Part 1
Green Chemistry for Sustainable Development

Green Separation Processes. Edited by C. A. M. Afonso and J. G. Crespo

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1.1
Green Chemistry and Environmentally Friendly Technologies

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1.1.1
Introduction

"Green Chemistry" is the universally accepted term to describe the movement towards more environmentally acceptable chemical processes and products [1]. It encompasses education, research, and commercial application across the entire supply chain for chemicals [2]. Green Chemistry can be achieved by applying environmentally friendly technologies – some old and some new [3]. 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 is fragmented and represents only a small fraction of actual chemistry. It is also important to realize that Green Chemistry is not something that is only taken seriously in the developed countries. Some of the pioneering research in the area in the 1980s was indeed carried out in developed countries including the UK, France, and Japan, but by the time the United States Environmental Protection Agency (US EPA) coined the term "Green Chemistry" in the 1990s, there were good examples of relevant research and some industrial application in many other countries including India and China [4].

The Americans launched the high profile Presidential Green Chemistry Awards in the mid-1990s and effectively disclosed some excellent case studies covering products and processes [5]. Again, however, it is important to realize that there were many more good examples of Green Chemistry at work long before this – for example, commercial, no-solvent processes were operating in Germany and renewable catalysts were being used in processes in the UK but they did not get the same publicity as those in the United States [2, 4].

The developing countries that are rapidly constructing new chemical manufacturing facilities have an excellent opportunity to apply the catchphrase of Green Chemistry "Benign by Design" from the ground upwards. It is much easier to build a new, environmentally compatible plant from scratch than to have to deconstruct before reconstructing, as is the case in the developed world.

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In this chapter I shall start by exploring the drivers behind the movement towards Green and Sustainable Chemistry. These can all be considered to be "costs of waste" that effectively penalize current industries and society as a whole. After a description of Green Chemistry I will look at the techniques available to the chemical manufacturers. This leads naturally into a more detailed discussion about methods of evaluating "greenness" and how we should apply sustainability concepts across the supply chain. It is important that, while reading this, we see Green Chemistry in the bigger picture of sustainable development as we seek to somehow satisfy society's needs without compromising the survival of future generations.

1.1.2
Objectives for Green Chemistry: The Costs of Waste

Hundreds of tonnes of hazardous waste are released to the air, water, and land by industry every hour of every day. The chemical industry is the biggest source of such waste [3]. Ten years ago less than 1% of commercial substances in use were classified as hazardous, but it is now clear that a much higher proportion of chemicals presents a danger to human health or to the environment. The relatively small number of chemicals formally identified as being hazardous was due to very limited testing regulations, which effectively allowed a large number of chemicals to be used in everyday products without much knowledge of their toxicity and environmental impact. New legislation will dramatically change that situation. In Europe, REACH (Registration, Evaluation, Assessment of Chemicals) will come into force in the first decade of the twenty-first century and whilst, at the time of writing, the final form of the legislation has yet to be decided, it is clear that it will be the most important chemicals-related legislation in living memory and that it will have a dramatic effect on chemical manufacturing and use [6]. REACH will considerably extend the number of chemicals covered by regulations, notably those that have been on market since 1981 (previously exempt), will place the responsibility for chemicals testing with industry, and will require testing whether the chemical is manufactured in Europe or imported for use there. Apart from the direct costs to industry of testing, REACH is likely to result in some chemical substances becoming restricted, prohibitively expensive, or unavailable. This will have dramatic effects on the supply chain for many consumer goods that rely on multiple chemical inputs.

Increased knowledge about chemicals, and the classification of an increasing number of chemical substances as being in some way "hazardous", will have health and safety implications, again making the use of those substances more costly and difficult. Furthermore, it will undoubtedly cause local authorities and governments to restrict and increase the costs of disposal of waste containing those substances (or indeed waste simply coming from processes involving such substances). Thus, legislation will increasingly force industry and the users of chemicals to change – both through substitution of hazardous substances in their processes or products and through the reduction in the volume and hazards of their waste.

The costs of waste to a chemical manufacturing company are high and diverse (Fig. 1.1-1) and, for the foreseeable future, they will get worse.

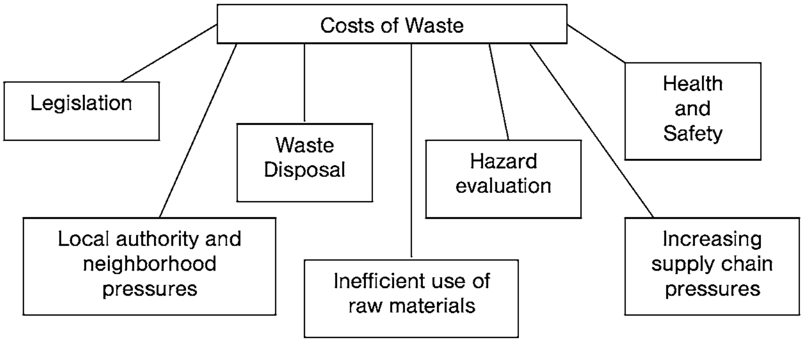


Fig. 1.1-1 The costs of waste.

These costs and other pressures are now evident throughout the supply chain for a chemical product – from the increasing costs of raw materials, as petroleum becomes more scarce and carbon taxes penalize their use, to a growing awareness amongst end-users of the risks that chemicals are often associated with, and the need to disassociate themselves from any chemical in their supply chain that is recognized as being hazardous (e.g. phthalates, endocrine disrupters, polybrominated compounds, heavy metals, etc.; Fig. 1.1-2)

1.1.3 Green Chemistry

The term Green Chemistry, coined by staff at the US EPA in the 1990s, helped to bring focus to an increasing interest in developing more environmentally friendly chemical processes and products. There were good examples of Green Chemistry research in Europe in the 1980s, notably in the design of new catalytic systems to replace hazardous and wasteful processes of long standing for generally important synthetic transformations, including Friedel–Crafts reactions, oxidations, and various base-catalyzed carbon–carbon bond-forming reactions. Some of this research had led to new commercial processes as early as the beginning of the 1990s [4].

In recent years Green Chemistry has become widely accepted as a concept meant to influence education, research, and industrial practice. It is important to realize that it is not a subject area in the way that organic chemistry is. Rather, Green Chemistry is meant to influence the way that we practice chemistry – be it in teaching children, researching a route to an interesting molecule, carrying out an analytical procedure, manufacturing a chemical or chemical formulation, or designing

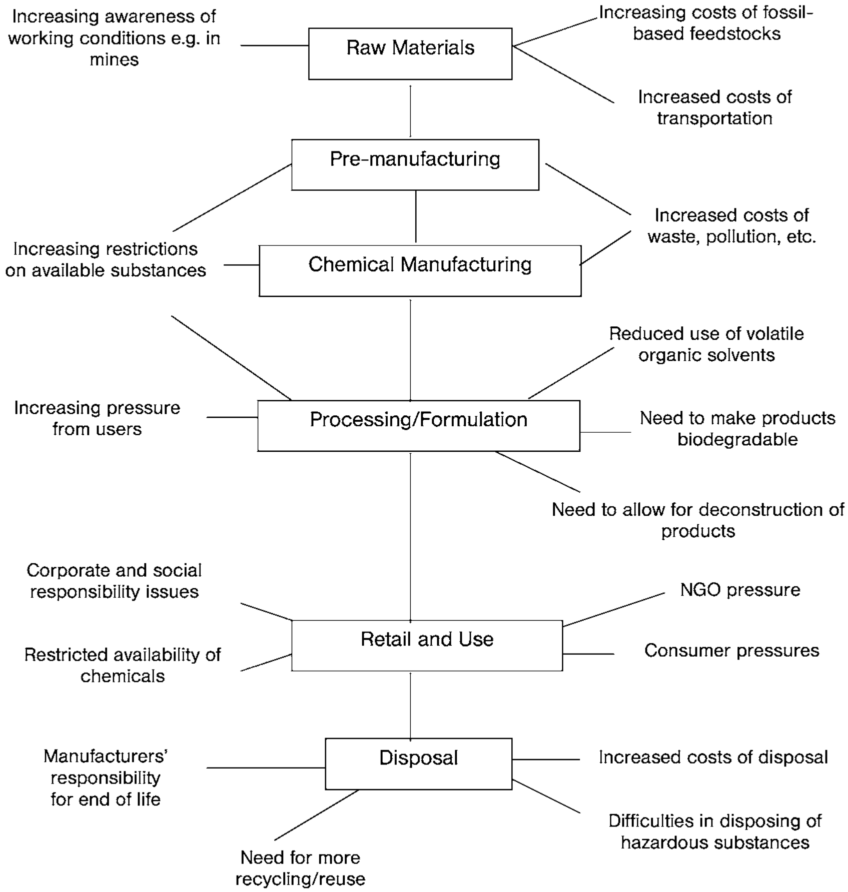


Fig. 1.1-2 Supply chain pressures.

a product [7]. Green Chemistry has been promoted worldwide by an increasing but still small number of dedicated individuals and through the activities of some key organizations. These include the Green Chemistry Network (GCN; established in the UK in 1998 and now with about one thousand members worldwide) [8] and the Green Chemistry Institute (established in the USA in the mid 1990s, now part of the American Chemical Society and with "chapters" in several countries around the world) [9]. Other Green Chemistry Networks or other focal points for national or regional activities exist in other countries including Italy, Japan, Greece and Portugal and new ones appear every year. The GCN was established to help promote and encourage the application of Green Chemistry in all areas where chemistry plays a significant role. (Fig. 1.1-3)

At about the same time as the establishment of the GCN, the Royal Society of Chemistry (RSC) launched the journal "Green Chemistry". The intention for this journal was always to keep its readers aware of major events, initiatives, and edu-

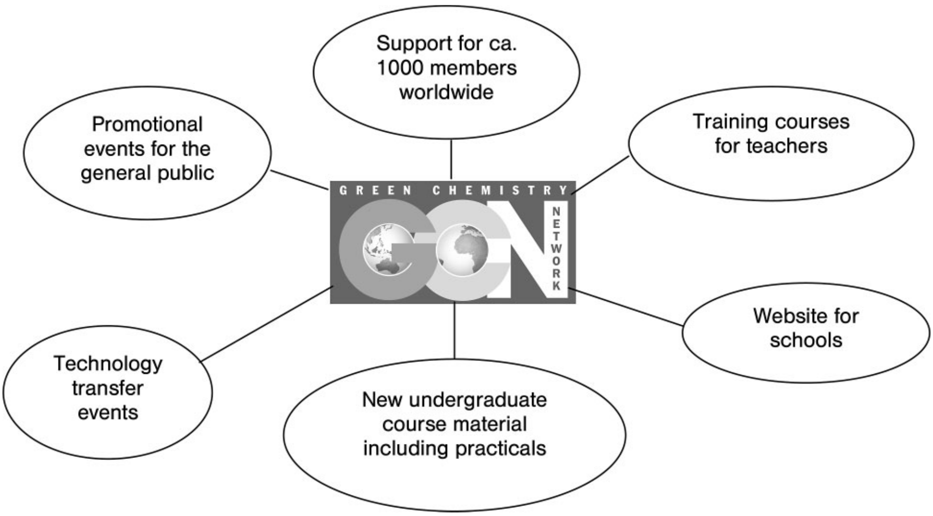


Fig. 1.1-3 The roles of the Green Chemistry Network.

cational and industrial activities, as well as leading research from around the world. The journal has gone from strength to strength and has a growing submission rate and subscription numbers, as well as having achieved one of the highest impact factors among the RSC journals (Fig. 1.1-4).

Green Chemistry can be considered as a series of reductions (Fig. 1.1-5). These reductions lead to the goal of triple bottom-line benefits of economic, environmental, and social improvements [11]. Costs are saved by reducing waste (which is becoming increasingly expensive to dispose of, especially when hazardous) and energy use (likely to represent a larger proportion of process costs in the future) as

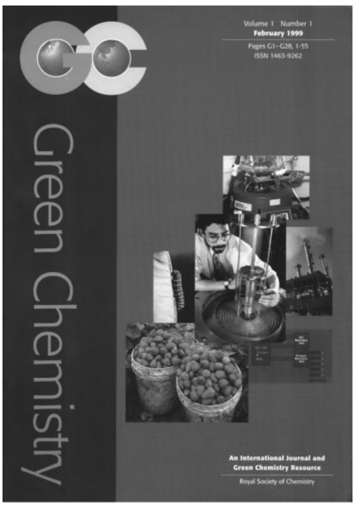


Fig. 1.1-4 The first issue of *Green Chemistry*.

well as making processes more efficient by reducing materials consumption. These reductions also lead to environmental benefit in terms of both feedstock consumption and end-of-life disposal. Furthermore, an increasing use of renewable resources will render the manufacturing industry more sustainable[12]. The reduction in hazardous incidents and the handling of dangerous substances provides additional social benefit – not only to plant operators but also to local communities and through to the users of chemical-related products.

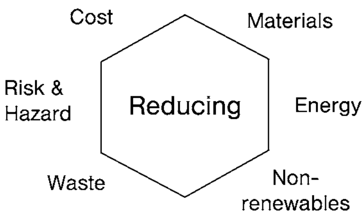


Fig. 1.1-5 "Reducing": The heart of Green Chemistry.

It is particularly important to seek to apply Green Chemistry throughout the lifecycle of a chemical product (Fig. 1.1-6) [13, 14].

Scientists and technologists need to routinely consider lifecycles when planning new synthetic routes, when changing feedstocks or process components, and, fundamentally, when designing new products. Many of the chemical products in common use today were not constructed for end-of-life nor were full supply-chain issues of resource and energy consumption and waste production necessarily considered. The Green Chemistry approach of "benign by design" should, when applied at the design stage, help assure the sustainability of new products across their full lifecycle and minimize the number of mistakes we make.

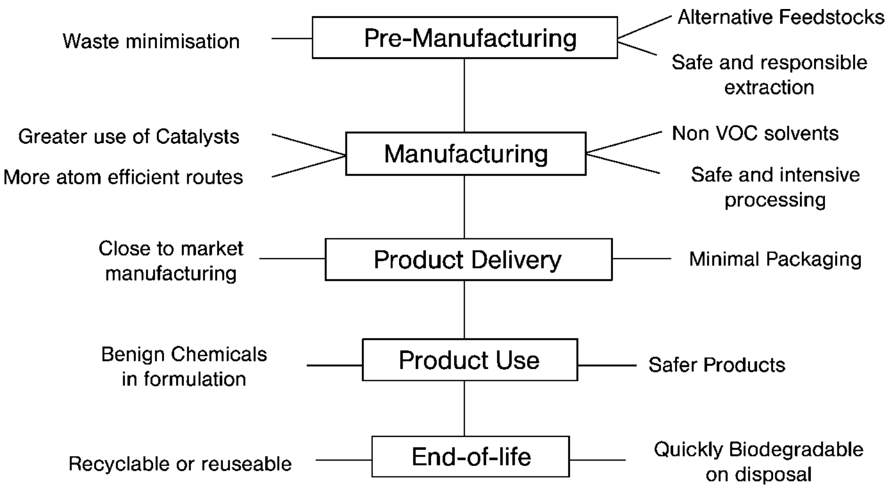


Fig. 1.1-6 Green Chemistry in the lifecycle of a product.

Much of the research effort relevant to Green Chemistry has focused on chemical manufacturing processes. Here we can think of Green Chemistry as directing us towards the "ideal synthesis" (Fig. 1.1-7) [3, 15].

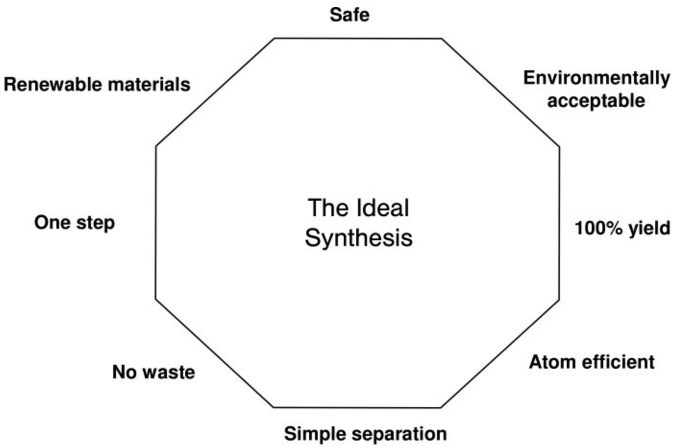


Fig. 1.1-7 Features of the "ideal synthesis".

Yield is the universally accepted metric in chemistry research for measuring the efficiency of a chemical synthesis. It provides a simple and understandable way of measuring the success of a synthetic route and of comparing it to others. Green Chemistry teaches us that yield is not enough. It fails to allow for reagents that have been consumed, solvents and catalysts that will not be fully recovered, and, most importantly, the often laborious and invariably resource- and energy-consuming separation stages such as water quenches, solvent separations, distillations, and recrystallizations. Green Chemistry metrics [16] are now available and commonly are based on "atom efficiency" whereby we seek to maximize the number of atoms introduced into a process into the final product. These are discussed in more detail later in this chapter. As indicated, simple separation with minimal input and additional outputs is an important target. An ideal reaction from a separation standpoint would be one where the substrates are soluble in the reaction solvent but the product is insoluble. The process would, of course, be further improved if no solvent was involved at all! Some of the worst examples of atom inefficiency and relative quantities of waste are to be found in the pharmaceutical industry. The so-called *E* factor (total waste/product by weight) is a simple but quite comprehensive measure of process efficiency and commonly shows values of 100+ in drug manufacture [17]. This can be largely attributed to the complex, multistep nature of these processes. Typically, each step in the process is carried out separately with work-up, isolation, and purification all adding to the inputs and amount of waste produced. Simplicity in chemical processes is vital to good Green Chemistry. Steps can be "telescoped" together for example, reducing the number of discrete stages in the process [18].

To achieve greener chemical processes we will need to make increasing use of technologies, some old and some new, which are becoming proven as clean technologies.

1.1.4
Environmentally Friendly Technologies [3]

There is a pool of technologies that are becoming the most widely studied or used in seeking to achieve the goals of Green Chemistry. The major “clean technologies” are summarized in Fig. 1.1-8. They range from well-established and proven technologies through to new and largely unproven technologies.

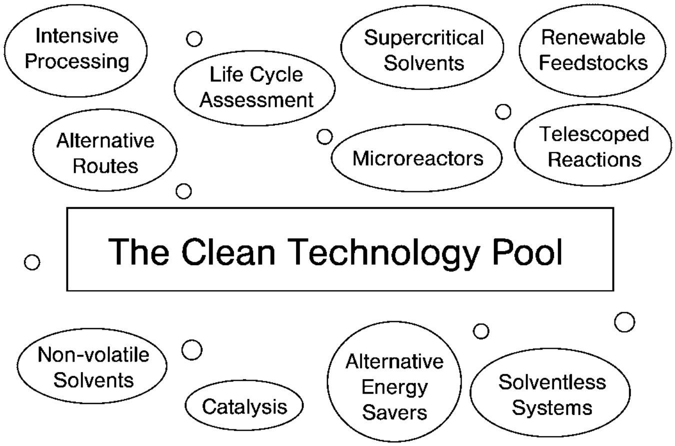
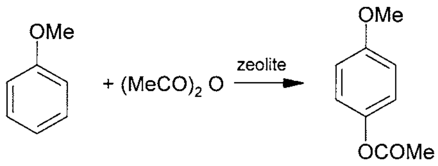


Fig. 1.1-8 The major clean technologies.

Catalysis is truly a well-established technology, well proven at the largest volume end of the chemicals industry. In petroleum refineries, catalysts are absolutely fundamental to the success of many processes and have been repeatedly improved over more than 50 years. Acid catalysts, for example, have been used in alkylations, isomerizations and other reactions for many years and have progressively improved from traditional soluble or liquid systems, through solid acids such as clay, to structurally precise zeolite materials, which not only give excellent selectivity in reactions but are also highly robust, with modern catalysts having lifetimes of up to 2 years! In contrast, the lower volume but higher value end of chemical manufacturing – specialties and pharmaceutical intermediates – still relies on hazardous and difficult routes to separate soluble acid catalysts such as H_2SO_4 and $AlCl_3$ and is only now beginning to apply modern solid acids. Cross-sector technology transfer can greatly accelerate the greening of many highly wasteful chemical processes [19]. A good, if sadly rare, example of this is the use of a zeolite to catalyze the Friedel–Crafts reaction of anisole with acetic anhydride (Scheme 1.1-1).

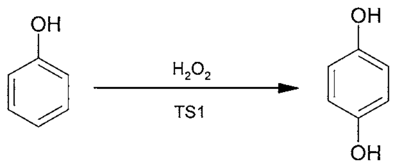


Scheme 1.1-1

In comparison to the traditional route using $AlCl_3$, the zeolite-based method is more selective. However, anisole is highly activated and the method is not applicable to most substrates – zeolites tend to be considerably less reactive than conventional catalysts such as $AlCl_3$.

Many specialty chemical processes continue to operate using traditional and problematic stoichiometric reagents (e.g. in oxidations), which we should aim to replace with catalytic systems. Even when catalysts are used, they often have low turnover numbers due to rapid poisoning or decomposition, or cannot be easily recovered at the end of the reaction. Here we need to develop new longer-lifetime catalysts and make better use of heterogenized catalysts, as well as considering alternative catalyst technologies (e.g. catalytic membranes), and to continue to improve catalyst design so as to make reactions entirely selective to one product [20].

Another good example of greener chemistry through the use of heterogeneous catalysis is the use of TS1, a titanium silicate catalyst for selective oxidation reactions [21] such as the 4-hydroxylation of phenol to the commercially important hydroquinone (Scheme 1.1-2).

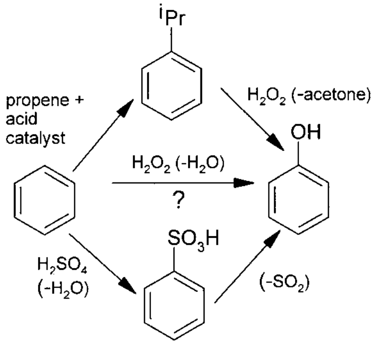


Scheme 1.1-2

TS1 has also been used in commercial epoxidations of small alkenes. A major limitation with this catalyst is its small pore size, typical of many zeolite materials. This makes it unsuitable for larger substrates and products. Again like many zeolites, it is also less active than some homogeneous metal catalysts and this prevents it from being used in what would be a highly desirable example of a green chemistry process – the direct hydroxylation of benzene to phenol. At the time of writing, commercial routes to this continue to be based on atom-inefficient and wasteful processes such as decomposition of cumene hydroperoxide, or via sulfonation (Scheme 1.1-3).

Of course, the direct reaction of oxygen with benzene to give phenol would be 100% atom efficient and based on the most sustainable oxidant – truly an ideal synthesis if we can only devise a good enough catalyst to make it viable!

The increased use of catalysis in the manufacture of low volume, high value chemicals will surely extend to biotechnology and, in particular, the use of enzymes



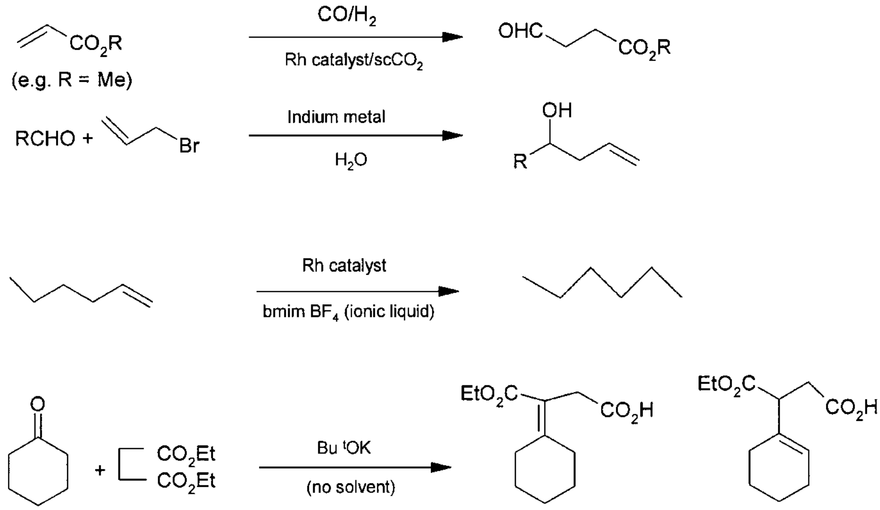
Scheme 1.1-3

[3, 22]. Enzymes provide highly selective routes to chemical products, often under mild conditions and usually in environmentally benign aqueous media. Drawbacks to their more widespread introduction include slow reactions, low space–time yields and, perhaps most importantly, a lack of familiarity with and even suspicions of the technology from many chemical compounds.

The replacement of hazardous volatile organic compounds (VOCs) as solvents is one of the most important targets for countless process companies including those operating in chemical manufacturing, cleaning, and formulation [23]. Some VOCs such as carbon tetrachloride and benzene have been widely prohibited and replaced but other problematic solvents, notably dichloromethane (DCM), continue in widespread use. While in many cases other, less harmful, VOCs are used to remove the immediate problems (e.g. ozone depletion) due to such compounds as DCM, more fundamental technology changes have included the use of non-organic compounds such as supercritical carbon dioxide or water, the use of non-volatile solvents such as ionic liquids (molten salts), and the total avoidance of solvent (e.g. through using a surface-wetting catalyst in a reaction, or simply relying on interfacial reaction occurring between solids). All of these alternative technologies have been demonstrated in numerous organic reactions such as those examples shown in Scheme 1.1-4.

Carbon dioxide has also been successfully introduced into some dry-cleaning processes and various consumer formulations now no longer contain a VOC solvent.

Green Chemistry needs to be combined with more environmentally friendly technologies if step-change improvements are to be made in chemical manufacturing processes. Synthetic chemists have traditionally not been adventurous in their choice of reactors – the familiar round-bottomed flask with a magnetic stirrer remains the automatic choice for most, even when the chemistry they plan to use is innovative e.g. the use of a non-volatile ionic liquid solvent or a heterogeneous catalyst as an alternative to a soluble reagent. However, an increasing number of research articles describing green chemical reactions are based on alternative reactors including [3, 24].



Scheme 1.1-4

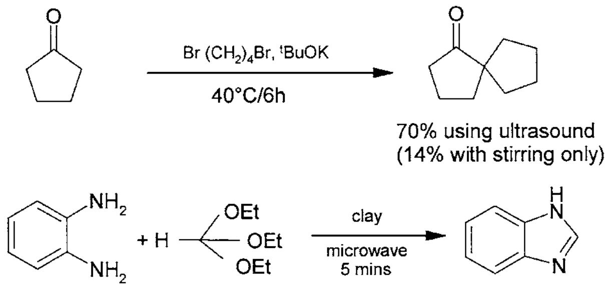
- continuous flow reactors (a technology that dominates the petrochemical industry but is little utilized in specialty chemical manufacturing)
- microchannel reactors whereby reaction volumes are kept small and scale is highly flexible thus reducing hazards and risk
- intensive processing systems such as spinning disc reactors which combine the benefits of low reaction volumes with excellent heat transfer and mixing characteristics
- membrane reactors that can maintain separation of aqueous and non-aqueous phases, hence simplifying the normally waste-intensive separation stages of a process

These alternative reactor technologies can be combined with Green Chemistry methods including, for example, catalytic membrane reactions and continuous flow supercritical fluid reactions.

Energy has often been somewhat neglected in the calculations of resource utilization for a chemical process. Batch processes based on scaled-up reaction pots can run for many hours or even days to maximize yield and often suffer from poor mixing and heat transfer characteristics. As the cost of energy increases and greater efforts are made to control emissions associated with generating energy, energy use will become an increasingly important part of Green Chemistry metrics calculations. This will open the door not only to better designed reactors such as those described earlier but also to the use of alternative energy sources. Of these, two of the more interesting are:

- ultrasonic reactors
- microwave reactors[25].

Both are based on the use of intensive directed radiation that can lead to very short reaction times or increased product yields and also to more selective reactions [3]. Examples of the use of these reactors are shown in Scheme 1.1-5.



Scheme 1.1-5

A lifecycle approach to the environmental performance and sustainability of chemical products demands a proper consideration of pre-manufacturing and specifically the choice of feedstocks. Today's chemical industry is largely based on petroleum-derived starting materials, a consequence of the rapid growth in the new petroleum-based energy industry in the early twentieth century. This industry was based on an apparently inexhaustible supply of cheap oil, which we could afford to use on a once-only basis for burning to produce energy. Petrochemicals was a relatively small (around 10%) part of the business, generating a disproportionately high income and helping to keep energy costs down, which in turn maintained ultra-high demand for the raw material even when extraction became more difficult and transportation more controversial. The parallel and mutually supportive growth in petro-energy and petrochemicals from the petro-refineries of the Middle East, Americas, Africa, and elsewhere is surely past its peak. It now seems likely that as we try to tackle the inevitable decline of oil as an energy source, so shall we attempt to seek alternatives for the manufacture of at least some of the many chemicals we use today. While forecasts seem to change every day and political parties can selectively use bits of the overwhelming amount of conflicting data to suit their own agenda, no one will argue that these changes must occur in the twenty-first century – "one hundred years of petroleum" is beginning to look about right.

The use of sustainable, plant-based chemicals for future manufacturing can involve several approaches (Fig. 1.1-9)' [3, 7 14].

Many of the earlier plans in this area were based on the bulk conversion of large quantities of biomass into the type of starting materials that the chemical industry has grown up on (CO, H_2, C_2H_4, C_6H_6, etc.). On one hand the logic behind this approach is clear – the manufacturing industries are equipped to work with such simple small molecules. On the other hand, it is perverse to consume resources and generate waste in removing functionality from albeit a soup of molecules, just so that we can then apply our chemical technology toolkit to consume more resources and generate more waste in converting the intermediate simpler molecules into ones we can use in the many industries that use chemicals. The scale of operation,

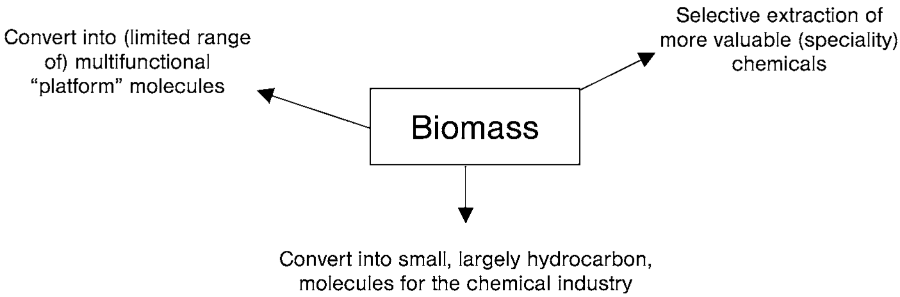


Fig. 1.1-9 Approaches to the use of plant-based chemicals.

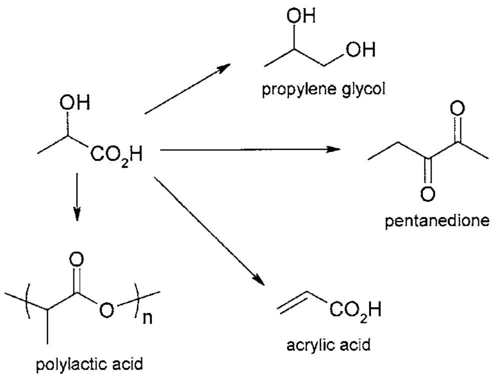
and the added costs of the extra steps, will always make this technology expensive and of limited appeal except in those situations where a large volume of waste biomass is in close proximity to suitable industrial plant.

Nature manufacturers an enormous array of chemicals to perform the many functions that its creatures need to survive, grow, and propagate. A tree contains some 30 000 different molecules ranging from simple hydrocarbons to polyfunctional organics and high molecular weight polymers. Many of these molecules have immediate and sometimes very high value, for example as pharmaceutical intermediates. The selective extraction of compounds from such complex mixtures is, however, often impractical and uneconomic and may lead to a very high environmental impact product as a result of enormous inputs of energy and outputs of waste. The extraction of families of compounds with high value themselves or through Green Chemistry modification is a more likely approach to take advantage of some of nature's gifts of sustainable and interesting molecular entities.

The third approach of using a large proportion of biomass to produce so-called "platform molecules" is worth close consideration. Here, we need to learn how to make best use of a number of medium-sized, usually multifunctional, organic molecules that can be obtained relatively easily by controlled enzymatic fermentation or chemical hydrolysis. The simplest of these is (bio) ethanol; others include levulinic acid, vanillin, and lactic acid. These are chemically interesting molecules in the sense that they can be used themselves or can quite easily be converted into other useful molecules – building on rather than removing functionality – as can be seen, for example, with lactic acid (Scheme 1.1-6).

One of these products, polylactic acid, has become the basis of one of the best recent commercial illustrations of the potential value of this approach. Cargill-Dow now manufacture polylactic acid polymer materials using a starch feedstock. The materials are finding widespread use as versatile, sustainable, and (importantly) biodegradable alternatives to petro-plastics. [14, 26].

Making more direct use of the chemicals in biomass and the functionality they contain, rather than reducing them to simpler, smaller starting materials for synthesis, makes sense from a lifecycle point of view as well as economically (Fig. 1.1-10).



Scheme 1.1-6

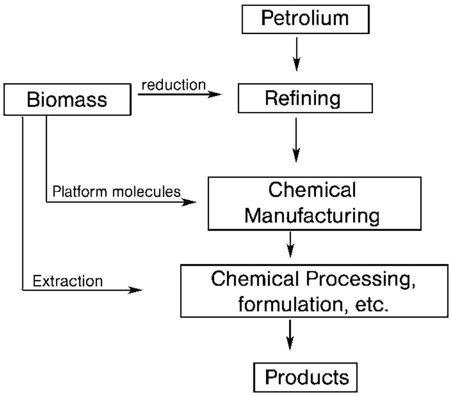


Fig. 1.1-10 The use of biomass chemicals in traditional chemical industry processes.

1.1.5
Green Chemistry Metrics

In its short history, Green Chemistry has been heavily focused on developing new, cleaner, chemical processes using the technologies described earlier in this chapter. Increasing legislation will force an increasing emphasis on products but it is important that these in turn are manufactured by green chemical methods. Industry is becoming more aware of these issues and some companies can see the business edge and competitive advantage that Green Chemistry can bring. However, the rate of uptake of Green Chemistry into commercial application remains very small. While the reasons for this are understandably complex, and also dependent on the economic vitality of the industry, it is important 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 they 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 to a petro-chemical 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 that can give hard, reliable data to prove its merits.

These needs and "reality checks" have led to the emergence of Green Chemistry-related metrics, although they are very new and by no means widely applied or tested. The ultimate metric can be considered to be lifecycle assessment (LCA), but full LCA studies for any particular chemical product are difficult and time consuming.[13, 14]. 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 [16, 25] are most widely considered in comparing chemical process routes, including limited, if easy-to-understand, metrics such as atom efficiency and attempts to measure overall process efficiency such as *E* factors, mass intensities, and mass efficiency [27]. As with LCA, these metrics have to be applied with definite 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. At the product end of the lifecycle we are used to testing for human toxicity and this will become much more prevalent through REACH [6]. 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 "sustainable solutions" to our healthcare, housing, food, clothes, and lifestyle needs, so we must be sensitive to the long-term availability of the inputs that go into the supply chain for a product [14]. With increasing 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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