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Green chemistry: what is the way forward?

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Green chemistry is now 20 years old. It has had many triumphs but, by no means, has it been adopted universally. This focus article explores some directions for its future development.

There is some argument over the precise date that Green Chemistry was born but it is generally agreed that the birth happened about 20 years ago. There is less argument over the fact that Green Chemistry was, and continues to be, promoted by the US Environmental Protection Agency (EPA) as a means of reducing and ultimately removing, the adverse environmental impact of chemical manufacture and use.

At the heart of Green Chemistry lies equation (1):

$$\text{Risk} = \text{Hazard} \times \text{Exposure} \quad (1)$$

Most environmental legislation worldwide seeks to mitigate Risk by limiting Exposure. The revolutionary step in Green Chemistry was to propose that Risk should be reduced by removing the inherent hazard of the chemicals or chemical operations. This led to the formal definition of Green Chemistry[1] as ‘the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances’. Obviously this is an ultimate ideal rather than an immediately achievable goal because, for example, pharmaceutical products would be useless if they had zero effect on human health. However, such products should be designed to degrade as rapidly as possible once they have passed through the human body so as to avoid adverse effects on the health of organisms in the wider environment.

Such ideas were indeed revolutionary, especially in the early 1990s. Now, after 20 years, it is reasonable to ask whether the revolution has indeed succeeded in changing the status quo and to consider how the field should move forward from its present position. So what has Green Chemistry achieved so far? Perhaps the most innovative concept of Green Chemistry has been the E-factor, introduced by Sheldon,[2] equation (2):

$$E = (\text{kg of waste})/(\text{kg of product}) \quad (2)$$

The E-factor is closely related to the concept of Atom Efficiency (also termed Atom Economy) introduced by Trost.[3] However, there is a big difference; the E-factor considers sources of waste (*e.g*. solvent, spent catalyst, unwanted by-products) which are not included in the stoichiometric equations used to determine Atom Economy. This is important because these “extra” sources of waste often dominate the total quantity of waste generated by actual industrial processes.

A few years later, Anastas and Warner introduced the 12 Principles of Green Chemistry,[4] a relatively simple checklist to enable chemists and engineers to gauge the ‘greenness’ of a particular process. There have been innumerable versions of the principles. We favour the ‘PRODUCTIVELY’ version (Figure 1), which is particularly suitable for use in lectures and seminars because it combines conciseness with simplicity.[5]

Principles of Green Chemistry

P – Prevent wastes
R – Renewable materials
O – Omit derivatization steps
D – Degradable chemical products
U – Use safe synthetic methods
C – Catalytic reagents
T – Temperature, pressure ambient
I – In-process monitoring
V – Very few auxiliary substances
E – E-factor, maximize feed in product
L – Low toxicity of chemical products
Y – Yes, it is safe

Figure 1 The condensed 12 Principles of Green Chemistry, reproduced from ref. 5.

The 12 Principles and the E-factor are demonstrably being taken up by industry. For example, Dunn and colleagues at Pfizer used a Green Chemistry approach to reduce the volume of solvent used

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to manufacture sildenofil citrate (Viagra) from 1300 $dm^3\ kg^{-1}$ of product at the medicinal chemistry stage to 6.5 $dm^3\ kg^{-1}$ at the production stage.[6] In addition, they changed the nature of the solvents from environmentally unacceptable chlorinated compounds to more benign solvents and reduced the E-factor of the process from 105 to 6. Their efforts were rewarded by a UK Green Chemistry Award. Similarly, the French cosmetics company, L'Oréal, wrote in its 2007 sustainability report:[7] '*Significant development of green chemistry and Pro-Xylane™, an agent resulting from green chemistry. pro-Xylane™ is an anti-ageing agent derived from xylose from beech trees, developed by l'Oréal, which conforms to green chemistry criteria, in solution its E factor is 13*.'

Other awards have been initiated across the world, particularly the US Presidential Green Chemistry Challenge Award,[8] the only branch of chemistry to be officially recognised by the US President. Now in their 16th year, these Awards recognise environmentally beneficial innovation from business and academia and have been supported by successive Presidents irrespective of their positions across the political spectrum. New journals have sprung up including *Green Chemistry*, *ChemSusChem*, *Green Chemistry Letters & Reviews*, all of which have achieved academically respectable impact factors. Well attended Green Chemistry conferences are proliferating with long-running series sponsored by the RSC, ACS, IUPAC and the Gordon Research Conferences.

The Challenge

Despite these successes, we believe that Green Chemistry needs to change its direction largely because the world has changed. Over the past 20 years there have been cataclysmic political and economic changes. Communist regimes have been replaced across wide areas of the world, the European Union has expanded enormously and there has been a huge shift in manufacturing from Europe and the USA to China and the Far East. At the same time, electronic communication and the internet have linked people across the world in a way that could hardly have been imagined 20 years ago.

These changes have been accompanied by increased pressures on the Earth's resource. We now live in a world where, for example, there are more mobile phones than toothbrushes and these phones are now reputed to contain more than 40 elements. Metals that used to be little more than chemical curiosities have become strategic commodities in increasingly short supply. And all of this has been occurring against a backdrop of dwindling reserves of oil and minerals, of increasing oil prices and a relentless growth in the global population which will reach 7 billion in early 2012. Furthermore, many people have increased expectations, aroused by the information learned about richer countries *via* the media and the internet.

All of this poses an enormous challenge to chemists namely how to supply the chemicals needed to meet the increasing aspirations of the world's population and to do so with reduced per capita resources and a shrinking palette of readily available elements. And Green Chemists have the extra challenge of doing this without using hazardous chemicals, generating toxic waste or causing other environmental harm.

No one yet knows how all of this will be achieved, but it must be achieved or else society as we know it cannot continue. Part of the solution will undoubtedly be found by applying or adapting technologies which already exist or are currently under development. Part will require the invention of radically new technologies. The remainder of this article indicates a few principles which might help Green Chemistry get started.

Recognizing Differences in Need

We believe that Green Chemists should recognise that the needs of people around the world are not uniform. Different people in different places have different needs and aspirations. Thus the 12 Principles (Figure 1) developed to reflect the needs in North America and Europe are not necessarily the most appropriate, for example, for Africa. Therefore, to coincide with the first Pan Africa Green Chemistry Congress[9] in Addis Ababa in November 2010, we and our Ethiopian colleagues proposed 13 Principles for Greener Africa (Figure 2),[10] which blend some of the UN Millennium Goals (*e.g.* to create wealth) with the 12 Principles of Green Chemistry. These 13 Principles were very well received by the Congress participants.

Principles for Greener Africa

G – Generate wealth not waste
R – Regard for all life & human health
E – Energy from the Sun
E – Ensure degradability & no hazards
N – New ideas & different thinking
E – Engineer for simplicity & practicality
R – Recycle whenever possible

A – Appropriate materials for function
F – Fewer auxiliary substances & solvents
R – Reactions using catalysts
I – Indigenous renewable feedstocks
C – Cleaner air & water
A – Avoid the mistakes of others

Figure 2 The 13 Principles of Green Chemistry and Engineering for sustainable development in Africa, reproduced from ref. 10.

Perhaps one of the most important of the 13 Principles is 'New ideas and different thinking' which seeks to underline the fact that solutions that work in the Developed World might not be the most appropriate for Africa. As a trivial example, one might take the packaging honey. In Great Britain, honey is normally sold in glass jars with metal screw lids. Such jars are resource- and energy-intensive to manufacture and are heavy to transport but are needed to avoid damage on the long journey from producer to customer. By contrast, honey is sold in Ethiopia in polyethylene bags (Figure 3), which require fewer resources to manufacture and weigh very little. Polyethylene is less robust than glass but, with more localized shopping in Africa, it serves its purpose. After submission of this article, we noticed that some brands of honey were on sale in plastic containers at a local supermarket in Nottingham. Perhaps we are learning from Africa?

Of course, polyethylene is made from oil and oil is unsustainable in the long term. However, the Brazilian company Braskem has demonstrated that polyethylene can be manufactured by a commercially competitive yet sustainable route; cane sugar (sucrose) is fermented to ethanol which is then dehydrated to ethylene.[11] This process underlines the important point that, at a time of rising oil prices and diminishing reserves, we will need to use

Figure 3 Photograph of honey being sold in polyethylene bags in a shop in the town of Jimma, Ethiopia; reproduced with permission, © M. Poliakoff.

biomass to make low value bulk chemicals rather than high value speciality and pharmaceutical chemicals. So bulk chemicals is an area where Green Chemists should be focusing.

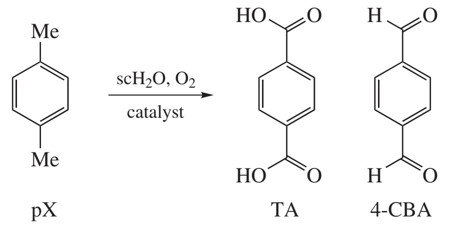
It is well known that only a small proportion of crude oil (*ca*. 5%) is used to manufacture chemicals and most of the oil is converted into transportation fuel. However, these chemicals contribute nearly 50% of the profit, and the ability to switch petroleum feedstocks between fuel production and chemicals is a vital factor in the 'petroleum economy'. Clearly the same will be true for biofuels and chemicals derived from biomass. Therefore, research into biofuels and the production of chemicals from renewable feedstocks need to be more closely linked than they are at present.

Identifying the Value Proposition

Although there are increasing numbers of publications which describe new 'greener processes' or reactions, very few of these publications try to identify which factor gives the new process a real advantage. Such factors are termed the 'value proposition' by chemical engineers. We suggest that identifying the value proposition for green chemistry will lead to greater understanding and new opportunities. The reason for this is that the true value proposition may not always be obvious. We give some examples.

Recently Kingman *et al*. have applied microwave heating to the continuous expansion vermiculite.[12] Vermiculite is an interleaved mineral with layers of water molecules which, on heating, cause the vermiculate to expand in a direction perpendicular to the layers to form the familiar insulating material. Conventionally, vermiculite is expanded by batch heating to 800 °C in ovens. The microwave equipment has a smaller footprint, is less noisy and dusty, has reduced maintenance and saves up to 95% of the energy compared to current technology. However, the real value of the process is that the vermiculite granules can be fed straight from the conveyor belt into a paper sack (Figure 4). By contrast conventionally heated material may require nearly two weeks to cool down.

Our own group in Nottingham has developed the use of supercritical H_2O as a medium for the aerobic oxidation of *p*-xylene (*p*X) to terephthalic acid (TA) (Scheme 1). Compared to the current widely used 'mid-century' oxidation in acetic acid,[13] the supercritical process totally eliminates the need for an organic solvent and has greatly increased energy recovery.[14,15] However, the real advantage is that supercritical oxidation avoids the co-precipitation of 4-carboxybenzaldehyde (4-CBA) with TA, which plagues the current process.



Scheme 1 Oxidation of *p*-xylene (*p*X) to terephthalic acid (TA) in supercritical water which avoids the 4-CBA impurity that contaminates TA produced by oxidation of *p*X in acetic acid.

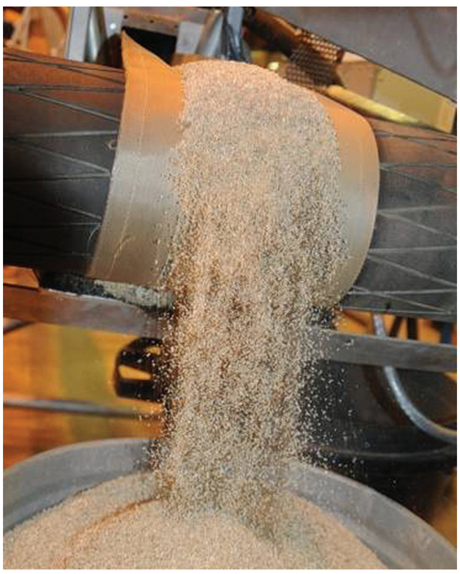
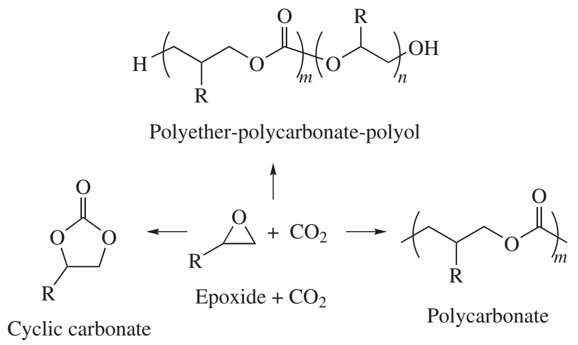


Figure 4 Photograph showing the collection of the product from the continuous microwave exfoliation of vermiculite; reproduced with permission, © The University of Nottingham.

At the Catalytic Center, a major collaborative project in Germany,[16] Leitner, Gürtler and co-workers are exploring various strategies for using CO_2 from Carbon Capture at power stations as a chemical feedstock. All of their favoured reactions involve organic epoxides which are sufficiently high-energy compounds to overcome the chemical inertness of CO_2. By varying the catalyst, the reaction can lead to cyclic carbonates, polycarbonates, or polyether-polycarbonate-polyols which are their preferred products because these polyols are precursors for polyurethanes (see Scheme 2). One might imagine that sequestering CO_2 could mitigate climate change but even the most optimistic forecast concludes that the amount of CO_2 sequestered would be $\ll 1\%$ of the anthropogenic CO_2 released each year. The real value comes from the fact that, by using CO_2 as a reactant, one can reduce the amount of organic feedstock needed to produce a given amount of polyol product by 15% compared to existing processes.[17]



Scheme 2 Use of CO_2 as a feedstock for producing materials by reaction with organic epoxides.[17]

Captured CO_2 as a Solvent

Over the past decade much of our research at Nottingham has focussed on the use of high pressure CO_2 as a replacement for petroleum-based solvents in continuous reactions of industrial interests including hydrogenation,[18,19] oxidation,[20,21] etherification[22,23] and other acid catalysed reactions.[24,25] One reaction, the hydrogenation of isophorone, has been scaled up to 1000 tons p.a.[26] Technically the process was highly successful but a sharp rise in global energy prices rendered it commercially uncompetitive. Now, with carbon capture and storage being proposed across Europe, the scene is changing. These proposals often involve transporting captured CO_2 in pipelines at pressures *ca.* 100 bar, similar to those needed for reactions in supercritical CO_2. Since the energy for compression will be expended at the CO_2 capture plants, this high pressure fluid could be used for reactions without need for further energy. Of course, captured CO_2 will be of relatively low purity; so recently we investigated the effects of N_2, CO and H_2O on the hydrogenation of isophorone. We found that the effects were either small or easily overcome by modest changes in reaction conditions.[27]

Automating Green Chemistry

In a 2007 review on Green Chemistry,[28] Horvath and Anastas stated that *'Today's scientific and technological establishment (or professors and managers) gives high rewards to those that discover and develop new chemical reactions or processes with high yields, mostly between 95–99%. While achieving the '100%' or an enzyme like performance is remarkably difficult, no rewards are given to those who get the last 1%.'* This final maximising of yield does not necessarily require the redesign of the system but can often be achieved by the optimisation of current reactions. Such optimisation, however, can be very time-consuming and boring to perform, and is often perceived as an unnecessary waste of time by cutting-edge researchers who want to move on to the next area of research as quickly as possible. We have recently been developing self-optimising continuous reactors using evolutionary search algorithms which can optimise a reaction typically in a period of 3 days.[29,30] Once programmed and started, our computerised system requires no human input and will tirelessly seek the optimal reaction conditions to provide the most sustainable parameters possible.

In conclusion, although the cleaner manufacture of chemicals is an important aspect of Green Chemistry, one should remember that most chemicals are bought for the effect which they can deliver rather than for their precise chemical structure. Thus people buy detergents, oils and paints because they clean, lubricate and look decorative and not because they have a particular chemical composition. Therefore, Green Chemists need to think more about producing effects rather than just making chemicals. A good example is cleaning windows. This requires chemicals and is dangerous (window cleaners fall off ladders). On the other hand, treating the windows with an appropriate coating can render them self-cleaning throughout their lifetime,[31] thereby eliminating both the chemicals and the danger. We believe that there is a real opportunity to apply such thinking to a wide range of effect chemicals. Such an approach can really move Green Chemistry to a new level. Of course, once a new strategy has been devised to achieve a given effect, one will still need to apply the Principles of Green Chemistry to realise the strategy in practice with minimum environmental impact.

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