綠色/永續化學資訊共享

化學中心◎2008.03.01

CONTENTS

你不會想錯過!!

1.劉廣定教授 2007年 9月份「永續化學概論」授課內容全公開。

(1)觀念與實例　(2)原則解說　(3)解決問題舉隅　(4)觸媒反應
(5)無溶劑反應　(6)水中反應　(7)微波反應　(8)續生性生質化學品
意者請電郵 ktliu@ntu.edu.tw。

2.本期內容「Pfizer建議使用以及避免使用之有機溶劑清單」~ p.5

*避免使用之有機溶劑其替代溶劑見 Green Chem., **2008**, 10, 31-36.*

3.如何降低離子液體之毒性 ? ~p.7-8

資料蒐集◎國立台灣大學化學系暨研究所　張煥宗教授

Research breakthroughs 2

Keeping dry without fluorine 2
Lignin — Nature's primary source of aromatics 2
Coating paper naturally 2
Bioprocessing + bioresources = bioproducts 3
A greener shade of black 3
A green shade of red 4
Preserving food — with food waste 4
Making sunscreens safe 4
Green leather tanning 5

Green chemistry tools to influence a medicinal chemistry and research chemistry based organization 5

What is a green solvent ?　a comprehensive framework for the environmental assessment of solvents 6

Defossiling fuel: how synthetic biology can transform biofuel production 6

Improved utilisation of renewable resources: New important derivatives of glycerol 7

Effects of different head groups and functionalized side chains on the aquatic toxicity of ionic liquids 7

Addressing the need for alternative transportation fuels: the Joint BioEnergy Institute 8

NCC report on greener supermarkets 9

It's not easy being green 9

Conference information 9

Research breakthroughs

(From http://www.chemsoc.org/networks/gcn/current.htm)

Keeping dry without fluorine

Water and soil repellency are important surface properties for fibres and fabrics. For many years we have used fluorinated coating to achieve these effects but concerns over the safety of some fluorinated compounds in the environment, including their persistence, has made this approach less popular. Nature has developed its own super-repellent surfaces on lotus leaves — this combines surface chemical structures and surface physics to achieve this. In a recent article from Clemson University in South Carolina, a new ultra-resistant textile surface has been developed without using fluorine. They mimic nature by combining a hydrophobic polymer coating with nanoparticles of silica.

K. Ramaratnam et al., *Chem. Commun.*, **2007**, 4510-4512.

Lignin — Nature's primary source of aromatics

Many of the chemical products in modern society are aromatic including personal care product constituents, additives in furnish and fabrics, and the engineering advanced materials used in modern aircraft. Almost without exception, these are derived from petroleum and we need to find alternatives based on renewable resources. The largest volume natural aromatic product is lignin and nature turns this over in enormous quantities every day — more than we could ever use. To add to its attractiveness, we produce huge volumes of lignin as a by-product in the paper and pulp industry and as cellulosic ethanol grows in volume, so will lignin by-product. Unfortunately, we have been quite inept at converting lignin into anything more sophisticated than energy (by burning): we need to be cleverer in exploring nature's most bountiful aromatic species. Two recent publications form Sweden and Portugal has disclosed significant developments.

Coating paper naturally

In an article from the Royal Institute of Technology in Stockholm, the fundamental problem of working with polymeric lignin has been overcome through the use of a technique known as nanofiltration, to separate the black lignin-rich liquor produced in the Kraft process. The smaller lignin-like units are more amenable to chemical transformations. The authors demonstrate this by reacting with a vegetable oil to produce an entirely sustainable product that has promising properties in paper coating due to its ability to interact well with wood fibres and to make paper water-resistant.
S. Antonsson et al., *Ind. Corps. Prod.*, **2008**, *27*, 98-103.

Bioprocessing + bioresources = bioproducts

In an article from the National Institute of Engineering and Industrial Innovation in Lisbon, a number of products made from lignin and using enzymes, are described. The authors argue that what they refer to as "environmentally friendly enzyme-based products" provide very promising methods for upgrading industrial (low value) lignins. Some of the bioproducts available by this methodology are chelating agents, coatings and paints. The authors suggest that much large scale production of enzymes is necessary if we are to progress these methodologies to large-scale commercial processes.

G. Sena-Martins et al., *Ind. Corps. Prod.*, **2008**, *27*, 189-195.

A greener shade of black

Twenty-five percent of the pigments used in the ceramic industry are black and these are generally derived from iron-cobalt-chromite and chromite-iron-nickel minerals. Other industrial pigments are based on other materials including manganese. Rather than use virgin raw materials, it would be environmentally (and economically)

advantageous to make use of the large volumes of industrial waste that contain metals, for example metal-rich sludges from galvanizing and surface coating. In a recent multinational study, it has been shown that black ceramic pigments can be prepared from chromium/nickel rich sludge from metal plating and steel wire galvanizing. The colors are comparable to traditional commercial products. The advantages are multiple — use of a waste that otherwise requires disposal and reducing use of minerals are the most obvious.
G. Costa et al., *Dyes Pigment.*, **2008**, *77*, 137-144.

A green shade of red

In a related discovery, an Indian group of researchers have developed novel inorganic red pigments suitable for coloring plastics. Classical red pigments can be toxic and unstable at high temperatures. The use of rare earth metal oxides should reduce any toxicity and the new report describes a ceramic-based example of this.
L. Sandhya Kumari et al., *Dyes Pigment.*, **2008**, *77*, 427-431.

Preserving food — with food waste

Chitosan is a polymer easily made from chitin, largely prepared from shellfish waste and representing one of the largest renewable sources of carbon on the planet. Chitosan has many interesting properties, however these are rarely sufficient to attract large-scale use. Chitosan is chemically reactive, and as shown in a recent article from a group in Mumbi can react with glucose to from a new material. This material shows some properties including antioxidant activity that are greater than the sum of its parts. It also has good antimicrobial activity comparable to chitosan. Together it appears to be superior to chitosan as a food preservative.
S. R. Kanatt et al., *Food Chem.*, **2008**, *106*, 521-528.

Making sunscreens safe

The use of titania nanoparticles in sunscreen was hailed as one of the most "visible" and everyday examples of the benefits of nanoscience to society. However, there are concerns that by generating electrons (a property the chemicals is also famous for doing in photovoltaic cells) it can create species that

can damage DNA. A group in New York have shown that the particles can be made safer by coating them with a thin layer of polymer. Whether the nanoparticles cab penetrate the skin surface and then go deep into the cells remains unknown.
W. A. Lee et al., *Chem Commun.*, **2007**, 4815-4817.

Green leather tanning

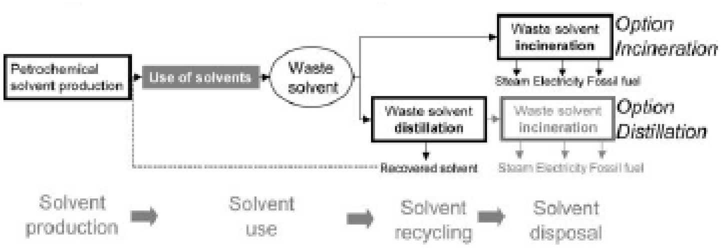
Conventional methods of pre-tanning, tanning and post-tanning leather are very polluting through the discharge of enormous amounts of waster liquors (ca. 30 L/kg leather), which contains salts, chromates and other species. Toxic gasses can also be produced during the process. Generally, it is believed that the conventional tanning methods are unacceptably complex, resource demanding, hazardous and wasteful. A group at the Central Leather Research Institute in India has published an article describing a "rationalized" process which involves salt-free curing and is lime and sulfide-free. The final leather is unaffected by the change in process, while the chemicals discharge is reduced by about three quarters, and the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are substantially decreased. There are also savings in water and energy production.
S. Saravanabhavan et al., *J. Chem. Technol. Biotechnol.*, **2007**, *82*, 971-984.

Green chemistry tools to influence a medicinal chemistry and research chemistry based organization

Influencing and improving the environmental performance of a large multi-national pharmaceutical company can be achieved with the help of electronic education tools, backed up by site champions and strong site teams. This paper describes the development of two of those education tools.
K. Alfonsi et al., *Green Chem.*, **2008**, *10*, 31-36.

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	Methyl *t*-butyl ether	Dichloromethane
Ethyl acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MethylTHF	Dimethyl formamide
Methyl ethyl ketone	Tetrahydrofuran	*N*-Methylpyrrolidinone
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

What is a green solvent ?　a comprehensive framework for the environmental assessment of solvents



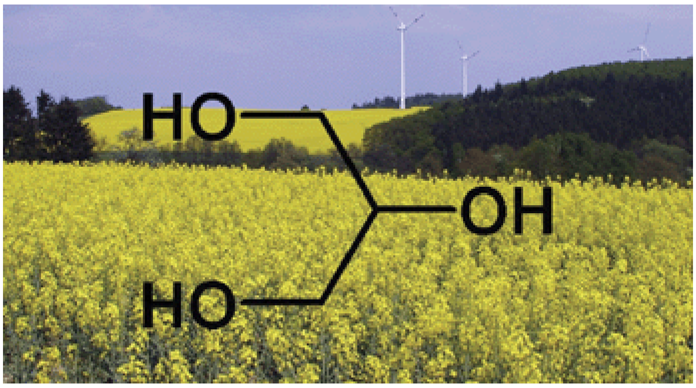
Solvents define a major part of the environmental performance of processes in chemical industry and also impact on cost, safety and health issues.　The idea of "green" solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production.　Here the question is raised of how to measure how "green" a solvent is.　We propose a comprehensive framework for the environmental assessment of solvents that covers major aspects of the environmental performance of solvents in chemical production, as well as important health and safety issues.　The framework combines the assessment of substance-specific hazards with the quantification of emissions and resource use over the full life-cycle of a solvent.　The proposed framework is demonstrated on 26 organic solvents. Results show that simple alcohols (methanol, ethanol) or alkanes (heptane, hexane) are environmentally preferable solvents, whereas the use of dioxane, acetonitrile, acids, formaldehyde, and tetrahydrofuran is not recommendable from an environmental perspective. Additionally, a case study is presented in which the framework is applied for the assessment of various alcohol–water or pure alcohol mixtures used for solvolysis of p-methoxybenzoyl chloride.　The results of this case study indicate that methanol–water or ethanol–water mixtures are environmentally favourable compared to pure alcohol or propanol–water mixtures.　The two applications demonstrate that the presented framework is a useful instrument to select green solvents or environmentally sound solvent mixtures for processes in chemical industry.　The same framework can also be used for a comprehensive assessment of new solvent technologies as soon as the present lack of data can be overcome.
C. Capello et al., *Green Chem.*, **2007**, *9*, 927-934.

Defossiling fuel: how synthetic biology can transform biofuel production

Although crude oil production is predicted to peak soon, it is reasonable to assume that unconventional fossil fuel sources can continue to meet society's increasing energy demands for many decades to come.　The real challenge is sustainability: stabilizing and reversing global climate change, minimizing political and economic energy volatility, and smoothing the transition from fossil fuels in the distant future. In response to this challenge, many are looking to biotechnology to develop biofuels, such as ethanol, butanol, biodiesel, and hydrogen (H_2), in which the energy ultimately derives from photosynthetic capture of sunlight. A fundamental issue with biofuels is efficiency. The pathway from sunlight through natural intermediates to final molecule is long, and biofuel production is perhaps the ultimate metabolic engineering problem. This challenge is made even greater by its inherent systems complexity, because any solution must be implemented in the context of an energy infrastructure with challenging engineering, economic, political, and environmental realities.

D. F. Savage et al. *ACS Chem. Biol.*, **2008**, *3*, 13-16.

Improved utilisation of renewable resources: New important derivatives of glycerol

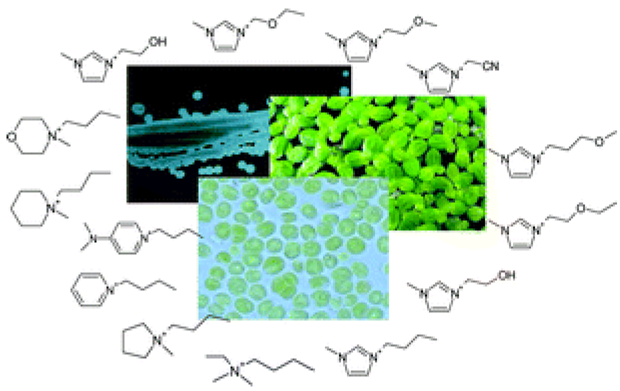


Although glycerol has been a well-known renewable chemical for centuries, its commercial relevance has increased considerably in the last few years because of its rising inevitable formation as a by-product of biodiesel production. The present review gives a broad overview on the chemistry of glycerol starting from the classic esters and oligomers to new products like glycerol carbonate, telomers, branched alkyl ethers, propanediols and epoxides. In particular, the novel possibilities to control the numerous addition, reduction and oxidation reactions via heterogeneous, homogeneous and biocatalysis will be presented. A benchmark will be given to determine the products which will have the best chances of entering the market and which processes are currently most developed.

A. Behr et al., *Green Chem.*, **2008**, *10*, 13-30.

Effects of different head groups and functionalized side chains on the aquatic toxicity of ionic liquids

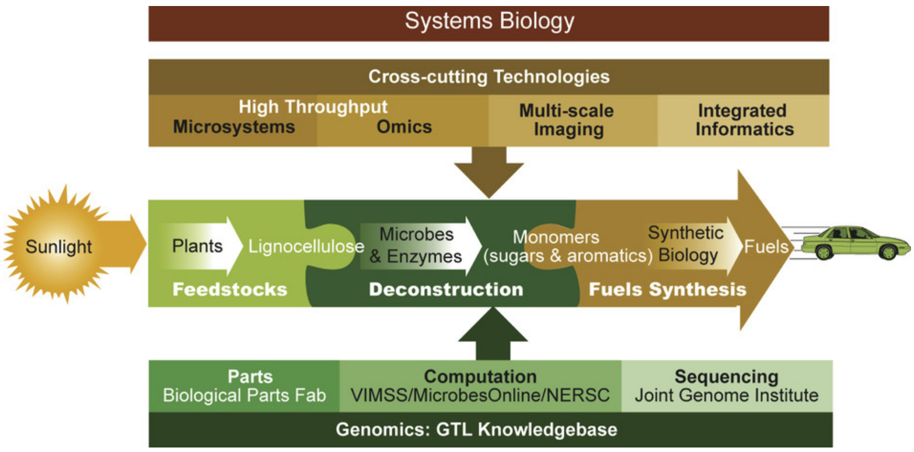
In this study, the influence of different head groups, functionalised side chains and anions of ionic liquids on the marine bacteria Vibrio fischeri, the limnic green algae Scenedesmus vacuolatus and the fresh water plant Lemna minor was investigated. The aim of these experiments is to improve the knowledge base for the molecular design of ionic liquids leading to a reduced (eco)toxicological hazard potential. The analysed set of about 40 ionic liquids confirmed the interdependency between lipophilicity—as derived from gradient HPLC—and (eco)toxicity. The toxicity was clearly reduced for the test organisms (partially by six to seven orders of magnitude) when short functionalised side chains were used instead of non-polar alkyl chains. Furthermore, we could demonstrate strong interactions of hydrophobic ionic liquid cations with two different types of common biological lipid bilayers, indicating that the membrane system of organisms is probably a primary target site of toxic action. These systematic studies are addressed to producers, developers and downstream users of ionic liquids in different fields of application, to facilitate the selection of (eco)toxicologically favorable structural elements and thus to contribute to the design of inherently safer ionic liquids.



S. Stolte et al., *Green Chem.*, **2007**, *9*, 1170-1179.

8

Addressing the need for alternative transportation fuels: the Joint BioEnergy Institute



Today, carbon-rich fossil fuels, primarily oil, coal, and natural gas, provide 85% of the energy consumed in the U.S. As world demand increases, oil reserves may become rapidly depleted. Fossil fuel use increases CO_2 emissions and raises the risk of global warming. The high energy content of liquid hydrocarbon fuels makes them the preferred energy source for all modes of transportation. In the U.S. alone, transportation consumes ~13.8 million barrels of oil per day and generates > 0.5 gigatons of carbon per year.

This release of greenhouse gases has spurred research into alternative, nonfossil energy sources. Among the options (nuclear, concentrated solar thermal, geothermal, hydroelectric, wind, solar, and biomass), only biomass has the potential to provide a high-energy-content transportation fuel. Biomass is a renewable resource that can be converted into carbon-neutral transporation fuels.
D. F. Savage et al. *ACS Chem. Biol.*, **2008**, *3*, 17-20.

NCC report on greener supermarkets

The National Consumer Council (NCC) of UK have recently published a report entitled "Green Grocers – how supermarkets can help make green shopping easier"……The top 8 food retailers in the UK were surveyed on a range of consumer-focused environmental indicators to ascertain what is already being done and what could be improved in future. To view this report visit http://www.ncc.org.uk/nccpdf/misc/greening2007.pdf

It's not easy being green

Those of us who, mindful of microbiological hazards, look askance at chicken on the buffet table and select a supposedly healthy salad instead, may need to adjust our perspective. For although recent improvements in animal husbandry have helped to stem and even reverse rising tides of salmonella, campylobacter, and toxigenic Escherichia coli infections in many countries, fresh fruit and vegetables are attracting increasing attention as vehicles of foodborne diseases.
B. Dixon, *Lancet Infect. Dis.*, **2007**, 7, 571.

Conference information

1. Green and Sustainable Conference for Developing Countries Cairo, Egypt, March 3-6, 2008 http://chem05.cu.edu.eg/

2. 1st International Conference on Sustainable Pharmacy Osnabruck, Germany, April 24-25, 2008 http://www.dbu.de/550artikel27309_788.html
3. 2nd International Symposium on Green Processing in the Pharmaceutical and Fine Chemical Industries Yale University, New Haven, CT, May 29-30, 2008 https://www.guidinggreen.com/Pharm_FineChem.html
4. The 12th Annual Green Chemistry & Engineering Conference Washington, DC, June 24-26, 2008 http://www.gcande.org/
5. Gordon Research Conference on Green Chemistry Bates College, Lewiston, ME, August 3-8, 2008 http://www.grc.org/programs.aspx?year=2008&program=green
6. 2nd International IUPAC Conference on Green Chemistry Moscow, Russia, September 14-20, 2008 http://www.icgc2008.ru/
7. 7th Green Chemistry Conference Barcelona, Spain, November 12-13, 2008 http://www.iuct.net/chem/7/index.html