Basic Principles of Green Chemistry

A combination of existing and new drivers makes it more likely that Green Chemistry will become increasingly important in the short term, and essential in the longer term.

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Professor James Clark has an international reputation for his work in Green Chemistry and is a Founding Director of the Green Chemistry Network. He was the founding Scientific Editor of the world’s leading journal in the field, Green Chemistry, and is also an author of numerous books on the subject. He now holds the Chair of Industrial & Applied Chemistry at York University (UK), and heads the Clean Technology Centre which integrates Green Chemistry research, industrial collaboration and educational developments and issues relevant to the public understanding of science. He is also the Director of the Greenchemistry Centre of Industrial Collaboration. Professor Clark’s research interests include heterogeneous catalysis and supported reagents and the exploitation of renewable resources. He has won medals and other awards for his research from the RSC, SCI, RSA and the EU.

Dr Paul Smith, BSc CChem FRSC, is currently the Commercial Manager of the Greenchemistry Centre of Industrial Collaboration based at York University (UK). He gained his first degree in Chemistry from the University of Nottingham (UK) and his PhD from the University of Cambridge (UK). His background is Chemical Development in the pharmaceutical industry, having worked for over 20 years at GlaxoSmithKline. The major focus of his work was to ensure that initial high quality supplies of potential new drug candidates were rapidly made available and that subsequent manufacturing routes would be developed in a safe, robust, efficient, cost-effective and environmentally sound manner. He also led a ‘Green Team’ which promoted Green Chemistry within the company.

Green Chemistry is the universally accepted term to describe the movement towards more environmentally acceptable and sustainable chemical processes and products (1). It encompasses education and promotional work, as well as research and commercial application of cleaner technologies – some old and some new (2).

While Green Chemistry is widely accepted as an essential development in the way that we practice chemistry, and is vital to sustainable development, its application has been fragmented and represents only a small fraction of today’s chemical education and chemical manufacturing. However, a combination of existing and new drivers now makes it more likely that it will become increasingly important in the short term, and essential in the longer term. These drivers include the increasing proportion of process costs due to energy and waste, availability and cost issues for traditional petroleum-based feedstocks, and perhaps most significantly the dramatic increase in legislation affecting chemical production, storage, use and disposal.

In Europe, REACH (Registration, Evaluation, Assessment of Chemicals) will come into force this decade and will undoubtedly be the most important chemicals-related legislation in living memory (3). Its effects are as yet unclear, but conservative estimates suggest that about 10% of existing chemicals will become restricted, prohibitively expensive or unavailable. REACH and other new legislation is also likely to bring many consumer product related chemicals to the public’s attention, and we have often seen how even the suggestion of a health or environmental-related problem
can result in media-induced public alarm and overreaction by retailers. Social as well as environmental and economic drivers will force change in chemical manufacturing which will require a shift in emphasis on chemistry research and education. This is being encouraged by a number of organisations (4).

GREEN CHEMISTRY IN THEORY

The principles of Green Chemistry should be applied at all stages in the life-cycle of a chemical product, and key technologies have been identified to help achieve this (Figure 1).

Over 90% of organic chemicals in current use are derived from petroleum. A truly sustainable industry will require a shift towards renewable feedstocks (5). Biomass can be better utilised in chemical manufacturing both to provide building blocks and (close to) final products (Figure 2). The ‘platform molecule’ concept is particularly interesting since it provides a range of useful synthetic intermediates which are both more functional and more valuable than conventional petroleum-based feedstocks, and also simple enough to allow us to build up a wide range of important products. One example of this is lactic acid which is readily derived from the fermentation of corn starch (Figure 3) (6).

Much of the Green Chemistry research effort and most of the good case studies of Green Chemistry at work are associated with chemical manufacturing (7). The substitution of volatile organic solvents is an important target for almost all chemical manufacturers – both in reactions and in work-ups and product purifications (2). A number of alternative reaction solvents have been proposed, including water (8), volatile supercritical CO2 (9) which is easily removed by a drop in pressure, and non-volatile ionic liquids such as butylmethylimidazolium tetrafluoroborate (BmimBF4) (10). Numerous examples of their use in the research literature are available, many of which also involve catalysis (Figure 4).

Some reactions can be carried out in the absence of solvent and are often accelerated using microwave activation – a methodology which shows considerable promise for the future, especially with the availability of commercial reactors including continuous flow systems. A number of other novel reactor technologies – often based on intensive processing such as microreactors – are also expected to become increasingly important. For example, we have recently described catalytic microreactors and catalytic spinning disc reactors (12) for high-throughput, safer and more flexible chemical processing, which combines state-of-the-art reactor technology with the latest examples of heterogeneous catalysis using mesoporous solid supports especially useful for liquid phase organic reactions.

At the product end of the life-cycle, ‘benign by design’ has an especially important significance since the product should not cause harm to its users nor harm the environment when it is released. While maximising reusability and recyclability of component parts are important goals, some inevitably does get into the
environment and rapid biodegradation to innocuous breakdown species is the final green chemistry goal in the product’s life-cycle.

GREEN CHEMISTRY IN PRACTICE

There are now enough examples of Green Chemistry at work in commercial processes that we can illustrate its application across the product life-cycle (Figure 5) (2, 7). We must not, however, get complacent at these successes since they only represent step-change improvements in a tiny fraction of industrial chemistry worldwide.

We continue to use diminishing, polluting and increasingly expensive fossil feedstocks for most chemical manufacturing. Hazardous reagents – including aluminium chloride and chromates along with volatile organic compounds such as dichloromethane – continue to dominate chemical processing. Products continue to be designed based on cost and effort with little consideration given to fate.

We must continue to innovate and design new processes and products but – just as importantly – we need to learn to more quickly adopt the new cleaner technologies if we are to achieve the triple bottom line of an economically, environmentally and socially effective industry (13).

However, the uptake of Green Chemistry by the pharmaceutical industry is particularly encouraging and this is well illustrated by the success seen in the US Environment Protection Agency’s (EPA) prestigious annual Presidential Green Chemistry Challenge (14). For example, Bristol Myers Squibb won the Alternative Synthetic Pathways Award in 2004 for the development of a green synthesis for the manufacture of Taxol® via plant cell fermentation and extraction.

Industry alone cannot be expected to discover and develop the novel green chemistry methods and technologies that are still needed. The good news is that, in the UK, university research is becoming more focused on industry’s needs – a good example being the recent setting-up of the Greenchemistry Centre of Industrial Collaboration, which is based at the University of York (15).

GREEN CHEMISTRY METRICS

In its short history, Green Chemistry has been heavily focused on developing new, cleaner, chemical processes using the type of technologies described here. Increasing legislation will force an increasing emphasis on products, but it is also important that these in turn are manufactured by green chemical methods – and that the advantages offered by Green Chemistry can be quantified. Legislation or supply-chain pressures may persuade a company that the use of a chlorinated organic solvent is undesirable, but how can it select a genuinely ‘greener’ alternative? How can a company add environmental data to simple cost and production factors when comparing routes to a particular compound? Can the environmental advantages of using a renewable feedstock compared with a petrochemical be quantified? In order to make Green Chemistry happen, we need to see the concept mature from an almost philosophical belief that it is the ‘right thing to do’, to one which can give hard, reliable data to prove its merits.

These needs, together with a ‘reality check’, have led to the emergence of Green Chemistry related metrics. The ultimate metric can be considered to be life-cycle assessment (LCA) (16), but full LCA studies for any particular chemical product are difficult and time-consuming. Nonetheless, we should always ‘think LCA’ – if only qualitatively – whenever we are comparing routes or considering a significant change in any product supply chain. Green Chemistry metrics (17, 18) are most widely considered when comparing chemical process routes, including limited – if easy-to-understand – metrics such as atom efficiency (how many atoms in the starting materials end up in the product) and attempts to measure overall process efficiency such as E Factors (amount of waste produced per kg product).

As with LCA, these metrics have to be applied with clear system boundaries, and it is interesting to note that for process metrics these boundaries generally do not include feedstock sources or product fate. Energy costs and water consumption are also normally not included, although – given the increasing concerns over both of these – it is difficult to believe that they can be ignored for much longer. We propose that process efficiency metrics such as E factor can be improved by including the CO2 equivalent of the energy used in the process when calculating the total waste for that process. At the product end of the life-cycle we are used to testing for human toxicity, but we will also need to pay more attention to environmental impact and, here, measures of biodegradability, environmental persistence, ozone depletion and global warming potential are all important metrics.

Last, but not least, we are moving towards applying Green Chemistry metrics to feedstock issues. As we seek
Figure 5: Examples of Green Chemistry in practice

’sustainable solutions’ to our healthcare, housing, food, clothes and lifestyle needs, so we must be sensitive to the long term availability of the raw materials that go into the supply chain for a product. With increasing financial and legislative pressures from the feedstock and product ends, and increasing restrictions and controls on the intermediate processing steps, chemistry must get greener!

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