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VIEWPOINT

Green Chemistry: Science and Politics of Change

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The chemical industry plays a key role in sustaining the world economy and underpinning future technologies, yet is under unprecedented pressure from the effects of globalization and change in many of its traditional markets. Against this background, what will be needed for the industry to embrace efforts to make it "greener"? We explore some of the issues raised by the development of "green chemistry" techniques and identify potential barriers to their implementation by industry.

Most processes that involve the use of chemicals have the potential to cause a negative impact on the environment. It is therefore essential that the risks involved be eliminated or at least reduced to an acceptable level. In its most simple form, risk can be expressed as

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

Traditionally, the risks posed by chemical processes have been minimized by limiting exposure by controlling so-called circumstantial factors, such as the use, handling, treatment, and disposal of chemicals. The existing legislative and regulatory framework that governs these processes focuses almost exclusively on this issue. By contrast, green chemistry (Table 1) (1–3) seeks to minimize risk by minimizing hazard. It thereby shifts control from circumstantial to intrinsic factors, such as the design or selection of chemicals with reduced toxicity and of reaction pathways that eliminate by-products or ensure that they are benign. Such design reduces the ability to manifest hazard (and therefore

risk), providing inherent safety from accidents or acts of terrorism.

Legislation has been effective in improving environmental conditions, but toxic materials are still discharged in considerable amounts—7 billion pounds (3.2×10^8 kg) in 2000 in the United States alone (4). Regulation clearly has a major and continuing role to play in lessening the environmental impact of the chemical industry (5). Green chemistry can potentially generate an even greater environmental benefit by removing the intrinsic hazard of particular products or processes, thereby moving them outside the scope of many environmental regulations.

Involvement of Academia and Industry

Green chemistry is a major component of the science underlying the "responsible care" program of the chemical industry (6) and of "sustainable development" (7). Making reduced hazard an important criterion for judging the performance of a product or process provides a new challenge for traditional academic research. Academic interest in green chemistry is reinforced by the increasing requirement by funding agencies that academic research should address quality-of-life issues and should be commercially more exploitable, and by increased "outsourcing" of industrial research to universities. As a result,

worldwide research aimed at cleaner processing has increased sharply (8).

Already in the 19th century, environmental regulation resulted in the cleanup of the LeBlanc soda process and other similarly polluting processes (9). More recently, the Montreal Protocol has led to the successful replacement of chlorofluorocarbons by compounds that do not affect the ozone layer appreciably. However, given society's demand for chemical products, most of these improvements could not have taken place in the absence of viable methods for reducing the environmental impact of the processes or introducing less harmful replacement products. Today, there is an increasing awareness that sophisticated technologies and radical new processes will be needed for the full potential for environmental improvement to be realized. Major advances in understanding the relation between the molecular structure of chemical products and their toxicity mean that we can begin to design "safer" chemicals.

The term "green chemistry" was coined only 10 years ago (10). Given that the development time for a new chemical process is often more than a decade, there has been insufficient time for green chemistry principles (Table 1) to be translated systematically into industrial processes. Nevertheless, many recently developed processes and products fulfill most of these principles. For example, the waste greenhouse gas, N_2O , from the manufacture of adipic acid (a component of nylon) is being reused as the oxidant in a greener route to phenol (11). Tetrakis(hydroxymethyl)phosphonium phosphate is used as a low-dose, low-toxicity control agent for

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microbial growth in industrial cooling systems (12); it breaks down rapidly in the environment without bioaccumulation. Similarly, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one is produced as a replacement for the environmentally problematic tri-butyl tin oxide in marine antifouling applications (13); unlike the tin compound, it degrades rapidly when released into seawater.

Academic research also has a considerable lead time. Only a few genuine green chemistry projects have been running long enough to make the transition from research laboratory to commercialization. The most striking example is the work on catalytic asymmetric synthesis by Knowles, Noyori, and Sharpless (14). Although predating the birth of green chemistry, this work reflects several of its ideals (1, 15), namely, high selectivity, atom economy, elimination of many steps from conventional synthesis, and avoidance of waste.

Ambitious Goals

Green chemistry aims to introduce radical new technologies that will transform the nature of chemical use and manufacture. Transformations on this scale are rare but not unprecedented. For example, the Haber-Bosch process for ammonia manufacture turned atmospheric nitrogen into a sustainable feedstock for nitrate production, marginalizing the use of nitrate minerals mined in remote, environmentally sensitive locations. New technologies of this type are not merely more profitable but render the existing technology virtually obsolete on economic grounds.

Novel, profitable, and environmentally benign processes are being reported across the world. Substantial funds are becoming available for green chemistry research worldwide, and environmental regulators actively promote green processing techniques. But green chemistry has barely begun to be integrated into the chemical enterprise. What further barriers need to be overcome to incorporate it systematically in industrial processes, academic research, and education?

Barriers to Implementation

Barriers to industrial innovation have been studied extensively in other technological areas. A recent European Union study on the barriers to energy efficiency (16) identified economic, behavioral, and organizational barriers, such as tax incentives, accountancy practices, and the lowly status of energy managers in some organizations.

Similar factors apply to green chemistry technology (7). In particular, current taxation strategies often punish polluters and emitters, rather than rewarding cleaner processes (17). Furthermore, there is often little incentive to improve processes beyond the limits set by existing environmental regulations, which frequently prescribe which technology should be used. Regulatory agencies have tried to make the rules more flexible, but industry still fears that any radical process changes could result in regulatory liability.

There is, however, a big difference between energy usage and green chemistry. Appropriate strategies for energy efficiency in different sectors are generally well estab-

lished. The implementation of green chemistry is much more radical and complex, resembling the introduction of fuel cells to replace fossil fuels or nuclear power generation. In only a few cases has green chemistry had time to establish a best practice. Few industrial processes have been explicitly labeled "green," and some of the most innovative examples are proprietary. Thus, it is difficult for industry to identify the economic and environmental benefits of the new technology. This barrier can be overcome by widespread dissemination of successful green chemical processes, such as the publication of case studies (17–19).

The key question is how one can judge whether new processes do indeed have a reduced environmental impact. Sheldon's E-factor (20)—the weight of waste per unit weight of product—has been used widely by chemists, and more practical and detailed assessment schemes have been suggested recently (21, 22). Establishing the true environmental impact of a new technology requires full life-cycle assessments as well as toxicological testing of any materials involved, such as reagents or solvents; unfortunately, many of these data cannot be obtained until the process has been tried out on a commercial scale (3, 23).

Despite its simplicity, Sheldon's E-factor is useful in highlighting the fine chemicals and pharmaceutical industries (Table 2) as the areas in which green chemistry is likely to have its most immediate impact. Fine chemical companies tend to produce a wide range of chemicals on a small scale (500 to 5000 tons per year). They therefore offer more diverse opportunities for introducing new technology than the bulk chemicals sector, and the scale-up from laboratory to plant is less daunting.

Businesses aim to maximize profitability without contravening regulation or excessively offending public opinion. Therefore, new green chemistry processes will be introduced only if they can provide a payback quickly enough to be attractive to managers and investors. A new, greener process will not be feasible unless it provides chemical advantage over current processes and is sufficiently profitable to offset the costs of shutting down

Table 1. The most widely accepted definition of green chemistry (1) is "the design, development and implementation of chemical processes and products to reduce or eliminate substances hazardous to human health and the environment." This definition has been expanded into 12 principles listed in the table.

Green chemistry principles

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g., solvents, separation agents, and so forth) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control before the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Table 2. Environmental acceptability, as measured by the E-factor. [Adapted from (20)]

| Industry | Product tons per year | Waste/product ratio by weight |
|-----------------|----------------------------------|-------------------------------|
| Oil refining | 10 ⁶ –10 ⁸ | ~0.1 |
| Bulk chemicals | 10 ⁴ –10 ⁶ | <1–5 |
| Fine chemicals | 10 ² –10 ⁴ | 5–50 |
| Pharmaceuticals | 10 ⁰ –10 ³ | 25–>100 |

the existing plant. Even then, companies that invest in successful new technologies are likely to use these as a means of gaining competitive advantage and, therefore, will resist sharing the technology with their competitors.

Perhaps the largest barrier is that proven green chemistry technologies are not as readily available as are more traditional alternatives. Speed is paramount in process development for most sectors of the chemical industry, so that profitability can be maximized within the life of a patent. Existing technologies that pollute within prescribed regulatory limits may be easier to implement than new technologies that pollute much less. Green chemistry needs the engagement of a wide cross section of the scientific community to enable it to deliver within the required time frame. A concerted research drive by industry, government, and academia is needed to develop a wide range of reliable, benign methodologies that will be available when needed.

An initiative just launched in the United Kingdom, the Crystal Faraday Partnership (24), shows the way ahead. This research forum with both industrial and government funding aims to promote research, education, and dissemination in green chemistry and processing. Experience at Nottingham University (United Kingdom) has shown that a balanced combination of industrial and government funding can lead to the rapid development of new, green chemistry-based processes. In collaboration with Thomas Swan & Co. Ltd., the university has developed a series of heterogeneously catalyzed supercritical fluid reactions (25–27), the basis of a 1000 ton per year chemical manufacturing plant (28) (Fig. 1) that successfully went on stream in March 2002.

The Scientific Challenge

Meeting the criteria of providing payback within a short time frame presents a major scientific challenge. Broadly, green chemical process research can be divided into three categories: alternative feedstocks, alternative solvents, and alternative synthetic pathways, many of which involve novel catalysis.

Alternative feedstocks. One proven approach, already widely implemented in industry, is to use the waste from one process as a feedstock or reagent in the next (29). A potential difficulty is that the production of many quite disparate products becomes linked, leading to problems if demand for one of them changes dramatically. A more radical approach is to move from hazardous, resource-depleting materials such as petroleum to those from renewable or biologically derived sources. For example, bio-derived lactic acid is now being used as a feedstock for large-scale industrial polymer production

(30, 31). Renewable feedstocks are often highly amenable to bioprocessing by enzymes, but represent a chemical challenge: Biomolecules such as sugars are far more oxygenated than petrochemical hydrocarbons, and may therefore require changing the chemistry from oxidation to reduction to manufacture a particular end-product.

The simplest alternative feedstock is CO₂. Making chemicals from CO₂ would not only conserve petroleum but also reduce CO₂ emissions. However, CO₂ is thermodynamically extremely stable and therefore difficult to activate chemically. Nevertheless, progress has been made in incorporating CO₂ into polymers, and in reacting it with H₂ to make formic acid, HCO₂H (32). The key is the design of new catalysts, and techniques such as immobilization or ultrafiltration, for separating high-value catalysts from the products so that they can be recycled.

Alternative solvents. Organic solvents are a major source of waste, and their efficient control can produce a substantial improvement in the environmental impact of a process (22). The most elegant way to avoid problems with solvents is not to use them, an approach that has been widely exploited in the paints and coatings industries. Recently, Raston *et al.* described organic reactions that can be carried out merely by grinding the

reagents together with a catalyst (33), a process that is both cleaner and quicker than the conventional reactions. The experiment may not be easy to scale up to an industrial scale, but it has nevertheless caused a paradigm shift in the synthesis of a whole class of compounds that were previously tedious or difficult to make.

Most reactions do, however, require a solvent, and a green chemical process must necessarily involve an environmentally acceptable solvent (34). Much current research focuses on two classes of alternative solvents (23): supercritical fluids (35) and ionic liquids (36). Supercritical fluids are gases that are nearly as dense as liquids (37), while ionic liquids are salts of highly asymmetrical organic ions with melting points below or close to room temperature (36). The cheapest supercritical fluid, CO₂, has solvent properties similar to those of light hydrocarbons, apart from an unusually high affinity for fluorocarbons (38). Its properties can be “tuned” by changing the applied pressure, leading to unusual chemical effects not easily achieved in more conventional solvents (25, 39, 40). Applications include dry cleaning (Fig. 2). Ionic liquids are chemically diverse owing to the huge number of possible cation/anion combinations that can be synthesized. A very broad range of chemical reactions from alkylation and polymerization to biocatalysis and electroplating have already been carried out in these solvents, although as yet none has been carried out on an industrial scale (41).

Alternative synthetic pathways. Most new pathways that lead to cleaner chemistry involve catalysts. A century ago, catalysts were not widely used in the chemical industry;



Fig. 1. Part of the multipurpose plant at Consett, Co Durham, United Kingdom, for chemical manufacture in supercritical CO₂. The plant is a good example of a green technology, developed in a university, being evaluated on a commercial scale in industry. More such trials are needed to implement new green chemical technologies. [Photo courtesy of Thomas Swan & Co. Ltd.]

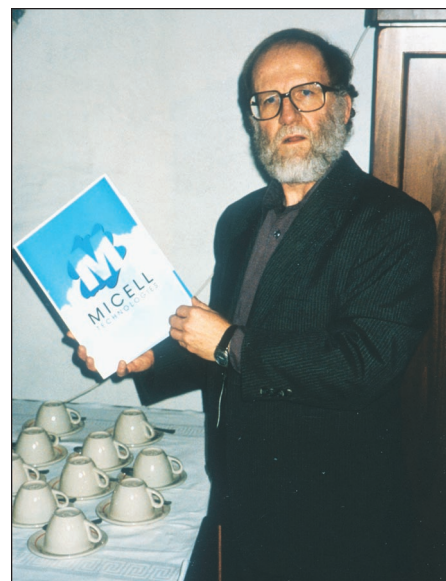


Fig. 2. The late Joe Breen, founding director of the U.S. Green Chemistry Institute (18), wearing one of the first suits dry-cleaned in CO₂. [Photo: M. Poliakkoff]

today, no petrochemical company and few chemical companies would be competitive without their use. The design of selective catalysts is crucial to the future of green chemistry because improved catalysis can reduce the number of stages in a given process and hence reduce its environmental impact. For example, a novel catalytic step has almost halved the number of stages needed to manufacture the analgesic ibuprofen (21) and has also eliminated the toxic solvent CCl_4 from the process. Similarly, Pfizer has introduced a new process, designed on green chemistry principles, that greatly reduces waste in manufacturing sertraline, the active ingredient in the antidepressive drug Zoloft (42).

The design of safer chemicals will necessarily change the detailed synthesis that is needed for a particular product. Nevertheless, there is still a major need for concerted research to improve the selectivity and performance of catalysts. Spent catalysts left at the end of a reaction also contribute to chemical waste, particularly because many contain toxic heavy metals. Research into catalyst reuse and recycling is still in its infancy. These factors should favor the use of enzymes as biocatalysts, which are often highly selective and do not involve toxic metals. Despite many commercially successful biocatalytic processes [such as the manufacture of the sweetener aspartame (43)], much research remains to be done before biocatalysts can be used routinely throughout the chemical industry.

Conclusion

Fundamental changes in technology are adopted by the chemical industry only when they provide real advantage. The challenge to green chemists is to develop such technolo-

gies on a short time scale. Increased collaboration between academia, governments, and industry will accelerate the pace of innovation in green chemistry along the supply chain from chemical innovators through scale-up to industrial end-users. Many in both industry and academia hesitate to take the plunge. Only when more universities teach green chemistry will graduates be able to apply these principles when they enter industry. For the full potential of green chemistry to be realized, young academics need role models to inspire them, and industry needs successful case studies to convince them.

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