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Introduction to Clean Technology and Catalysis*James H. Clark*

1.1

Green Chemistry and Clean Technology

Traditional chemical manufacturing is resource demanding and wasteful, and often involves the use of hazardous substances. Resources are used throughout the production and including the treatment of waste streams and emissions (Figure 1.1).

Green chemistry focuses on resource efficiency and on the design of chemical products and processes that are more environmentally benign. If green chemistry is used in a process, it should be made simpler, the inputs and outputs should be safer and more sustainable, the energy consumption should be reduced and costs should be reduced as yields increase, and so separations become simpler and less waste is generated [1]. Green chemistry moves the trend toward new, clean technologies such as flow reactors and microwave reactors, as well as clean synthesis. For instance, lower temperature, shorter reaction time, choice of an alternative route, increased yield, or using fewer washings at workup improve the “cleanness” of a reaction by saving energy and process time and reducing waste [2].

At present, there is more emphasis on the use of renewable feedstocks [3] and on the design of safer products including an increasing trend for recovering resources or “closed-loop manufacturing.” Green chemistry research and application now encompass the use of biomass as a source of organic carbon and the design of new greener products, for example, to replace the existing products that are unacceptable in the light of new legislation (e.g., REACH) or consumer perception.

Green chemistry can be seen as a tool by which sustainable development can be achieved: the application of green chemistry is relevant to social, environmental, and economic aspects.

To achieve sustainable development will require action by the international community, national governments, commercial and noncommercial organizations, and individual action by citizens from a wide variety of disciplines. Acknowledgment of sustainable development has been taken forward into policy by many governments including most world powers notably in Europe [4], China [5], and the United States [6].

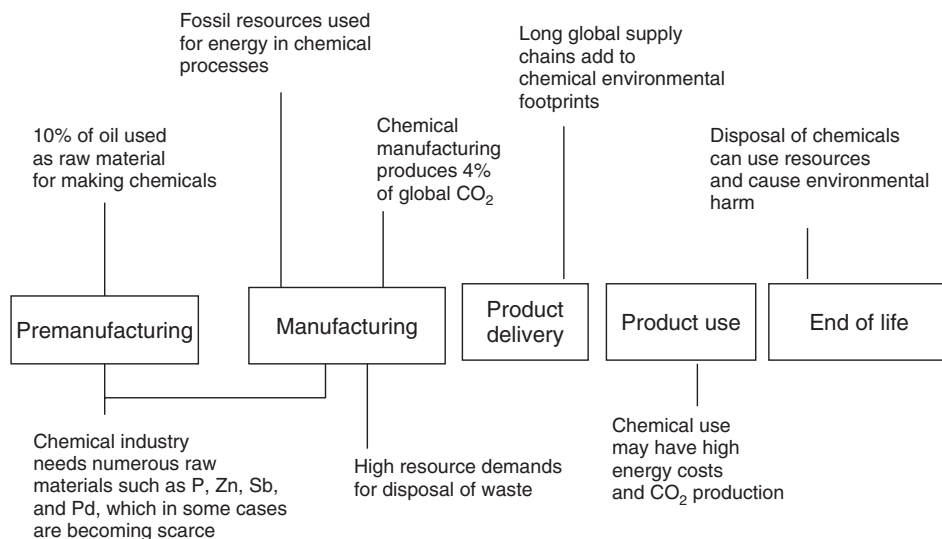


Figure 1.1 Resource demands of traditional chemical manufacturing.

1.1.1

Ideals of Green Chemistry

In Figure 1.2 and Figure 1.3, the ideals of green chemical synthetic design are shown.

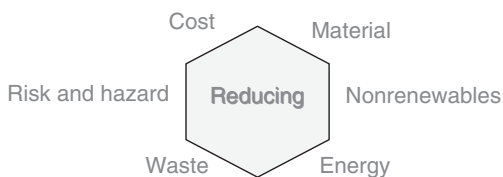


Figure 1.2 Factors for reduction in syntheses.

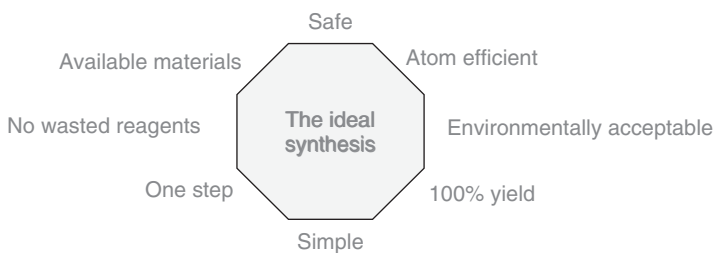


Figure 1.3 The eight parts of an ideal synthesis.

It is important to note that these green chemistry goals are most effectively dealt with and are easier to apply if they are considered at the design stage rather than retrospectively – green chemistry is not an end-of-pipe solution.

Chemical plants have traditionally concentrated on mechanical safety devices, reducing the probability of accidents. However, mechanical devices are not infallible and safety measures cannot completely prevent the accidents that are happening. The concept of inherently safer design (ISD) was designed with the intention of eliminating rather than preventing the hazards and led to the phrase “What you don’t have can’t harm you” [7]. ISD means not holding significant inventories of hazardous chemicals or not using them at all.

This approach would have prevented the accident at Bhopal, India in 1984, where many thousands of people were killed or seriously injured. One of the chemicals used in the process at the Union Carbide factory was highly water sensitive, and when a watertight holding tank was breached, the accident occurred, releasing the chemicals into the air, affecting the villages surrounding the factory. The chemical is nonessential and the ISD approach would have been used as an alternative, thus eliminating the risk altogether.

Green chemistry research has led to the invention of a number of clever processing technologies to save time and energy or reduce waste production, but these technologies mostly exist in academia and, with very few exceptions, industry has been slow to utilize them. Green chemical technologies include heterogeneous catalysis (well established in some sectors but much less used in fine chemicals and pharmaceuticals, see the subsequent text), use of supercritical fluids (as reaction and extraction media), photochemistry, microwave chemistry, sonochemistry, and synthetic electrochemistry. All these replacements for conventional methods and conductive heating can lead to improved yields, reduced reaction times, and reduced by-product formation. Engineered greener technologies also exist, including a number of replacements for the stirred tank batch reactor, such as continuous stirred tanks, fluidized bed reactors, microchannel reactors, and spinning disc reactors as well as microwave reactors, all of which increase the throughput, while decreasing the energy usage and waste. Unfortunately, despite these many new processes, industry is reluctant to use these hardware solutions because of the often massive financial expenditure involved in purchasing these items and the limited number of chemistries that have been demonstrated with them to date. There is also a reluctance to change well-established (and paid for) chemical plant so that newer, cleaner technologies may well have more success in the developing (e.g., the Brazil, Russia, India, and China (BRIC)) nations, where the chemical industry is growing and new plant is required to meet the increasing expectations of local and increasingly affluent markets.

1.2

Green Chemistry Metrics

It is important to be able to quantify the change when changes are made to chemical processes. This enables us to quantify the benefit from the new technology

introduced (if there are benefits). This can aid in in-house communication (to demonstrate the value to the workforce) as well as in external communication. For yield improvements and selectivity increases, simple percentages are suitable, but this simplistic approach may not always be appropriate. For example, if a toxic reagent is replaced by a less toxic one, the benefit may not be captured by conventional methods of measuring reaction efficiency. Equally, these do not capture the mass efficiency of the process – a high-yielding process may consume large amounts of auxiliaries such as solvents and reagents, as well as those used in product separation and purification. Ideally, we also need to find a way to include energy and water, both of them have been commonly used in a rather cavalier way but they are now subject to considerable interest that they can vary depending on the location of the manufacturing site.

Numerous metrics have been formulated over time and their suitability discussed at great length [8–12]. The problem observed is that the more accurate and universally applicable the metric devised, the more complex and unemployable it becomes. A good metric must be clearly defined, simple, measurable, objective rather than subjective, and must ultimately drive the desired behavior. Some of the most popular metrics are

- E factor (which effectively measures the amount of product compared to the amount of waste – the larger the E factor is, the less product-specific is the process; the fine chemical and pharmaceutical manufacturing sectors tend to have the highest E factors) [13];
- effective mass yield (the percentage of the mass of the desired product relative to the mass of all nonbenign materials used in its synthesis – this includes an attempt to recognize that “not all chemicals are equal” – important and very real but very difficult to quantify);
- atom efficiency/economy (measures the efficiency in terms of all the atoms involved and is measured as the molecular weight of the desired product divided by the molecular weight of all of the reagents; this is especially valuable in the design “paper chemistry” stage when low atom efficiency reactions can be easily spotted and discarded);
- reaction mass efficiency (essentially the inverse of E factor).

Of course, the ultimate metric is life cycle assessment (LCA); however, this is a demanding exercise that requires a lot of input data, making it inappropriate for most decisions made in a process environment. However, some companies do include LCA impacts such as greenhouse gas production in their in-house assessment, for example, to rank solvents in terms of their greenness. It is also essential that we adopt a “life cycle thinking” approach to decision making so that we do not make matters worse when greening one stage in a manufacturing process without appreciating the effects of that change on the full process including further up and down the supply chain.

1.3

Alternative Solvents

Most chemical processes involve solvents – in the reactions and in the workups as well as in the cleaning operations [14, 15]. The environmental impact of a chemical process cannot be properly evaluated without considering the solvent(s). For some time there has been a drive toward replacing or at least reducing the use of traditional volatile organic solvents such as dichloromethane, tetrahydrofuran, and *N*-methylpyrrolidone – commonly used solvents in, for example, catalytic processes.

Ionic liquids, fluoruous biphasic systems, and supercritical fluids have all been studied as alternatives to conventional organic solvents. However, because of their nature, some of these novel systems require additional hardware for utilization. For example, some suppliers have designed advanced mixing systems to enable polyphasic systems to be intimately mixed at the laboratory scale. There has also been considerable rethinking of the green credentials of some of these alternative solvents in recent years and many ionic liquids are no longer considered suitable because of their complex syntheses, toxicity, or other unacceptable properties, or difficulty in separation and purification. Fluoruous solvents (which are based on heavily fluorinated usually aliphatic compounds) are not considered to be environmentally compatible (as they persist in the environment).

Supercritical solvents are difficult to manipulate because of the high pressures and temperatures often employed. In the case of supercritical water, equipment had to be designed, which could contain the highly corrosive liquid. Vessels for creating supercritical solvents such as supercritical CO₂ (scCO₂) are now available and are capable of fine adjustments in temperature and pressure to affect the solvents' properties. Very high pressure and temperatures are not required to produce scCO₂ and it is becoming an increasingly popular reaction medium as its properties are controllable by varying the temperature and pressure or by the use of a cosolvent [16]. The main environmental benefit of scCO₂ lies in the workup, as the product mixture is obtained free from solvent by simply returning to atmospheric conditions. Additionally, carbon dioxide is nontoxic, nonflammable, recyclable, and a by-product of other processes. However, there are energy and safety concerns associated with the elevated temperatures and pressures employed and in particular, there are high capex costs to install a plant. These must be balanced against the benefits of its use.

scCO₂ can be a good medium for catalysis, although its low polarity means that either catalysts are heterogeneous or they have to be modified to enable them to dissolve (e.g., by introducing solubilizing substituents on the catalyst ligands).

Ionic liquids are molten salts and are liquid at relatively low temperatures: room-temperature ionic liquids are the most widely studied. Their lack of vapor pressure has been their biggest selling point but the enormous flexibility of choice of ions enables ionic liquids to be designed as catalysts as well as solvent. In particular, they can be powerful combined solvent–acid catalysts. The use of ionic liquids

has been reported in various synthetic transformations such as Friedel–Crafts reaction, Diels–Alder reaction, and metal-catalyzed asymmetric synthesis. The problems with their use include toxicity (in some cases), cost of manufacture, and difficulties in separation/purification (they cannot be distilled), and these have hampered their industrial uptake, although they are certainly interesting at least for niche applications [17, 18].

Biphasic systems can be an effective method by which catalyst, substrates, and products can be easily separated into different liquid phases and therefore simplifying and “greening” reaction workup. Fluorous biphasic solvent systems, where the homogeneous catalyst is soluble within the fluorous phase and reactants are soluble within an immiscible conventional solvent, have been extensively studied. Heating leads to the two solvents becoming miscible, enabling the reaction to occur. On completion of the reaction, when cooled, the phases return to being immiscible with the product partitioning into the conventional solvent phase for isolation. However, there have been serious concerns expressed over the “green” credentials of these heavily fluorinated molecules as they persist in the environment and can be hazardous to operators. Phase transfer catalysts (PTCs) have been used for many years in biphasic systems for transferring species into a phase they would not normally be soluble in. They aid the reaction by improving the availability of the substrates [19]. PTCs are commonly quaternary ammonium or phosphonium compounds; they mostly do not present major environmental concerns and continue to be popular for greening organic reactions. Perhaps, the biggest concern is with regard to their recovery from reactions as they are usually very soluble in both phases of the biphasic system, although heterogeneous PTC, involving, for example, silica-supported onium compounds have been reported.

1.4

Heterogeneous or Homogeneous

While homogeneous catalysis generally offers good activity and a homogeneous distribution of active sites, as explained earlier, it is not without problems notably with regard to separation and reuse. Here, heterogeneous catalysis has clear advantages. There are in fact a number of advantages of heterogeneous catalysis compared to homogeneous [20, 21].

- *Safety* – heterogeneous catalysts are often environmentally benign and safe to handle because of the active species being bound to a support material (e.g., silica-supported sulfonic acid for acid catalysis compared to sulfuric acid).
- *Separation and reusability* – the solid catalyst can either be used in a fixed bed configuration or simply filtered or centrifuged from a stirred tank reaction and then, in many cases reactivated for reuse (e.g., zeolites used in petroleum refining can be reactivated and reused for years before disposal).
- *Activity* – while homogeneous catalyst are commonly the most active, there are many cases where perhaps counterintuitively, the heterogeneous analog is more

- active often because of the cooperative effect of surface sites with the introduced catalyst sites (e.g., clayzic for Friedel–Crafts catalysis compared to zinc chloride).
- *Selectivity* – a very important plus for many heterogeneous catalysts whereby the pore structure limits the diffusion in for reactants or out for products effectively restricting the chemistry that occurs and the shape and size of molecules that can react or be formed; shape selectivity can also affect the stereochemistry through the control of reaction pathways (e.g., use of zeolites to limit the alkylation of benzene to mono-substituted products).

The disadvantages of heterogeneous catalysis include added synthesis costs, need for larger amounts of materials, and blocking of catalyst sites. Overall, heterogenization of catalysts (and sometime reagents) is one of the most widely favored green chemical technologies.

1.5

Alternative Energy Reactors for Green Chemistry

There are a number of types of equipment associated with high-energy transfer to the reactants including microreactors, microwave reactors, radio frequency heating, electric pulses, ultrasonication, and spinning disc reactors. Some of these are briefly discussed later.

1.5.1

Microchannel Reactors

The principle of the microreactor is based on the simple fact that having very small volumes of reactants coming together at any given time, the risk of a potentially hazardous thermal runaway is minimized. This is an example of “process intensification,” which has many benefits including uniform treatment of all molecules and transport rates that match the reaction rates. These can lead to improved selectivity and yield and reduced processing time as well as reduced risk through limited exposure. Typically, submillimeter channels are etched into quartz or plastic units [22]. These units have been successfully demonstrated for liquid/liquid reactions, for example, fixing palladium cross-coupling catalysts to fine glass pipes.

Using a “scaling out” rather than “scaling up” approach, a more flexible production capacity is available with the opportunity to rapidly switch product output as market demands change, and very importantly (in the light of such disasters as Bhopal), the storage of hazardous product should become redundant.

1.5.2

Microwave Reactors

Microwave irradiation is a high-frequency electric field, with wavelength in the centimeter range, which places it between radio waves and infrared in the

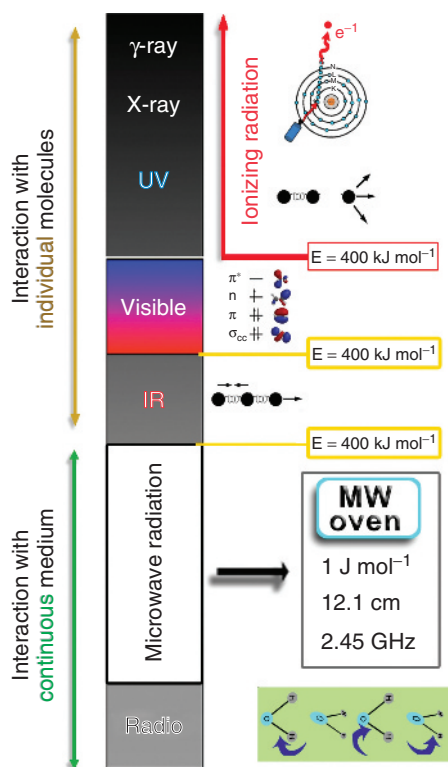


Figure 1.4 Microwaves in the electromagnetic spectrum.

electromagnetic spectrum (Figure 1.4). Microwave energy is very low, around 1 J mol^{-1} , which means that microwaves cannot directly break the bonds. Microwaves interact with dipoles or ions, and create “molecular heating” by causing dipole rotations (or ionic conduction). Both of these mechanisms of receiving energy are caused by the molecules attempting to align with the rapidly oscillating microwave field. Thus, microwave reactors are capable of enhancing reaction rates as they allow more molecules to have sufficient energy to overcome the activation barrier of the reaction. These high-energy molecules are created by preventing the molecules from relaxing from the excited state: kinetic relaxation occurs in 10^{-5} s , whereas microwaves apply energy in 10^{-9} s , which creates a nonequilibrium state.

There has been an exponential growth in microwave-related publications from the first articles involving organic synthesis in 1986 [23]. Early studies used domestic ovens and gave erratic results that are often caused by hot spots, which in some cases led to explosions. A number of companies have now manufactured systems designed for chemistry, using mono-mode microwave generators and laboratory-scale apparatus usually on a scale of 1–100 ml. With these more reliable systems, chemists have reported microwave benefits including decreased reaction

times, reduced overall energy consumption, and improved yield and selectivity. Microwave technology is “enabling a wide range of reactions to be performed easily and quickly” [24].

Microwave processing has now been shown to be effective at large continuous processing scale, for example, in waste treatment including food waste gasification. Microwave-assisted organic chemical reaction can be considerably more energy efficient than that using conventional heating [25] and as such is another example of process intensification, especially when combined with flow systems that can help overcome limitations of microwave penetration and allow optimum continuous operation. Furthermore, because of the instantaneous nature of the heating, microwaves offer a major advantage in controllability over conventional heating. Microwave activation of the active center of heterogeneous catalysts has also been proposed [26], but it must be noted however that this is a little understood reaction and no detailed explanation or theories have been proposed.

Microwave reactions have been successfully demonstrated for many different organic reactions including metal-mediated catalysis, cyclo-additions, heterocyclic chemistry, rearrangements, electrophilic and nucleophilic substitutions, and reduction. Many reactions work well in water, adding to the techniques green credentials [27].

1.6

Concluding Remarks

Green chemistry shows many great challenges for the future and many opportunities where technologies such as catalysis can play an important role. It also teaches us that we must only introduce changes in full recognition of the effects across the life cycle including resources and all aspects of the process.

The development of new heterogeneous catalysts, which can be integrated into emerging intensive processes or can be operated with alternative solvents, is critical to establish viable clean technologies for industry. Catalyst design requires improved understanding of the mechanism of catalyzed processes and ability to probe catalyst active sites under operation as is discussed in the subsequent chapters of this book.

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