



NEWSLETTER

January 2012

Green Chemistry Network and Green Chemistry and the Consumer News, Views and Solutions for Sustainable Supply Chains

EDITORIAL

2011 was another good year for Green Chemistry events. I was lucky enough to attend excellent events in places as far apart as Brazil, China, France, India, Korea, and the US. While I was in Boston, I enjoyed the benefit of a personal tour of John Warner's new facility, the Warner Babcock Institute for Green Chemistry. Being with John at two major events (CleanTech in Boston and the extremely impressive Industrial Green Chemistry World in Mumbai) I was reminded of the continued importance of his 12 Principles of Green Chemistry and how they continue to be meaningful after almost 20 years. Our excitement at the growth in interest must however be tempered by a determination not to allow the concept and the principles that underpin it to be undermined by basic misunderstandings of what is green and sustainable. The term has been high-jacked in some cases to label an entire area as "green" and thus make it more acceptable or favourable without a proper appreciation of what it really means to be green. So in the spirit perhaps more of Ebenezer Scrooge than Father Christmas I now propose the **12 Misunderstandings of Green Chemistry**.

1. **Hazardous chemicals must be immediately replaced.** Through REACH and other instruments we are now identifying chemicals which are hazardous to human health and/or the environment: these should be replaced but only with alternatives we are confident are genuinely safer (as well as being effective) across their lifecycle. There is a tendency for chemical users to demand all "red-

listed" chemicals be immediately replaced but we must be careful that we don't make matters worse through hasty and ill-conceived substitution. What is clear is that we must invest more in R&D directed to finding genuinely greener alternatives to these unwanted chemicals.

2. **Chemicals should be biodegradable.** All substances end up in the environment and when they do it is important that they don't persist or bio-accumulate. However, degradation can prevent (immediate) reuse and while the eco-system will recycle the carbon and other elements, it may be preferable to maximize the useful lifetime of complex (molecular) substances. For example, food waste is rich in interesting and useful complex molecules that can be used for other applications.
3. **Water is the greenest solvent.** Water has many attractions as a solvent but it is not a good solvent for many organic compounds, it can affect the reactivity of many reagents and catalysts, and it can be difficult to work with. Its ability to dissolve small amounts of most substances means that water effluent can be difficult to treat. We do need to make more use of water as a solvent but using water does not automatically make the process green!
4. **Fossil-derived (non-renewable) chemicals should be replaced by bio-derived (renewable) chemicals.** Petroleum-derived chemicals are not sustainable in the long term and we must accelerate their replacement with non-food biomass-derived chemicals, however, we must not let this be an excuse for developing impractical alternatives based on scarce resources or complex, wasteful synthesis routes. Bio-derived chemicals are not automatically green; they must be processed using green chemical methods to make genuinely green and sustainable products.
5. **Conventional sources of energy must be replaced by renewable sources.** The most wasteful use of our diminishing fossil resources is single use burning to make energy. A more intelligent use of these increasingly precious resources is to make chemicals (see 4 above). However, we must be more holistic in our selection of alternative energy sources. Some of these are based on the large scale use of elements that have not previously been used in large quantities: we must look at the whole periodic table when making

major changes to our energy and manufacturing infrastructure.

6. **Involatile solvents are better than volatile ones.** Legitimate concerns about the damage to the atmosphere caused by volatile solvents have led to a general belief that all volatile organic compounds should be replaced and that involatile solvents are preferable. Apart from the difficulty of finding enough involatile solvents to replace the very many roles VOCs have in today's society, we are also in danger of replacing one environmental impact with another. Involatile solvents such as ionic liquids are a useful addition to the green chemistry toolkit but due consideration must be given to all of their "green credentials" including resources, preparation, separation and toxicity as well of course, as cost.
7. **Catalysts are better than reagents.** The replacement of widely used hazardous reagents such as aluminium chloride and sodium chromate with catalytic alternatives rightly remains one of the great challenges in clean synthesis but we must be careful about the choice of catalyst and catalytic process. Many of the most interesting catalytic metals are also becoming scarce and the process for making some catalysts can in itself have high resource demands and produce large amounts of waste. Efficient catalyst recovery and reuse is also essential.
8. **Halogenated compounds are harmful to the environment and should be replaced.** While there are some large volume halogenated compounds that need to be phased out, we must not bundle all halogenated compounds in the same "red" basket. Nature turns over enormous quantities of organohalogen compounds and we need to learn from nature and avoid, as much as possible, those compounds that it cannot deal with (e.g. perhalogenated compounds).
9. **Bio-processes are preferable to chemo-processes.** Nature has developed some supremely elegant processes which function in a benign environment using non-toxic species to give highly selective processes. However, we have chosen to create a society based on the engineering of resources that goes beyond natural systems and it is unreasonable to believe that we can perform all resource-to-product processes using natural organisms. We can expect an increase in

the number of industrial bio-processes but chemical processes can be expected to continue to dominate for some time to come.

10. **Alternatives need to be assessed by full life-cycle analysis before they are validated.** The appreciation that if 'we cannot measure it we cannot improve it' has been one of the most important developments in green chemistry in the last 10+ years - green chemistry metrics are now very much part of the toolkit. Part of this is the awareness that you cannot change one stage in a product life-cycle without affecting other stages and hence life-cycle awareness is important. But this needs to always extend to a full LCA which is time-consuming and dependent on the quality of input data.
11. **Waste minimization should be a priority for any process optimization.** Clearly we do not want to produce something that needs to be disposed of since this is a loss of resource and causes harm to the environment. However, processes that only produce the one desired product are unrealistic. We need to fundamentally change our attitude and see what we currently refer to as waste as co-products with value either within that process or elsewhere. We can no longer afford the luxury of waste.
12. **Hazardous or non-renewable chemicals in formulations should be replaced.** Almost all chemicals are ultimately used in formulations and we need to recognize this more in green chemistry. An additional complication of formulations is that changing any one component is likely to lead to a change in more than one property. While undesirable components need to be replaced we must be careful that a direct X for Y substitution (for example to make the product more "natural" or "bio") may lead to deterioration in performance and the need to add other components to compensate for this. We must treat formulations as a whole and find ways to simplify them, not make them more complicated.

Happy New Year!

James Clark
Honorary President

BREAKTHROUGHS

Green 1,4-butanediol is a winner

Genomatica has been named 2011 winner of the US EPA's Presidential Green Chemistry Challenge Award in the Greener Synthetic Pathways category for its 1,4-butanediol (BDO) technology. BDO is a high-volume chemical building block used to make many common polymers, such as spandex. Using sophisticated genetic engineering, Genomatica has developed a microbe that makes BDO by fermenting sugars. When produced at commercial scale, Genomatica's Bio-BDO will be less expensive, require about 60% less energy, and produce 70% less CO₂ emissions than BDO made from natural gas. Genomatica is partnering with major companies to bring Bio-BDO to the market. Over time they plan to roll out plants in the United States, Europe, and Asia.

Feedstocks	Process	Products
✓?	✓	✓
Sugar-based so entirely non-renewable. Must avoid any food competition	Good attention to detail e.g. recycled water, no solvent, ambient temperature	Product is biodegradable. No significant harmful by-products

<http://epa.gov/greenchemistry/pubs/pgcc/winners/gspa11.html>

Green Polymers from Glycerin

Recent increases in biodiesel production has created a glycerin surplus and caused its price to erode. Being water soluble and biodegradable, glycerin is a good reactant for green chemistry. When reacted with polyacid, polyester is produced. The products' physical properties – strength and flexibility - can be adjusted by varying the acid and/or the reaction conditions. The resulting polyesters can replace those manufactured from petrochemical raw materials. The reaction does not require catalyst or solvent, takes place around 100 °C and may be performed in standard compression molding equipment to make simple plastic objects. These green polyesters offer a sustainable alternative to commodity plastics.

Feedstocks	Process	Products
✓~	✓	✓?
No longer readily available due to problems in biodiesel production (in Europe) but likely to be available in many regions	Catalyst- and solvent-free Simple processing, moderate energy consumption	Expect products to be biodegradable but needs verifying

http://www.ars.usda.gov/research/publications/publications.htm?SEQ_NO_115=270323

Paint Wins Greener Chemicals Award

The Sherwin-Williams company has won the US EPA's Presidential Green Chemistry Challenge Award in the Designing Greener Chemicals category for its Water-based Acrylic Alkyd Technology. Oil-based "alkyd" paints have high levels of volatile organic compounds (VOCs) that become air pollutants as the paint dries. Previous acrylic paints contained lower VOCs, but could not match the performance of alkyds. Sherwin-Williams developed water-based acrylic alkyd paints with low VOCs that can be made from recycled soda bottle plastic (PET), acrylics, and soybean oil. These paints combine the performance benefits of alkyds and low VOC content of acrylics. In 2010, Sherwin-Williams manufactured enough of these new paints to eliminate over 350 metric tons of VOCs.

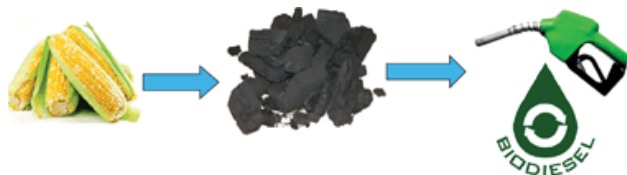
Feedstocks	Process	Products
~	~	✓?
Uses a combination of recycled waste, bio-derived components, and (presumably) some non-renewable components	Not clear but avoids solvents and surfactants	Definite improvement over traditional products through being water-based though not clear if fully and quickly biodegradable

<http://epa.gov/greenchemistry/pubs/pgcc/winners/dqca11.html>

BREAKTHROUGHS continued

Double Green Biodiesel

Despite recent problems in the European bio-refinery market it seems likely that biodiesel will continue to be widely used as a renewable transport fuel. It is interesting that even in a country such as Brazil that has a very large home-grown bioethanol market, biodiesel is a major consumer product. There is an increasing interest in valorising food wastes as a means of producing biofuels and several companies in Europe, for example, have built businesses on this. In a recent report from Spain, a large user of waste cooking oils for biofuel production, a new process has been proposed that is based on a catalyst derived from corncob waste.



Feedstocks	Process	Products
✓ ~	✓ ~	✓
Abundant feedstocks, at least in some regions. Like most biodiesel production it continues to rely on petro-methanol	Not an entirely simple process but process steps are kept to a minimum and energy consumption is modest	Expect both the product fuel and process residues to be biodegradable

<http://pubs.rsc.org/en/content/articlelanding/2011/qc/c1qc15908a>

POSTCARD FROM SPAIN

Is the landfill site the chemical factory of the future?

The environmental complex of Montalban, Spain (Empremasa, Complejo Medioambientale de Montalban), is a unique example of integrated waste management. It was built to meet the new E.U. directives regarding waste management; concentrating, recovering and valorising waste in order to avoid landfilling as much as possible. The company is responsible for waste management operations in the province of Cordoba, Andalusia. It provides home collection of municipal solid waste (household waste, paper, cardboard, glass and electric appliances), transportation, processing and landfill management for 74 municipalities (approximately 475,500 inhabitants). This strategy and the scale of operations allows the facility to be cost-effective with more flexible

working procedures and a rationalisation of human and material resources involved in the cycle.

The complex is an integrated facility which combines high efficiency waste scanning and segregation, recycling, composting, electricity generation and landfilling activities on the same site. The complex is able to produce high quality recycled plastic by sacrificing 40% of the organic waste through the use of a more rigorous process. Its efficiency is 90% as only 10% of the plastic arriving at the facility is landfilled (e.g. mainly plastic contained in Tetrapack[®] packaging). As a result, the higher quality plastic meets the specifications for being used in further plastic packaging applications which, up to now, was limited. In addition, compost is commercially produced

from organic waste, as well as 1.2 MW of electricity as the composters are connected to a biogas plant.

This process illustrates how the valorisation of waste can provide 1st generation waste-derived feedstocks (i.e. recycled plastic, compost, biogas/energy) as an alternative source of carbon. Such applications limit the use of virgin land and finite resources such as oil.

There is a growing recognition that the twin problems of waste management and resource depletion can be solved together through the utilisation of waste as a resource. The Montalban waste treatment plant represents an example of a waste biorefinery, producing commercial high quality recycled plastic, compost and electricity from waste. But such applications only have marginal economic value.

On the other hand, the major quantity of waste being landfilled in the E.U. is food supply chain waste (FSCW). In the context of the Landfill directive, policy makers in the E.U. are examining alternatives to landfill such as value recovery from FSCW.

90 million tonnes of food waste are generated every year in the E.U.²⁷ (including industrial and household waste). The carbon content of food waste in the E.U. is equivalent to the carbon content of all the chemicals produced from imported oil in the E.U. Therefore, 2nd generation valorisation of FSCW into

concentrated feedstocks for the production of chemicals and materials, represents a more valuable solution. The valorisation of FSCW presents many advantages: it is a rich source of functionalised molecules (i.e. biopolymers, proteins, carbohydrates) and contains valuable extracts for a number of applications (e.g. resins from cashew nut shell liquid). Furthermore, the use of FSCW should reduce the need to functionalise hydrocarbon feedstocks derived from oil; processes that use dangerous chemistries, generate hazardous wastes and have high energy demand.

Symbiotic recovery and re-use of all waste streams for the production of chemicals, materials and fuels can therefore be very economically and environmentally beneficial, leading to closed loop manufacturing where all materials are fully valorised (waste raw materials and products), as illustrated in figure 1, promoting a closed-loop economy.

Lucie Pfaltzgraff & James Clark, Green Chemistry Centre of Excellence, University of York.

Both authors would like to thank Emepmasa for their instructive visit of the environmental complex of Montalban. We would also like to thank Dr Rafael Luque for his assistance on the research.

<http://www.epremasa.es/index.php/quienes-somos>
Preparatory study on food waste across E.U.27- European Commission report (DG ENV)

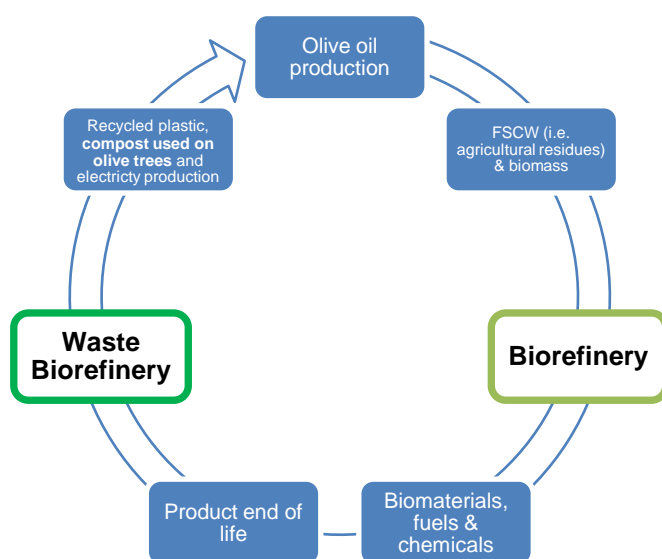


Figure 1: 2nd generation closed loop manufacturing

NEWS ITEMS

Walk the Walk

Bayer MaterialScience has developed a unique concept for a “green shoe” that uses a range of sustainable materials and technologies. These include polyurethane raw materials based on natural resources, products for solvent-free coatings and adhesives, and a polycarbonate blend and thermoplastic polyurethane based on renewable resources. Up to 90 per cent of all components in the “Ecotrekker” concept shoe can be given eco-compatible properties by using the company’s products.



<http://www.research.bayer.com/en/the-green-shoe.aspx>

Pee Power

UK Scientists have published the world's first research paper on the viability of urine as a potential fuel for Microbial Fuel Cells (MFCs) to produce electricity. This project aims to produce electricity from urine through stacks of small-scale MFCs whilst at the same time cleaning the urine stream and getting rid of any pathogens that present. MFCs consist of two half-cells – an anode and a cathode – that are separated by an ion selective membrane. Bacteria are in the anode side, and the urine in the cathode side completes the reactions (i.e. closes the circuit) to generate power. The output from one MFC is small but by miniaturisation and multiplication of the number of MFCs into a stack and regulating the flow of urine, it may be possible to produce useful levels of power, for example in a domestic or small village setting. The MFCs also ‘clean’ the urine so that it could be safely discharged to the environment without the need for wastewater treatment.

<http://www.rsc.org/chemistryworld/News/2011/October/31101103.asp>

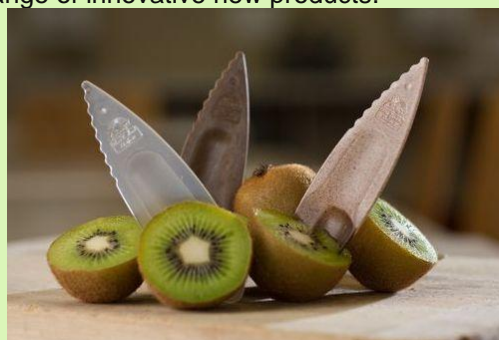
Eco-Friendly Lab Opens in China

East China Normal University, France's Centre National de la Recherche Scientifique, Ecole Normale Supérieure de Lyon and French chemical producer Rhodia, jointly announced the opening of a new laboratory, the International Research Laboratory of Eco-efficient Products and Processes (E2P2L). Located in Rhodia's Shanghai Research Centre, it will work as an open laboratory bringing together leading researchers and academics from the various fields and countries. It aims to invent the chemistry of the future that will significantly reduce the environmental impact of existing products or processes and especially greenhouse gas emissions. In particular, it targets to deliver new eco-efficient technologies that can reduce dependence on oil by using renewable feedstocks such as biomass.

<http://www.adsalecprj.com/Publicity/MarketNews/lang-eng/article-118292/Printing.aspx>

Greener Kiwifruit

In New Zealand Scion, a bioproducts research organisation and ZESPRI®, the country's major kiwifruit exporter, have together developed a novel bioplastic product to retail with the fruit and also for packaging. They have produced the biospife (a ‘spife’ is a spoon-knife), made from bioplastics, such as polylactic acid (PLA), mixed with formulations of waste kiwifruit, including pulp, skin and hairs. The biospife is also compostable - in an industrial composting facility a biospife will degrade in under three months, slower in a garden composter. Currently, thousands of tonnes of kiwifruit not suitable for fresh sales are fed to livestock each year. These valuable raw materials could be turned into bioplastics and used to make a range of innovative new products.



http://www.biotechlearn.org.nz/news_and_events/news/kiwifruit_into_plastic

Green Chemistry Events 2012

3rd Annual Next generation Bio-Based Chemicals, 23-26 January 2012, San Diego, California, USA
<http://informationforecastnet.com/index.php/conference/biobased12>

Manufacturing Using Sustainable Chemistry, 16 February 2012, York, UK
<http://www.musc-network.co.uk/flyer%20and%20form.pdf>

Green Polymer Chemistry 2012, 20-22 March, Cologne, Germany
<http://www2.amiplastics.com/Events/Resources/Programme/Green%20Polymer%20Chemistry%202012.pdf>

Bio Based Chemicals 2012, 13-14 March, Rotterdam, Netherlands
Bio Power Generation 2012, 13-14 March, Rotterdam, Netherlands
World Biofuels Markets 2012, 13-15 March, Rotterdam, Netherlands
<http://www.greenpowerconferences.com/EF/?sSubSystem=Prospectus&sEventCode=BC1203NL&sSessionID=272285d7ce1fa5c931d630f5a07c7fb7-5373340>

Environmental Microbiology & Biotechnology Conference, 10-12 April 2012, Bologna, Italy
http://www.suschem.org/en/_event/emb-2012-10-12-april-bologna

Biopolymer World Congress, 23-24 April 2012, Mestre-Venice, Italy
<http://www.biopolymerworld.com/>

Royal Society of Chemistry Symposium 2012: Not Costing the Earth – Profit from Green and Sustainable Chemistry, 13-14 June 2012, Barcelona, Spain
<http://www.rsc.org/ConferencesAndEvents/conference/alldetails.cfm?evid=108490>

International Symposium on 'Catalysis for Clean Energy and Sustainable Chemistry', CCESC 2012, 27-29 June, Alcobendas, Madrid, Spain
<http://www.ccesc2012.net/index.html>

4th International Eco Summit, 30 September – 5 October 2012, Columbus, Ohio, USA
<http://www.ecosummit2012.org/index.htm>

Minnesota Green Chemistry Conference 2012: Strategies for Growth, 26 January, Minneapolis, USA
<http://www.iatp.org/event/minnesota-green-chemistry-conference-2012-strategies-for-growth>

ACSEE 2012: The Asian Conference on Sustainability, Energy & the Environment, 3-6 May, Osaka, Japan
<http://acsee.iafor.org/>

7th Annual Green Chemistry & Commerce Council (GC³) Innovators Roundtable, 9-11 May 2012, Ann Arbor, Michigan
<http://www.greenchemistryandcommerce.org/events.upcoming.php>

16th Annual Green Chemistry & Engineering Conference, 18-20 June 2012, Washington, D.C., USA
<http://acswebcontent.acs.org/gcande/>

The Green Chemistry Gordon Research Conference, 22-27 July 2012, Lucca, Italy
<http://www.grc.org/programs.aspx?year=2012&program=greenchem>

4th International IUPAC Conference on Green Chemistry, 25-29 August 2012, Foz do Iguaçu, Brazil
<http://congresscentral.com.br/sbq/ufscar/icgc4/index.php>

The [Green Chemistry Network](#) (GCN) aims to promote awareness and facilitate education, training and practice of Green Chemistry in industry, commerce, central, regional and local government, academia and schools. The network was initially launched in 1998 with funding from the Royal Society of Chemistry and is now funded on a project-by-project basis. The GCN is a not-for-profit Company Limited by Guarantee (Registered in England and Wales, No: 6879262).

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