# 1

# From Green to Sustainable Industrial Chemistry

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## 1.1

## Introduction

The concept of "Green Chemistry" was introduced in the early 1990s in the USA. After the introduction of the US Pollution Prevention Act, the Office of Pollution Prevention and Toxics (OPPT) explored the idea of developing new or improved chemical processes to decrease hazardous to human health and the environment. In 1991, OPPT launched a research grants program called "Alternative Synthetic Pathways for Pollution Prevention." This program was focused on pollution prevention in the design and synthesis of chemicals.

In 1993, the program was expanded to include other topics, such as greener solvents and safer chemicals, and was renamed "Green Chemistry." Since then, the Green Chemistry Program, led by the US Environmental Protection Agency (EPA), has built many collaborations with academia, industry, other government agencies and non-government organizations to promote the use of chemistry for pollution prevention through completely voluntary, non-regulatory partnerships. Further information can be found in the web site: http://www.epa.gov/gcc/index.html.

Notable among the initiatives is the "Presidential Green Chemistry Challenge" (launched in 1995), which promotes pollution prevention through partnerships with the chemistry community. The current focus of the challenge is the Presidential Green Chemistry Challenge Awards. Table 1.1 gives the 2008 award recipients to exemplify the initiative. Further details can be found in the web site cited above.

In addition, in the USA the Green Chemistry Institute (GCI) was created in 1997 – a not-for-profit corporation devoted to promoting and advancing green chemistry. In January 2001, GCI joined the American Chemical Society (ACS) in an increased effort to address global issues at the intersection of chemistry and the environment. The institute developed the Green Chemistry Resource Exchange as a place for users to exchange green chemistry information resources. Development was part of a

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**Table 1.1** Recipients of the 2008 US Presidential Green Chemistry Challenge Awards.

| Topic | Award | Motivations |
|---|---|---|
| Greener Synthetic Pathways | Battelle for the development and commercialization of Biobased Toners | A soy-based toner that performs as well as traditional ones, but is much easier to remove |
| Greener Reaction Conditions | Nalco Company for 3D TRASAR Technology | 3D TRASAR technology monitors the condition of cooling water continuously and adds appropriate chemicals only when needed, rather than on a fixed schedule |
| Designing Greener Chemicals | Dow AgroSciences LLC for Spinetoram: enhancing a natural product for insect control | The new insecticide replaces organo-phosphate pesticides for tree fruits, tree nuts, small fruits and vegetables. It reduces the risk of exposure throughout the supply chain |
| Small Business | SiGNa Chemistry, Inc. for new stabilized alkali metals for safer, sustainable syntheses | A new way to stabilize alkali metals by encapsulating them within porous, sand-like powders, while maintaining their usefulness in synthetic reactions |
| Academic | Robert E. Maleczka, Jr., Milton R. Smith, III Michigan State University for green chemistry for preparing boronic esters | New catalytic method to make in a greener way precursors with a carbon–boron bond for Suzuki “coupling” reactions |

cooperative agreement with the US EPA Design for the Environment program. One of the notable results is the development of the “Green Chemistry Expert System” (GCES), which allows users to build a green chemical process or product, or survey the field of green chemistry. The system is equally useful for new and existing chemicals and their synthetic processes.

Education is of critical relevance to effectively incorporate green chemistry into chemical product and process designs. For green chemistry to enter widespread practice, chemists must be educated about green chemistry during their academic and professional training. To accomplish this goal the EPA, in collaboration with ACS, supports various educational efforts that include the development of materials and courses to assist in the training of professional chemists in industry and education of students. Consequently, the chemical industry has discovered that when their professional chemists are knowledgeable about pollution prevention concepts they are able to identify and implement effective pollution prevention technologies.

Over the years, the EPAs Green Chemistry Program has collaborated with several organizations internationally. The most important being the Organization for Economic Co-operation and Development (OECD), the International Union of

Pure and Applied Chemistry (IUPAC) and the G8 Ministers for Research (Carnegie Group). In 1999 the OECD adopted the following priority recommendations:

- supporting and promoting the research and development;
- recognizing sustainable chemistry accomplishments;
- disseminating related technical and event information, for example, on the Internet;
- developing guidance on implementing sustainable chemistry programs for OECD member countries and outreach to non-member international interests;
- incorporating sustainable chemistry principles into chemical education.

The OECD Sustainable Chemistry Initiative Steering Group includes over 40 representatives from ten countries.

In 2005, the G8 Ministers for Research founded a research and training network on green sustainable chemistry called the International Green Network (IGN). The Interuniversity Consortium “Chemistry for the Environment” (INCA, in Venice, Italy) was selected as the hub of the IGN. The goals of IGN are to sponsor, coordinate and provide information for scientific collaborations; provide training for young chemists; and support applications of green chemistry in developing nations.

In 1976, IUPAC set up a standing committee called CHEMRAWN (Chemistry Research Applied to World Needs). Over the years, there have been several CHEMRAWN conferences and projects to advance chemical technologies that help to achieve a sustainable society. IUPAC has also established in 2001 a working party on “Synthetic Pathways and Processes in Green Chemistry” and the Interdivisional sub-Committee on Green Chemistry.

Other multi-national organizations, including the United Nations, are now beginning to assess the role that they can play in promoting the implementation of green chemistry to meet environmental and economic goals simultaneously. There are rapidly growing activities in government, industry and academia worldwide.

Also in Europe, starting from about 1998, various green chemistry initiatives were launched. In the UK the Green Chemistry Network (GCN) and the Environment, Sustainability & Energy Gateway were launched by the Royal Society of Chemistry, which also started a new journal entitled *Green Chemistry* (http://www.rsc.org/). The 10th anniversary of this journal was celebrated recently with a special issue [1]. Also in UK the CRYSTAL Faraday Partnership was created – a virtual center of excellence in green chemical technology aimed at promoting lower-cost, sustainable manufacturing, for the chemical industry. GCN also launched the Green Chemistry Center for Industry to provide competitive, tailor-made solutions, which reduce waste and environment damage to obtain better profits in chemical industry.

In Italy, the Interuniversity National Consortium “Chemistry for the Environment” (INCA) was founded in 1993 and rapidly become an internationally recognized reference center for green chemistry. The many initiatives include the periodical *School on Green Chemistry*, the organization of the first International IUPAC Conference on Green Chemistry and the Green Chemistry Publication Series. INCA is also the hub center for IGN, as indicated above.

In Germany, activities related to green chemistry are widespread throughout scientific and governmental organizations [2], as well as in other European countries such as France, Spain, Netherlands, Denmark, and so on. Many symposia and international congresses on green chemistry have been organized in these countries.

In Australia the Center for Green Chemistry was established at Monash University, and the Green Chemistry Challenge Awards by the Royal Australian Chemical Institute. In Brazil there is the "Química Verde" (Green Chemistry) program. Japan created, in 1998, the Green Chemistry (GC) Initiative, a task force consisting of representatives from Japanese chemical organizations. In 2000 the Green & Sustainable Chemistry Network (GSCN) was launched. Many other activities on green chemistry have been implemented worldwide and for reasons of space cannot be cited here. However, this short overview evidences the numerous activities concerning green chemistry starting from the first reporting of the phrase "green chemistry" by Paul Anastas (EPA) in 1991.

To further strengthen this concept, Figure 1.1 reports the number of publications per year, over the last 15 years, reporting the concept "green chemistry" (*SciFinder*: as entered, journals, English only). The exponential growth of activity is clear; indeed, the actual number of publications is higher because, often, the concept of green

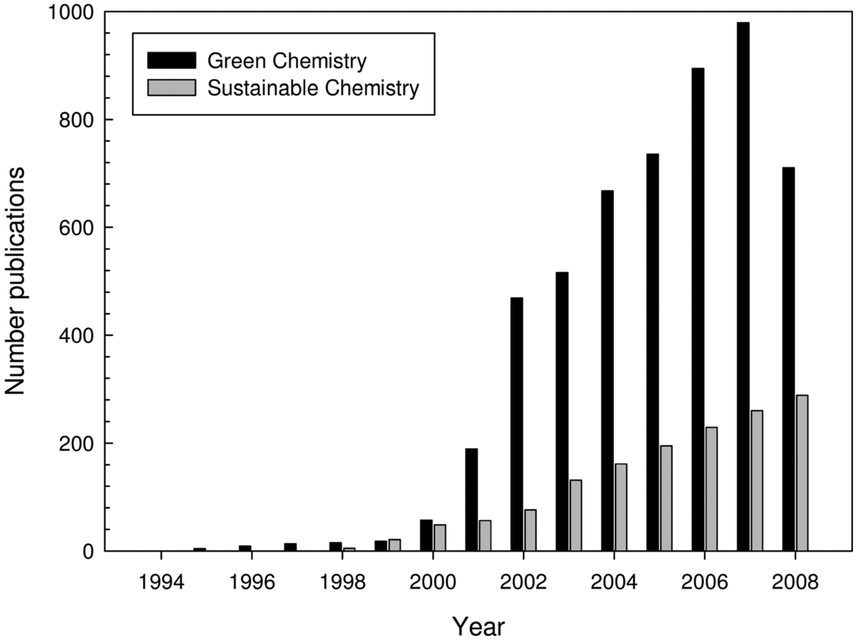


**Figure 1.1** Number of publications per year in the last 15 years reporting the concept "Green Chemistry" (*SciFinder*: as entered, journals, English only) or the concept "Sustainable Chemistry." Values for 2008 extrapolated to full year from data available in July 2008.

chemistry is indicated differently and/or is simply not reported, even if the research falls under this area.

Figure 1.1 also reports the number of publications per year using the concept "Sustainable Chemistry," which is often considered as synonymous with green chemistry.

### 1.1.1
### Green versus Sustainable Chemistry

About a decade ago, Hutzinger [3] discussed the topic of "green versus sustainable" chemistry. The controversial debate was a response to discussions within the Federation of European Chemical Societies, Division for Chemistry and the Environment, the only truly multinational (European) Environmental Chemistry Section. Hutzinger [3] argued that whilst most scientists use English as the *lingua franca* of science, cultural-sociological factors giving different meanings to terms and words should also be considered. "Green," for instance, in a cultural context simply means something different in countries such as the USA and Germany.

As pointed out before, in the USA and UK "green chemistry" has become synonymous with chemical industrial processes that avoid (toxic) by-products as much as possible: the greening of industry. The following sections analyze in more detail the principles and some examples of this green chemistry. In many countries, concepts such as "green accounts," "green procurement" and "green taxes" are accepted.

In Germany, the term "green" in many cases elicits political-sociological feelings – for instance, fear of production shutdowns in chemical industry – and general opposition to genetic engineering projects and atomic energy by members of the Green Party. There has been strong opposition to the term "green chemistry" by IUPAC, OECD, CEFIC and GDCh headed by the German speaking members. In addition, "green" was abandoned by the European Commission in the section of the fifth Framework program, likewise headed by the German speaking members.

Furthermore, the underlying meaning of the terms "green chemistry" and "sustainable chemistry" is different. Sustainable chemistry is the maintenance and continuation of an ecological-sound development, whereas green chemistry focuses on the design, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible. In Europe, apart from in the UK, the term sustainable chemistry is now preferred over green chemistry, but this practice is extending worldwide, as pointed out in Figure 1.1, which shows that the use of the term sustainable chemistry is expanding.

We could add that sustainable chemistry is not synonymous with green chemistry, for example, of a chemistry having a lower impact on environment and human health, but goes beyond the latter concepts, seeing chemistry as part of an integrated vision where chemistry, sustainability and innovation are three key components for the future of our society [4, 5].

### 1.1.2
### Sustainability through Chemistry and the $F^3$-Factory

A key driving force promoting this change from green to sustainable chemistry vision is the European Technology Platform on Sustainable Chemistry (ETP SusChem) [6] promoted by Cefic (European Chemical Industry Council) and EuropaBio (European Association for Bioindustries). To implement this vision, however, requires not only a concerted strategy of the stakeholders of the sector (objective of the cited platform), but also the progressive introduction of radical new approaches to chemical industrial production that foster innovation in chemical industry as the key factor to meeting sustainability. Two relevant concepts are:

1. down-size and integrate (chemical) production to minimize transport and storage, avoid large plants and concentration in one single location;
2. integrate processes (multi-step reactions – catalysis, reaction & separation).

Down-sizing chemical production, for example, break-down of scale economy though a modular design, is a new challenge for production of chemicals. To reach this objective, the development of many tools is necessary, ranging from microreactors and process intensification, integration of reaction-separations, to new ways to supply energy (from heat to photo, electro, microwave, etc.), new catalysis and nanotechnology, smart products (on-line microsensors), and so on. The advantages are to make production compatible with environmental sustainability (self-cleaning capacity), reduce investment (accelerate the introduction of new processes) and facilitate the introduction of cleaner production to non-chemical areas.

Realizing new processes for small-scale modular production also requires the development of new solutions for direct syntheses that avoid multistep reactions even in cascade mode.

The three main documents prepared by the European Technology Platform on Sustainable Chemistry (Vision Paper, Strategic Research Agenda, and Implementation Action Plan; they can be download free from cited ETP SusChem web site) evidence how *sustainability through chemistry* (probably a better definition than sustainable chemistry) requires a far more concerted and integrated effort than only a greener chemistry, which, nevertheless, is a core part of this vision.

These concepts are an integral part of the strategy for the future $F^3$-Factory (future, fast, flexible), the visionary idea promoted by ETP SusChem for the future of chemical production (Figure 1.2). Future sustainable $F^3$ chemicals production will combine a much broader range of production scales with interlinking technologies and logistics. An important strategy to meeting the $F^3$ challenge is process intensification. This is a strategic and interdisciplinary approach employing different tools (such as microreaction technology and modularization) to improve processes holistically. A core technology to achieving process intensification is a new design of catalysts (e.g., to develop catalysts suitable for micro-reactor technology), evidencing how advances in catalysis are strictly related to innovation and sustainability in chemical production.

Faster, more flexible and environmentally benign chemical production are the three base elements for the $F^3$-Factory visionary project. Rapid response to market

**Figure 1.2** Vision of the $F^3$-Factory (future, fast, flexible).
Source: elaborated by ETP SusChem (http://www.suschem.org).

demand, an ability to handle a diverse product portfolio and improved sustainability are the key characteristics of tomorrow's chemical production facilities. The goal is to produce chemical products and intermediates that have minimal environmental impact through the use of highly eco-efficient, scalable and adaptive process that have smaller physical and ecological footprints.

One of the major drivers for this change is fierce competition from emerging countries, where large quantity production is cheaper and potentially more flexible. New competitive business models should be thus based on novel manufacturing technologies and a holistic approach to process development, where sustainability through chemistry, safety and respect of the environment are the driver for innovation and not the elements slowing down the development, the cultural model that has often dominated the business in the past.

The synthetic processes of traditional chemical industry will be strongly affected by new opportunities offered by biotechnology and process intensification (such as micro-reaction technology). The flexible integration of inherently safe process technologies with small holding volumes will be a key to success for future products.

The $F^3$-Factory is not only a crucial step and a prerequisite for successful and competitive future processes in Europe and worldwide, but is also the basis to implementing a new sustainable industrial chemistry. A major objective will be a substantial drop in capital expenditure for new plant and/or for retrofit of high-performance intensified devices into existing infrastructure.

Achieving these objectives requires that the whole chain for production processes is revised in an holistic approach that enables new products by new processing technologies and production concepts, encompass full lifecycles to optimize the whole production chain, and minimizes the use of resources and improves eco-efficiency, and delivers demonstration plants and a technology platform for future processes.

Integrated process units and combined unit operations should be linked with advanced process modeling tools, in-line monitoring, model-based process management and advanced process control to form centers of excellence for fast process development.

Sustainability through chemistry, for example, a sustainable industrial chemistry, is thus an approach that starts from green chemistry concepts and goes on to a vision for the future sustainability of society. This is clearly a process in evolution and this book aims to contribute to this goal by presenting, on one hand, some of the concepts and tools necessary to reach this scope and, on the other hand, some examples of interesting case histories, written from researchers operating in companies, and which could be used to better understand with practical cases the opportunities and problems in developing this new sustainable industrial chemistry.

This evolution from green to sustainable chemistry parallels the change in the concept of sustainability that has occurred in the last few years. The original concept of sustainability [7] emphasized the needs to combine social objectives (health, quality of life, employment) to the management of scarce resources (energy and raw materials) and the preservation of the natural bases for life, for example, the need to adopt all actions such as cleaner processes, recycle waste, reduce pollutant emissions necessary to preserve biodiversification. The actual concept of sustainability is broader and takes into account that sustainability is also the engine for innovation. In fact, the fast modifying socio-economic and geo-strategic context requires a societal change and adaptation to put the capacity of innovation at the core of competitiveness and economics.

### 1.1.3
### Role of Catalysis

Emphasis throughout this book is given to catalysis, because it is a driver for sustainability and societal challenges [8]. Catalysis plays a critical role in promoting the feasibility, eco-efficiency and economics of over 90% of chemical processes. However, catalysis is also one of the critical enabling factors for sustainability in the specific field of chemical processes. In the mobility sector, without the introduction of catalytic converters starting from the 1960s, it was not possible to counterbalance the increasing level of emissions of pollutants such as $NO_x$, CO and hydrocarbons associated with the worldwide expansion of the car market. In particular, without the introduction of catalytic converters it was not possible to reduce the total NOx emissions below values sustainable for the society, for example, to limit issues such as smog formation, acid rain and the increase of diseases and allergies due to pollutants.

The achievement of a sustainable mobility was thus linked to the capacity to develop and consecutively further improve the catalytic converters for emissions from cars, buses and trucks. Several challenges remain in this area, particularly related to the need to find more effective catalysts for the reduction of NOx in the presence of oxygen (a very relevant problem to address the increasing share of diesel engines), better catalytic filters for particulate and catalysts more active at low temperature (to reduce cold start emissions). Catalysis was thus one of the enabling factors for a critical societal need such as mobility, and will continue to play a critical role in this area, because further R&D is needed. Regulations on $CO_2$ emissions from vehicles under discussion currently also poses new challenges for catalysis, because new requirements for catalytic converters derive from the necessary changes in engines to meet these limits.

In chemical and refinery productions, catalysts are not simply components functional to the process economy, for example, which allow improvements in yields/productivity, and reduce process costs (longer catalyst life, milder reaction conditions, reduction of separation and environmental costs). A new catalytic process is an opportunity to gain market share or to enter into new markets. New regulations (REACH in Europe, in particular), which impose the need to record the production process of the chemicals, will further change the use of catalysis from being a tool to achieve process targets to be part of the strategic vision of the companies. Not only the quality of a chemical product will be important in the future but also the quality of their production chain. It will thus no longer be possible to produce in remote areas where the environmental criteria or controls are less severe. The environmental performance indexes, from energy efficiency to greenhouse gases and pollution emission factors (and other factors which may be estimated from life cycle assessments) will be the key parameters for evaluation in a society, which should include in the production cost also the use of the limited natural resources. The actual dramatic lack of some raw materials is already a clear signal of the need for progress in this direction. The increasing concerns over greenhouse gas emissions is another signal.

The lack of energy and natural resources are two main factors that have determined a drastic change in the priorities for society and thus for chemistry in the last few years. The progressive revolution in chemical and fuel areas deriving from the socio-political pressure of new uses in biomass and in general terms of renewable resources [9] has largely changed R&D priorities. Handling biomass is far more complex than oil and converting biomass into a concentrated and easy transportable form of energy is more difficult than for the equivalent based on oil derivatives. Biomass utilization requires therefore an intense research effort. Many process steps require the development of novel catalysts and processes, starting from the need for efficient and stable solid catalysts for vegetable oil transesterification, to solid catalysts for cracking, hydrolysis or selective depolymerization of (hemi)cellulose and lignin, and to new enzymes for fermentation to products other from ethanol. The passage from first- to the second-generation biofuels requires intensified research on new catalysts.

A recent study by the US Department of Energy (DoE) [10] “Catalysis for Energy” indicated the following three priority research directions for advanced catalysis science for energy applications:

1. Advanced catalysts for the conversion of heavy fossil energy feedstocks.
2. Advanced catalysts for conversion of biologically derived feedstocks and specifically the deconstruction and catalytic conversion to fuels of lignocellulosic biomass.

3. Advanced catalysts for the photo- and electro-driven conversion of carbon dioxide and water.

Fuel cells, due to their higher efficiency in the conversion of chemical into electrical energy with respect to thermo-mechanical cycles, are another major area of R&D that has emerged in the last decade. Their effective use, however, still requires an intense effort to develop new materials and catalysts. Many relevant contributions from catalysis (increase in efficiency of the chemical to electrical energy conversion and the stability of operations, reduce costs of electrocatalysts) are necessary to make a step forward in the application of fuel cells out of niche areas. This objective also requires the development of efficient fuel cells fuelled directly with non-toxic liquid chemicals (ethanol, in particular, but also other chemicals such as ethylene glycol are possible). Together with improvement in other fuel cell components (membranes, in particular), ethanol direct fuel cells require the development of new more active and stable electrocatalysts.

Fuel cells should also be considered as an element of a broader area in which catalysis is used in combination with electrons to perform selective reactions. For example, it is possible to feed waste streams from agro-food production to an electrochemical device essentially analogous to a fuel cell to produce at the same time electrical energy and chemicals [8]. This approach is interesting in SMEs (Small Medium Enterprises) for using wastewater or by-product solutions derived from agro-food production. A limiting factor is the need to develop new nanostructured electrocatalysts, because conventional fuel cell electrodes have limited effectiveness and they are tailored for total oxidation. The challenge is to develop new electrocatalysts that do not break the C−C bond, have a high activity to make the process industrially feasible (e.g., have close to 100% Faradaic efficiency, and current densities of about 100–150 $\mathrm{mW\,cm^{-2}}$ at temperatures lower than 90 °C) and are stable in the strong basic medium required to use anion-exchange membranes. Target products are low-molecular weight oxygenates of industrial valuable interest. Recent results [11] have shown that it is possible to oxidize selectively ethanol, glycerol, 1,2- and 1,3-propanediol and ethylene glycol to the corresponding (di)carboxylic acids, hydroxy- or keto-acids, in DAFC-type cells (polymeric membrane fuel cells fed with alcohols).

Catalytic chemistry with fuel cells may be thus considered part of the general effort towards new delocalized chemical productions, because this approach is especially suited for SMEs.

### 1.1.4
### Sustainable Industrial Chemistry

The above few examples (more are discussed later in this book) show that a very rapid change in priorities, methodologies and issues has occurred in chemistry over the last few years, driven by the fast evolving socio-economical context. There is thus the need to re-consider chemistry in the light of these changes, in addition to the motivations discussed before, for example, to re-address the topic from the point of view of sustainable industrial chemistry, the aim of this book. The present book is in agreement with the philosophy of the journal *ChemSusChem*, published by Wiley-VCH Verlag (Weinheim, Germany).

Although recently, various books have been published on green catalysis [12–16], often also with focus on catalysis, we consider this further book necessary focused in particular on highlighting the new vision for sustainable industrial chemistry, but complemented by a series of industrial examples that could be used either for educational purposes or as case histories.

The present chapter introduces the basic concepts of green and sustainable chemistry and engineering as a background for subsequent chapters. An outlook for future needs is also provided with a short analysis of the key priorities identified in the cited documents of the ETP SusChem.

## 1.2
## Principles of Green Chemistry, Sustainable Chemistry and Risk

The previous section outlined briefly the historical development of the Green Chemistry Movement, which started in the early 1990s as a means of encouraging industry and academia to use chemistry for pollution prevention. More specifically, the green chemistry mission was: "To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products." Practical motivations, however, were to counteract the negative image of chemistry, deriving from several factors:

- The limited attention to impact on the environment and human health given by companies (apart few of them) during the period of fast development of industrial chemical productions (approximately the 1960–1980s).
- The progressive increase in the size of chemical plants (due to scale economy) and concentration of many plants in the same locations (due to the integration of chemical production and need of common utilities, services, etc.), which led to an amplification of local impact on environment.
- Major chemical accidents that reinforced this poor public image [17–19]. Examples are (i) the Bhopal accident in 1984, in which 3000 people were killed and more than 40 000 injured and (ii) the grounding of the Exxon Valdez [20] in the Prince William Sound in Alaska in 1989, which still affects the marine ecosystem nearly 20 years later.

Figure 1.3 reports the results of a poll made by the UK Chemical Industries Association to analyze the general public's view of the chemical industry by (MORI survey) [21, 22]. Although the survey was limited to UK, it is indicative of the general perception of the chemical industry by the public [23]. A constant decline, with a maximum of unfavorable opinions around the end of the 1980s, is evident.

The practical consequences were a rapid increase in environmental legislation, and public opposition to building new plants, and also a decline in the number of young people interested in R&D in chemistry, for example, the number of applicants

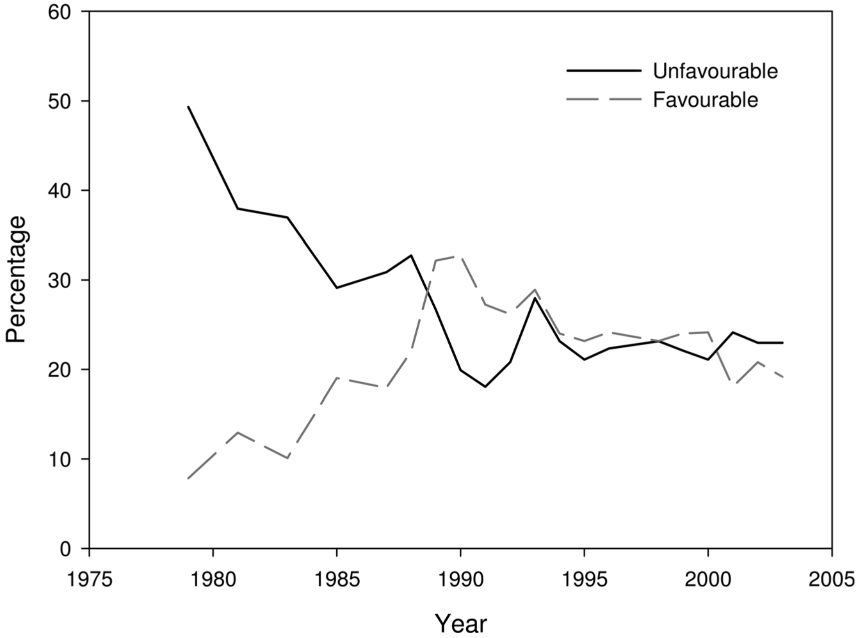


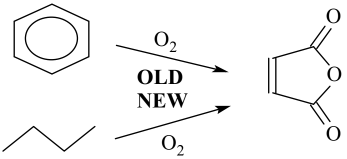
**Figure 1.3** Chemical industry favorability. Source: elaborated from Lancaster [21].

reading chemistry at university had been falling steadily for several years during the cited period. Therefore, an effective push from both academia and the chemical industry was needed to give chemistry a different image.

This was the general cultural context of the green chemistry movement, which explains both the rapid increase in interest (Figure 1.1) and the limitations of the approach. Often, the term green chemistry was adopted to indicate with a new term, apparently more attractive and ecologically-sound, the natural evolution of R&D in the field. We could cite, as an example, the industrial process for the synthesis of maleic anhydride from butane as a substitute for the old process starting from benzene. This industrial process was introduced about 15 years before the concept of green chemistry. Although the process could be read in terms of green chemistry principles (Table 1.1), the effective motivations were industrial [5]. A series of other examples of industrial motivation versus principles of green chemistry in the development of new processes have been reported by Centi and Perathoner [5].

There is, thus, often no contrast between industrial objectives and the principles of green chemistry, but the right motivations in R&D should be clearly pointed out (Table 1.2). Voluntary programs for reducing environmental impact are present in several chemical companies, even if the driving force for process selection has for long been economics. With the rising costs of technologies to reduce emissions to levels compatible with legislation limits, a change of philosophy from end-of-pipe pollutant elimination to avoid waste formation is a natural trend. However, the introduction of new processes is costly and the effective introduction of cleaner industrial processes has been limited in the last decade.

**Table 1.2** Comparison of industrial motivation and the principles of green chemistry in the industrial synthesis of maleic anhydride from *n*-butane. Source: adapted from Centi and Perathoner [5].



| Green chemistry principle | Industrial motivation |
|---|---|
| Atom economy | The loss of two carbon atoms (as starting from benzene) is avoided. Thus better yield by weight |
| Simple and safe process | Easy maleic anhydride recovery and separation, due to the reduced by-products |
| No waste | Only by-products $CO_x$ and $CH_3COOH$ (minor amount) |
| Avoid toxic chemicals or solvents | Toxicity aspects related to use of benzene were avoided |

An effective increase in the rate of introduction of new cleaner processes could derive only from a change of perspective, in which “greener technologies” are not only seen as a strategy to improve the image of chemistry but as a novel business strategy for innovation. This is the concept of sustainable industrial chemistry versus green chemistry. It uses green chemistry concepts and integrates them into a larger vision to create an effective strategy for sustainability though chemistry. Green and sustainable chemistry are thus not synonymous, as indicated in the cited books [12–16], but instead green chemistry is the core around which a new strategy for chemistry should be built up.

In addition, we may observe that the principles for green chemistry (see later) are of general validity, but their implementation was often questionable and/or with limited impact. We note, for example, that no relationship could be seen between the growing of publications on “green chemistry” (Figure 1.1.) and public perception of importance of chemistry (Figure 1.3). This is more evidence as to why a further step is necessary, for example, to pass from green to sustainable industrial chemistry.

In conjunction with the American Chemical Society, the EPA has developed a set of 12 guiding principles for green chemistry [24]. These principles can be summarized as being concerned with ensuring that:

- the maximum amounts of reagents are converted into useful products (atom economy);
- production of waste is minimized through reaction design;
- non-hazardous raw materials and products are used and produced wherever possible;
- processes are designed to be inherently safe;
- greater consideration is given to use of renewable feedstocks;
- processes are designed to be energy efficient.

**Table 1.3** Principles of green chemistry [24, 25].

| | |
|---|---|
| 1 | Waste prevention is better than treatment or clean-up |
| 2 | Chemical synthesis should maximize the incorporation of all starting materials |
| 3 | Chemical synthesis ideally should use and generate non-hazardous substances |
| 4 | Chemical products should be designed to be nontoxic |
| 5 | Catalysts are superior to reagents |
| 6 | The use of auxiliaries should be minimized |
| 7 | Energy demands in chemical syntheses should be minimized |
| 8 | Raw materials increasingly should be renewable |
| 9 | Derivations should be minimized |
| 10 | Chemical products should break down into innocuous products |
| 11 | Chemical processes require better control |
| 12 | Substances should have minimum potential for accidents |

Table 1.3 lists all twelve principles. The underlying objective of these principles is that green chemistry encompasses much more of the concepts of sustainability than simply preventing pollution. However, a more detailed reading evidences that these principles focus mainly on the reaction (especially on organic syntheses) rather than on the industrial processes, even if relevance is given to the design for energy efficiency and the use of renewable feedstocks.

The concept of green chemistry is defined as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products” [24, 25].

### 1.2.1
### Sustainable Risk: Reflections Arising from the Bhopal Accident

The focus of green chemistry on the reaction more than on the process and its industrial feasibility, even considering the attention given to aspects such as green chemistry and engineering [16], indicates that aspects related to the safety of a chemical or manufacturing process, measured in terms of risk, are not given enough consideration. In its simplest form risk can be expressed as:

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

To date, legislation has sought to minimize risk by limiting exposure to chemicals, that is, controlling use, handling, treatment and disposal. Green chemistry seeks to improve safety by minimizing hazard and so shifts the risk from circumstantial to intrinsic factors. Methods of providing this inherent safety in chemical processes are the generation of hazardous intermediates *in situ*, avoiding storage of large quantities of chemicals on site and avoiding the use of dangerous chemicals altogether.

The example of the well-known Bhopal accident (in 1984) is instructive and is a good lesson [26–28]. Bhopal is located in North Central India. It is a very old town in a picturesque lakeside setting and was a tourist center. It is the capital of Madhya Pradesh and industry was encouraged to go there as part of a policy of bringing industry to less developed states. The annual rent was $40 per acre and thus Union Carbide took the decision in 1970 to build a plant to produce the pesticide SEVIN, a DDT substitute (brand name for Carbaryl-1 – naphthyl methylcarbamate). The initiative was greatly welcomed and was cited at that time as part of India's Green Revolution.

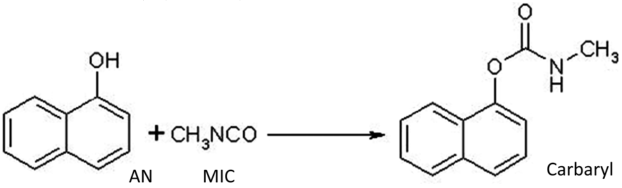
SEVIN was manufactured from carbon monoxide (CO), monomethylamine (MMA), chlorine ($Cl_2$), alpha-naphthol (AN) – the first two imported by truck and the latter two made on site. The process route was as follows:

$$CO + Cl_2 \rightarrow COCl_2(\text{Phosgene}) \tag{1.1}$$

$$COCl_2 + MMA \rightarrow MMC + MIC \tag{1.2}$$

MIC is stored in three $\sim 50\,m^3$ tanks.

$MIC + AN \rightarrow \text{Carbaryl}(\text{SEVIN})$:



(1.3)

Figure 1.4 shows a simplified flow chart of the process. An intermediate in the processes is methyl isocyanate (MIC), which was stored in a series of tanks partially underground and equipped with cooling systems and a series of safety control devices (Figure 1.5). In fact, MIC is a highly toxic (maximum exposure: TLV-TWA, during an 8-hour period is 20 parts per billion), flammable gas that has a boiling point near to ambient temperature and gives a runaway reaction with water unless chilled below 11 °C. Table 1.4 gives the list of MIC safeguards.

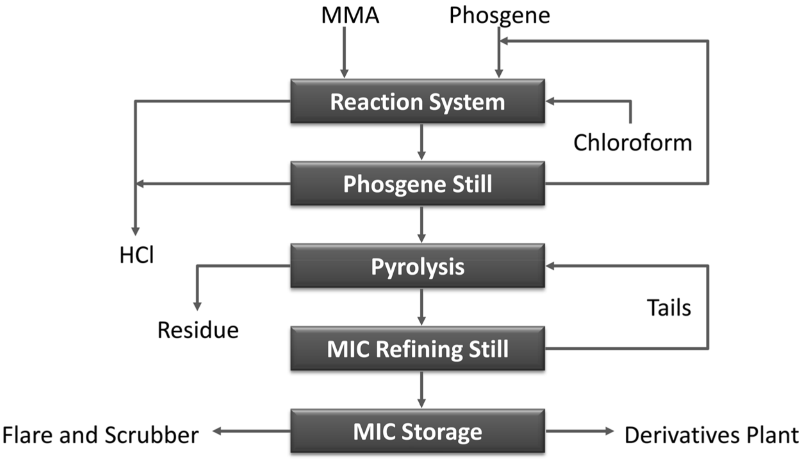


**Figure 1.4** Simplified flow chart of the Bhopal Union Carbide process.

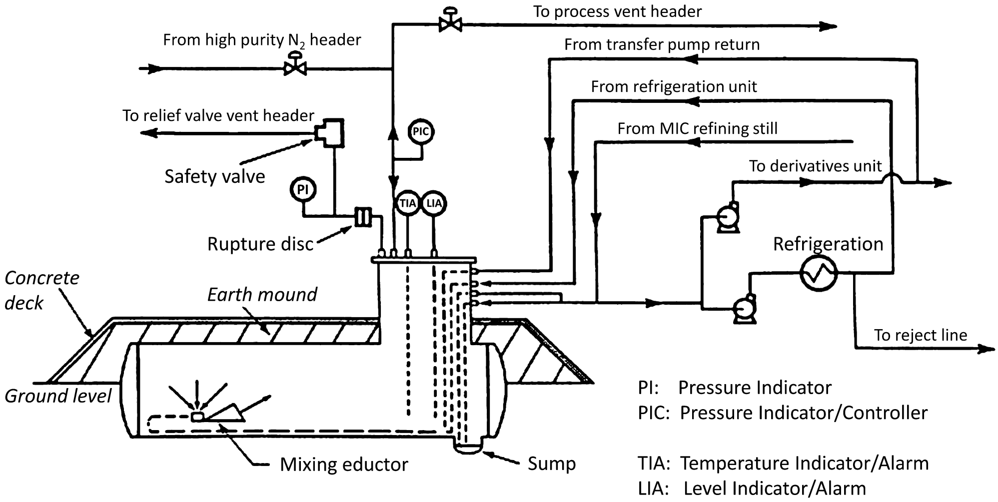


**Figure 1.5** Methyl isocyanate (MIC storage) tank used in the Bhopal Union Carbide process. Source: adapted from Reference [31].

Safeguards may be equipment items or procedures designed to prevent the initiating event, limit or terminate the propagation, or mitigate the outcome. In fact, accidents are normally characterized by a sequence of events leading from the initiating event, propagation of the accident and realization of the undesired outcome.

Active safeguards are those that require human procedures or mechanical initiation to operate (e.g., work permit procedures, scrubber caustic circulation). Passive safeguards are those that do not require any initiation (e.g., concrete fire-proofing, elevated vent stack for dispersion).

Both active and passive safeguards can be defeated through inadequate safety management systems. A safety management system is the most efficient way to

**Table 1.4** Safeguard devices for the methyl isocyanate (MIC) tank employed in the Bhopal Union Carbide process.

| Safeguards | Type |
|---|---|
| Mounded/insulated MIC Tanks | Passive |
| Refrigeration below reaction initiation temperature | Active |
| Refrigeration uses non-aqueous refrigerant (Freon) | Active |
| Corrosion protection (cathodic) to prevent water ingress | Active |
| Rigorous water isolation procedures (slip blinds) | Active |
| Nitrogen padding gas used for MIC transfer not pumped | Active |
| Relief valve and rupture disk | Passive |
| Vent gas scrubber with continuous caustic circulation | Active |
| Elevated flare | Active + Passive |
| Water curtain around MIC Tanks | Active |

allocate resources for safety, since it not only improves working conditions but also positively influences employees' attitudes and behavior with regards safety, consequently improving the safety climate [29]. The Bhopal accident was crucial for widespread adoption of more rigorous process safety procedures and management systems [30]. Process safety is a comprehensive, systematic approach encompassing the proactive identification, evaluation and mitigation or prevention of chemical releases that could occur as a result of failures in process, procedures or equipment.

We may note in Table 1.4 that the vent gas scrubber was an active safeguard, while a passive type (as well as a change from active to passive of the other safeguards) would probably have avoided the accident, as discussed later.

In December 1984 water leaked into a storage tank and reacted to cause an increase in pressure that subsequently blew the tank. Around 41 tonnes of methyl isocyanate was released into the atmosphere and rained back down on the local population. It killed 3800 people instantly and several thousand others through long-term exposure effects. Several hundred thousand people have suffered permanent disabilities.

To understand the motivations of this accident, within the frame of the general context of green/sustainable chemistry, it is necessary to clarify first the industrial context of the accident, and in particular the plant problems that are the effective precursors to disaster. The first observation is that the alpha-naphthol plant was shut down and thus SEVIN production was no longer profitable, and the plant run intermittently. This situation determined a series of critical issues:

- minimum maintenance,
- safety procedures simplified for small jobs,
- refrigeration unit shut down and Freon sold,
- scrubber circulation stopped,
- manning cut to 600 and morale low,
- slip blinding no longer mandatory during washing,
- high temperature alarm shut-off as $T$ now >11 °C,
- relief valve and process vent headers joined (for maintenance),
- emergency flare line corroded, disconnected.

The chemistry causing the accident is well established. Forty-one tonnes of MIC in storage reacted with 500 to 900 kg water plus contaminants. The resultant exothermic reaction between MIC and water caused an increase of temperature that reached 200–250 °C. As a consequence, the tank pressure rose to 200 + psig (14 + bar); the tank was designed for 70 psig (4 bar). The MIC tank thus overheated was over-pressured and vented through the scrubber, which was out of operation. This caused an elevated discharge of a massive quantity of MIC (approximately 25 tonnes). The source of water was clearly the determining element for the accident. The following observations could be made:

- filters were flushed using high-pressure water;
- drain line from filter was blocked, operator observed no flow to drain;

- flushing continued despite blockage;
- high pressure could cause valve leak; this forced water into the relief header.

Figure 1.6 shows the probable route of entrance of water into tank number 610 containing the MIC. The admission of water to the MIC tank was thus caused by a series of concomitant events:

- relief valve (RV) and process vent headers were joined by a jumper pipe, no blinds;
- MIC tank was not pressurized;
- head of water sufficient for flow;
- slow initial reaction between MIC and $H_2O$ allowed enough water to enter into the tank.

Notably, no universally accepted cause exists [31], and sabotage, for example, whereby somebody deliberately connected a water hose to piping that directly entered into the storage tank, is still supported by some authors. However, this theory would require (i) an intimate knowledge of piping around the tank, where to physically make the correct connection, (ii) removal of a pressure indicator and then (iii) the re-attachment of piping fittings. This theory is thus unlikely.

When water started to react with MIC, no control of the temperature/pressure started, because it was late at night and the operational staff was reduced to a minimum, and the MIC tank's alarms had not worked for 4 years. The gas leakage followed, for the first 30 min, approximately the inverse route of water entrance (Figure 1.6), except that which reached the atmosphere through the vent collection system (VCS). However, the flare tower and the vent gas scrubber (Figure 1.7) had been out of service for 5 months before the disaster. After the first 30 min, the rupture disk bursts and this increased the rate of release of MIC.

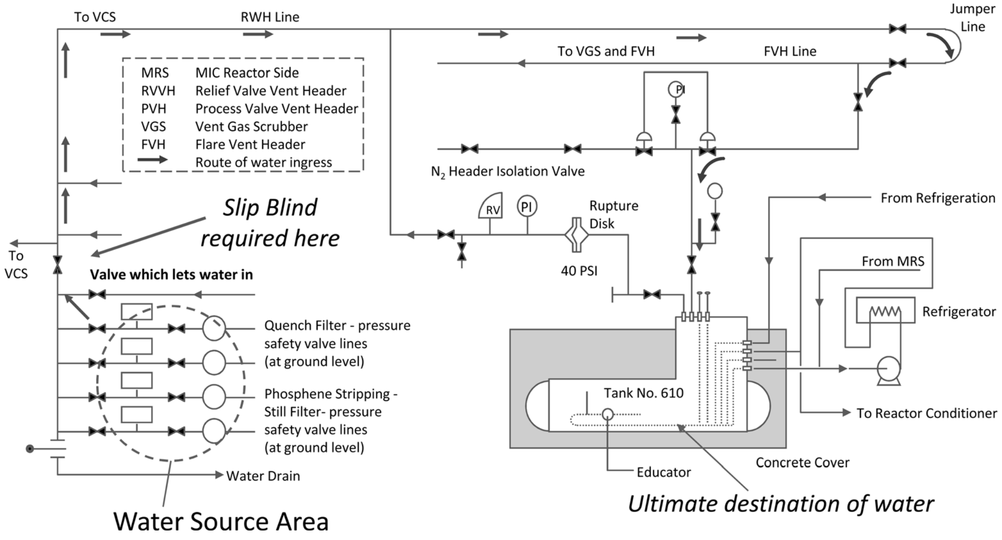


**Figure 1.6** Probable route of entrance of water into the MIC tank in the Bhopal Union Carbide process.

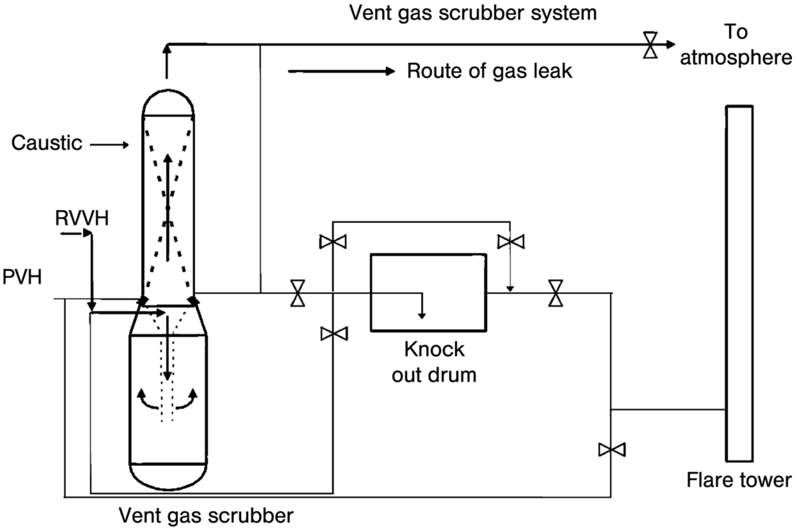


**Figure 1.7** Schematic diagram of the emergency relief effluent treatment system that includes a scrubber and flare tower in series in the Bhopal Union Carbide process.

Owing to a poor design, the maximum pressure that could be handled by the NaOH scrubber was only one-quarter of that developed after the first 30 min, and thus, even if working, the scrubber was not effective in preventing the accident [32]. Finally, a further cause of the release was that the refrigeration system, designed to inhibit the volatilization of MIC, had been left idle – the MIC was kept at 20 °C, not the 4.5 °C advised by the manual, to reduce energy costs, and to allow the use of the coolant elsewhere.

Other causes that contributed to the accident include (i) lack of slip-blind plates that would have prevented water from pipes entering into the MIC tanks via faulty valves, and (ii) use of carbon-steel valves, despite the fact that they corrode when exposed to acid (the leaking carbon-steel valve that allowed water to enter the MIC tanks was not earlier repaired as this was too expensive).

However, neither of above is a root cause. The root causes were management decisions:

- to neglect to repair the flare system;
- to place a scrubber system on stand-by to save on operating expenses;
- to remove coolant from the refrigeration system used to cool the MIC storage tank.

Additional root causes made the accident more severe:

- inadequate emergency planning and community awareness;
- lack of awareness of the potential impact of MIC on the community by the people operating the plant;
- lack of communication with community officials before and during the accident;

- inadequate community planning, allowing a large population to live near a hazardous manufacturing plant. This situation was not unusual in the chemical industry in the early 1980s, and one major impact of Bhopal was to warn all chemical plants about the importance of these considerations in the siting and operation of facilities.

It may be also noted that (i) between 1981 and 1984 six accidents with phosgene or MIC occurred, (ii) a 1982 audit was critical of the MIC tank and instrumentation and (iii) in 1984 a warning of a potential runaway reaction hazard was given. Therefore, clues to this accident were available before it happened.

The roots of this accident extend even further back. Optimistic market-size expectations led to an oversized plant – and therefore MIC storage capacity oversized by a factor of three. Failure of state and local government to control the shantytown growth near the plant meant a considerably larger impacted population was unable to take shelter.

### 1.2.2
### Risk Assessment and Sustainable versus Green Chemistry

The above paragraph shows that the reasons and dimensions of the accident at Bhopal are connected to many factors, but principally to a lack of management responsibility in plant management and procedures of maintenance of partially decommissioned plants, which were oversized due to poor market-size projections, and to a lack of control by the authorities.

Sheldon, in an editorial on the first year of activity of the journal *Green Chemistry* [33], citing a conference of Guy Ourisson (President of the French Academy of Science), invoked the terms black chemistry and red chemistry to describe two shortcomings of many traditional processes:

“Black chemistry stands for waste = pollution and conjures up images of the industrial revolution, black smoking chimneys and Blake’s *dark satanic mills*. Red chemistry, on the other hand, denotes danger and evokes associations with incidents such as Bhopal and Seveso. Many chemical processes in use today are black or red, or both. Hence, the goal of the chemical industry is, or should be, the replacement of red and/or black chemistry with green alternatives.”

The example of the Bhopal accident shows that instead it is not a problem of bad versus good (green) chemistry but of correct design and management of risky processes. When the risk (intended in its larger meaning, which includes risk for environment, health and process safety) is less than the benefits (for society, which includes economic access to goods produced directly by the process or though further consecutive steps), the risk is acceptable, even if it is better to further minimize it. A sustainable risk, which implies the accounting for sustainability and the use of tools such as life-cycle assessment (LCA) for a correct analysis of the risk, which will be discussed later, is what differentiates the concept of sustainable industrial chemistry from green chemistry.

Minimizing risk means reducing both the magnitude of the possible event and its frequency, by proper design of both the engineering and chemistry of the process, but which could be only effective by proper risk assessment. For example, as shown later, there is the possibility of substituting phosgene with other chemicals, which are less toxic or risky. This solution was discussed in several papers and indicated as the necessary route for a green chemistry [34–45].

However, the minimization of the risk, both in terms of environment and process safety, could be equally reached by adopting an on-demand synthesis of phosgene and MIC [46]. This is the approach preferred industrially and evidences that the same goal could be reached by a different philosophy, other than the substitution of chemicals indicated by green chemistry principles.

### 1.2.3

### Inherently Safer Process Design

In general, there are two approaches to design safety into a chemical process – either handling the hazards with engineering and management controls or eliminating them altogether [47]. If a process hazard cannot be eliminated, it may still be possible to reduce its potential impact sufficiently as far it is not capable of causing major injury or damage. Whenever feasible, it is desirable to eliminate or minimize process hazards. Engineering and management controls have been effective in reducing risk to very low levels in the chemical process industries, as demonstrated by the industries' excellent safety record. However, no engineering or management system can ever be perfect, and the failure of these systems can result in major accidents. Moreover, the original installation and ongoing operations and maintenance of these safety and risk-management systems is often expensive. If the manufacturing technology can be changed to eliminate the hazards, the result will be a safer and a more cost-effective plant design.

We refer to a process that eliminates or minimizes hazards as "inherently safer," because the safety basis of the design is inherent in the process chemistry and operations, rather than coming from added safety equipment and procedures. The process designer is challenged to change the process to eliminate hazards, rather than to develop add-on barriers to protect people, the environment, and property. This is best accomplished early in the product and process design cycle, but it is never too late to apply these concepts. This concept is discussed more in detail in the next section.

There are four major strategies for inherently safer process design [48–50]:

1. Minimize the size of process equipment.
2. Substitute a less-hazardous substance or process step.
3. Moderate storage or processing conditions.
4. Simplify process and plant design.

As mentioned before, scaling-down chemical processes and making them modular is an essential element for a new vision of sustainable industrial chemistry.

This is also fully in line with the concept of process intensification (see below) and the strategy of minimizing the size of process equipment for a inherently safer process design.

Reducing the size of chemical process industry (CPI) equipment generally improves safety by reducing both the quantity of hazardous material that can be released in case of loss of containment and the potential energy contained in the equipment. This energy may derive from high temperature, high pressure or heat of reaction.

There are many opportunities to minimize the inventory of hazardous materials in a CPI plant without fundamental changes in process technology. Following the accident in Bhopal, India, in 1984, most CPI firms reviewed their operations to identify opportunities to reduce quantities of toxic and flammable materials on-hand. These companies did not rebuild their plants using a different technology, or make dramatic changes to the process equipment, as both solutions were too costly. Instead, they carefully evaluated existing equipment and operations, and identified changes that would allow them to run with a reduced inventory of hazardous materials. Some of the possibilities are:

- **Storage**: The need for storing large quantities of raw materials and intermediates was often simply adopted to make “easier” the operations of a plant, for example, more flexibility in ordering raw materials, secure from fluctuations and transportation delays. However, when the associated risks are fully considered, it is often worth significantly reducing the quantities on-hand and devoting additional resources to ensure a reliable supply. Modern inventory-control systems, improved communications with raw materials suppliers and transport companies, and strategic alliances with raw materials manufacturers also allow plants to function with a smaller stock of hazardous substances. Often, large storage tanks for hazardous in-process intermediates are used. This storage decouples sections of a plant from each other. Parts can continue to run, either filling or emptying these tanks, while a unit at the facility is shut down for maintenance or operating problems. However, by reducing plant shutdowns it is possible to greatly reduce or eliminate such storage.

- **Piping**: When designing piping for hazardous materials, one should minimize the “inventory” (holdup) in the system. Piping should be large enough to transport the quantity of material required, but not greater. The quantity in pipes can be also minimized by using the material as a gas rather than a liquid. The Dow Chemical Exposure Index [51] is a tool to measure inherent safety with regards to potential toxic exposure risks. For example, the risk related to a pipe carrying liquid chlorine from a storage area to a manufacturing building, where chlorine should be vaporized and fed to a process, could be reduced by installing the vaporizer in the storage area. This reduces the inventory of chlorine in the pipe by a factor of over ten.

- **Process intensification** means using significantly smaller equipment. Examples include novel reactors, intense mixing devices, heat- and mass-transfer designs that provide high surface-area per unit of volume, equipment that performs one or more unit operations, and alternative ways of delivering energy to processing equipment – for example, via ultrasound, microwaves, laser beams or simple electromagnetic radiation. These technologies can increase the rate of physical and chemical processes, allowing high productivity from a small volume of material. A small, highly efficient plant can be expected to be cheaper and more cost-effective, but also can reduce the magnitude of potential accidents. If the plant is small enough, the maximum possible accident may not pose any significant hazard. This will reduce the safety equipment, emergency alarms and interlocks, and other layers of protection required to manage the risk. Installation and ongoing operation of this safety equipment is often a major expense; if it can be eliminated, there will be additional cost savings. Safety needs not necessarily mean spending money. Safer can also be cheaper, if a small, efficient inherently safer process can be developed.

- **On-demand (on-site) synthesis**: The use of novel equipment/technologies for process intensification avoids the storage/transport of hazardous chemicals. They could be generated on-site and immediately converted into final product. In the Bhopal process, the introduction of on-demand synthesis of methyl isocyanate (MIC) has reduced the total inventory of less than 10 kg of MIC, for example, which is 0.024% of the amount released during the accident [48, 49]. Phosgene, the other hazardous chemical present in the Bhopal process, could be also produced on-demand. A continuous tubular reactor has been developed to make this chemical on-demand available for immediate consumption by batch processing vessels [52]. One plant using the new design contains 70 kg of gaseous phosgene, compared to an inventory of 25 000 kg of the liquid in equipment and storage in the old facility. As the new unit is quite small it is also possible to provide secondary containment for the phosgene, further enhancing the process safety [53].

### 1.2.4
### On-Demand Synthesis and Process Minimization

Novel developments in micro-reactor technology offer new possibilities to combine process intensification, safer operations and on-demand production. For example, in the phosgene on-demand synthesis it is possible to use a silicon micropacked-bed reactor to achieve complete conversion of chlorine for both a 2:1 $CO:Cl_2$ feed at $4.5\,cm^3\,min^{-1}$ and a 1:1 feed at $8\,cm^3\,min^{-1}$ [54]. The latter gives a projected productivity of approximately $100\,kg\,yr^{-1}$ from a ten-channel microreactor, with the opportunity to produce significant quantities by operating many reactors in parallel. The increased heat and mass transfer inherent at the submillimeter reactor length scale provides a larger degree of safety, control and suppression of gradients with respect to those present in macro-scale systems.

Phosgene is widely used as a chemical intermediate for the production of isocyanates used in polyurethane foams and in the synthesis of pharmaceuticals and pesticides [55]. Processes using phosgene require specialized cylinder storage, environmental enclosures, pipelines, fixtures under negative pressure and significant preventative maintenance. Moreover, phosgene is under various transportation restrictions. As a consequence, most phosgene is consumed at the point of production today. Micro-chemical systems stand to provide an opportunity for flexible point-of-use manufacturing of chemicals such as phosgene. Banks of reactors can be turned on or off as needed to maintain close to zero the storage. Single reactor failures would lead to extremely small chemical release.

The cited micro-fabricated silicon packed-bed reactor for phosgene on-demand production (Figure 1.8) was made out of single crystal silicon with standard micro-fabrication processes developed for integrated circuits and MEMS. The geometry is defined using photolithography and created with silicon etching. The reactor consists of a 20 mm long, 625 mm wide, 300 mm deep reaction channel (3.75 mL volume) capped by Pyrex. Figure 1.8b shows a scanning electron micrograph (SEM) of the inlet where the flow is split among several interleaved channels (25 mm wide) that meet at the entrance of the reaction channel. Perpendicular to the inlet channels are 400-mm wide loading channels used to deliver catalyst particles to the reactor. Catalyst is loaded by placing a vacuum at the exit of the reactor and drawing in particles through the loading channels. At the outlet of the reaction chamber, a series of posts with 25 mm gaps acts as a filter to retain the catalyst bed (Figure 1.8c).

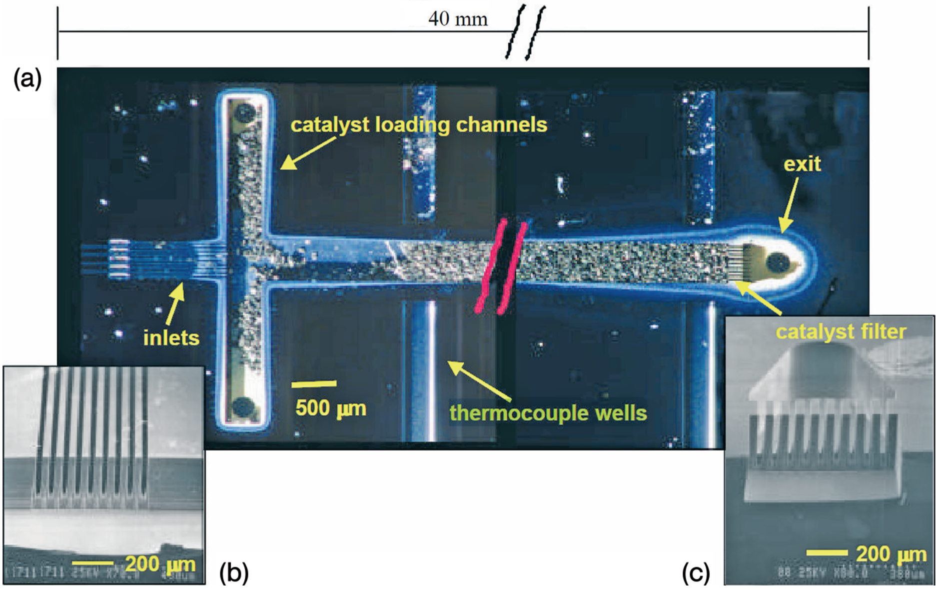


**Figure 1.8** Microfabricated silicon packed-bed reactor for phosgene on-demand production. (a) Top-view of reactor partially loaded with 60-mm activated carbon particles – the reactor channel is 20 mm long, and the image is spliced to fit the 20 mm reaction channel by omitting the long channel midsection; (b) SEM of the 25 mm wide interleaved inlets; (c) SEM of the catalyst filter structure. Source: adapted from [53].

There are also four 325-mm wide channels perpendicular to the reaction channel along its length for holding thermocouples. Access ports for flow come from underneath at the inlet (not shown in Figure 1.8), the reactor exit and at the ends of the catalyst loading channels.

There has been great interest recently in micro-reactor technology (as discussed also later in this book) as a new efficient tool for process intensification and risk reduction [56–58]. They will be one of the key tools for decentralized chemical production. Actual chemical production is still at the stage where the large, centralized production facility dominates. Although not for all processes, we believe that this will change, and that small, dedicated plants producing on-demand specific materials at the site where the material is needed will be an important component of the future chemical production industry (CPI). Changes in this direction in other industries have been largely driven by the need for flexibility and convenience, along with the development of economically competitive, small, distributed systems.

The CPI has an additional factor that will drive the change to small, distributed facilities – the greatly reduced inventory of hazardous materials of an inherently safer, small plant. These plants will be highly automated and largely unstaffed, and use commonly available and relatively nonhazardous raw materials. They will contain small quantities of hazardous material and energy, and will not be capable of causing a major incident. The *scale economy* leading to large, centralized plants should be substituted with the *smart economy* of building small, cheap plants that can be set down where they are needed, used and then taken away or recycled. In addition, this modular design would greatly reduce the costs in developing new process (increasing the production would only need an increase in the number of reaction/separation modules) and will significantly boost the introduction of new processes/technologies (reduced cost of investment). This future vision of the CPI has, for example, been described in articles by Benson and Ponton [59], Ponton [60], Hendershot [47] and also us as well [5]. However, the increasing energy and raw materials costs, global competiveness, and social pressure on safety and environment protection, has forced chemical companies to re-consider their strategy of development. For this reason, this concept of modular-design and small/distributed production is now a key part of the vision for the future of chemical industry indicated in the documents prepared by the European Technology Platform of Sustainable Chemistry [6], which derives from a joint effort of the main chemical companies in Europe and the scientific community.

Long term, it will even be possible to manufacture many hazardous materials in plants as small as a silicon chip, using large numbers of “plants on a chip” in parallel to produce the quantity of material required [61, 62]. It is unlikely that the large, world-scale petrochemical plant will ever completely disappear. However, distributed manufacture of chemicals in small plants will become an important part of the industry, in particular for the improved safety through distributed manufacturing of hazardous chemicals. There are many relevant examples besides those cited previously of phosgene and methyl isocyanate synthesis, for example HCN [63] and aqueous peracetic acid [64] on-demand syntheses.

### 1.2.5
### Replacement of Hazardous Chemicals and Risk Reduction

The replacement of hazardous chemicals with benign and inherently safer alternatives indicated by green chemistry principles is certainly a valuable measure, because a hazardous chemical that is no longer present can no longer be involved in an accident. However, from industrial point of view there are often alternative solution that reduce the risk to a sustainable level at a much lower cost than that required by completely changing the production.

The problem of cost is a key element for an effective introduction of cleaner and safer technologies. Green chemistry approaches [12, 13, 24, 25, 65, 66] often stress the need for replacement of a hazardous ingredient in chemical synthesis or process, with respect to alternatives such as on-site/on-demand production of high-risk compounds, and reduced reliance on those hazardous chemicals that cannot be replaced. However, a sustainable industrial technology, for example, which reaches the optimum in the triangle of process economy, safety of operation and environment protection, is preferable to a "greener" technology that may have a lower impact on the environment or better intrinsically safer operations, but which will be not implemented due to too higher costs in a global economy.

Sustainability is step-by-step progressive development with a moving frontier. It is necessary to consider and teach this concept; a realistic approach will lead to a faster implementation of better industrial technologies, with an effective reduction of risks and waste, and improved use of resources. Owing to the large cost of investment, substitution of chemicals is often not cost-effective with respect to alternative engineering solutions, even if it should be discussed case-by-case. There are, however, often discrepancies between the emphasis given in scientific research to the issue of substituting hazard chemicals and industrial solutions to reduce risk to a sustainable level. We can further discuss this issue by returning to the problem of the Bhopal synthesis of SEVIN.

After the Bhopal accident, new regulations were introduced in almost all countries to limit the amount of methyl isocyanate (MIC) that may be stored in a plant. The EU allows a maximum of half a tonne storage on site – around 67 tonnes were stored at the Bhopal facility. The use of MIC could be avoided by changing the order of synthesis, as illustrated in the alternative route reported in Figure 1.9 [67].

Avoiding the use of MIC removes a significant amount of the hazard associated with the process and as a result gives an inherently safer process. However, the alternative process still uses phosgene, which is extremely toxic. A process that avoids phosgene would provide further intrinsic safety.

### 1.2.6
### Replacement of Hazardous Chemicals: the Case of DMC

Dimethyl carbonate (DMC) is a versatile compound that is an attractive alternative to phosgene [68, 69] and which could be synthesized in a eco-friendly process by catalytic oxidative carbonylation of methanol with oxygen (Enichem, Italy [70] and

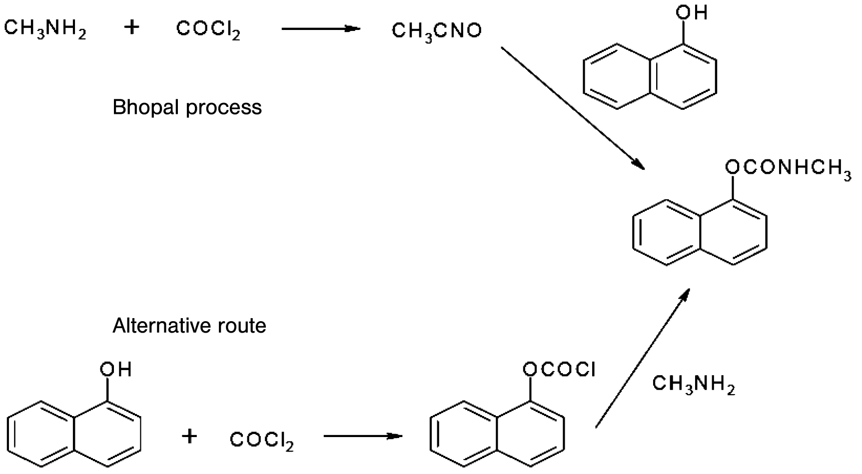


**Figure 1.9** Bhopal and alternative routes to *N*-methyl 2-naphthyl carbamate [67].

UBE, Japan [71] processes). DMC can act as a substitute for phosgene and toxic methylating agents like dimethyl sulfate and methyl chloride, and can also find use as a safe solvent and as a possible emission-reducing, high-oxygen-containing additive for fuels [69, 72]. The topic of phosgene substitution is of high relevance because its high reactivity has been known since the beginning of the chemical industry. However, owing to the high reactivity and toxicity its utilization is increasingly burdened by growing safety measures to be adopted during the production, transportation, storage and use and by growing waste disposal costs to be faced. The reasons for phosgene substitution stem not only from considerations relating to its high toxicity, but also to the fact that its production and use involves chlorine as a raw material and results in the generation of large amounts of halogenated by-products. The formation of HCl and chlorine salts as by-products gives rise to contaminated aqueous streams that are difficult to dispose of, or the credited value of the by-produced HCl may render uneconomical its recovery, purification and re-use. Moreover, reactions involving phosgene often require the use of halogenated solvents, like $CH_2Cl_2$ and chloro- or *o*-dichlorobenzene, which are likely to raise environmental problems.

Phosgene ranks highly among the industrially produced chemicals. Although its production output is most exclusively captive and, therefore, only approximate production statistics are available, a yearly worldwide production of about 5–6 t $yr^{-1}$ can be estimated. The main uses of phosgene are in the production of isocyanates and polycarbonates. The production of isocyanates represents the major output. Of exceeding importance is the production of di- and polyisocyanates, both as commodities, like TDI (toluene diisocyanate) and MDI (diphenylethane diisocyanate), and as specialties, like the aliphatic isocyanates (HDI – 1,6-hexane diisocyanate, IPDI – isophorone diisocyanate and HMDI – dicyclohexane diisocyanate), for the production of polyurethanes. Monofunctional isocyanates like methyl isocyanate, cyclohexyl isocyanate and aryl or phenyl isocyanate are used in lower amounts for agrochemicals and pharmaceutical products.

The production of polycarbonates, mostly the aromatic polycarbonates derived from bisphenol A, is the second largest area of phosgene usage and is probably the most important growing area. It accounts for about $1.5\,\mathrm{t\,yr^{-1}}$ of polycarbonates, corresponding to a yearly phosgene consumption over $0.6\,\mathrm{t\,y^{-1}}$.

DMC is classified as a non-toxic and environmentally compatible chemical [69]. In addition, the photochemical ozone creation potential of DMC is the lowest among common VOCs (2.5; ethylene = 100). The areas in which DMC acts, or can act, as a potential phosgene substitute correspond to the main areas of phosgene industrial exploitation, that is, production of aromatic polycarbonates and isocyanates, leading the production of these important chemicals out of the chlorine cycle.

The traditional production of DMC involves phosgene:

$$COCl_2 + 2CH_3OH \rightarrow (CH_3O)_2CO + 2HCl \tag{1.4}$$

Therefore, any possible use of DMC as substitute of phosgene should be based on a different synthesis of DMC, not involving phosgene. Non-phosgene alternative routes for DMC production, basically, have relied on the reaction of methanol with carbon monoxide (oxidative carbonylation) or with carbon dioxide (direct carboxylation with $CO_2$, or indirect carboxylation, using urea or alkylene carbonates as $CO_2$ carriers) (Figure 1.10) [72].

Oxidative carbonylation of methanol to DMC, which takes place in the presence of suitable catalysts, has been developed industrially by EniChem (later Polimeri Europa). Carbonylation/transesterification of ethylene oxide to DMC via ethylene carbonate is also an attractive route. However, this route is burdened by the complexity of the two-step process, the co-production of ethylene glycol (even if it

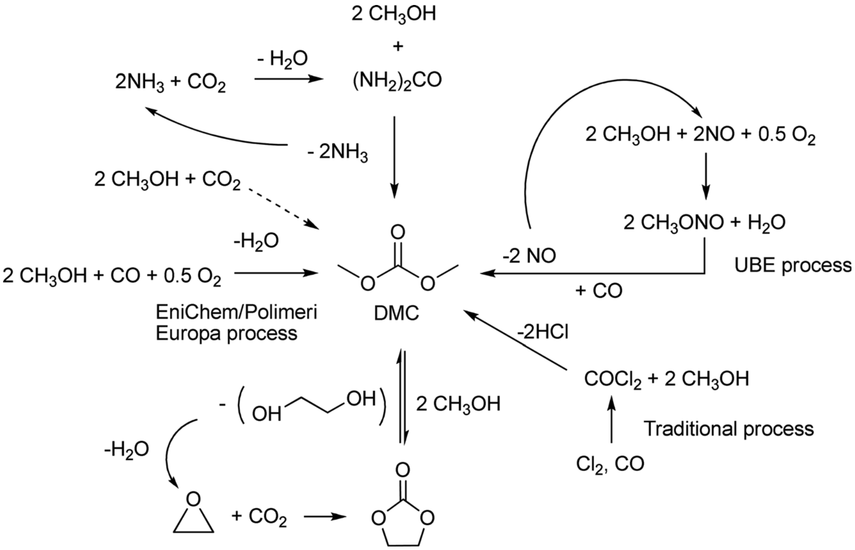


Figure 1.10 DMC synthesis routes.

could be recycled) and the use of toxic and risky ethylene oxide, which is presented as carbon-friendly because it allows the use of $CO_2$ instead of CO.

The UBE process was also developed on a commercial scale, in Japan, and uses methyl nitrite as intermediate for the gas-phase palladium-catalyzed ($PdCl_2/CuCl_2$ on active carbon) carbonylation to DMC.

Copper compounds, besides being the most widely used co-catalysts for palladium re-oxidation, are themselves active in DMC formation. Exploiting the catalytic properties of CuCl, EniChem developed its DMC production process of one-step oxy-carbonylation of methanol. This process has operated industrially since 1983. The single step is carried out in the liquid phase in a continuous reactor fed with $CH_3OH$, CO and $O_2$. Reaction conditions are in the range of 120–140 °C and 2–4 MPa. The $CO:O_2$ ratio is kept outside the explosion limits by the use of a large excess of CO and the adopted high oxygen conversion per pass. As depicted in Figure 1.11, the reactor-evaporator concept is adopted: the catalyst is kept inside the reactor, where the products are vaporized, mainly taking advantage of the heat of reaction ($\Delta H_r = -74\ \mathrm{kcal\,mol^{-1}}$), and removed from the reaction system together with the excess gas leaving the reactor [73]. This design allows the use of high catalyst concentrations and simplifies catalyst separation from the products. Quite high DMC productivity (up to $250\ \mathrm{g\,L^{-1}\,h^{-1}}$) is achieved under optimized reaction conditions.

The use of CuCl as a catalyst affords minimization of by-products, high purity of the product and practically endless catalyst life. The only co-products are water and $CO_2$, which are produced in substantial amounts. By adopting a suitable process, the co-produced $CO_2$ can be re-utilized as a carbon source in the CO generation. All these features characterize the presented DMC production process as a clean technology.

Since a halide free, non-corrosive catalyst for DMC production would be a further process improvement, alternative catalytic systems have been investigated. Cobalt(II) complexes with N,O ligands, such as carboxylates, acetylacetonates and Schiff bases, have been shown to produce DMC with a good reaction rate and selectivity [74].

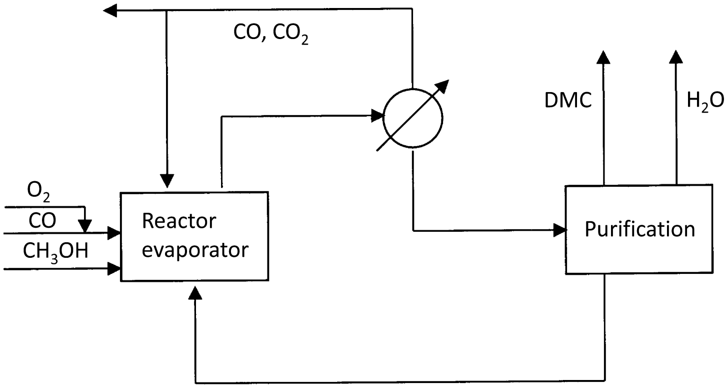


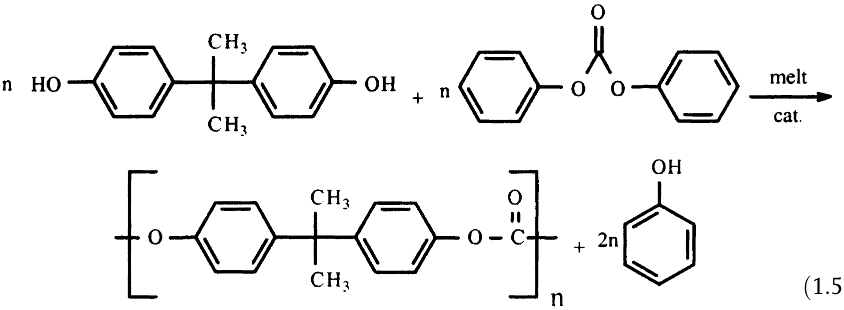
**Figure 1.11** Conceptual scheme of the EniChem one-step DMC production process. Source: Rivetti [72].

**Table 1.5** Comparison between DMC- and phosgene- or dimethyl sulfate (DMS)-based reactions. Source: Tundo [75].

| Phosgene or DMS | DMC |
|---|---|
| Dangerous reagent | Harmless reagent |
| Use of solvent | No solvent |
| Waste water treatment | No waste water |
| NaOH consumption | The base is catalytic |
| By-products: NaCl, $Na_2SO_4$ | By-products: MeOH, $CO_2$ |
| Exothermic | Slightly or not exothermic |

DMC is thus considered a prototype example of a green reagent, since it is nontoxic, made by a clean process, is biodegradable and it reacts in the presence of a catalytic amount of base, thereby avoiding the formation of undesirable inorganic salts as by-products [75–77]. Table 1.5 shows the major environmental benefits of DMC-based procedures. DMC Enichem/Polimeri Europa technology has been licensed to (i) General Electric Japan for a DMC/DPC unit at Chiba (DMC unit was 11.7 kt yr$^{-1}$ capacity and started up in 1993) and (ii) General Electric España for a DMC/DPC unit at Cartagena (DMC unit was 48.3 kt yr$^{-1}$ capacity and started up in 1998; in 2004 the total capacity has been increased to 96.6 kt yr$^{-1}$ with the start up of a second unit).

DMC has been proven to perform advantageously as a substitute for phosgene in several reactions. A non-phosgene process for the melt polymerization production of aromatic polycarbonates has been established commercially [69, 72]:



(1.5)

This process also avoids the use of methylene chloride as a solvent and the co-production of NaCl salt. Another well-established application of DMC in the field of polycarbonates relates to the production of poly[diethyleneglycol bis(allylcarbonate)], a thermosetting resin used in the production of optical glasses and lenses. The non-phosgene process involves the intermediate formation of diallyl carbonate from DMC – whereas the traditional process was based on the use of diethyleneglycol bis(chloroformate) that in turn was obtained from phosgene – and allows high flexibility in terms of customer-tailored products.

The non-phosgene production of isocyanates takes place through thermolysis of the corresponding carbamate. The carbamate synthesis may involve several alternative possible ways, such as the reaction of a nitro-compound with CO, or the reaction of an amine with CO and $O_2$, with urea and alcohol, or with a carbonic ester. Among these routes, the reaction of DMC, or DPC (diphenyl carbonate), with aliphatic amines is a very efficient way to produce carbamates.

A non-phosgene process for the production of methyl isocyanate, starting from methylamine and diphenyl carbonate as raw materials, has been established by EniChem/Polimeri Europa, resulting in the commercialization of two production units in the USA (1988) and China (1994) [78].

Recently, a comparative evaluation of dimethyl carbonate versus methyl iodide, dimethyl sulfate and methanol as methylating agents has been made in terms of green chemistry metrics [79]. These provide a quantitative comparisons based on measurable metrics able to account for several aspects of a given chemical transformation, including: (i) the economic viability, (ii) the global mass flow and the waste products and (iii) the toxicological and eco-toxicological profiles of all the chemical species involved (reagents, solvents, catalysts and products) [80–83].

Figure 1.12 summarizes the result of this comparative evaluation of DMC as green methylating agent. The assessment was based on atom economy (AE) and mass index (MI) for three model transformations: O-methylation of phenol, the mono-C-methylation of phenylacetonitrile and the mono-N-methylation of aniline. In terms of chemical and toxicological properties, DMC shows the lower toxicity index ($LD_{50}$, e.g., lethal dose for 50% of rats in toxicology experiments) and irritating properties, but costs about twice as much as methanol.

The atom economy (AE, as percentage) was calculated considering the mass-balance of a process related to its stoichiometric equation, that is, the percentage of atoms of the reagent that end up in the product:

$$AE = \frac{MW\ \text{product}}{\Sigma MW\ \text{of all reagents used}} \times 100$$

where MW is the mass weight in $\text{g mol}^{-1}$. To include the chemical yield and the selectivity towards the desired product, as well as the mass of all reagents, solvents, catalysts, and so on, used in the examined reactions a more all-encompassing metric, the mass index (MI), could be used. All values are expressed by weight (kg).

$$MI = \frac{\Sigma\ \text{reagents} + \text{catalysts} + \text{solvents} + \text{etc.}}{\text{Desired product}}$$

The atom economy generally follows the trend (Figure 1.12a):

$$\text{MeOH} \gg \text{DMC} \geq \text{DMS} > \text{MeI}$$

Two factors account for this behavior: (i) for methanol, 47% of its mass is incorporated in the final products, more than twice as much as the other reagents (DMC 16%, DMS 12%, or 24% when both methyl groups are incorporated, MeI 11%) and (ii) methanol and DMC require catalytic base or zeolites, as opposed to DMS and MeI. MeOH and DMC offer similar low values of MI (on average, in the range 3–5.5), which are better than those achievable with DMS and MeI (Figure 1.18b).

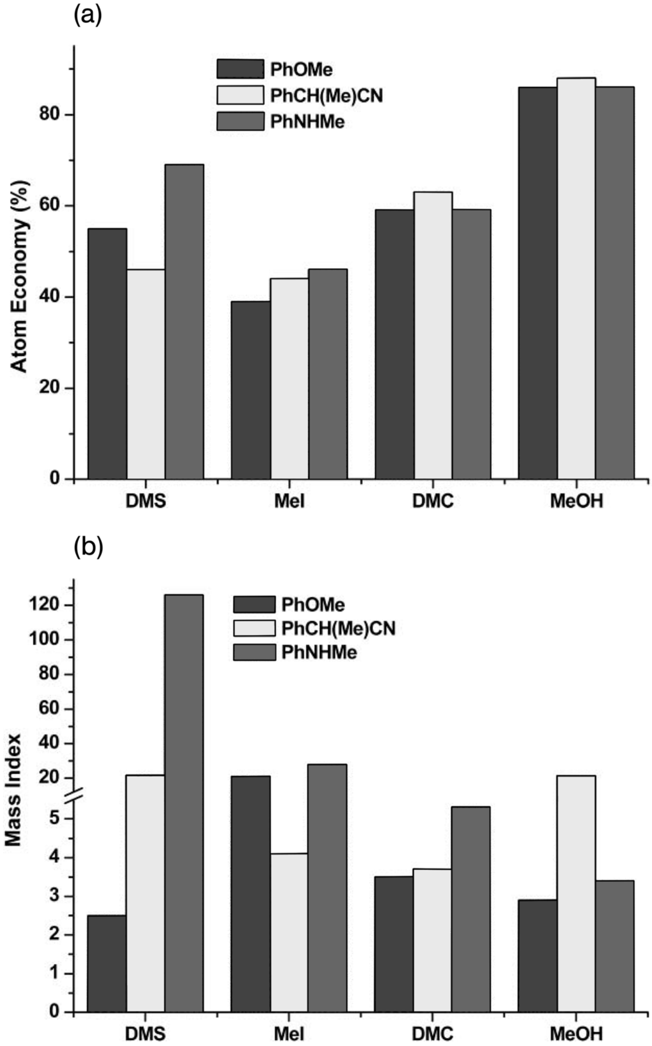


**Figure 1.12** Atom economy (a) and mass index (b) for the reaction of phenol, phenylacetonitrile and aniline with different methylating agents. Source: Selva and Perosa [79].

DMC thus yields very favorable mass indexes (in the range 3–6), indicating a significant decrease of the overall flow of materials (reagents, catalysts, solvents, etc.) and thereby providing safer greener catalytic reactions with no waste.

One conclusion that may be derived from these studies is that DMC is an ideal reactant and that no reasons could exist to still use phosgene. As mentioned above, the process of clean DMC production has been commercialized for over 15 years, an apparently long time and long enough for a substantial substitution of phosgene by DMC. It is thus interesting to look at the market for phosgene in comparison with DMC.

The United States, Western Europe and Asia are currently the major producing and consuming regions for phosgene – primarily consumed captively to manufacture *p,p′*-methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI) and polycarbonate resins. In 2006, global production/demand was estimated at over 7 million metric tons. Demand for phosgene grew by about 3.25% per year in the period 2001–2006, while it was about 6.4% per year in the period1997–2002. About 75–80% of global phosgene is consumed for isocyanates, 18% for polycarbonates and about 5% for other fine chemicals. Fine chemical applications are further broken down to 50% for intermediates, 25% for agrochemicals, 20% for pharmaceuticals and 5% for monomers and coloring agents.

By contrast, total global dimethyl carbonate capacity was about 170 000 $t\,y^{-1}$ in 2002 and output and consumption were both about 90 000 tonnes. Production was concentrated in Western Europe, the USA and Japan and capacity in these regions accounts for about 70% of the total. Consumption was in polycarbonate synthesis (about 50 000 tonnes, accounting for 56.1% of the total), pharmaceutical production (about 20 000 tonnes, accounting for 22.5%), pesticide production (about 7000 tonnes, accounting for 7.9%) and other sectors (about 12 000 tonnes, accounting for 13.5%).

With respect to the global production of polycarbonate, three companies (GE, Cartagena, Spain; Bayer, Antwerp, Belgium; and Asahi Kasei, Taiwan in 2002) use non-phosgene based manufacturing units, with a market share of 12% of the polycarbonate produced by this phosgene-free technology. This market share increased to ca. 20% in 2007.

We may thus conclude that more than 15 years after the introduction of clean processes of DMC synthesis and the large amount of advertising by the scientific community, which still continues, about the use of DMC as clean and safer reactant as a replacement for phosgene, the market penetration of DMC is still quite limited. The reasons for this are several, some general, as discussed in the following section, and some more specific. These include, first, the already noted observation that a safer use of phosgene is possible. There are two main options:

- **On-demand (or on-site) production**. Over 99% of produced phosgene is not transported and is consumed on-site to avoid risk of transport. New legislations limit the amount of phosgene that can be stored on-site, and on-demand production is spreading. Davy Process Technology – DPT (Switzerland) offers modular phosgene generators with production ranging from 3 to 10 000 $kg\,h^{-1}$ [55]. These modular generators produce phosgene from CO and $Cl_2$ over carbon-supported catalysts (carbon itself is active or may by doped with 0.1–2% of active metal, in particular to reduce the formation of $CCl_4$ side product to less that 150 ppm). Figure 1.13 shows the process flow of the phosgene generation section of a phosgene generator from DPT [55]. It consists of two sections, a phosgene generator (Figure 1.13) and a safety absorption module. Note that for safety the reactors are located in a secondary containment and all the lines and systems could be vented with an inert gas. Novartis Crop Protection Inc. (Monthey, Switzerland) has developed an intrinsically safe equipment for the on-demand manufacture of phosgene [84]. Furthermore, confinement in a double envelope of the phosgene

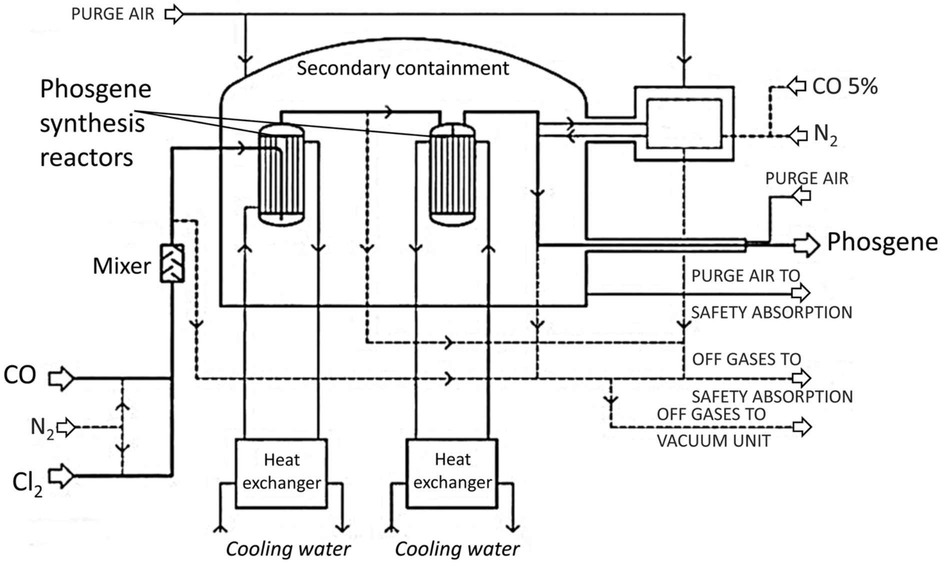


**Figure 1.13** Process flow of the phosgene generation section of a phosgene generator of Davy Process Technology. Source: adapted from Cotarca and Eckert [55].

production, supply and utilization equipment makes it possible to collect any leakage with ultimate destruction of the phosgene in specific installations. Chemical Design, Inc. (US) (http://www.chemicaldesign.com/Phosgene.htm) has also designed and built phosgene plants ranging from 0.5 to over 160 tons per day of high purity phosgene. State-of-the-art bellow seal valves are used to virtually eliminate emissions. They use a compact, skid mounted phosgene reactor design that allows the entire reaction system to be installed inside a controlled building that acts as secondary containment. The complete plant allows phosgene to be safely produced on-site, on demand, thereby eliminating transportation and storage concerns.

- **Use of a safer phosgene source**. Triphosgene is used as a phosgene source. It may be used in pre-packaged cartridge for on-demand production of phosgene by triphosgene catalytic depolymerization. Laboratory generators for on-demand production of phosgene are available. In cooperation with Buss ChemTech, Sigma-Aldrich offers a safe and reliable phosgene generation kit, giving simple access to small quantities of high purity, gaseous phosgene exactly when needed, while no transport and storage of liquid phosgene is necessary. The generator converts safe triphosgene into phosgene on demand using a patented catalyst [85]. Phosgene generation can be stopped at any time. A total containment approach eliminates the risk that phosgene can reach the environment.

Phosgene substitution is thus an emblematic case for sustainable industrial chemistry and how this question should be considered in view of a rational risk assessment more than on generic principles. Phosgene is still central to the chemistry of pharmaceutical, polyurethanes and polycarbonates. This is a very large market and still about eight million tons of phosgene are used industrially worldwide. New uses have also been discovered, from the synthesis of high purity synthetic diamonds to the production of the nutritive sweetener aspartame; it was also used as fuel in molecular motors. The book *Phosgenations – A Handbook* [55] discusses in detail novel and old uses of phosgene (see Sections 1.4 and 1.5, in particular).

However, phosgene is clearly highly toxic (threshold limit value – TLV of 0.1 ppm), but acrolein, for example, has the same TLV and is produced in quantities of several millions worldwide. Acrolein is also produced at barbecue parties by roasting foods, without provoking health alarms. Clearly, a low TLV implies the adoption of special safety procedures and limited storage. On-demand production and other safety procedures, such as those discussed above, are the solution to minimizing the risk to a sustainable level.

The substitution of phosgene with other chemicals (DMC, in particular) should be thus weighted between intrinsic (yield, reactivity, handling, work-up) and extrinsic (safety, toxicity, environmental impact) criteria [55]. Modern technologies for industrial chemical production allow proper and safe operation with toxic chemicals. Their sustainability (or green content) in terms of effective impact on environment and safety of workers is not necessarily lower than their substitution. It is only a problem of economy. More toxic feedstocks means higher costs in safety devices and thus alternative, less toxic reactants are implemented when the overall cost is lower. However, in terms of risk assessment, a more toxic reactant could be equally used, when the appropriate measures are adopted. This is why phosgene is still largely used.

The example of Bhopal teaches that the background for the accident is a poor design (actual processes no longer have this problem) but the reason is a poor management. The human factor is a critical element for all industries, but particularly for chemical ones. It is wrong to give the image of a clean and safe (“green”) chemistry in opposition to the “red” and/or “black” chemistry cited in Section 1.2.2. All chemical production should be sustainable, but unavoidably they handle risky substances, not only in terms of intrinsic toxicity but also of explosive/flammable nature and so on. There are proper procedures and technologies to operate safely, and their progress is in continuous evolution. However, these need skilled operators, high-quality management, continuous maintenance and training. Under these conditions risk could be sustainable, and therefore exporting chemical production to regions of cheap labor could be a problem, owing to weakness in education and sensibility to risk.

### 1.2.7
### Final Remarks on Sustainable Risk

We end this section with a further question arising from the discussion in the previous section. Should the slow substitution of phosgene by DMC be associated only with the slow turnover of chemical processes? No. There are various examples of faster changes of technology even in large-scale chemical productions, while in small-scale applications, for example, production of fine chemicals turnover is typically fast. The problem is that the substitution of chemical processes by more sustainable ones is a complex issue. It clearly involves a techno-feasibility and environmental assessment. The use of toxic reactants implies the use of special safety procedures and monitoring devices, and the production of waste, particularly that which is difficult to treat, determines additional costs of raw materials and disposal treatments. They are thus an integral part of a techno-economic assessment.

The problem is the boundary limit of the techno-economical assessment, for example, which costs are effectively considered (see also later discussion regarding life-cycle assessment). This is a moving boundary that should be determined from the best-available-technology (BAT) and the related legislative limits on emissions. However, a more advanced concept is to consider the chemical process as a component of the environment and set the local legislative limits on emissions to values that do not decrease the biodiversity in the specific area where the process is localized. There are many problems in implementing this concept which introduces the idea that emissions from chemical production (and in general from all industrial and human activities) should have a value connected to the capacity of the environment to sustain the life (biodiversity).

However, global competiveness and market should be considered. This is the real barrier for a more sustainable industrial chemistry. Therefore, the real step forward could derive only when the product value of chemical compounds also includes components related to the process of production, its impact on environment and safety of operations. We live in a global world, not only economically but also environmentally, where the impact of industrial production and human activities is no longer on a local scale. The value of products should thus not be related only to the "local" cost of production, which hides part of the effective costs (for the environment, for example, or for society, when risk is too high). It is thus necessary to adopt transparent procedures where cost is not only determined from the market but also includes the production procedures. This concept of traceability of chemical products is one of the concepts around which the new REACH legislation was built. The next section discusses in more detail this legislation, because it is an important component for the sustainability of chemistry and industrial chemical production not only inside Europe.

## 1.3
## Sustainable Chemical Production and REACH

REACH is a new European Community Regulation on chemicals and their safe use (EC 1907/2006) (http://www.reachlegislation.com, http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm). It deals with the Registration, Evaluation, Authorisation and Restriction of Chemical substances. The new law entered into force on 1 June 2007. The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, the innovative capability and competitiveness of the chemicals industry should be enhanced. The

**Table 1.6** REACH timeline.

| Date | Action |
|---|---|
| June 2007 | New law entered into force |
| June 2008 | European Chemicals Agency to become operational |
| 2008–2010 | The first phase of registrations. This will apply to substances supplied at 1000 tonne or more, as well as some other priority high-risk substances |
| By 2013 | The second phase of registrations, to be completed 6 years after REACH comes into force, and will apply to substances supplied at 100 tonne or more |
| By 2018 | The final phase of registrations for substances supplied at 1 tonne or more |

benefits of the REACH system will arrive gradually, as more and more substances are phased into REACH (Table 1.6).

Under REACH, manufacturers, importers and downstream users are required to demonstrate that the manufacture/import/use of a substance does not adversely affect human health and that risks are adequately controlled. Information on chemical properties and safe uses of chemicals will be communicated up and down the supply chain.

The main elements characterizing REACH are the following:

- **Registration**. Each producer and importer of chemicals in volumes of 1 tonne or more per year and per producer/importer – around 30 000 substances – will have to register them with a new EU Chemicals Agency, submitting information on properties, uses and safe ways of handling them. The producers and importers will also have to pass the safety information to “downstream users” – manufacturers that use these chemicals in their production processes – so that they know how to use the substances without creating risks for their workers, the end consumers and the environment.

- **Evaluation**. Through evaluation, public authorities will look in more detail at registration dossiers and at substances of concern. They can request more information if necessary. At this stage, they will also scrutinize all proposals for animal testing to limit it to the absolute minimum. REACH makes data sharing on animal test results compulsory and prescribes the use of alternative methods wherever possible.

- **Authorisation**. Use-specific authorisation will be required for chemicals that cause cancer, mutations or problems with reproduction, or that accumulate in our bodies and the environment. Authorisation will be granted only to companies that can show that the risks are adequately controlled or if social and economic benefits outweigh the risks where no suitable alternative substances or technologies are available. This will encourage substitution – the replacement of such dangerous chemicals with safer alternatives.

- **Restrictions**. The use of certain dangerous substances at EU level could be still restricted, but REACH will introduce clearer procedures and allow decisions to be taken more quickly than currently. The provisions for restrictions will act as a safety net.

The REACH Regulation gives greater responsibility to industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers will be required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database run by the European Chemicals Agency (ECHA, fully operational on June 2008) in Helsinki. The Agency will act as the central point in the REACH system: it will manage the databases necessary to operate the system, co-ordinate the in-depth evaluation of suspicious chemicals and run a public database in which consumers and professionals can find hazard information.

The Regulation also calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified. The main legislative texts of REACH are the following:

- Regulation (EC) No 1907/2006 is the central act of the new European chemicals policy. It is often referred to as the "REACH Regulation."
- Directive 2006/121/EC contains technical adaptations of Directive 67/548/EEC that are necessary in the light of the new REACH Regulation (Directive 67/548 concerns the classification, packaging and labeling of dangerous substances and applies in parallel with REACH).

The latter Directive originates from the need of an internationally-harmonized approach for classification and labeling to ensure the safe use, transport and disposal of chemicals. The new system, which is called "Globally Harmonized System of Classification and Labeling of Chemicals" (GHS, a United Nations system) addresses classification of chemicals by types of hazard and proposes harmonized hazard communication elements, including labels and safety data sheets. It aims to ensure that information on physical hazards and toxicity from chemicals is available to enhance the protection of human health and the environment during the handling, transport and use of these chemicals. GHS also provides a basis for harmonization of rules and regulations on chemicals at national, regional and worldwide level, which is an important factor for trade facilitation. The GHS aims to identify hazardous chemicals, and to inform users about these hazards through standard symbols and phrases on packaging labels and through safety data sheets (SDSs).

### 1.3.1
### How does REACH Works

The REACH legislation is by far the largest legislative project adopted by the EU in recent years. It replaces 40 legislative texts and creates a single EU-wide system for the management of chemicals produced in Europe or imported into Europe.

Before REACH, there was a general lack of knowledge regarding 99% of the chemicals (around 100 000 substances) that were placed on the market before 1981. Prior to that date, no stringent health and safety tests were needed to market chemicals.

REACH is based on the idea that industry itself is best placed to ensure that the chemicals put on the market in the EU do not adversely affect human health or the environment. This requires that industry has certain knowledge of the properties of its substances and manages potential risks. REACH creates a single system for both "existing" and "new" substances; substances are now described as *non-phase-in* substances (i.e., those not produced or marketed prior to the entry into force of REACH) and *phase-in* substances. Its basic elements are described below:

- All substances are covered by the REACH Regulation unless they are explicitly exempted from its scope.
  - REACH is very wide in its scope, covering all substances, whether manufactured, imported, used as intermediates or placed on the market, be that on their own, in preparations or in articles, unless they are radioactive, subjected to customs supervision or are non-isolated intermediates. Waste is specifically exempted. Food that meets the definition of a substance, on its own or in a preparation, will be subject to REACH, but such substances are largely exempted from Registration, Evaluation and Authorisation.

- Manufacturers and importers of chemicals should obtain relevant information on their substances and to use that data to manage them safely.
  - To reduce testing on vertebrate animals, data sharing is required for studies on such animals.
  - For other tests, data sharing is required on request by other registrants.
  - Better information on hazards and risks and how to manage them safely will be passed down and up the supply chain.
  - Downstream users are brought into the system.

- Evaluation is undertaken by the agency for testing proposals made by industry or to check compliance with the registration requirements. The agency co-ordinates substance evaluation by the authorities to investigate chemicals with perceived risks. This assessment may be used later to prepare proposals for restrictions or authorisation.

- Substances with properties of very high concern will be made subject to authorisation; the agency will publish a list containing such candidate substances. Applicants will have to demonstrate that risks associated with uses of these substances are adequately controlled or that the socio-economic benefits of their use outweigh the risks.
  - Applicants must also analyze whether there are safer suitable alternative substances or technologies. If there are, they must prepare substitution plans, if not they should provide information on research and development activities, if appropriate.
  - The European Commission may amend or withdraw any authorisation on review if suitable substitutes become available.

- The restrictions provide a procedure to regulate as to whether the manufacture, placing on the market or use of certain dangerous substances shall be either subject to conditions or prohibited.
  - Restrictions act as a safety net to manage EC wide risks that are otherwise not adequately controlled.
  - A classification and labeling inventory of dangerous substances will help to promote the agreement within industry on the classification of a substance. For some substances of high concern a EC wide harmonization of classification by the authorities should be made.

### 1.3.2
### REACH and Sustainable Industrial Chemistry

The REACH legislation will improve the life of all citizens because it concerns more than 30 000 substances currently used in everyday products. At the same time, REACH will provide important opportunities for European industry. This is true for the chemicals industry itself. But REACH will also provide important opportunities to other industries that look to the chemicals industry as a driver of innovation and as key to resolving critical challenges, such as higher energy efficiency and combating climate change.

There are several beneficial characteristics of REACH for both companies and society [86–88]:

- closure of data gaps, for example, missing knowledge on hazards is no longer an advantage;
- equal data requirements for new and existing chemicals;
- authorisation of the most dangerous chemicals (CMR, PBT, vPvB) keeps them under control;
- substitution of most hazardous substances encouraged;
- improved confidence of consumers by better information on hazards and risks.

REACH plays a relevant role for innovation:

- encourages market entrance of new chemicals by lower data requirements up to a production volume of $10\,\mathrm{t\,yr^{-1}}$;
- no competitive advantage for existing substances because of equal requirements;
- use of substances for R & D purposes facilitated;
- improved knowledge about chemicals, allowing better predictability of their risks;
- downstream users receive improved information to help find innovative solutions;
- incentives for manufacturers through improved knowledge about their uses and exposure patterns.

On a long-term view REACH legislation represents the way to introduce traceability of chemical products, for example, to include in the products and their chain of production the information on the production method and their impact on the environment. Notwithstanding the obvious strong resistance and difficulties in implementation, this is the only real possibility to include the cost for environment and society in the production cost and to avoid the excuse of global competitiveness to introduce new cleaner and sustainable chemical processes and technologies. Note that this concept is quite distant from the concepts of "green taxes," which have shown great limits.

Including the method of production and its impact on environment and health on the trading cost of chemical products will be a relevant boost to the introduction of new advanced processes/technologies and thus for innovation and sustainability. The chemical industry is a high-tech sector in which competiveness has long been dominated by the capacity of companies to be innovative. The percentage of annual budget dedicated to R&D was thus nearly twice that of the mean value in the manufacture sector. This picture has changed in the last one–two decades, in parallel with the change of the overall market and the situation of chemical production in the world.

However, new sustainability issues require R&D to be put back at the core of chemical industry. The first element to move in this direction is the development of a longer term vision for the chemical industry, which contrasts the very short term view (few years) planning of several companies and the continuous restructuring of the chemical industry in the last one–two decades. One of the positive signals in this direction is the cited European Technology Platform on Sustainable Chemistry and the related prepared document [6], which plans to define the scenario for R&D for the next 20 years.

REACH is another important step towards sustainability of chemicals, because:

- Information on hazardous properties of chemicals is generated.
- Information upstream and downstream the supply chain will be improved (enhanced dialogue).
- Most hazardous chemicals must be authorised and will be under control.
- Chemicals can only be marketed if it is proven that their identified use is safe.

### 1.3.3
### Safety and Sustainability of Chemicals

A chemical substance is safe for a certain use if it is demonstrated that it poses no risk when taking into consideration risk reduction measures that reduce exposure of man or environment [86–88]. However, this is not enough to indicate that it is also a sustainable chemical. A sustainability target consists of the development of inherently safe chemicals (ISCs), for example, without risks for human health and the environment, even without specific exposure control.

We may distinguish two aspects for ISC: those used at workplaces (in particular, in SMEs), where in principle only substances not classified as dangerous for human health should be used, and those released to the environment, which should be not persistent and bioaccumulative or not persistent and highly mobile.

**Table 1.7** Inherent safety of chemicals. Source: adapted from Steinhäuser [86].

| Unsustainable | Sustainable |
|---|---|
| CMR properties | No irreversible and chronic effects |
| Respiratory sensitizers | Low acute (eco) toxicity |
| Extreme acute (eco) toxicity | Low persistence |
| PBTs/vPvBs | No bioaccumulation |
| High persistence and mobility | Low spatial range |

Table 1.7 summarizes some of the characteristics for unsustainable versus sustainable chemical substances. The combination of persistence with bioaccumulation is of great concern, because:

- bioaccumulation enhances probability of toxic effects;
- persistence causes irreversibility of environmental exposure;
- long-term adverse effects are unpredictable.

The combination of persistence with mobility is also of great concern, because:

- mobility enhances probability of exposure to large areas;
- persistence causes irreversibility of environmental exposure;
- long-term adverse effects are unpredictable.

Sustainable chemicals should be short-range chemicals, that is, in which their (i) spatial range is low (mobility), (ii) temporal range is low (persistence) and (iii) effects are not irreversible. Clearly, not all chemicals that should be used can have the above characteristics because, for example, fuels must be inflammable, pesticides must be toxic (even with controlled properties) and reactive reagents must be aggressive/corrosive. The challenge is thus a careful control of the properties ("just needed") and hazardous properties should be not linked to not-necessary functionalities.

However, it is necessary to go beyond inherent safety sustainable chemicals, because they should be produced with low resource demand (energy, feedstock, auxiliaries), high yield and low discharges of sewage and waste. Three steps towards sustainability of chemicals should be evidenced:

1. **Safety:** A chemical is safe if it is demonstrated that it poses no risk, taking into consideration risk reduction measures.
2. **Inherent safety**: Chemicals unlikely to pose a risk for human health and environment – even without specific exposure control – due to the lack of hazardous properties.
3. **Sustainable chemicals:** in addition low energy and resource demand.

Sustainability in chemistry is not only a qualitative target, but also a quantitative one, because chemical production has increased since 1930 from 1 million to 500 million tonnes per year in 2000. As a consequence, measures needed to reduce chemicals' use in various branches are very important. One of these actions consists in selling services instead of substances. "Chemical leasing" may reduce chemical consumption up to 30–50%. Chemical leasing (ChL) is an initiative of the United Nations Industrial Development Organisation (UNIDO) (http://www.-chemicalleasing.com). The idea is to promote sustainable management of chemicals and close the material cycles between suppliers and users of chemicals ("closing the loops").

Traditionally, chemicals are sold to a customer, who becomes the owner of the substances and therefore responsible for its use and disposal. Their suppliers have a clear economic interest in increasing the amount of chemicals sold, which is usually related to a negative release to the environment. Compared to this approach, the concept of ChL is much more service-oriented. In this business model the customer pays for the benefits obtained from the chemical, not for the substance itself. Consequently, the economic success of the supplier is no longer linked with product turnover. Chemical consumption becomes a cost rather than a revenue factor for the chemicals supplier. The supplier will thus try to optimize the use of the chemical and improve the conditions for recycling to reduce the amount consumed, which again reduces the environmental pollution.

Against this background ChL can be seen as a key element of sustainable chemicals management systems. The application of ChL models brings economic advantages for all partners involved, provides concrete solutions for efficient chemicals management and ways to reduce negative releases to the environment. Since chemical products provide a broad variety of services such as "cleaning," "coating," "coloring" and "greasing" the ChL model is applicable in a multitude of industry sectors.

When applying ChL business models, the producer does not just provide the chemical but also his know-how on how to reduce the consumption of chemicals and how to optimize the conditions of use. While in the traditional model the responsibility of the producer ends when the chemical is sold, in ChL business models the producer remains responsible for the chemical during its whole life cycle, including its use and disposal.

## 1.4
## International Chemicals Policy and Sustainability

Sustainable development was originally defined in the Brundtland report "Our Common Future" in 1987 as follows: "Sustainable Development should meet the needs of the present without compromising the ability of future generations to meet their own needs." Sustainable Development balances three principal requirements:

- the needs of society (the social objective);
- the efficient management of scarce resources (the economic objective);
- the need to reduce the load on the eco-system to maintain the natural basis for life (the environmental objective).

Although this original definition has evolved (see, for example, the United Nations Commission on Sustainable Development – CSD: http://www.un.org/esa/desa/

aboutus/dsd.html), and new definitions have been proposed to consider, for example, dynamic models that describe the inter-relationships of environmental, economic and social variable [89], the background concepts remain valid. One of the central aspects is the need for cooperation on a worldwide scale, and for a sustainable industrial chemistry the definition of international chemicals policies is of fundamental importance.

At the United Nations (UNs) level, the commitment to sound management of chemicals was renewed in an action plan on chemicals, agreed by Heads of State at the Johannesburg World Summit on Sustainable Development in September 2002. This plan – welcomed by the global chemical industry – provides that by 2020, chemicals be used and produced in ways that lead to minimization of significant effects on human health and the environment. The approach is based on sound risk assessment and risk management, and follows the precautionary approach. Following this, two initiatives were developed in parallel by UNEP (United Nations Environmental Program): the Marrakech process and the Strategic Approach to International Chemicals Management (SAICM).

From chemical industry side, the commitment to sustainable development has resulted in a wide range of programs and initiatives. The most known are the Responsible Care Global Charter, the Global Product Strategy, the Long Range Research Initiative and the HPV program. These programs and initiatives being global are managed by ICCA (International Council of Chemical Association; http://www.icca-chem.org). ICCA is the worldwide voice of the chemical industry, representing chemical manufacturers and producers all over the world. It accounts for more than 75% of chemical manufacturing operations with a production exceeding US$ 1.6 trillion annually. ICCA has a central role in the exchange of information within the international industry, and in the development of position statements on matters of policy. It is also the main channel of communication between the industry and various international organizations that are concerned with health, environment and trade-related issues, including the United Nations Environment Program (UNEP), the World Trade Organization (WTO) and the Organisation for Economic Co-operation & Development (OECD).

Through the above programs and initiatives the chemical industry is contributing to the SAICM objectives as well as to the goal of the Marrakech process to achieve sustainable consumption and production (SCP). Achieving the objectives of SAICM is essential to improving public confidence in the safe management of chemicals and to further promote the benefits of chemistry. SAICM will provide the framework for future international chemicals management globally and will influence the direction of national regulatory systems until 2020.

Figure 1.14 shows a roadmap of governmental initiatives and regulations and industry programs and initiatives. The Rio and Johannesburg Summits (in 1992 and 2002, respectively) are the Earth Summits organized by United Nations to discuss the growing environmental and development problems facing the planet. In Rio the 178 governments attending the Earth Summit signed up to *Agenda 21*, an ambitious global action plan for achieving sustainable development. This document set out a long-term vision for balancing economic and social needs

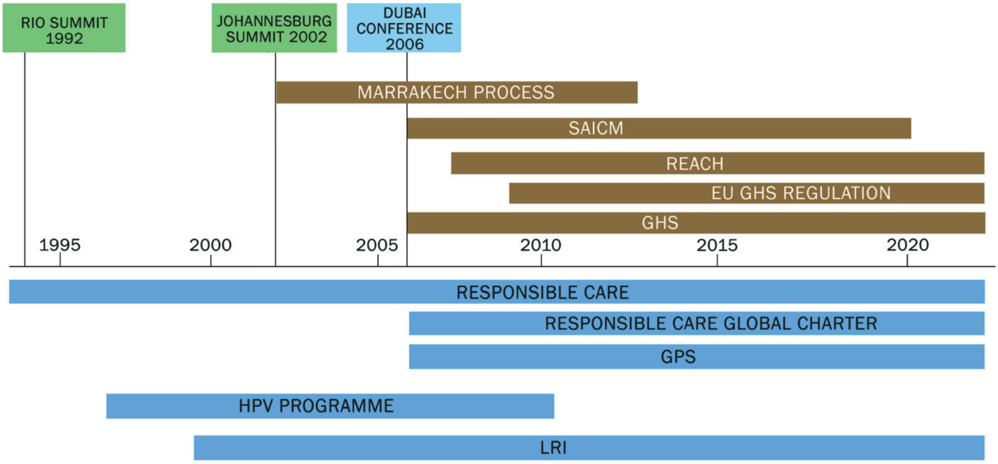


**Figure 1.14** Roadmap of governmental initiatives and regulations and industry programs and initiatives. Source: European Federation of Chemical Industry – Cefic – web site: www.cefic.org.

with the capacity of the earth's natural resources. In the immediate aftermath of Rio, governments, NGOs (non-governmental organizations) and other stakeholders joined forces to implement the plan. There was a real belief that global leaders were on their way to tackling issues such as poverty eradication, social injustice and environmental degradation. However, a decade on, it had become clear that the vision and commitment shown at the Rio Summit did not last. While some real progress was made – for instance with the convention on climate change and other national and regional initiatives – many of the actions agreed have been still not implemented. The movement towards a more sustainable world has been slower than many expected.

In 2002, the international community met in Johannesburg to once again take up the challenge of sustainable development. The World Summit on Sustainable Development was one of the largest and most important international gatherings ever held on the subject.

The International Conference on Chemicals Management (Dubai, 2006) was a critical turn-out point for strategies in chemical production. During the conference the chemical industry made a public commitment to enhance chemical safety throughout the value chain. At the same time, the Responsible Care Global Charter and the Global Product Strategy (GPS) were launched. Related programs and initiatives include the Long-range Research Initiative (LRI), the HPV Chemicals program and the SusChem platform.

The Marrakech process is a global process to support regional and national initiatives to promote the shift towards Sustainable Consumption and Production (SCP) patterns. In the European Union, the Marrakech process is leading the development of an EU SCP Action Plan that entails amongst other things the Integrated Product Policy (IPP) and Green Public Procurement (GPP).

The International Conference on Chemicals Management (ICCM) organized by UNEP (United Nation's Environmental Program) in Dubai (2006) led to the "Dubai Declaration on the Strategic Approach to International Chemicals Management (SAICM)." At the same time, the Johannesburg Summit called for technical and financial assistance for developing countries to strengthen their capacity for the sound management of chemicals and hazardous waste, as well as for the national implementation of a new globally harmonized system of classification and labeling of chemicals (GHS).

In the European Union the Marrakech process has led to a renewed European Sustainable Development Strategy, which identifies Sustainable Consumption and Production (SCP) as one of the key objectives to be achieved in the context of the European Union's commitment of sustainable development. SCP aims to "promote sustainable consumption and production by addressing social and economic development within the carrying capacity of ecosystems and decoupling economic growth from environmental degradation."

The two key pillars in the context of SCP Action Plan in Europe are the Green Public Procurement (GPP) and the Integrated Product Policy (IPP). One of the main pillars of European SCP Policy is GPP, which means that "public purchasers take account of environmental factors when buying products or services."

Another key pillar is the Integrated Product Policy (IPP). IPP aims to reduce the environmental impact of products. Relevant initiatives include pilot projects, the creation of an EU Platform on life cycle assessment (LCA), and product prioritization.

The Strategic Approach to International Chemicals Management (SAICM) is a non-binding agreement launched in 2003 and aimed to improve the sound management of chemicals throughout their entire life cycle. More than 100 countries represented by their environment and health ministers have adopted this international approach to stimulate the safe production, transport, storage, use and disposal of chemicals. The objectives of the Global Plan of Action are (i) risk reduction, (ii) knowledge and information, (iii) governance, (iv) capacity-building and technical cooperation, and (v) stopping illegal international traffic.

Worldwide hazard communication of chemicals requires a change from the existing systems to a more harmonized one. This gave rise to the elaboration of a "Globally Harmonized System of Classification and Labeling of Chemicals" (GHS) by the United Nations Economic Commission for Europe (UNECE, 2002). This system proposes harmonized hazard communication elements, including labels and safety data sheets.

Regarding the trade of chemicals, the following conventions should be finally remembered:

- The "Basel Convention," a multilateral agreement to reduce the movement of hazardous wastes between nations, and specifically to prevent transfer of hazardous wastes from developed to less developed countries (LDCs). The convention entered into force in 1992.

- The "Rotterdam Convention," a multilateral agreement that became legally binding on its parties in 2004 to promote shared responsibilities in relation to the international trade of certain hazardous chemicals and to contribute to the environmentally sound use of those chemicals by facilitating exchange of information about their characteristics. The convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure.

## 1.5
## Sustainable Chemistry and Inherently Safer Design

Process safety, a discipline that focuses on the prevention of fires, explosions and accidental chemical releases at chemical process facilities, is a key element for a sustainable industrial chemistry, as indicated in the previous sections. There are three key elements for process safety: behavior, system and process.

Thorough and effective analyses of workplace incidents are critical components of a comprehensive safety management system. Yet, many incident analysis processes (i.e., accident investigations) fall short. They frequently fail to identify and resolve the real root causes of injuries, process incidents and near misses. Because the true root causes of incidents are within the system, the system must change to prevent the incident from happening again.

Process safety differs from the traditional approach to accident prevention [90]:

- there is greater concern with accidents that arise out of the technology;
- attention is given to foreseeing hazards and taking action before accidents occur;
- accidents that cause damage to plant and loss of profit but do not injure anyone should be considered in addition to those that do cause injury.

In general, there is greater emphasis on a systematic rather than a trial-and error approach, particularly on methods that identify hazards and estimate their probability and consequences. The term loss prevention can be applied in any industry, but is widely used in the process industries (particularly chemical industries), where it usually means the same as process safety.

Chemical plants, and other industrial facilities, may contain large quantities of hazardous materials. The materials may be hazardous due to toxicity, reactivity, flammability or explosivity. A chemical plant may also contain large amounts of energy – the energy is required either to process the materials or is contained in the materials themselves. An accident occurs when control of this material or energy is lost. An accident is defined as an unplanned event leading to undesired consequences. The consequences might include injury to people, damage to the environment, or loss of inventory and production, or damage to equipment.

The practices to process safety have been progressively changed with time, as briefly shown in Table 1.8. Process safety does not depend only on human errors or faults in equipments but on the whole system management. From the end of the 1970s there has thus been a large effort to develop risk assessment techniques and systematic approaches, as well as suitable strategies for successful process safety management (PSM). In the 1980s, the Bhopal accident pushed the chemical industry

**Table 1.8** Process safety milestone practices.

| Period | Type approach | Practice |
|---|---|---|
| Pre-1930s | Behavior | Identify who caused the loss and punish the guilty |
| Pre-1970s | Process | Find breakdown in, and fix man–machine interface |
| 1970s, 1980s | Management systems | Development of risk assessment techniques and systematic approaches |
| 1980s + | Comprehensive | Performance-, risk-based standards, regulations; sustainable and inherent designs |

towards a further step for a more comprehensive approach, for example, to an inherent safer design.

Inherently safer design of chemical processes involves the use of smaller quantities of hazardous materials, the use of less hazardous materials, the use of alternative reaction routes or process conditions to reduce the risk of runaway exothermic reactions, fires, explosions and/or the generation or release of toxic materials.

Notably, in some cases changes made to improve the environment have resulted in inherently less safe designs. For example, the collection of vent discharge gases for incineration or for absorption on carbon beds has resulted in explosions when the composition of the gases in the vent system has entered the flammable range.

Chemical process safety strategies can be grouped into four categories [91]:

1. **Inherent**: when the safety features are built into the process, not added on; for example, replacement of an oil-based paint in a combustible solvent with a latex paint in a water carrier.

2. **Passive**: for example, safety features that do not require action by any device – they perform their intended function simply because they exist; for example, a blast resistant concrete bunker for an explosives plant, or a containment dike around a hazardous material storage tank.

3. **Active**: for example, safety shutdown systems to prevent accidents (e.g., a high level alarm in a tank shuts automatic feed valves) or to mitigate the effects of accidents (e.g., a sprinkler system to extinguish a fire in a building). Active systems require detection of a hazardous condition and some kind of action to prevent or mitigate the accident. Multiple active elements involve typically a sensor (detect hazardous condition), a logic device (decide what to do) and a control element (implement action).

4. **Procedural**: or operating procedures, for example, operator response to alarms, emergency response procedures, safety rules and standard procedures, training. An example is a confined space entry procedure.

In general, inherent and passive strategies are the most robust and reliable, but elements of all strategies will be required for a comprehensive process safety management program when all hazards of a process and plant are considered.

**Table 1.9** Examples of process risk management strategies. Source: adapted from Mannan [90].

| Risk management strategy category | Example | Comments |
|---|---|---|
| Inherent | An atmospheric pressure reaction using nonvolatile solvents that is incapable of generating any pressure in the event of a runaway reaction | No potential for overpressure |
| Passive | A reaction capable of generating 22 kPa pressure in case of a runaway; carried out in reactor which may operate up to 36 kPa | The reactor can contain the runaway reaction, but 2 kPa pressure is risky and reactor could fail due to a defect, corrosion, physical damage or other cause |
| Active | A reaction capable of generating 22 kPa, realized in a reactor with a 1 kPa high-pressure interlock to stop reactant feeds and a properly sized 3 kPa rupture disc discharging to an effluent treatment system | The interlock could fail to stop the reaction in time, and the rupture disk could be plugged or improperly installed, resulting in reactor failure in case of a runaway reaction.<br>The effluent treatment system could fail to prevent a hazardous release |
| Procedural | The same reactor described in example 3 above, but without the 1 kPa high-pressure interlock. Instead, the operator is instructed to monitor the reactor pressure and stop the reactant feeds if the pressure exceeds 3 kPa. | There is a potential for human error, the operator failing to monitor the reactor pressure, or failing to stop the reactant feeds in time to prevent a runaway reaction |

Table 1.9 gives some examples of process risk management strategies. Note, however, that these examples refer only to the categorization of the risk management strategy with respect to the hazard of high pressure due to a runaway reaction. The processes described may involve trade-offs with other risks arising from other hazards. For example, the non-volatile solvent in the first example may be extremely toxic, and the solvent in the remaining examples may be water. Decisions on process design must be based on a thorough evaluation of all the hazards involved.

Table 1.9 refers to a batch chemical reactor as an example. The hazard of concern is a runaway reaction causing high temperature and pressure and potential reactor rupture. The preferable (inherent) approach is to develop a chemistry that is not exothermic, or mildly exothermic, for example, where the maximum adiabatic exothermic temperature is lower than the boiling point of all ingredients and onset temperature of any decomposition or other reactions. In a passive approach, the maximum adiabatic pressure of a reaction is lower than the maximum reactor pressure design. The hazard (pressure) still exists, but is passively contained by the pressure vessel. In an active strategy the maximum adiabatic pressure for 100% reaction is higher than the reactor design pressure, but an active control is present, for example, progressive introduction of the limiting reactant with temperature control to limit potential energy from reaction. In addition, high temperature and pressure interlocks to stop feed and apply emergency cooling are used and emergency relief systems are provided. In the procedural approach, the automatic devices are substituted by a trained operator to observe temperature, stop feeds and apply cooling, if the temperature exceeds critical operating limit.

There are various techniques to achieve classical risk reduction, but generally these approaches to safety are mostly an afterthought in the design. They may use a safety review or process hazards analysis (PHA), such as a hazard and operability study (HAZOP) or a "what if?/checklist study", merely as a project check instead of a preemptive hazards reduction tool. If these studies are carried out at the latter stages of engineering or during construction there is a natural tendency to avoid expensive redesign or rework. In the inherently safer design, elimination or significant reduction of the process hazards occurs during the design by adopting suitable approaches, which fall into the following categories:

- **Minimize**: Significantly reduce the quantity of hazardous material or energy in the system, or eliminate the hazard entirely if possible. It is necessary to use small quantities of hazardous substances or energy in (i) storage, (ii) intermediate storage, (iii) piping and (iv) process equipment, as discussed in the previous sections. The benefits are to reduce the consequence of incident (explosion, fire, toxic material release), and improve the effectiveness and feasibility of other protective systems (e.g. secondary containment, reactor dump or quench systems). Process intensification (see below) is also a way to reach this objective.

- **Substitute**: Replace a hazardous material with a less hazardous substance, or a hazardous chemistry with a less hazardous chemistry. Examples are water-based coatings and paints in place of solvent-based alternatives. They reduce fire hazard, are less toxic, have a better smell and lower VOC (volatile organic compound) emissions, and reduce hazards for end user and also for the manufacturer. Safer use and better sustainability thus go in the same direction. Another example is substitution of chemicals used for refrigeration. Initially, ammonia, light hydrocarbons and sulfur dioxide were used. They were later substituted by inherently safer alternatives, for example, CFCs (chloro-fluorocarbons). However, in around the 1980s, CFCs were discovered to be active in stratospheric ozone destruction and thus were later banned (Montreal Protocol entered into force in 1989). CFCs were initially substituted by HCFCs, where not all the C-H bonds in alkanes were substituted by C-X bonds (X is an halogen group), but the phasing out of also these chemicals is programmed. New substitutes for hydrofluorocarbons (HCFC) should be thus developed, but their impact should be also minimized both by severe regulations on their disposal and by re-design of refrigerators to minimize the quantity of flammable hydrocarbons. Currently, in home refrigerators as little as 120 grams of hydrocarbon refrigerant is used. This example shows that substitution of chemicals sometimes is not a simple problem. In fact, this is one of the critical points in REACH legislation discussed in the previous section.

Substitution of an hazardous chemical is often an even more complex problem, in particular regarding the trade-off between inherently safer design and sustainable chemistry. Several examples are discussed in subsequent chapters. We thus limit our discussion here to a few aspects. Up until around the 1960s the Reppe process was employed for of synthesis of acrylic esters:

$$CH \equiv CH + CO + ROH \xrightarrow[HCl]{Ni(CO)_4} CH_2 = CHCO_2R \tag{1.6}$$

It was substituted by the new process of oxidation of propylene to acrylic acid via acrolein using heterogeneous Bi-molybdate based catalysts followed by acid-catalyzed reaction of acrolein with the alcohol:

$$\begin{aligned} &CH = CHCH_3 + 1.5\,O_2 \xrightarrow{\text{Solid Cat.}} CH_2 = CHCHO \\ &CH_2 = CHCHO \xrightarrow{\text{Solid Cat.}} CH_2 = CHCOOH + H_2O \\ &CH_2 = CHCOOH + ROH \xrightarrow{H^+} CH_2 = CHCO_2R + H_2O \end{aligned} \tag{1.7}$$

Although substitution was motivated by the availability at that time of propylene and lower cost of the process, it was also a significant improvement in terms of safety, because acetylene is flammable and extremely reactive, carbon monoxide is also toxic and flammable, nickel carbonyl catalysts are toxic, environmentally hazardous (heavy metals), and carcinogenic, and anhydrous HCl (used in the reaction) is toxic and corrosive. However, the new process from propylene cannot be considered inherently safer. Hazards are primarily due to the flammability of reactants, corrosivity of the sulfuric acid catalyst for the esterification step (new solid acids have eliminated this hazard, as discussed in subsequent chapters), small amounts of acrolein as a transient intermediate in the oxidation step, and reactivity hazard for the monomer product.

- **Moderate:** Reduce the hazards of a process by handling materials in a less hazardous form, or under less hazardous conditions, for example at lower temperatures and pressures. Dilution is one of the key words. Aqueous ammonia should be used instead of anhydrous $NH_3$. Aqueous HCl in place of anhydrous HCl. Sulfuric acid in place of oleum. Figure 1.15 shows an example of the relevant effects observed for the concentration of ammonia measured in air as a function of distance from the place of rupture of a tank containing anhydrous or diluted ammonia solution. Less severe processing conditions are also another keyword. The use of improved catalysts is a critical element in reaching this objective and will be discussed extensively in the following chapters.

- **Simplify:** Eliminating unnecessary complexity to make plants more "user friendly" and less prone to human error and incorrect operation. In the previous section we emphasized how an objective of sustainable chemistry is the development of novel solutions to reduce complexity of chemical processes, which also allows a better control and an improvement of safety.

One way to simplify processes is to eliminate equipment, by combining reaction and separation. The use of membranes is discussed in Chapter 4. Another relevant example is reactive distillation. Figure 1.16 compares the traditional methyl acetate process with that based on reactive distillation (Eastman Chemical) [97–99]. Eastman

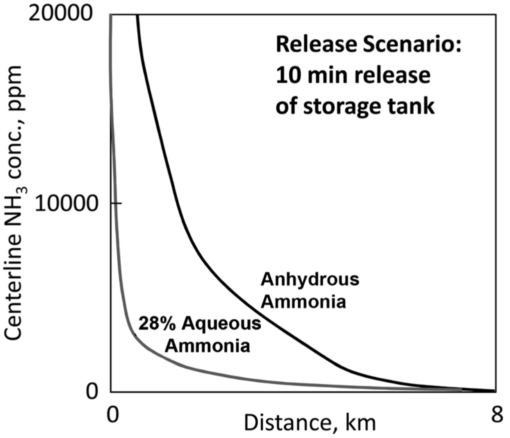


**Figure 1.15** Concentration of ammonia measured in air as a function of the distance from the place of the rupture of a tank containing anhydrous or diluted ammonia solution.

Chemical Co.'s methyl acetate reactive distillation process and processes for the synthesis of fuel ethers are classic success stories in reactive distillation. Improvements for the Eastman process are very high: five-times lower investment and five-times lower energy use than the traditional process. However, combining reaction and distillation is not always advantageous and in some cases it may not even be feasible. The methyl acetate process based on reactive distillation has fewer vessels, pumps, flanges, valves, piping and instruments. This is an advantage also in terms of safety and maintenance. However, a reactive distillation column itself is more complex (multiple unit operations occur within one vessel) and thus more difficult to control and operate. It is thus not possible to make unique conclusions.

The concept of inherently safer design was first proposed by Kletz, who developed a set of specific design principles for the chemical industry [92] (see also [50]), but it has been publicized and promoted later by many technologists from petrochemical and chemical companies such as Dow, Rohm and Haas, ExxonMobil, and many others. A relevant source of information is the book *Inherently Safer Chemical Processes: A Life Cycle Approach* [49].

For inherent safety, while prevention, detection and mitigation are all considered, the emphasis should be on prevention. For example, moving the proposed location of a flammable liquid storage tank away from a public fence line may greatly reduce the consequences of a release and may reduce or eliminate the costs of providing the added protection system required if it is not. Inherent safety includes the consideration of more than just design features of a process. Inherent safety principles include human factors, in particular those related to the design and operating conditions. Finding an error-likely situation, such as controls being too difficult to access or too complicated, and working to reduce the clutter and confusion or to improve the accessibility to reduce the chance of a human error is an example of inherent safety in action.

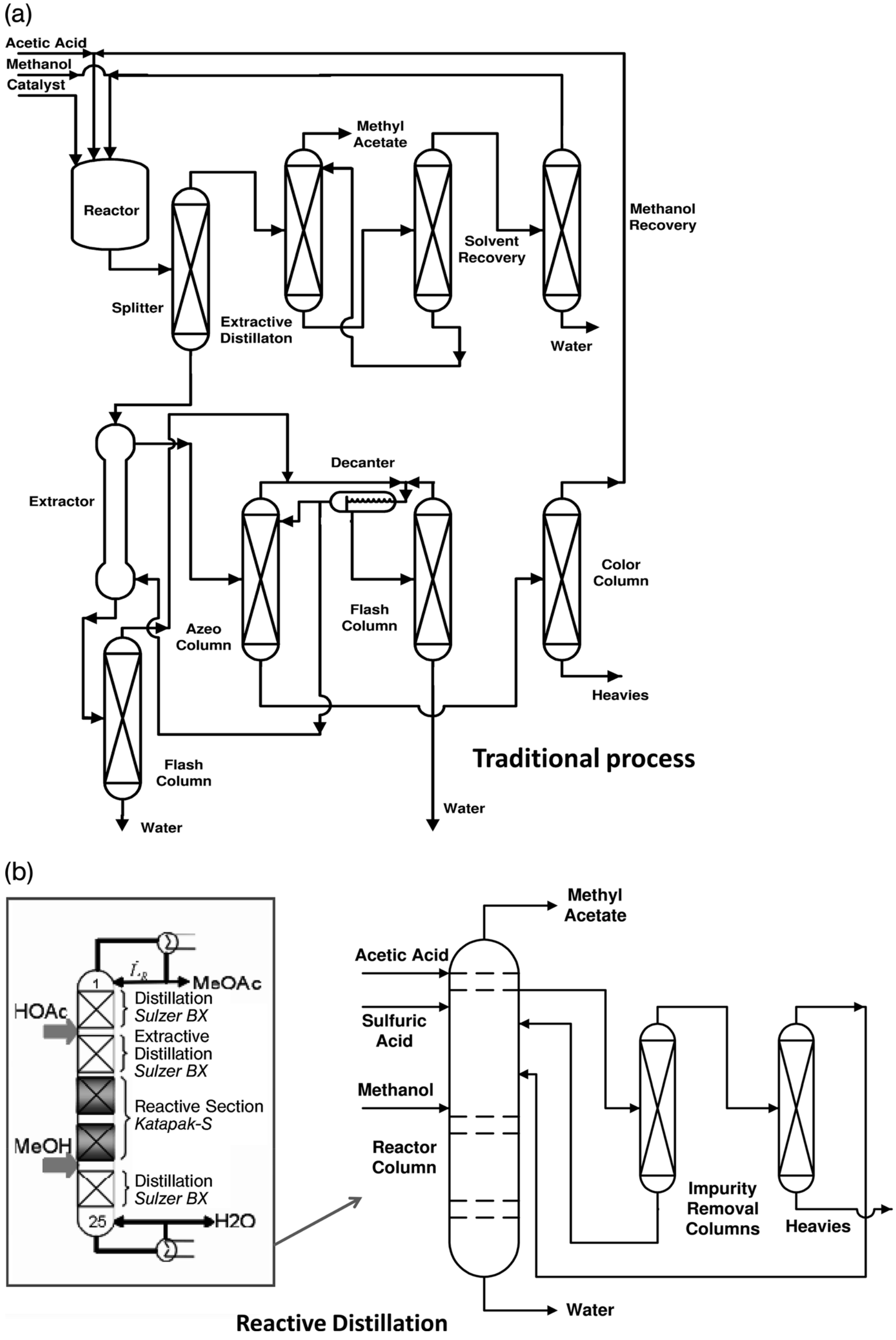


**Figure 1.16** Traditional (a) versus reactive (b) distillation process for the synthesis of methyl acetate.

Inherently safer design includes the following strategies and approaches:

1. **Hazard elimination**
   - Concept – eliminate hazards as a first priority rather than accepting them and mitigating them as a risk reduction strategy once they exist.
   - Potential methods:
     - eliminate the hazardous materials;
     - substitute with a non-hazardous material;
     - discontinue the operations.

2. **Consequence reduction**
   - Concept – where hazards cannot be completely eliminated, find less hazardous solutions to accomplish the same design objective by focusing on the consequences.
   - Potential methods:
     - reduce the quantity of the hazardous material;
     - provide a curbed area with a drain to contain and evacuate a spill and produce a smaller pool area of a spill;
     - separate the operation by adequate spacing to reduce exposure to adjacent operations and personnel.

3. **Likelihood reduction**
   - Concept – where hazards cannot be completely eliminated and after consideration of consequence reduction, consider ways to reduce the likelihood of events occurring.
   - Potential methods:
     - reduce the potential for human error through simplicity of design;
     - control ignition sources;
     - provide redundant alarms.

Inherently safer design is thus an intrinsic part of the sustainable chemistry and engineering [93]. It focuses on “safe” accidents, for example, immediate consequences of single events (fires, explosions, immediate effects of toxic material release) and includes considerations of chemistry as well as engineering issues such as siting, transportation and detailed equipment design. Several methodologies are relevant for an inherently safer design and implementation of the above strategies [92–96]:

- **Intensification:** The most widely used method of an inherently safer design is intensification. This involves the use of minimal amounts of hazardous materials so that a major emergency is not created even if all the plant contents are released. For example, hazardous reactants, such as phosgene, are often generated as required in an adjacent plant so that the actual amount in the pipeline is kept to an absolute minimum. Intensified designs are also available for reactors, liquid–vapor contacting equipment, heat exchangers, mixers, scrubbers, dryers, heat pumps and so on. “Inherently safer” designed equipment is smaller than conventional equipment, often cheaper, as well as being safer because less add-on protective equipment is needed.

- **Substitution:** If intensification cannot be achieved an alternative is substitution with safer materials. Nonflammable or less flammable, less toxic solvents, refrigerants or heat transfer materials should be used instead of flammable or toxic ones. For example, some ethylene oxide plants use hundreds of tonnes of boiling paraffin to cool reaction tubes and this represents a bigger hazard than the mixture of ethylene and oxygen in the tubes. Modern plants now use water for cooling instead of paraffin. Care must be taken to avoid the introduction of new hazards and risks as a result of substitution. For example, to protect the environment and prevent damage to the ozone layer, chlorofluorocarbon refrigerants are being replaced by liquefied petroleum gas and ammonia. However, this change can cause additional fire, health and safety risks, if not properly controlled.

- **Alternative reaction routes:** In addition to safer chemicals, it is also possible to reduce the risks associated with manufacture introducing changes in the reaction routes. We discussed extensively this case above with reference to the Bhopal accident. For the design of alternative reaction routes it is important to consider, in turn, reactants, catalysts, solvents, intermediates and the compatibility of all materials used. For example, in a particular process, acetone was used as a solvent. However, due to the heat of reaction, the uncontrolled addition of one of the reactants, or the loss of cooling, could led to a vigorous boiling of the mixture. The consequence is the possible over-pressurization of the reactor and loss of containment. The simple replacement of acetone with toluene, which has a higher boiling point, eliminated this hazard.

- **Modified storage arrangements:** If the above alternatives to achieve inherently safer processes cannot be applied and large quantities of hazardous material are still needed, then it should be handled in the least hazardous form or in minimum quantities. Consequently, large quantities of ammonia, chlorine and liquefied petroleum gas are now usually stored as refrigerated liquids, at low pressure below their boiling point rather than under pressure at atmospheric temperature. If a leak occurs in such circumstances the driving force is low and the evaporation rate is comparatively small. The inventories of toxic or flammable materials that are not manufactured on site can be reduced significantly from hundreds of tonnes to tens of tonnes if reliable and regular supplies can be delivered, perhaps on a daily basis or on a just-in-time basis. In these circumstances a release of such materials, although still involving a comparatively large quantity, reduces the potential to cause injury or damage. This approach does not necessarily involve modifications of existing plants, though smaller storage tanks would prevent inadvertent increases in the inventories in the future.

- **Energy limitation:** Consideration should also be given to limit the amount of energy available in the manufacturing process. For example, it is better to prevent overheating by limiting the temperature of the heat exchange fluid than to rely on interlocks that may fail or be disconnected.

- **Simplicity:** The final method to achieve inherently safer processes is to consider simplicity. Simple plants are inherently safer, because less equipment can fail and fewer opportunities for human error exist.

To develop inherently safer processes along the lines reported above, several formal review procedures are available that can be applied to a new chemical process or during the review of an existing process. These procedures include hazard and operability (HAZOP) studies and life cycle assessment (LCA) Studies. HAZOP studies are normally carried out late in the design when detailed diagrams are available and it is then too late to make significant changes. However, similar detailed studies should be made at the beginning of a project when decisions are made about products, routes, and so on. Figure 1.17 gives a flow diagram identifying the stages where inherently safety issues could be addressed within the process life cycle, starting with conceptual research and development through plant decommissioning and environmental fate.

It is at the conceptual stage in the process development where inherent chemical and process safety benefits can be best introduced. It becomes progressively more difficult to achieve such benefits in the later stages of process development.

In conclusion, inherent safety is achievable through safer processes, improved engineering and stringent safety procedures. Inherent safety will be cost-effective in the medium and long terms, even if higher costs may be incurred in the short term. It should be pursued to safeguard the health and safety of all involved, including consumers, and to protect the environment.

## 1.6
## A Vision and Roadmap for Sustainability Through Chemistry

To realize and implement a sustainable industrial chemistry requires not only the development of suitable methodologies and tools, and a legislative and social framework, as shown in this chapter, but also a vision and roadmap for sustainability through chemistry that is shared between all the stakeholders, from companies and research institutions to NGOs and civil/environmental associations. In fact, while industry has made great progress in adopting processes and chemistry with sustainable characteristics, a further decisive step towards a true sustainability requires long-term planning of R&D activities, for example, to establish a roadmap that can overcome the typical short-term R&D planning that has characterized the last decade. In fact, future progress requires technical and political challenges to be addressed. Industrial biotechnology appears to be a particularly fruitful area for building industrial sustainability, but new problems are posed. Radical improvements can also be achieved by new process design, including new reactor configurations, integration of operations both within and between enterprises and through a focus on recycling and reusing materials [100].

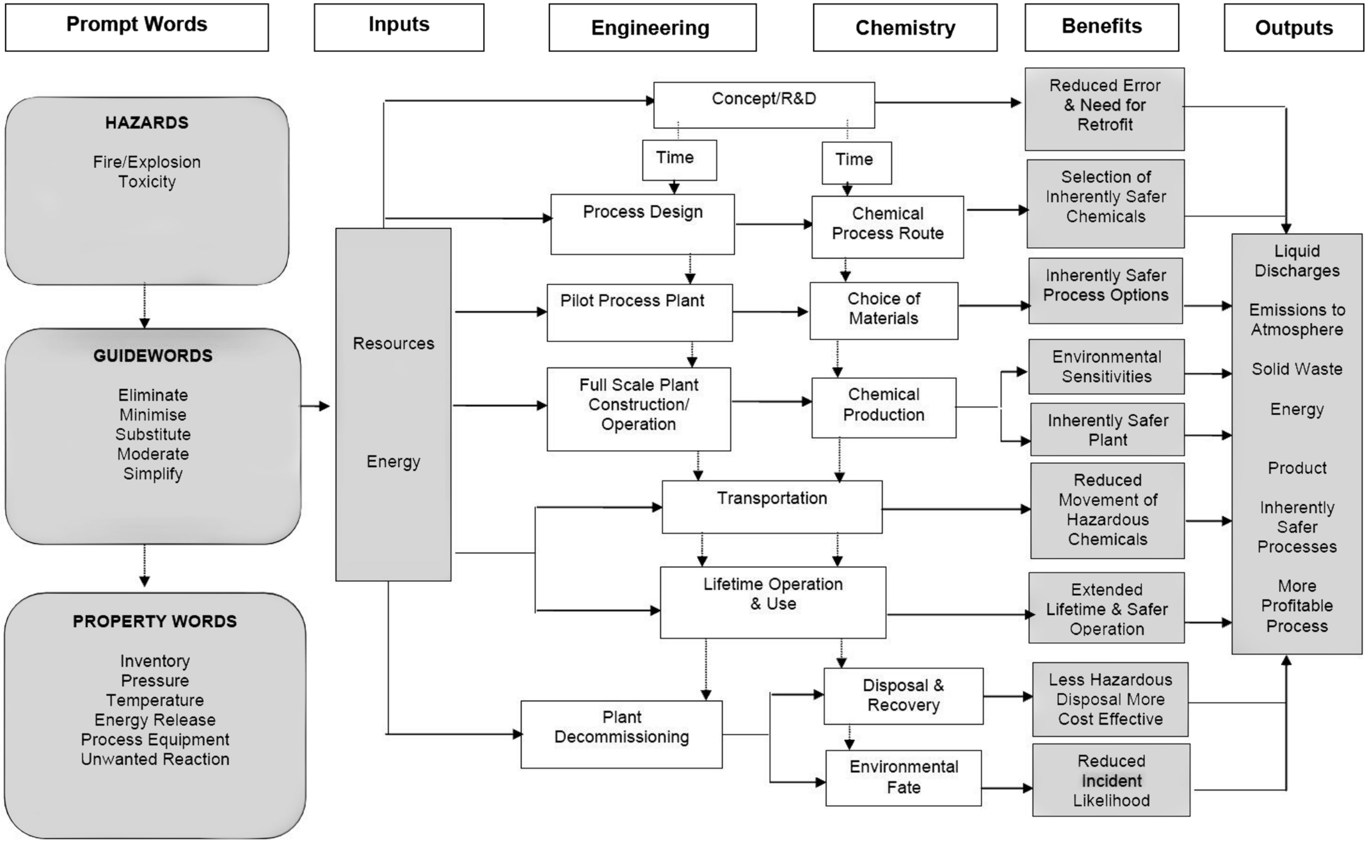


**Figure 1.17** Inherent safety life cycle. Source: Wrightson [94].

Many barriers exist to limit the implementation of radical improvements to industrial performance: incremental debottlenecking of plant and expansion is preferred in times of slow growth and a ‘first-of-a-kind’ process faces a high investment hurdle. The economic and regulatory environment needs to support investment in new technologies that demonstrates sustainable advantage but carry also higher technical risk than conventional operations.

To overcome these barriers and foster innovation and sustainability through chemistry requires a more synergetic integration of fundamental and applied research, and to effectively coordinate the effort along common priorities. One of the problems affecting the chemical industry in the last one–two decades has been the continuous re-organization and short-term view of the objectives that has caused a progressive worsening of the innovation index of the chemical industry; the index is defined as the number of new products/processes introduced on the market versus the number of products/processes already presented for more than five years. At the same time, new problems and issues have arisen: the increase in the cost of energy and raw materials, the double-digit economic growth in Asia and Latino/America, the increasing social pressure for sustainability, the need to use bioresources, and so on. It is thus necessary to reconsider the market strategies for development in chemical companies and put again innovation at the heart of chemical production. Defining a roadmap and an alliance to implement this roadmap is the first step in this direction.

These were the motivations for developing in Europe a Technology Platform for Sustainable Chemistry, which was promoted by Cefic (European Chemical Industry Council, http://www.cefic.be) and EuropaBio (The European Association for Bioindustries, http://www.europabio.org), but which involved also the active participation of many researchers and managers from academy, companies and other public or private organizations. The results of this effort are three documents: the initial Vision document, the Strategic Research Agenda (SRA) and the Implementation Action Plan (IAP) [6]. Although a roadmap exercise has also been made in other countries, these documents have probably seen the largest active participation in their preparation. They represents thus a genuinely shared effort to define priorities and planning actions for R&D in chemistry. Notwithstanding some limits and possible disagreement on some specific aspects, it is useful to summarize here the main aspects of these documents, as a good and reliable basis to define the needs and priorities to develop an industrial sustainable chemistry.

The original structure of the Technology Platform for Sustainable Chemistry (SusChem, http://www.suschem.org), which is then reflected in the cited document, was an organization in three main technology-oriented sections: (i) Industrial Biotechnology, (ii) Materials Technology and (iii) Reaction & Process Design. In addition, a horizontal section was also present. The actual structure has changed, reflecting the need for reorganization of objectives after completing the preparation of the cited documents.

While the SRA document was structured along the three sections indicated above, the IAP document was instead organized along eight areas (bio-based economy, energy, healthcare, information and communication technologies, nanotechnology, sustainable quality of life, sustainable product and process design, and transport) which reflected the structure of the seventh European Framework Program (http://cordis.europa.eu/fp7/home_en.html) in support of R&D in Europe. The SRA describes which science questions need to be answered to accomplish the vision, will define themes for future research and will contain technology roadmaps for those thematic areas aimed at providing 'fertile ground' for subsequent commercial development and exploitation in Europe. The IAP defines how the research themes, as identified in the SRA, are to be implemented and how the innovation framework conditions in Europe need to be altered to enable or accelerate innovation to directly promote the competitiveness of the EU chemical industry and optimize the benefits for all stakeholders.

The IAP also contains an introduction to three visionary projects that will practically demonstrate the benefits and impact on daily life of the sustainable industrial chemistry: (i) the Smart Energy Home, (ii) the Integrated Biorefinery, and (iii) the $F^3$ Factory; the latter has already been discussed in this chapter.

For conciseness, it is not possible to discuss in depth all the research themes and priorities identified, and the issues that need to be addressed in the short-, medium- and long-term to realize the full potential of research and innovation. We thus outline here only the general aspects, with references given to cited documents for details.

### 1.6.1
### Bio-Based Economy

Industrial biotechnology is a key technology to realizing the knowledge-based bioeconomy by transforming the knowledge of life sciences into new, sustainable, eco-efficient and competitive products. This includes an optimized combination of the biotechnology processes with classical and new biochemical processes – especially in the chemical, materials and biofuels sectors. The following three topics have been identified as being of major importance to facilitate the development of a bio-based economy and industrial biotechnology:

1. Biocatalysis – novel and improved enzymes and processes. Biocatalysis focuses on two aspects: (i) the discovery and improvement of novel selective biocatalysts suitable for industrial use and (ii) the development of a systematic process design technology for a quick and reliable selection of new and clean high-performance manufacturing process configurations. The aim of research in biocatalysis is to: (i) employ nature's toolkit to enable cleaner, safer and more cost-efficient processes, (ii) address the increasing need for selectivity, stability and efficiency using enzymes as catalysts, (iii) enable novel chemo-enzymatic processes through the discovery, evolution and/or design of enzymes and (iv) solve reaction and process problems through the search for novel biocatalytic functions and the selection of new high-performance process configurations. We may cite that

**Table 1.10** Case studies that demonstrate sustainability. Source: adapted from Kamm *et al.* [101].

| Selected case studies | Environmental impact | | | Economic |
|---|---|---|---|---|
| | Energy efficiency | Raw materials | $CO_2$ emissions | Production costs |
| Vitamin B2 (BASF) | + | ++ | + | + |
| Antibiotic cephalexin (DSM) | ++ | ++ | + | + |
| Scouring enzyme (Novozymes) | + | + | 0 | + |
| NatureWorks (Cargill Dow) | + | ++ | ++ | 0 |
| Sorona (DuPont) | + | ++ | + | + |

several environmental studies in which the impact of replacing chemical synthesis with biotech routes has demonstrated the benefits of industrial biotechnology [101]. In particular, two reports – one authored by the OECD [102], which includes 21 case studies on the impact of biotechnology on the environment, the other by a consortium of companies, industry associations, the Öko-Institut, and McKinsey [103] – have demonstrated clearly that industrial biotech can help to create jobs, boost profits and benefit the environment (Table 1.10). The German chemical company BASF was able to adopt biotech processes to transform the production of vitamin B2. Traditionally, its synthesis requires a complicated eight-step chemical process, but biotech reduces it to just one step. Soy oil is fed to a mould and vitamin B2 is recovered as yellow crystals directly from the fermentation process. This has cut production costs by 40% and reduced $CO_2$ emissions by 30% and waste by 95%. The antibiotic cephalexin has been produced on an industrial scale by the Dutch chemicals firm DSM for several years. Metabolic pathway engineering helps to establish a bio-route that reduce substantially the number of steps needed in the process. The biotech process uses 65% less energy, 65% less input chemicals, is water-based and generates less waste. In total, the variable costs of the process decreases to nearly half. Novozymes, a Danish biotech company, produces enzymes for the scouring process in the textile industry. Scouring, which removes the brown, non-cellulose parts of cotton, traditionally requires a harsh alkaline chemical solution. Use of enzymes not only reduces discharges into the water by 60% but reduces also energy costs by a quarter. Environmental and economic benefits go hand in hand: the new process is also 20% cheaper than the chemical treatment. Cargill Dow's bio-polymer PLA made from corn requires 25 to 55% fewer fossil resources than the conventional polymers against which it competes. With the help of biomass and potentially other forms of renewable energy for processing, the joint venture between Cargill and Dow Chemical believes PLA could even become a net carbon sink. In the near future DuPont's Sorona polymer will be based on propanediol (PDO) produced by fermentation, in collaboration with Tate and Lyle. This is estimated to reduce greenhouse gas emissions by approximately 40%.

2. Developing the next generation of high efficiency fermentation processes, including novel and improved production of microorganisms/hosts. Fermentation processes are commonly used today to manufacture numerous products; however, major technological improvements are needed to increase competitiveness. Current bottlenecks include low volumetric productivity and low yield of the microorganisms under non-optimal fermentation conditions in bioreactors. Another setback is the limited understanding of cellular behavior in bioreactor surroundings. Therefore, the major aims are to (i) enhance existing or new microorganisms to reach optimum production capacities under industrial conditions, (ii) develop analytical tools for monitoring the events in the bioreactor and mathematical models to control better processes and to improve their understanding for strain optimization and (iii) improve fermentation process engineering through better bioreactors and downstream processing.

3. Process eco-efficiency and integration: the biorefinery concept. Since it produces multiple products a biorefinery maximizes the value derived from the complex biomass feedstock. It relies on the best use and valorization of feedstock, optimization and integration of processes for a better efficiency, optimization of inputs (water, energy, etc.) and waste recycling/treatment. The main focus points of research are: (i) improving biorefining technologies, (ii) integrating the products into existing value chains and (iii) establishing strategies and business models for sustainability and competitiveness.

Regarding biorefinery, the recently published book *Biorefineries – Industrial Processes and Products* [101] provides an excellent overview of the status quo and future directions in this area.

Biotech also plays a critical role in rekindling chemical innovation. At a time of increasing competition from Asia in established products and the subsequent commoditization and strong price decline, chemical companies are once again looking at innovation as a key source of differentiation, as commented in previous sections. The importance of stimulating innovation can be seen by looking at the introduction of new polymers. During the twentieth century the development of fossil-fuel-based polymers increased steadily through to the post-war period, stimulated by the abundance and low cost of basic petrochemicals. It has, however, declined dramatically since 1960. Innovation in the traditional polymer industry today is mainly related to the application and blending of these polymers, rather than to the invention of new ones (Figure 1.18). Just as low-cost petrochemical building blocks such as ethylene, propylene and butadiene became available with the introduction of crackers in the 1930s it is necessary now to introduce new bio-based building blocks. These include lactic acid, which can be polymerized to the biopolymer PLA (polylactic acid). PLA has started to replace polyester because of its competitive cost and new applications. Lactic acid can also be processed into chiral drugs, acrylic acid, propylene glycol, food additives, and more. Other examples of innovation abound – Cargill is exploring the potential of 3-hydroxyproprionic acid as a new building block; BASF is looking into new chemistry around the simple organic molecule succinic acid; and DuPont will use cheap propandiol (PDO) as a monomer for its Sorona polymer.

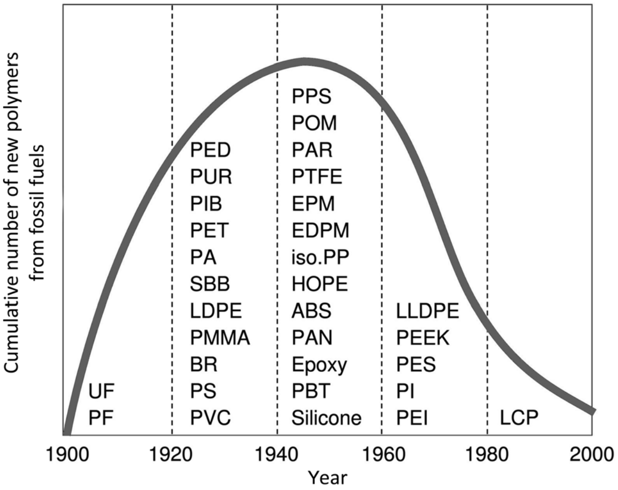


**Figure 1.18** Polymer innovation based on fossil-fuel building blocks. Source: adapted from Kamm *et al.* [101].

### 1.6.2
### Energy

A sustainable, safe and efficient energy supply is crucial for every country's economy. There is a critical need to rethink energy supply and use, since existing energy resources are limited both in volume and geographical distribution in the light of exploding global energy requirements. The problem of energy is complex and multifaceted. In terms of sustainable chemistry, there are three critical aspects: (i) developing alternative energy sources, (ii) saving energy by reducing energy loss through the smart application of materials and technologies and (iii) ensuring the safer and better storage of energy through innovative ways of use and transport.

The diversification of energy sources tailored to the requirements and resources of each country using nature's renewable resources such as the sun (photovoltaics), wind power, geothermal energy and biomass is a definite requirement. If solar cells are chosen to provide an alternative to fossil fuels, significant research work is needed: (i) to develop new routes for the production of crystalline silicon, (ii) in the development of amorphous silicon hybrid materials that could result in enhanced efficiencies, (iii) for further development of thin-layer technology, (iv) in concerted efforts for cheaper and more stable dyes, (v) in improving the efficiency of the dye-sensitized cells and (vi) in process development to deliver enhanced device performances, ensure sustainability and reduce production costs on an industrial scale.

However, to overcome present barriers, sustainable energy vectors should be developed in a harmonized way, taking into account all possibilities and related technologies, and not be limited to one or few sources. For example, in the transportation sector, several technologies present great potential: biomass conversion into biofuels, hydrogen fuel cells, hybrid engines and the exploration of metal nanoparticles as a fuel source. In the specific area of fuels from biomass, the production of liquid fuels, to be competitive, needs cheap and reliable sources of renewable raw materials and efficient production processes. The attention is on organic fuels such as methanol, ethanol, butanol and their derivatives, ETBE, MTBE, which can be produced by fermentation or gas to liquid technologies. Other points of attention are biodiesel and biogas, which can provide interesting biomass-based alternatives to diesel and LPG.

Bio-fuels should be not in competition with food. Therefore, new technologies need to be developed to efficiently convert cellulosic, fiber or wood-based, waste biomass into fermentable sugars. Similarly, to make biodiesel competitive as a transport fuel, efforts should be directed to diversify the use of raw materials and to improve the processes while making them more economic by developing added-value uses for by-products such as glycerol. Catalysis plays a critical role in achieving these objectives [9].

More efficient use and conservation of energy is possible, for example, by using OLEDs for lighting or novel nanofoams for insulation. Portable technologies require novel materials for the storage of energy, such as supercapacitors or new batteries. Higher specific energy, shorter charging times and long cycle life batteries need to be attained to keep pace with the increasingly demanding needs of personal electronic equipment. Lithium ion technology is currently the most promising for rechargeable batteries. Here, safety is key for the development of new systems (e.g., hybrid vehicles, energy networks, electronic devices).

Nanomaterials are expected to have a huge impact on active material design, due in part to their better resistance to structural strains and improved kinetics whatever the electrochemical system used (lead-acid, Li-ion or Ni-MH).

The envisaged hydrogen economy requires an efficient and safe hydrogen storage system. Hybrid organic-inorganic materials are a promising family of materials that includes dispersions of inorganic nanoparticles in organic (polymer) matrices; the converse, porous metal organic framework materials; pure nanoporous polymers; and organic macromolecules into mesoporous oxides such as silicas.

Supercapacitors containing electronically conducting polymer electrodes are of great interest, in particular for hybrid and electric vehicles due to their potential in the storage of large amounts of energy in a small volume. The largest hurdles towards marketable products are material development, production scale up and quality control.

### 1.6.3
### Healthcare

The challenges for the next century in healthcare are (i) an ever increasing number of patients with allergic, inheritable or contagious diseases and cancers, (ii) demographic trends and (iii) the exploding costs of healthcare.

Nanotechnology has the potential to revolutionize medical technologies and therapies, by providing the tools to cope with these challenges. The health sector will greatly benefit from the new products and technologies provided by materials science: treatments, medical devices and delivery systems. Drug delivery, whether targeted or smart, may be achieved through the novel design of materials, in the form of coatings or formulations. These materials enhance the binding of the active ingredient/pharmaceutical to receptor sites or delivery/entry into specific cell types (e.g., cancer).

Functionalized (magnetic) metal nanoparticles with suitable polyfunctional organic groups or polymer chains are able to link to specific biomolecules or receptor sites. Different nanostructured inorganic matrices are suitable as bone tissue substitutes and, furthermore, have the potential for controlled drug delivery, specific to bone pathologies. Currently, there are several problems with the application of nanoparticles in delivery systems, for example, their tendency to aggregate during storage or under physiological conditions. Understanding and preventing aggregation is thus extremely important.

Exploiting nanoparticulate formulations with nanoscale functionalities for new applications will have an immense impact on healthcare and quality of life. This will be achieved through effective drug applications, faster and non-invasive medical diagnostics, and through treatments. An important task will be to establish appropriate safety standards for these new products and formulations. Many of these actions require extensive research to be realized, particularly in the understanding of how structure–property relationships affect the interactions between biological cells/organs and pharmaceuticals, how sensors work in the body, and how to interface biological systems with signal transporting materials/devices.

Note that the focus here was on materials for healthcare, because this is the area that needs to be fostered from recent developments in science. The identification and design of new active pharmaceutical ingredients is clearly equally important, but innovation in this area is already a driver.

### 1.6.4
### Information and Communication Technologies

Information and communication technology (ICT) is a fast-moving consumer sector with a strong need for new materials and products to meet demands. The adoption of newly developed architectures and materials will lead to fundamental changes in the concepts and design paradigms of integrated circuits. Integration of nanostructures in device materials is thus a priority. Several new nanostructured materials, including carbon nanotubes, and silicon and germanium nanowires, are of potential interest for future device applications. Note that this problem of advanced nanoarchitecture of materials is critical not only for ICT but also in several other sectors (e.g., novel materials for energy). However, the mechanisms that control nanostructure, composition and size are not yet understood or mastered.

The role of catalyst composition and structure, in conjunction with temperature and gas composition (and other factors), in the production of, for example, carbon nanotubes is not understood in determining the structure. Understanding the mechanisms of how to control growth, structure, composition and orientation on predefined templates will be vital.

New methodologies of preparation are also vital to go beyond metal-oxide-semiconductor (CMOS) technology. Already, the semiconductor industry is investigating some very interesting areas such as spintronics, quantum computing and optical computing. Priorities will thus be as follows: (i) the application and introduction of new materials (polymers, nanomaterials, etc.), (ii) the control, production and integration of these new materials into devices with respect to cost and (iii) energy consumption.

Important facets are the understanding of interfaces between various materials, whether organic or inorganic; the use of self-assembly and patterning techniques in production; and the identification of new semiconductors, for example, carbon nanotubes. Furthermore, materials for information storage have also been addressed, such as holographic or new forms of switches (e.g., DNA, picosecond).

The need to fully characterize interfaces between nanomaterials integrated in an IC chip is of critical importance for their controlled production. Here, novel metrology techniques will be required to characterize the electronic and structural interactions at nanometer scale interfaces.

Studying the interaction forces between molecules and interfaces by means of atomic force microscopy and fluorescence-based technologies on the nanometer scale will provide valuable information on interfaces. Investigating surface functionalization processes with organic and biomolecular moieties, as well as self-assembly at surfaces, will enable insights into the basic properties of the interfaces.

### 1.6.5
### Nanotechnology

Nanotechnology is enabling new developments in material science, while providing innovations for industries such as construction, information and communications, healthcare, energy, transportation and security. The sustainable development of nanomaterials, including their potential for environmental protection and the appropriate assessment of possible risks, will contribute to sustainable economic growth.

The discovery of new materials with tailored properties and developed processing are the rate-limiting steps in new business development for many industries. The development of novel nanomaterials is necessary: their synthesis and production, their analysis and their design by computer modeling. A priority topic is synthesis, surface chemistry and processing. Innovations in materials technology and the design of advanced materials with tailored macroscopic properties based on their molecular structure are prerequisite for innovations in many industries. Interesting applications are nanostructured biosensors, smart packaging with enhanced barrier properties and functional surfaces.

The demands of tomorrow's technology translate directly into increasingly stringent demands on the chemicals and materials involved, for instance their intrinsic properties, costs, processing and fabrication, their benign health and environmental attributes, and their recyclability when focusing on eco-efficiency. There is a pressing industrial need to better understand complex physical, chemical and biological phenomena relevant to the mastering and processing of multifunctional and eco-efficient materials.

Another priority is the understanding of structure–property relationships, particularly at the nanometer scale. To understand the phenomena arising at this scale and to gain the ability to control structure, and integrate new properties related to a reduction of the material size, it is necessary to understand the structure–property relationship, including the control of materials' shape and size. There is a need to be able to analyze individual components, but also to analyze the properties of the whole system at the macroscopic level. Computational modeling will lead the way in providing insights into nanophenomena and thus assist the design of new materials.

### 1.6.6
### Sustainable Quality of Life

Sustainable industrial chemistry core goal is to improve the quality of life of citizens by applying new technologies and at the same time making citizens' lifestyles more sustainable, by achieving a lower environmental impact by consuming less energy, using fewer resources and reducing emissions. The focus revolves around the home – from energy collection via photovoltaic cells, novel insulation and lighting technologies, to eco-efficient processes. Particular attention is paid to the actions for waste treatment, for example, water purification and recycling to maintain this precious resource. The cited SusChem visionary project, the Smart Energy Home, will demonstrate how these technologies integrate in a home that produces, instead of consumes, energy and which minimizes the use of other resources such as water.

Reaching this objective requires the development of new energy-efficient construction materials, smart appliances, alternative energy systems in the home environment, insulation and sustainable products for the consumer.

### 1.6.7
### Sustainable Product and Process Design

The building blocks for sustainable product and process design are engineering, catalysis and chemical synthesis to achieve intensified, more eco-efficient, environmentally benign and competitive processes and production technologies.

Five main areas need to be developed to implement innovative process technologies and knowledge-based design as well as plant operation methodologies in chemical, pharmaceutical and biotechnological production:

1. Diversification of the feedstock base.
2. Innovative eco-efficient processes and synthetic pathways.
3. Knowledge-based manufacturing concepts for targeted and tailored products.
4. Implementation and integration of intensified process technologies.
5. Life cycle analysis.

Development in these areas will also provide opportunities for new business models, utilizing various feedstocks and directly targeting specific product end-use properties. A holistic approach is depicted to rationally integrate innovative chemistry and engineering developments and to develop the most viable option regarding the whole process.

The following research activities specifically aim to innovate processes and chemical/pharmaceutical manufacturing excellence in Europe:

- Innovative eco-efficient processes and synthetic pathways. This activity aims to achieve more eco-efficient chemical syntheses and corresponding processes with high resource efficiency and reduced amounts of waste. Some examples addressed are (i) specific transformations of functional groups, (ii) the utilization of highly selective multifunctional catalysts, (iii) the increased use of benign and easy-to-handle oxidants and (iv) alternative solvents. Targeted process technologies are the development of integrated reactive and hybrid separations and the utilization of non-conventional forms and sources of energy. There is clearly some coincidence with the topics discussed above regarding the green chemistry approach, but it may be noted that the general context and philosophy is different, further stressing the core concept of this chapter of the need to pass from a green chemistry to a sustainable industrial chemistry approach.

- Knowledge-based manufacturing concepts for targeted and tailored products. It is necessary to master product's end use properties through process design. Intensified product engineering requires extending the capabilities of continuous processing, in particular those of highly viscous and/or solid-containing process fluids with the ultimate goal of intelligent, self-adapting process devices. Other requirements are advanced formulation technologies, high-throughput tools for formulation engineering and process systems engineering techniques, as well as reliable scale-up methods for microencapsulation and the production of fine particles and nanoformulations.

### 1.6.8
### Transport

Chemistry plays an important role in realizing sustainable mobility and developing vehicles with improved eco-efficiency and recyclability, while increasing the safety and mobility of citizens. Key priorities are:

- sustainable management of materials, including the development of elastomeric products and materials to catalyze the decomposition of COx, NOx and SOx;
- development of new assembly technologies;
- onboard $H_2$ production;
- production of fuels containing low sulfur and aromatic components.

In the area of sustainable materials management, the need for lightweight but strong materials, which combine high performance with reduced environmental impact, should be noted. Reducing weight can be accomplished by developing innovative thermoplastic products for structural parts, leading to lower fuel consumption: (i) tough thermoplastic foams, (ii) organic filler-based thermoplastic composites and (iii) polymers with improved thermal resistance for further metal replacement (body panels).

More efficient airbag systems need to be developed to bring the best degree of protection together with weight reduction. Fibers offering a better cost–performance compromise could replace metal chords in tires, resulting in a significant weight reduction, thus producing less rolling resistance and reducing fuel consumption.

Alternative body assembly technologies – gluing versus welding and reversible assembly – need to be pursued to complement the move away from rigid assembly processes. The use of adhesives in the assembly process gives also the potential to reverse the process cheaply and efficiently. This can easily be done by dissolving the glue, particularly at the end of the lifecycle. Research should focus on high-throughput formulations and testing techniques as well as on the development of nondestructive analytical tools.

Chemistry also is central for the development of materials and technologies for traffic management sensors (collision avoidance, night vision), instant diagnostics, constant repairing materials (coatings), and silent cars and roads.

### 1.6.9
### Risk Assessment and Management Strategies

The introduction of emerging technologies requires reconsideration of the overall approach to risk assessment and management in the early stages of development. This is needed to ensure that the objectives for growth and innovation, and the protection of health and environment, are not compromised.

Especially in the light of long-term investments in innovation, a reliable consistent risk-based framework is essential on the regulatory side and in the public debate. The goals are the following:

- Identification and development of a reliable consistent risk management framework for the introduction of emerging technologies – addressing the critical points throughout product use to allow faster and more effective innovation.
- Capture and dissemination of integrated approaches for safety assessment within the context of regulatory decision processes for emerging/breakthrough technologies.
- Evaluation of how the gap between risk and perceived risk can be closed for new technologies.

The work should aim to define and characterize (i) risk, (ii) perceived risk, (iii) risk management options and (iv) risk communication options to meet stakeholder concerns. Key activities to reach these scopes are:

- intelligent risk management strategies;
- integrated assessment and acceptance;
- safety assessment of new technologies.

## 1.7
## Conclusions

The central concept of this chapter is the idea that sustainable industrial chemistry is more than green chemistry or engineering, and not an alternative politically-correct definition, as is usually reported in the literature and cited in lectures. Sustainable industrial chemistry is an holistic approach that has as its final aim the realization of sustainability through chemistry. It includes green chemistry and engineering concepts, and inherently safer design as well, but in a general framework and vision centered on the balance between economic growth and development, environment preservation and society promotion (health protection and quality of life), where innovation plays the driving role to realize this balance.

We have discussed a series of examples and aspects, such as the problem of risk and sustainability assessment, tools and principles for a sustainable industrial development (in particular, the issue of scaling-down and intensification of chemical processes, and the role of catalysis), and problems and opportunities in substituting chemical and processes (also in the view of REACH legislation, and of the international chemicals policy on sustainability). These topics are expanded in the following chapters, while the final section on industrial case histories for sustainable chemical processes provides further hints on these aspects.

The final section of this chapter has been dedicated to a concise discussion of a vision and roadmap for sustainability through chemistry, taken from the implementation action plan prepared by the European Technology Platform on Sustainable Chemistry. This plan evidences the pervasive role of chemistry for our society and thus how a next step is necessary in R&D to really realize a sustainable world through chemistry innovation.

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