined. The extraction techniques employed, namely solid–liquid extraction, and microwave-assisted and ultrasound-assisted extractions, are emphasized and discussed in terms of extraction yields and purification factors. Furthermore, the evaluation of the IL chemical structure and the optimization of the process conditions (IL concentration, temperature, biomass–solvent ratio, etc.) are critically addressed. Major conclusions on the role of the ILs towards the extraction mechanisms and improved extraction yields are additionally provided. The isolation and recovery procedures of the value-added compounds are ascertained as well as some scattered strategies already reported for the IL solvent recovery and reusability. Finally, a critical analysis on the economic impact versus the extraction performance of IL-based methodologies was also carried out and is here presented and discussed.

Metal-free Synthesis

Metal-free Multicomponent Syntheses of Pyridines

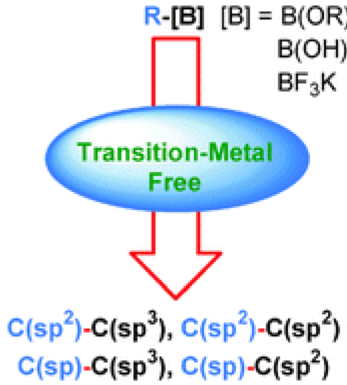
Chem. Rev., Article ASAP **DOI**: 10.1021/cr500099b

Since developing "green chemistry" methodologies has never been such an emergency in our environmental and economical context, we will focus in this article on recent selected advances in the development of metal-free multicomponent strategies toward pyridines. The compilation of the existent literature focuses on the pyridine ring construction and has been organized according to the main reaction involved in each process. It is interesting to note that although they have known significant developments in the past decade, most of them are based on old but well-known reactions.

Transition-metal-free C–C bond Forming Reactions of Aryl, Alkenyl and Alkynylboronic Acids and Their Derivatives

Chem. Soc. Rev., **2014**, Advance Article **DOI**: 10.1039/C4CS00195H

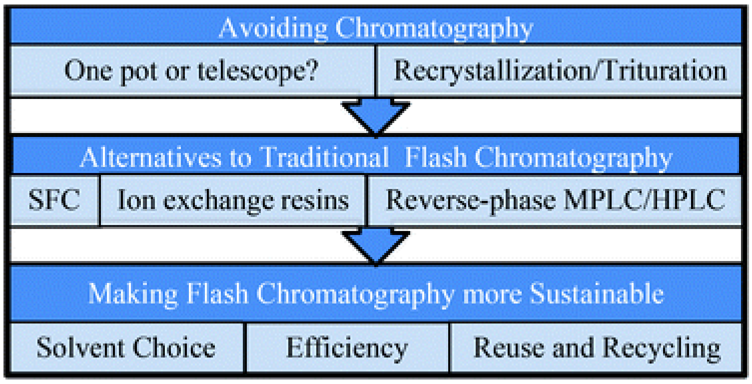
Investigation of new methods for the synthesis of C–C bonds is fundamental for the development of new organic drugs and materials. Aryl-, alkenyl- and alkynylboronic acids and their derivatives constitute attractive reagents towards this end, due to their stability, low toxicity and ease of handling. However, these compounds are only moderately nucleophilic. Consequently, the most popular C–C bond forming reactions of these boronic acids, such as the Suzuki–Miyaura, Heck, and Hayashi–Miyaura reactions, or additions to C=O and C=N bonds, require catalysis by transition metals. However, due to the toxicity and cost of transition metals, some new methods for C–C bond formation using aryl-, alkenyl- and alkynylboronic acids under transition-metal-free conditions are beginning to emerge. In this tutorial review, the recent synthetic advances in this field are highlighted and discussed.



Green Separation

Sustainable Chromatography (An Oxymoron?)

Green Chem., **2014**, *16*, 4060-4075. **DOI**: 10.1039/C4GC00615A

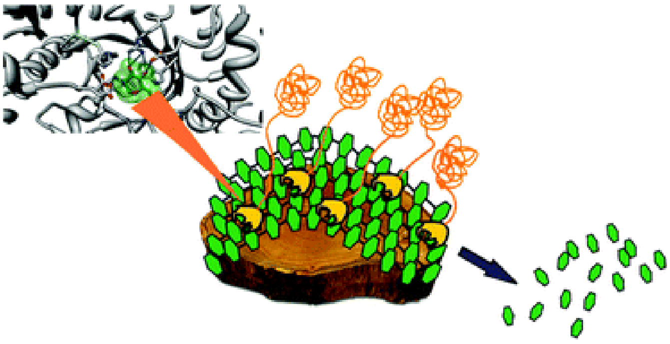


Chromatography is routinely used in drug discovery as a means to isolate intermediates and final compounds. From a sustainability perspective, it is one of the largest contributors of solvent waste in the drug discovery process. The medicinal chemistry subgroup within the American Chemical Society's Green Chemistry Institute Pharmaceutical Roundtable (ACS GCI PR) offers a perspective aimed at providing chemists with practical tools and easily implemented techniques to improve the sustainability of drug discovery through reduction of the waste generated during chromatography. This perspective also offers alternatives to traditional, silica gel-based chromatography as well as information on how to avoid chromatography completely through use of crystallization and reaction telescoping.

Biomass and Biofuel

Enzymatic Breakdown of Biomass: Enzyme Active Sites, Immobilization, and Biofuel Production

Green Chem., **2014**, Advance Article **DOI**: 10.1039/C4GC01405G

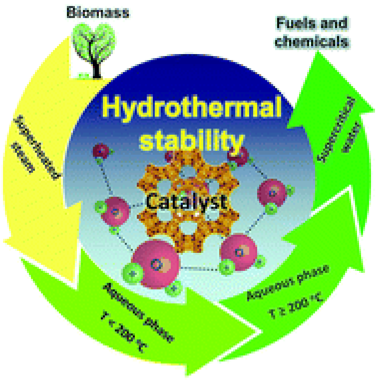


A bacterial enzyme efficiently breaks down cellulose and hemicellulose without the cooperation of other enzymes. An emerging trend in the versatile development of biomass breakdown techniques involves multidomain cellulase enzymes of bacteria, which efficiently hydrolyze microcrystalline cellulose by outperforming enzyme cocktails typically used commercially to break down biomass produced by the fungus Hypocrea jecorina. This article presents a review of current developments in the understanding of the microstructure of plant biomass, treatment of biomass using bacterial hydrolase enzymes, active site structures of hydrolytic and oxidative enzymes, and their overall impact on the biomass degradation process. This article addresses the nanoscale features of a biomass surface during enzymatic reactions, the implication of enzyme-based biorefineries in biofuel production, and the mechanism of action of cellulases and other enzymes in the degradation of insoluble biomass substrates. The environment and roles of the active sites of the hydrolytic and oxidative enzymes are also discussed. The concept of immobilized cellulase on a solid surface is emphasized, which is an effective alternative for developing biorefineries for biofuel production driven by enzyme function.

Hydrothermally Stable Heterogeneous Catalysts for Conversion of Biorenewables

Green Chem., **2014**, Advance Article **DOI**: 10.1039/C4GC01152J

The catalytic conversion of biomass-derived molecules to fuels and chemicals involves reactions carried out in the aqueous phase. The corrosive effects of the reactive environment can cause degradation of heterogeneous catalysts, but the detrimental effects depend on the state of water. For example, water vapor, superheated steam and sub- and supercritical liquid water can behave very different from each other. In this review, we focus on the hydrothermal stability of the heterogeneous catalysts in order of the increasing severity of the reaction medium: superheated steam, liquid water at temperatures below 200 °C, liquid water at temperatures above 200 °C and supercritical water. This review addresses changes in the physical structure of heterogeneous catalysts used for biomass conversion



reactions. These physical changes influence the catalytic performance, but other causes for deactivation include sintering of the metal phase or coking or carbon deposition on catalysts. The latter phenomena are not the primary focus of this review. We also describe recent approaches designed to improve the hydrothermal stability of heterogeneous catalysts in biomass conversion reactions.

Characterization of Biomass and Its Derived Char Using ^{13}C-solid State Nuclear Magnetic Resonance

Green Chem., **2014**, Advance Article **DOI**: 10.1039/C3GC42570C

The role of ^{13}C solid state nuclear magnetic resonance (ssNMR) in the elucidation of the structure of biomass and carbonaceous solids derived from biomass has been crucial since the mid-70s, which gives it a more than 30-year history. As soon as magic angle spinning was coupled to cross-polarization, ssNMR suddenly became of high use to approach structural resolution in cellulose, lignin, coals and various types of carbonaceous materials, up to the more recent hydrothermal carbons (HTC). This review focuses on the specific contribution that ssNMR has made to this field and in particular, the technical advances in the field of ssNMR (advanced pulse sequences for spectral editing, more advanced Magic Angle Spinning probes, high-field spectrometers) will be outlined in terms of their usefulness for the specific purpose of studying the structure of complex biomass (lignin, cellulose) and their char obtained either via a pyrolytic or hydrothermal approach.

Sonochemistry: What Potential for Conversion of Lignocellulosic Biomass into Platform Chemicals?

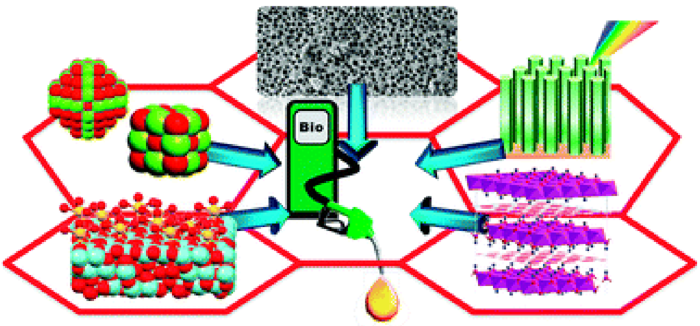
ChemSusChem **2014**, *7*, 2774 – 2787. **DOI**: 10.1002/cssc.201402289

This Review focuses on the use of ultrasound to produce chemicals from lignocellulosic biomass. However, the question about the potential of sonochemistry for valorization/conversion of lignocellulosic biomass into added-value chemicals is rather conceptual. Until now, this technology has been mainly used for the production of low-value chemicals such as biodiesel or as simple method for pretreatment or extraction. According to preliminary studies reported in literature, access to added-value chemicals can be easily and sometimes solely obtained by the use of ultrasound. The design of sonochemical parameters offers many opportunities to develop new eco-friendly and efficient processes. The goal of this Review is to understand why the use of ultrasound is focused rather on pretreatment or extraction of lignocellulosic biomass rather than on the production of chemicals and to understand, through the reported examples, which directions need to be followed to favor strategies based on ultrasound-assisted production of chemicals from lignocellulosic biomass. We believe that ultrasound-assisted processes represent an innovative approach and will create a growing interest in academia but also in the industry in the near future. Based on the examples reported in the literature, we critically discuss how sonochemistry could offer new strategies and give rise to new results in lignocellulosic biomass valorization.

Heterogeneous Catalysis for Sustainable Biodiesel Production via Esterification and Transesterification

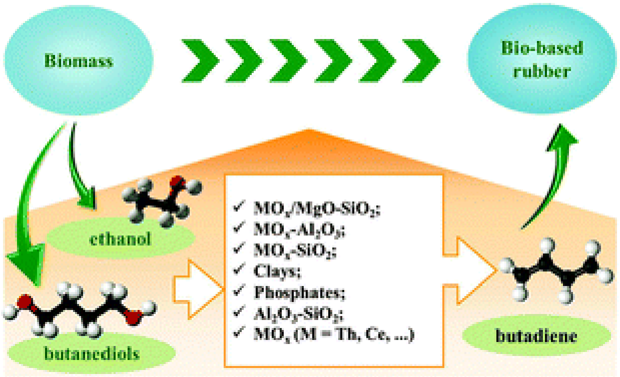
Chem. Soc. Rev., **2014**, Advance Article **DOI**: 10.1039/C4CS00189C

Concern over the economics of accessing fossil fuel reserves, and widespread acceptance of the anthropogenic origin of rising CO_2 emissions and associated climate change from combusting such carbon sources, is driving academic and commercial research into new routes to sustainable fuels to meet the demands of a rapidly rising global population. Here we discuss catalytic esterification and transesterification solutions to the clean synthesis of biodiesel, the most readily implemented and low cost, alternative source of transportation fuels to meet future societal demands.



Review of Old Chemistry and New Catalytic Advances in the On-purpose Synthesis of Butadiene

Chem. Soc. Rev., **2014**, Advance Article **DOI**: 10.1039/C4CS00105B



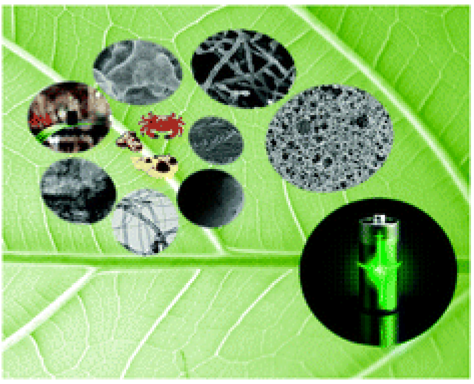
Increasing demand for renewable feedstock-based chemicals is driving the interest of both academic and industrial research to substitute petrochemicals with renewable chemicals from biomass-derived resources. The search towards novel platform chemicals is challenging and rewarding, but the main research activities are concentrated on finding efficient pathways to produce familiar drop-in chemicals and polymer building blocks. A diversity of industrially important monomers like alkenes, conjugated dienes, unsaturated carboxylic acids and aromatic compounds are thus targeted from renewable feedstock. In this context, on-purpose production of 1,3-butadiene from biomass-derived feedstock is an interesting example as its production is under pressure by uncertainty of the conventional fossil feedstock. Ethanol, obtained via fermentation or (biomass-generated) syngas, can be converted to butadiene, although there is no large commercial activity today. Though practised on a large scale in the beginning of the 20th century, there is a growing worldwide renewed interest in the butadiene-from-ethanol route. An alternative route to produce butadiene from biomass is through direct carbohydrate and gas fermentation or indirectly via the dehydration of butanediols. This review starts with a brief discussion on the different feedstock possibilities to produce butadiene, followed by a comprehensive summary of the current state of knowledge regarding advances and achievements in the field of the chemocatalytic conversion of ethanol and butanediols to butadiene, including thermodynamics and kinetic aspects of the reactions with discussions on the reaction pathways and the type of catalysts developed.

Materials

Sustainable Carbon Materials

Chem. Soc. Rev., **2014**, Advance Article **DOI**: 10.1039/C4CS00232F

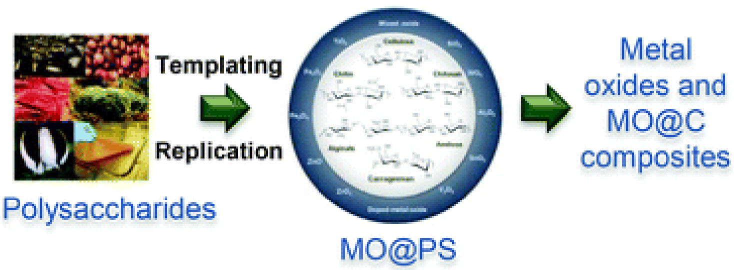
Carbon-based structures are the most versatile materials used in the modern field of renewable energy (i.e., in both generation and storage) and environmental science (e.g., purification/remediation). However, there is a need and indeed a desire to develop increasingly more sustainable variants of classical carbon materials (e.g., activated carbons, carbon nanotubes, carbon aerogels, etc.), particularly when the whole life cycle is considered (i.e., from precursor "cradle" to "green" manufacturing and the product end-of-life "grave"). In this regard, and perhaps mimicking in some respects the natural carbon cycles/production, utilization of natural, abundant and more renewable precursors, coupled with simpler, lower energy synthetic processes which can contribute in part to the reduction in greenhouse gas emissions or the use of toxic elements, can be considered as crucial parameters in the development of sustainable materials manufacturing. Therefore, the synthesis and application of sustainable carbon materials are receiving increasing levels of interest, particularly as



application benefits in the context of future energy/chemical industry are becoming recognized. This review will introduce to the reader the most recent and important progress regarding the production of sustainable carbon materials, whilst also highlighting their application in important environmental and energy related fields.

Metal Oxides and Polysaccharides: An Efficient Hybrid Association for Materials Chemistry

Green Chem., **2015**, Advance Article **DOI**: 10.1039/C4GC00957F

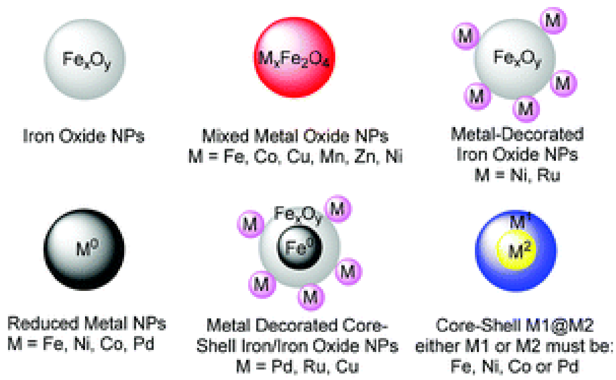


Metal oxides and polysaccharides in nature and in laboratories: limits and aims of the review. Part 1: Different ways to associate metal oxides and polysaccharides. Part 2: Controlled growth of metal oxide nanoparticles throughout polysaccharide fibers. Part 3: Biotemplating and bio-replication on the micro- to nanoscale. Part 4: Chemical transformation of polysaccharide fibers by mineralisation. Perspectives and concluding remarks. Biopolymers and inorganic minerals are often associated in nature, and living organisms benefit from these materials with a sophisticated and hierarchical architecture. Inspired by nature, chemists have tried to extend these combinations by associating natural polymers with inorganic materials that do not occur naturally in living organisms. In this review, we propose to focus only on research conducted on the association between polysaccharides and metal oxides. Over the last 10–15 years, substantial research has been focused on finding ways to combine these two types of materials, with the goal of mastering the morphology, porosity, composition and structure of the hybrid materials (metal oxide@polysaccharide) or pure metal oxides obtained after polysaccharide elimination. There are many possibilities for interactions between metal cations and the chemical functionality of the carbohydrate, thus allowing different approaches, as the structure and functionality of the polysaccharide are of major importance. Because of the sophisticated architecture that can be achieved on the one hand, and the potential sustainable use of these biopolymers (a green approach) on the other hand, these material elaboration processes offer a unique way for chemists to prepare functional hybrid materials and metal oxides (e.g. luminescent materials, catalysts, absorbent materials, magnetic composites, anode and photocatalyst materials). To be as comprehensive as possible, this review is limited to some natural polysaccharides. After contextualisation, we successively considered metal oxide growth control by biotemplating, the replication of raw and refined polysaccharide templates, ending with a discussion of the most recent approaches like mineralisation.

Sustainable Nanotechnology

Bare Magnetic Nanoparticles: Sustainable Synthesis and Applications in Catalytic Organic Transformations

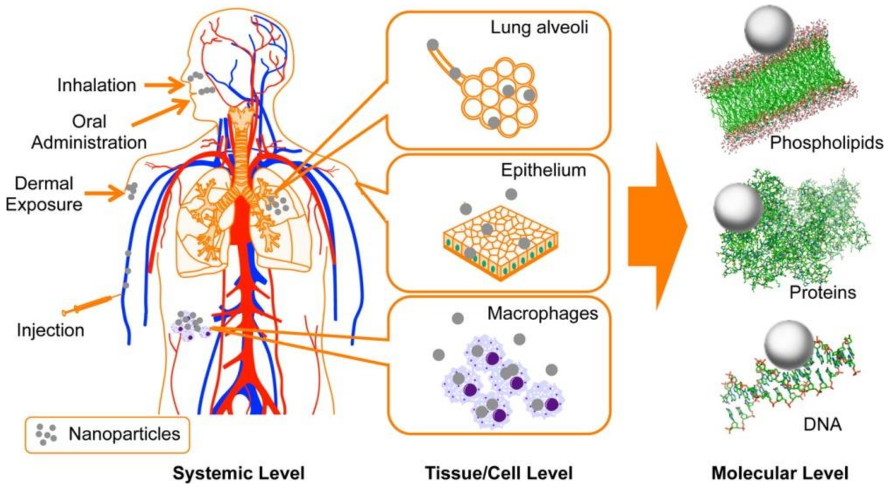
Green Chem., **2014**, *16*, 4493-4505. **DOI**: 10.1039/C4GC00418C



Magnetic nanoparticles have become increasingly attractive in the field of catalysis over the last decade as they combine interesting reactivity with an easy, economical and environmentally benign mode of recovery. Early strategies focused on the use of such nanoparticles as a vehicle for supporting other catalytic nanomaterials or molecules to facilitate recovery. More recently, research has shown that bare magnetic nanoparticles may serve the dual role of a catalyst and a magnetically recoverable entity. At the same time, emerging sustainability concepts emphasize the utility of earth abundant and less toxic resources, especially iron. Herein, we review the recent progress made in the assembly of such systems and their direct application in catalysis. Examples of such bare nanoparticles include iron oxide (Fe2O3 and Fe3O4), metal ferrites (MFe2O4, M = Cu, Co and Ni), Fe(0), Co(0), Ni(0), and multi-component nanoparticles. Features such as reactivity, recoverability and leaching are discussed in a critical fashion.

Chemical Basis of Interactions between Engineered Nanoparticles and Biological Systems

Chem. Rev., **2014**, *114*, 7740–7781. **DOI**: 10.1021/cr400295a



A breakthrough technology cannot prosper without wide acceptance from the public and society, that is, it must pose minimal harm to human health and the environment. Nanotechnology is now facing such a critical challenge. We must elucidate the effects of engineered nanomaterials (ENMs) on biological systems (such as biological molecules, human cells, organs, and physiological systems). Accumulating experimental evidence suggests that nanoparticles interact with biological systems at nearly every level, often causing unwanted physiological consequences. Elucidating these interactions is the goal of this review. This endeavor will help regulate the proper application of ENMs in various products and their release into the environment. A more significant mission of this review is to direct development of “safe-by-design” ENMs, as their demands for and applications continue to increase.

Exploiting Intrinsic Nanoparticle Toxicity: The Pros and Cons of Nanoparticle-Induced Autophagy in Biomedical Research

Chem. Rev., **2014**, *114*, 7581–7609. **DOI**: 10.1021/cr400372p

The current review will provide a clear overview of reports on nanomaterial-mediated modulation of autophagy and will focus on the importance of autophagy in both health and disease. We will briefly discuss the different ways in which this process can possibly be manipulated, and in the final part, we will examine how and why nanoparticle-induced autophagy can be exploited as a novel therapeutic tool.

Five papers addressed nanotoxicity and ways to lower it. Raveendran et al. discussed how to stabilize and lower toxicity by coating ZnSiMn quantum dots with a polysaccharide produced by extremophilic bacteria. Veronesi et al. studied the effects of coating, size, and aggregation for Ag nanoparticles on neural cells. Shvedova et al. found differences in the toxicity of nanocellulose depending on processing of the material. Coated polymer nanoparticles were studied by Zuo et al. to obtain different surface charges to study the effects of hydrophobicity on lung cells. Reed et al. examined nanoscaled metals contained in dietary supplement drinks and determined their effects on intestinal cells. Potential exposures from wastewater were also discussed.

Green Approach for Augmenting Biocompatibility to Quantum Dots by Extremophilic Polysaccharide Conjugation and Nontoxic Bioimaging

ACS Sustainable Chem. Eng., **2014**, *2*, 1551–1558. **DOI**: 10.1021/sc500002g

The Physicochemistry of Capped Nanosilver Predicts its Biological Activity in Rat Brain Endothelial Cells (RBEC4)

ACS Sustainable Chem. Eng., **2014**, *2*, 1566–1573. **DOI**: 10.1021/sc5000896

In Vivo Evaluation of the Pulmonary Toxicity of Cellulose Nanocrystals: A Renewable and Sustainable Nanomaterial of the Future

ACS Sustainable Chem. Eng., **2014**, *2*, 1691–1698. **DOI**: 10.1021/sc500153k

Increasing Hydrophobicity of Nanoparticles Intensifies Lung Surfactant Film Inhibition and Particle Retention

ACS Sustainable Chem. Eng., **2014**, *2*, 1574–1580. **DOI**: 10.1021/sc500100b

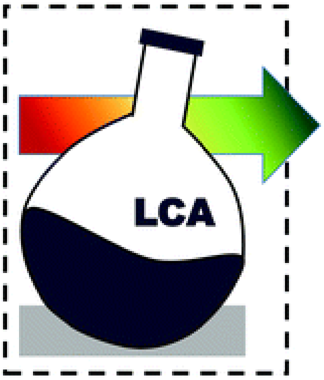
Characterization of Nanomaterials in Metal Colloid-Containing Dietary Supplement Drinks and Assessment of Their Potential Interactions after Ingestion

ACS Sustainable Chem. Eng., **2014**, *2*, 1616–1624. **DOI**: 10.1021/sc500108m

Life Cycle Assessment

Rules and Benefits of Life Cycle Assessment in Green Chemical Process and Synthesis Design: A Tutorial Review

Green Chem., **2015**, Advance Article **DOI**: 10.1039/C4GC01153H

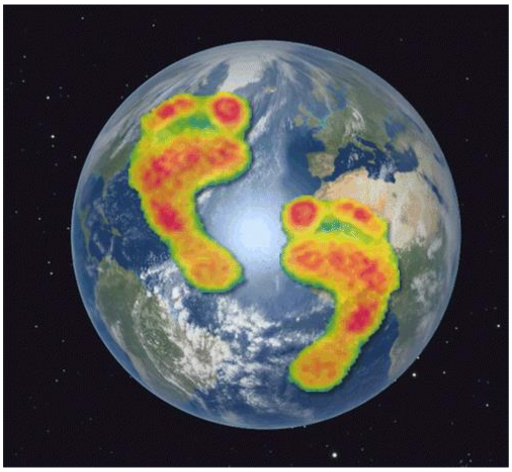


The implementation of Life Cycle Assessment and related methods in green chemical process and synthesis design strongly supports the development of greener concepts on the basis of deep and profound insights into the dependences between the selection of compounds and process parameters and the resulting environmental impacts. This review article provides an overview on things to know about LCA in general, specifics to be considered during its application in the field of chemical (re-)designs and current application examples from emerging research areas such as active pharmaceutical ingredient manufacturing, nanotechnology, flow chemistry, process intensification under harsh synthesis conditions, process integration, waste treatment, the use of alternative energy sources or solvents as well as chemistry based on renewable resources.

Education

Infusing Sustainability Science Literacy through Chemistry Education: Climate Science as a Rich Context for Learning Chemistry

ACS Sustainable Chem. Eng., Article ASAP **DOI**: 10.1021/sc500415k



Global science is paying increasingly urgent attention to sustainability challenges, as evidenced by initiatives such as the working group determining whether Earth has moved from the Holocene to the Anthropocene Epoch on the geologic time scale and the interdisciplinary efforts to define and quantify our planetary boundaries. Despite the fact that much of the scientific work underlying these initiatives is based on measurements of fundamental chemistry parameters, sustainability literacy has not been incorporated in any systematic way into the undergraduate chemistry curriculum. We report here on the philosophy and implementation of a NSF-funded initiative, Visualizing the Chemistry of Climate

Change (VC3), which provides an exemplar for developing strategies to fill that gap, focusing on climate change, one of the defining sustainability challenges of the 21st century. VC3 targets the strategic first year university and college chemistry courses that are common to the program requirements of many science and engineering majors. The overall goals of the VC3 project are to infuse climate literacy principles into the learning of representative core topics in North American general chemistry courses for science majors, while demonstrating that learning core chemistry topics by starting with an important rich context is a viable approach.

Education Resources

Green Chemistry 101 Video Training Modules

http://wsppn.org/p2-training/green-chemistry-101-video-training-modules/

Green Chemistry: The Nexus Blog

https://communities.acs.org/community/science/sustainability/green-chemistry-nexus-blog