12

Green Chemistry

12.1 The Principles of Green Chemistry

12.1.1 What is Green Chemistry

Many chemical products can be manufactured using a wide variety of synthetic routes. The designer of a chemical process must choose from alternative raw materials, auxiliary materials such as solvents and catalysts, reaction pathways, and reaction conditions, and these design choices can have a significant impact on the overall environmental performance of a chemical process. *Green chemistry*, refers to the design of chemical products and processes that reduces or eliminates the use and generation of hazardous and polluting substances.

The identification of environmentally preferable chemical processes requires extensive chemical and process knowledge and creativity. Since the number of alternative process pathways is very large and the implications of the alternatives so complex, it is not feasible to develop a systematic, quantitative design tool covering all possible process alternatives of all conceivable products.

Ideal chemical reactions would have attributes such as:

- Simplicity.
- Safety.
- High yield and selectivity.
- Energy efficiency.
- Use of renewable and recyclable raw and auxiliary materials.
- Use of raw materials with no or low content of impurities.

In general, chemical reactions cannot achieve all of these goals simultaneously, and it is the task of chemists and chemical engineers to identify pathways that optimise the balance of desirable attributes.

If the agenda specifically includes the use of renewable and recyclable resources and energy generation without fossils, the term *sustainable chemistry* is often used. Often the concepts of green chemistry and sustainable chemistry are used interchangeably, although green chemistry is the more common expression. Below we will most often use "green chemistry" although we also include issues of renewable resources and avoidance of fossils in energy generation.

The concept of green chemistry is here presented in two basic parts – one qualitative and the other quantitative.

In this Chapter

12.1.2 The History of Green Chemistry

Green chemistry was first promoted by IUPAC, the International Union of Pure and Applied Chemistry, in the late 1980s. The focus was first on the avoidance of environmentally hazardous products. Later the agenda broadened and the chemical processes themselves grew more important. More recently the fact that both raw materials and energy in the chemical industry mostly relies on fossils, and that these should be avoided, have been added. This is a large source of both pollution and un-sustainability, as the energy source is non-renewable.

OECD, the Organisation for Economic Cooperation and Development, later rephrased the IUPAC principles for Green Chemistry to principles for Sustainable Chemistry as the following:

- Design, manufacture and use of efficient, effective and environmentally more benign chemical products and processes.
- Maximise resource efficiency, energy and non-renewable resource conservation.
- Risk minimisation, pollution prevention, waste minimisation.
- Reuse and recycling of products.

OECD continues by pointing to areas where Research and Development, R&D, in sustainable chemistry is needed:

- Use of alternative synthetic pathways.
- Use of alternative reaction conditions.
- Design of chemicals that are inherently safer than current materials.
- Use of renewable or recycled feedstock.
- Avoidance of persistent, toxic or bioaccumulative substances.
- Increased energy efficiency.
- Use of green analytical methods in processing.

It will be clear from this chapter that much remains to be done to strengthen the knowledge background for making chemistry sustainable. OECD says:

Chemical production is still far from being sustainable; substance and energy flow is too high, as are the emissions of hazardous substances both during production and from the products themselves. The whole design of chemical processes and chemicals is a challenge that needs to be met by a new chemicals policy. Issues that need to be considered include atom economy, less hazardous chemical synthesis, design of safer and degradable chemicals, and the need to avoid auxiliary substances and unwanted by-products. A paradigm shift is necessary.

Bernd Jastorff, Johannes Ranke, and Reinhold Störmann, who have written the first textbook on sustainable chemistry, say that we need to add three new dimensions to the classical triangle (synthesis, analysis, and reaction mechanisms) of Organic Chemistry education: First the principles of saving energy and resources, secondly the assessment of toxicological and eco-toxicological consequences of chemicals, and thirdly the understanding of the principles of sustainable development.

12.1.3 Green Chemistry Methodologies

A qualitative approach to chemical process design involves raw material selection, selection of auxiliary materials such as solvents, catalysts, and other materials and the selection of reaction pathways and conditions.

Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. The *12 principles of green chemistry* [Anastas and Warner, 1998], provide a road map for implementing green chemistry. These principles have been adopted world wide.

1. *Prevent waste:* Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. *Design safer chemicals and products:* Design chemical products to be fully effective, yet have little or no toxicity.
3. *Design less hazardous chemical syntheses:* Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. *Use renewable feedstocks:* Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. *Use catalysts, not stoichiometric reagents:* Minimise waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. *Avoid chemical derivatives:* Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. *Maximise atom economy:* Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. *Use safer solvents and reaction conditions:* Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

9. *Increase energy efficiency:* Run chemical reactions at ambient temperature and pressure whenever possible.
10. *Design chemicals and products to degrade after use:* Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. *Analyse in real time to prevent pollution:* Include in-process real-time monitoring and control during syntheses to minimise or eliminate the formation of by-products.
12. *Minimise the potential for accidents:* Design chemicals and their forms (solid, liquid, or gas) to minimise the potential for chemical accidents including explosions, fires, and releases to the environment.

The first step is thus to avoid pollution. This principle is well established and in a way inherited from the earlier concerns about environmental impacts. The methods are those developed in product design and cleaner technologies. A careful monitoring of this aspect requires the use Life Cycle Assessment or some of the simpler life cycle methods. A more careful toxicological or eco-toxicological assessment of the chemicals and products themselves will be requested as part of proper chemicals management, and will be required for all bulk chemicals in the new EU chemicals directive, REACH.

The second step is to use renewable resources. Several possibilities of replacing non-renewable oil products exist. These include cellulose, starch, vegetable oils, etc. From them it is possible to produce bulk chemicals such as methanol, ethanol, etc. Many standard chemicals are also made microbiologically, including acetic acid, citric acid etc. This is also called vegetable chemistry.

The third step is to use biological or biologically inspired conditions. Ordinary petrochemical reactions are usually far from that state, with their high temperature, organic solvents, and moderate yields. Biological reactions are normally conducted at body temperature, in water solution, and without toxic components such as heavy metals. The methods used to approach this are found in biotechnology or biotech-inspired chemistry.

12.2. Selecting Raw Materials

12.2.1 Criteria for Green Chemicals

The synthesis and manufacture of any chemical substance begins with the selection of raw materials from which the final product will be synthesised. In many cases, the selection of a raw material can be the most significant factor of the impact of a chemical manufacturing process on the environment. There are a number of criteria that can be used in evaluating the potential environmental impacts of materials. One set of criteria that may be important in evaluating the environmental performance of a material is that it should have low persistence in the environment, low or no bioaccumulation potential, and low or no eco-toxicity and human toxicity. The scarcity of the material, and whether it is a renewable or non-renewable resource, may also be considered. The environmental impacts associated with creating the raw material are also important factors.

In selecting the raw material for a chemical process a number of general principles can be applied.

Innocuous. The selection of raw material for a process should start with the evaluation of the material itself, in order to ensure that it does not possess any hazardous properties.

Generate Less Waste. An important consideration associated with the use of a particular raw material is whether it is responsible for the generation of more or less waste than other raw materials. The type of waste generated is also an important factor to be considered.

Selectivity. Utilising a raw material or reaction pathway that is more selective means that more of the raw materials will be converted into the desired product. High product selectivity does not, however, always translate into high product yield (and less waste generated). Both high selectivity and high conversion must be achieved for a synthesis to generate little or no waste.

Efficiency. Reaction efficiency, like product selectivity, will offer cleaner production benefits. If the overall yield of a reaction is increased, less material ends up in the waste streams and more is converted into product.

Renewability. If chemistry is to be sustainable the raw material needs to be renewable. Considering that the chemical industry today is dominated by petrochemicals, this is a big challenge.

12.2.2 Selecting Raw Materials

Raw materials below will refer to organic chemicals, metals, and biological materials, especially wood.

The chemical industry is today dominated by oil products, petrochemicals. About 10% of all petroleum products are used as raw materials in the chemical industry. Oil is used to produce everything from simple hydrocarbons, solvents, aromatics, up to complicated compounds. Part of this production is polluting, e.g. through emissions of by-products such as sulphuric compounds, SO_x, and heavy metals, especially mercury.

To replace this with materials from renewable resources is difficult and will take time. It is perhaps not entirely necessary if the use of oil products for energy purposes is drastically reduced. Biological sources include forest products and cultivated crops. Rape seed oil, corn, and sunflower oil are already used as alternative raw materials. Various crops (corn, sugar cane, wheat etc) are used for the production of ethanol through fermentation; organic waste is used for the production of methane, biogas, through fermentation; and wood can be used for the production of methanol. All these chemicals can be used for the production of more complicated compounds. A long series of raw materials can also be produced from recycled products. To some extent this is true of petrochemicals, as returned plastic products are processed into chemicals for new products.

Metals such as iron, aluminium, and copper are less controversial as raw materials as they are present in abundance and are non-toxic. However, the extraction of iron and aluminium is combined with environmental impacts. The alternative is to use recycled metals. Thus recycled iron, scrap iron, copper, and aluminium are common as raw materials in industry.

Wood as raw material is renewable. It can be used to the extent that its long-term production rate allows. Still one needs to know that it is not a threatened resource, such as tropical wood. This can be guaranteed if only certified sources are used.

Below we will give a few examples of how selection of raw material can improve the environmental profile of manufacturing.

12.2.3 Hydrogen and Fuel Cells vs Fossil Fuels and Combustion

Fossil oil products are totally dominant as fuel, that is, energy carrier, for many purposes, especially transports. Alternatives now on the market include ethanol and biogas. In the long term hydrogen appears to be an even more interesting alternative energy carrier, as it may be used in fuel cells. Hydrogen and fuel cell technology is in the starting blocks. Fuel cells are now a viable technology that can readily be put into production, and billions are being spent throughout the world on the further development of this technology. Proton exchange membrane fuel cells (PEM) and solid oxide fuel cells (SOFC) appear to be particularly promising areas of fuel cell development. An interesting new development are nano-biological fuel cells that are using the photo synthesis reaction for generating electrons for the electrical circuit.

The largely oil-based European Union transportation sector gives rise to about a third of the total CO_2 emissions. Once the mass production of fuel cells begins, this source of carbon dioxide would be reduced. It requires that automobiles propelled by fuel cells will become competitive in price with conventional cars. In the transportation sector, the first fuel cell driven cars, buses and light motorcycles have already been introduced on the market.

Like the transportation sector, the energy sector is heavily based on the use of fossil fuels. It is estimated that 85% of the world's commercial energy sales are based on fossil sources of energy. A renewable energy system based on hydrogen would preclude any pollution and contamination from the power stations, and the idea of building large entities would become obsolete. Fuel cells are efficient, even in small units, and they are very scaleable. Hence a single installation can easily be expanded to higher output by increasing the number of fuel cell units. Another advantage of fuel cells is that the efficiency is quite high even at a low load. This is particularly important in power production.

However these promising scenarios depend on that hydrogen can be produced in a renewable way. We will now look into this challenge for green chemistry.

12.2.4 Production of Hydrogen Based on Fossil Raw Materials

There are no barriers to the introduction of hydrogen and fuel cells either from a technological perspective or from the vantage point of safety. In fact hydrogen has been produced and utilised industrially for over a hundred years.

Hydrogen can be produced from a number of different sources using different techniques. If hydrogen is produced from coal, oil, or natural gas, the ensuing by-products will be harmful to the environment if they are not handled in an environmentally sound way.

The majority of hydrogen production processes based on fossil raw materials are based on heating up hydrocarbons, steam, and in some instances air or oxygen, in a reactor, producing a mixture of hydrogen, carbon monoxide, and carbon dioxide.

Steam reforming of natural gas is currently the cheapest way to produce hydrogen, and accounts for about half of the world's hydrogen production. Steam, at a temperature of 700-1000 ºC, is fed methane gas in a reactor with a catalyst, at 3-25 bar pressure. In addition to the natural gas being part of the reaction process, an extra 1/3 of natural gas is used as energy to power the reaction.

The formula for the chemical reaction is:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

and for the following "shift reaction":

$$CO + H_2O \rightarrow CO_2 + H_2$$

giving the overall reaction:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

In this process 4 mol hydrogen is produced for each mol of methane. The percentage of hydrogen from water is 50%.

Autothermal reforming is a combination of partial oxidation and steam reforming. Burning hydrocarbons with reduced amounts of oxygen is called partial oxidation. The term autothermal reforming reflects the heat exchange between the endothermic steam reforming process and the exothermal partial oxidation. The hydrocarbons react with a mixture of oxygen and steam in a "thermo reactor" with a catalyst.

The processes described above produce gas with a high content of carbon monoxide – CO. It is therefore necessary to put the gas through the CO-shift process to increase the conversion to hydrogen. The shift reaction (see earlier) is a two-step process to achieve the most complete reaction between CO and steam. Initially steam is added in a high-temperature step (300-500 ºC), followed by a low-temperature step (200 ºC), with different catalysts in the two steps.

Each of the processes described above produces CO_2 in addition to H_2. In order to produce pure hydrogen gas, the CO_2 and H_2 must be separated. To separate hydrogen and CO_2, it is common to use amine-based absorption processes. This is conventional technology. Methods based on selective membranes or sorbents are under development.

12.2.5 Hydrogen Production Using Renewable Raw Materials

Over 70% of the earth is covered with water. The percent of hydrogen in water, measured by weight, is 11.2%. There is definitely an abundant supply. The advantage in using hydrogen as fuel is that, during combustion, it binds itself to the oxygen in the air, and creates water. Hydrogen is therefore totally renewable, and with this in mind, it could be said that we only "borrow" the hydrogen.

Breaking down water to hydrogen and oxygen is a process that requires energy. Heat, electricity, light, or chemical energy can be used for this purpose. If renewable energy is used, the resulting hydrogen will also be a clean and renewable energy carrier.

Water electrolysis is splitting water into hydrogen and oxygen. An electrolyser is a device for electrolysis. Water is subjected to electrical power and the result is hydrogen and oxygen.

$$2H_2O + \text{energy} \rightarrow 2H_2 + O_2$$

This is the opposite reaction of what happens in a fuel cell.

In the short term renewable electricity, green electricity, will have to come from hydro, wind, or wave power. In the longer term one may rely to some extent on electricity supplied by direct conversion of the solar radiation to electricity.

Case Study 12.1 Soldering of Integrated Circuit Boards – Lead vs Alternatives

Traditionally electronic components are connected on an Integrated Circuit Board by making an electrical and mechanical joint between the components connection pins and the copper connection network to make the electronic circuit, with *soft solder*. A solder is a low temperature melting metal or metal alloy. The most commonly used solder is an alloy of lead and tin.

The EU WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction of Hazardous Substances) Directives require that by 2006 all (with a few exemptions) electronic applications have to comply with the elimination of lead in the manufacture. The reason is that lead is a toxic and cumulative poison that causes damage to the nervous system.

This has driven the electronics industry to develop alternative lead-free soldering materials. Most of the alternative soldering materials are alloys between tin and one or more other metals. The first major difference between tin lead (SnPb) and lead free soldering is the melting temperature. The majority of lead free solders require higher melting temperatures (Table 12.1); therefore, the soldering processes must have sufficient heating capacity to solder the assemblies without damaging the hardware.

The second major difference between tin-lead and lead-free soldering is wetting. Lead free solders do not wet as well as tin lead. To improve wetting, nitrogen or more active solder fluxing additives must be used.

Table 12.1 Melting temperatures of soldering materials.

Solder alloys	Melting temperature
SnPb	183 ºC
SnBi	138 ºC
SnAgCuBi	215 ºC
SnAgCu	218 ºC
SnAg	221 ºC
SnAgCuSb	222 ºC
SnCu	227 ºC
SnSb	240 ºC
AuSn	280 ºC

Sources:
Kester, http://www.kester.com/en-us/leadfree/alloys.aspx
EFD, http://www.efdsolder.com/prod_alloys.htm

The sun's light energy can be converted directly into electricity in a single process using Photovoltaic (PV) cells, otherwise known as solar cells. A PV cell is a thin plate of light sensitive material made primarily of silicon, the second most abundant element in the earth's crust, and the same semiconductor material used for computers.

When the silicon is combined with one or more other materials, it exhibits unique electrical properties in the presence of sunlight. Electrons are excited by the light and move through the silicon. This is known as the photovoltaic effect and results in direct current (DC) electricity.

Many PV cells are linked together to create a standard PV module, which in turn are linked together into a PV array. PV modules have no moving parts, are virtually maintenance-free although they should be kept clean and clear of shading, and have a working life of 20-30 years.

12.2.6 Alternatives to Heavy Metals

In the classical chemical industry several heavy metals are important. As the toxic effects of heavy metals have become more obvious, alternatives to the use of heavy metals have developed. A well-known case is the replacement of organic *lead* (tetraethyl lead, $PbEt_4$) as anti-knocking agents in petrol with other compounds. This may be the single most significant step to reduce the toxic effects of heavy metals in our societies. Another case is the replacement of lead in soldering of metals (Case Study 12.1).

Another often cited large-scale alternative to heavy metal use is the replacement of *copper* wires with optical fibres in various electrical equipment.

Cadmium poisoning is increasing in the Baltic Sea region. One way to reduce cadmium use is to replace cadmium containing dies with alternatives. Cadmium may also be removed from phosphorus fertilisers.

The replacement of *mercury* in the process of production of chlorine gas and caustic soda is described below under "processes". Mercury has also been replaced in a series of other products. Thus amalgamates for repairing teeth can today be replaced with either plastics or ceramics. Ceramics, the most appealing alternative as it mimics the natural material hydroxyl-apatite, is still under development.

Below we will describe in some detail alternatives to the use of *chromium* in leather tanning. In this case it is the various toxic chromium compounds which are avoided by using alternative procedures.

12.3 Auxiliary Materials

12.3.1 Solvents

The most commonly used auxiliary materials in the chemical and the chemical-related industries are solvents. According to Toxic Release Inventory (TRI) data, 5 of the top 10 chemicals released or disposed of in the environment were solvents and include methanol, toluene, xylene, methyl-ethyl-ketone, and dichloromethane. With increasing regulatory pressure focusing on solvents, significant attention is being paid to the use of alternatives to traditional solvents. There are a number of general guiding principles in the selection of "solvents".

Use of less solvent. The amounts of solvents used can often be reduced. This is true both in processes as well as for cleaning applications, paints, etc. A reduced amount of solvent in a process as a rule results in physical changes in the product or for the process; viscosities of the process liquids are changed, process flows are reduced etc. This has to be taken into account by making equipment or process alterations, but normally these changes, e.g. replacing pumps, will not entail large costs.

Use of solvents with lower volatility. Often alternative solvents having similar properties, but with higher boiling temperature and/or lower vapour pressure, can be used. A replacement will result in lower emissions to the atmosphere. As in the former case one must be observant about secondary effects in the production process.

Use of less hazardous solvents. Solvents have been developed focusing on safety since they are used in such large volumes. The earliest and most obvious hazards that were addressed in the design of solvent molecules were their ability to explode or ignite. With the greater understanding of the health and environmental effects that could be caused by a large number of solvents, new solvents are being examined for other health hazards as well. Solvents are of particular concern because the likelihood of significant levels of exposure is high. Many solvents, by their nature, have high vapour pressures and, in combination with their use in large volumes, can result not only in the risk of explosions but also in significant exposures, with both acute and chronic health effects. Halogenated solvents such as carbon tetrachloride, perchloroethylene, and chloroform have been implicated as potential and/or suspect carcinogens while other classes of solvents have demonstrated neurotoxicological effects. Especially in these cases finding alternatives are important.

Use of solvents with less environmental impact. There are also a number of environmental implications of the use of large volumes of solvents. The use of solvents has caused both global and local environmental concerns. At the global level, the role of chlorofluorocarbons (CFCs) in stratospheric ozone depletion has led to a global phase-out of these substances from virtually all uses. Other solvents have been found to possess significant global warming potential and are thought to contribute to the overall greenhouse gas loading in the environment. At a more local level, the use of certain volatile organic compounds (VOCs) as solvents and in other applications has generated concern about their ability to contribute to the formation of secondary pollutants such as tropospheric ozone and other photochemical oxidants.

In investigating possible alternative solvents for an application, it is useful to refer to one of the ranking lists that have been developed. An example of such a list is given in Table 9.1 (Chapter 9). It is however important to realise that in replacing a solvent used in a process more factors than the potential hazard of the alternative must be considered.

12.4 Reaction Pathways

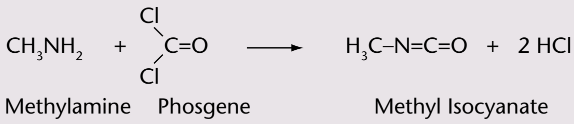
12.4.1 Finding Alternatives to Chemical Reactions

To identify chemical reaction pathways that may lead to better environmental performance of the production process of a product is complex and requires extensive chemical knowledge. But it is essential that a process engineer be able to identify classes of chemical reactions that have potential for environmental improvements.

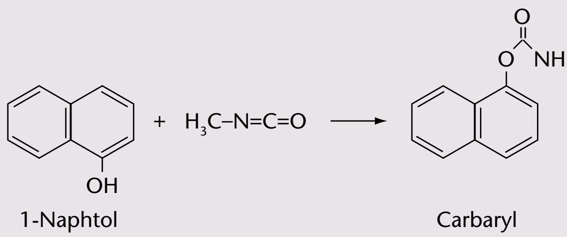
Addition reactions (A + B → AB), substitution reactions (AB + C → AC + B), and elimination reactions (AB → A + B), for example, all have different degrees of impact on human health and the environment. Addition reactions incorporate the starting materials into the final product and, therefore, do not produce waste that needs to be treated, disposed of, or otherwise dealt with. Substitution reactions, on the other hand,

Case Study 12.2 How to avoid the Bhopal Disaster

In the Bhopal disaster (Case Study 1.2 in Chapter 1) the pesticide produced was carbaryl or 1-naphthalenyl-methyl-carbamate from methyl amine, phosgene and 1-naphtol with methylisocyanate, MIC, as an intermediate product (Reactions 1 and 2). In the accident 40-45 tonnes of methylisocyanate was emitted due to a run-away polymerisation reaction in a MIC storage tank combined with inadequate safety precautions.



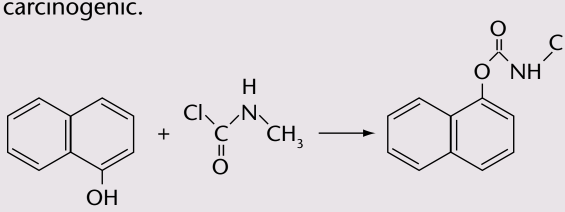
$$CH_3NH_2 + Cl_2C{=}O \longrightarrow H_3C{-}N{=}C{=}O + 2\,HCl \qquad (1)$$



(2)

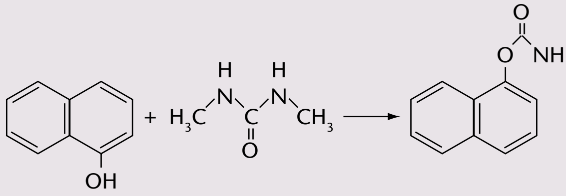
In this reaction sequence, two of the reactants are extremely toxic. Phosgene was used during the 1st World War as a chemical weapon and as such was responsible for the great majority of deaths due to chemical attacks. Methylisocyanate is the substance responsible for the toxic effects of the Bhopal accident.

There are a number of alternative reaction routes that will avoid the formation of MIC. In one such process 1-naphtol is reacted with methylcarbamoyl chloride to yield carbaryl and one mole of HCL (Reaction 3). However, the reactant methylcarbamoyl chloride is also toxic as well carcinogenic.



(3)

A recently proposed reaction uses dimethylurea in a catalytic reaction with 1-naphtol giving carbaryl directly and methylamine as a by-product (Reaction 4). Hereby the problem with toxicity of the raw material is solved.



(4)

However the product itself, being a pesticide, is of course a serious environmental problem. Pesticides can only be avoided by finding other methods to control crop damage.

necessarily generate equivalent quantities of substances as by-products and waste. Elimination reactions do not require input of materials during the course of the reaction other than the initial input of a starting material, but they do generate equivalent quantities of substances that are not part of the final target molecule.

Side reactions, which will generate by-products that need to be separated from the product mix, constitute another problem that needs to be dealt with. It is essential to minimise by-products both for efficiency and economic reasons, and if they are toxic or environmentally problematic, it is even more important. A semi-quantitative tool that a process engineer or chemist can use in evaluating reaction pathways is the concept of *atom and mass efficiencies*. The atom efficiency and mass efficiency characterise the fraction of starting materials that are incorporated into desired products.

Case Study 12.3 Alternative Ways for Chlor-alkali Production

The three dominating ways of producing chlorine and sodium hydroxide are the mercury, the diaphragm, and the membrane methods. In all three a solution of sodium chloride (NaCl) is electrolysed in electrolysis cells using a low-voltage direct electric current. All methods have the same gross formula:

$$\mathrm{NaCl + H_2O \rightarrow NaOH + ½Cl_2 + ½H_2} \qquad \Delta H = 218\ \mathrm{kJ}$$

or

$$\text{1.7 tons salt + water + 3300 – 5000 kWh} \rightarrow$$
$$\text{1.13 tons NaOH + 1 ton } \mathrm{Cl_2} \text{ + 0.03 ton } \mathrm{H_2}$$

The electrical energy for the electrolytic process has more the character of raw material than electricity. About half of the energy provided is found as chemically bound energy in the products, which can be seen in the reaction enthalpy, ΔH, being 218 kJ/mol or 1710 kWh/ton produced chlorine. It is the energy bound in the chlorine that gives it its remarkable reactivity. The requirements on the process are that the cell and process designs will give:

- Cl_2 and H_2 separate from each other
- Cl_2 free from O_2 and H_2
- NaOH free from NaCl
- Concentrated NaOH

The Mercury process

In the mercury process the anode for the electrolysis is made of carbon, and the cathode is liquid mercury. The reason for the choice of mercury as cathode material is that it enables the separation of the spaces where the chlorine is formed from where NaOH and hydrogen are. This will give a practically chloride-free NaOH and a hydrogen free chlorine. At the same time it effectively suppresses the mixing of hydrogen and chlorine which is a very explosive mixture. The electrolysis reactions are:

$$\mathrm{Na^+Cl^- \rightarrow Cl_2 + Na^+ + e^-} \tag{1}$$

$$\mathrm{Na^+ + nHg(liq) + e^- \rightarrow NaHg_n}\ \text{(Na – amalgam)} \tag{2}$$

$$\mathrm{NaHg_n + H_2O \rightarrow NaOH + ½H_2 + nHg\ (liq)} \tag{3}$$

Total:

$$\mathrm{NaCl + H_2O \rightarrow NaOH + ½H_2 + ½Cl_2}$$

The reactions are carried out in two steps. The part where the salt solution is electrolysed is called the primary cell, and where the NaOH solution is formed is the secondary cell.

In the primary cell, sodium ions migrate towards the mercury cathode, where they are converted to sodium metal that reacts with the mercury to sodium-amalgam (reaction 2). The chloride ions migrate towards the anode where the chlorine gas is formed (reaction 1). The mercury with the sodium amalgam is circulated to the secondary cell.

In the secondary cell the amalgam is decomposed with water to sodium hydroxide, hydrogen, and liquid mercury (reaction 3). The mercury is pumped back to the primary cell (Figure 12.1a).

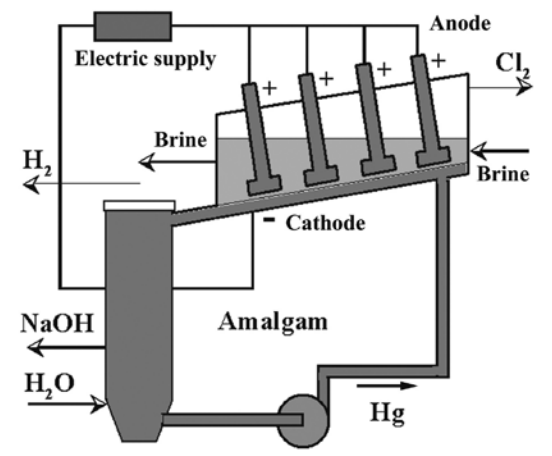


Figure 12.1a *The construction of an electrolysis cell for the mercury method used in the chlor-alkali process. See also the Cleaner Production Practice section.*

The Diaphragm process

In the diaphragm process a warm (70º) almost saturated solution of NaCl is fed to the anode compartment of the electrolysis cell where Cl_2 is formed. The solution flows through the diaphragm into the cathode compartment where H_2 and OH^- are formed. Continuous flow is

As an example of how it is possible to rethink a reaction pathway, the production of the pesticide carbaryl, 1-Naphthalenyl-methyl-carbamate, in an alternative way is described in Case Study 12.2. The classical way of synthesis involves very toxic compounds. It is this production that led to the disaster in Bhopal in India in 1984 (Case Study 1.2 in Chapter 1).

A recent example of how changing one reaction in a reaction sequence can cascade through the entire process pathway is the development of a new synthetic route for the production of ibuprofen. Ibuprofen is the active ingredient of a number of analgesic (pain reliever) drugs. The world production of ibuprofen exceeds 13,500 tons per year.

The traditional process for production of ibuprofen consists of a six-step synthesis with an atom efficiency of 40%, which means that only 40% of the raw materials for the process appear in the final product. The remaining 60% are undesired

achieved by hydrostatic pressure, different liquid levels in the two compartments. The diaphragm separating the anode and the cathode compartments allows ions to pass through the diaphragm but stops a mixing of hydrogen and chlorine gases. The flow direction from anode to cathode compartment was chosen to limit the migration of hydroxide ions into the anode compartment. The solution leaving the electrolysis cell contains ca 12% NaOH and 16% NaCl. The solution is evaporated in a crystalliser where NaCl is precipitated, yielding a final product with about 50% NaOH and 1% NaCl.

The Membrane process

In the membrane process the anode and the cathode compartments are separated by an ion-selective membrane that is impregnable by negatively charged ions like Cl^- and OH^-. The main reactions are:

Anode: $Cl^- \rightarrow \frac{1}{2}Cl_2(g) + e^-$

Cathode: $H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2(g)$

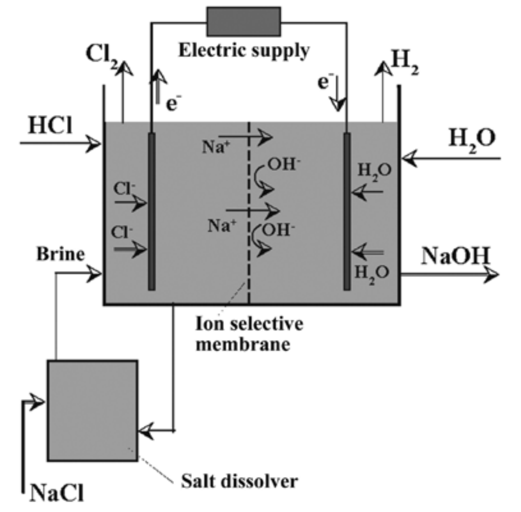


Figure 12.1b *The construction of a electrolysis cell for the membrane method used in the chlor-alkali process. See also the Cleaner Production Practice section.*

The main objective with the membrane is to hinder all side reactions. This enables the production of a practically chloride-free NaOH. The membrane technology also allows the cells to be made very compact. A plant with the membrane process takes up a floor space only a fraction of that required by a mercury process with the same production capacity (Figure 12.1b).

A comparison between the three processes

The Mercury process

This method yields a concentrated NaOH solution (ca 60%) that is chloride free. This entails major economic advantages. The hydrogen is free from other gases, but the chlorine can be contaminated with oxygen and hydrogen gas. But environmentally the mercury method is unacceptable since, despite large efforts towards process encapsulation and improved separation and recovery methods, there are still small but unacceptable emissions of Hg from the process.

The Diaphragm process

It is the technically least complicated method but requires extensive purification and concentration of the products. The diaphragms in the electrolysis cells are made of asbestos fibres which is a serious environmental and health risk. The process gives an almost hydrogen free chlorine gas but a contamination of oxygen is difficult to completely avoid. The NaOH produced is about 50% and the residual chloride concentration is about 1%.

The Membrane process

This is the latest development of the technology of chlor-alkali production. It has technical advantages over the mercury method and economic advantages compared to the diaphragm method. The major difficulty is finding a suitable membrane material. The most commonly used membrane is currently a thin ion-selective membrane based on a matrix similar to PFTE (Teflon). The gases produced have at least the same purity as in the diaphragm method. The NaOH is about 40% with a chloride concentration of no more than 50 ppm.

by-products and waste. The new process has only three catalytic steps and an approximately 80% atom utilisation, which easily can be increased to 99% if the recovered by-product, acetic acid, is utilised. In addition the new process saves 20-40% of the total energy required in the traditional process. All starting materials are either converted to products, recovered as by-products, or completely recycled in the process, virtually eliminating the production of waste.

12.4.2 Finding Alternatives to Chemical Processes

A number of industrial production processes may also be remade completely. There are several examples where new processes have been developed using e.g. new membrane technologies, heating with microwave radiation, separation using chromatography, etc. A creative approach is needed to find new alternatives, and no routine methods for this development seem to be available.

The conventional process for production of chlorine gas and sodium hydroxide, i.e. caustic soda, from sodium chloride, i.e. ordinary salt, is the mercury method. Here chlorine gas and caustic soda is produced by electrolysis of a concentrated solution of sodium chloride. The positive electrode (the anode) made of mercury dissolves metallic sodium produced in the process to form sodium amalgam. The amalgam is later transformed into (recycled) mercury and caustic soda. Even if the mercury is recovered, a significant amount of mercury leaks into the surroundings and is a major source of pollution. A chlorine alkali factory uses hundreds of tonnes of mercury.

Today alternative methods are used for production of chlorine and sodium hydroxides have found increased use. The most common are the diaphragm method and the membrane method, which are both mercury free. A disadvantage is that the caustic soda produced is less concentrated.

The description of the two technologies are found in Case Study 12.3 and in the Cleaner Production Practices section.

12.5 Biotechnology

12.5.1 The Promises of Biotechnology

Industrial production is too often characterised by use of organics solvents, high temperature, long reaction times, and not very good yields. This is very different from the way that the biological cell produces materials. Biological reactions occur mostly in a water environment, at room or body temperature, and with a very high yield. These reactions are typically catalysed by enzymes, which by themselves provide the hydrophobic environment that may be required for typical organic reactions to take place.

Biotechnological alternatives to traditional chemical processes are being developed and more and more introduced in large-scale production processes. Micro-organisms are being used in industrial production to produce many important chemicals, antibiotics, organic compounds, and pharmaceuticals. Using living organisms as chemical synthesis factories reduces many of the risks and complexities of industrial syntheses, allowing costly and polluting raw materials to be replaced, and

Figure 12.2 The mercury cell hall in the Skoghall chlor-alkali industry. *This hall houses 200 tonnes of metallic mercury. The production of chlorine from electrolysis of sodium chlorine solution was changed from using mercury cells to the so-called membrane method in 1987. Still there are two factories using the mercury cell method in Sweden and some 60 in Europe, many of them in Russia, 40 in Germany and 2 in Poland. These factories were the largest mercury polluters as metallic mercury was lost from the cells, which were yearly receiving large refills of the metal. Today the refills are reduced to 100 tonnes/year in western Europe, of which at least 10 tonnes are lost to air, water and products. In Sweden, mercury cells will be outlawed in 2010. (Photo: Courtesy of AkzoNobel Industries)*

the introduction of less expensive processes. The by-products of biosynthetic reactions are usually less toxic and hazardous than those of traditional industrial chemical reactions. The transition to cleaner industrial manufacturing does not necessarily require completely new and costly plant and equipment investments. Often, an introduction of biotechnological stages or a modification of an existing plant will achieve the desired result. However, we still await the introduction of biotechnology on a larger scale.

12.5.2 The Components of Biotechnology

Biotechnology usually refers to three distinct types of technologies.

Firstly, it refers to the *cultivation of biological cells* for technical purposes. Most common by far is the use of micro-organisms, bacteria and yeast cells. Classical biotechnological processes include the fermentation of sugar to produce alcohol, the oxidation or ethanol to produce acetic acid, and fermentation of organic material to produce methane. However a number of other processes rely on the use of biological cells. Chemicals produced on a large scale using bacterial processes include e.g. lactic acid, citric acid, and penicillin. The tanks used for the fermentations vary from hundreds of litres for special chemicals in the pharmaceutical industry to hundreds of cubic meters for bulk chemicals. Chemicals may also be produced in cultures of higher cells, both from animals and plants, e.g. in the pharmaceutical industry.

Secondly, biotechnology refers to the genetic change of cells, also called *genetic engineering*. With today's very highly developed DNA technologies, it is possible to make directed genetic changes in cells, and to introduce or block specific genes. Micro-organisms have been cultivated as special strains for very many years. More recently it has been possible to modify plant cells by genetic engineering; the resulting variants of plants are then referred to as Genetically Modified Organisms (GMOs). In animals the genetically changed individuals are often referred to as transgenic animals. Practically all micro-organisms used in biotechnology have been genetically fine-tuned for their purpose. Modified plant cells can be used for the production of several new components, which later have to be purified from the plant after harvest. Products from transgenic animals used for production, so-called genetic farming, include complicated bioproducts such as proteins, e.g. blood coagulation factors. Most of these are today either produced in cultivated animal cells or in micro-organisms.

A third very important part of biotechnology is the *use of isolated bio-molecules*, especially enzymes, for technical purposes. Enzymes are very sophisticated biocatalysts. Enzymes may be isolated from all sources mentioned above, especially from bacteria. Some of them are used in bulk without much purification, such as proteases for dissolving dirt in washing of clothes, or beta-galactosidase to reduce the lactose content in milk. Others are used as attached, immobilised, to a surface. The most common materials for this immobilisation are those used in chromatography. The resulting chromatographic column will then function as a bioreactor, conducting the process that the immobilised enzyme catalyses.

Enzymes are normally known as very delicate molecules, which cannot in any way be treated as the traditional chemicals used in the chemicals industry. However, more recently it has been possible to change them to survive the conditions typical of technical processes in two ways. One is that enzymes are isolated from bacteria found in hot springs. These are adapted to stand some 100°C heat and low pH, often close to 2. Another way is to genetically modify the enzymes to make them more resistant to tough conditions. This has been done e.g. for the proteases used in detergents.

Biotechnology is far from fully developed. The potential of biological methods to improve the performance of the chemical industry is huge, and systematic efforts to harvest this immense source of new environmentally friendly and non-toxic processes are just in their infancy. Ethical issues connected with this development exist, however, and should be considered carefully.

12.5.3 Textiles and Leather – Chromium vs Enzymatic Tanning

Leather tanning is the process of converting raw hides or skins into leather. The objective of the tanning process is to treat the hides and skins in such a way that the material is prevented from decaying, made resistant to wetting, and kept supple and durable.

During the tanning operation, collagen, the principal protein of the skin, will fix a tanning agent to its reactive sites, thus stopping the biological decaying of the material. The products which are capable of being fixed to skin to achieve tanning are many and varied.

Leather tanning is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Figure 12.3 presents a general flow diagram for the leather tanning and finishing process. The first steps of the process, trimming, soaking, fleshing, and unhairing, are operations in which the skins are prepared for the actual tanning process.

The tanning process itself includes the process steps bating, pickling, tanning, wringing, and splitting. Finally the material go through finishing processes that include conditioning, staking, dry milling, buffing, spray finishing, and plating.

In traditional chrome tanning, the skins and hides are washed and re-moisturised, remaining meat and fat is cut out and the hair on the outside of the skin is removed by soaking in a lime and sulphide solution, which either loosens or dissolves the attached hair. In some operations, the hair is only loosened through the caustic action of the lime, with the hair removed mechanically, followed by washing and drying. However, the more common approach for hair removal is to completely dissolve the hair and discharge it to the wastewater stream.

Following the pre-tanning processes the actual tanning starts with de-liming and bating in which non-leather-forming proteins are removed in order to give the leather softness, stretch, and flexibility properties. This is done by soaking the skins and hides in a solution of an ammonium salt and proteolytic enzymes. In the subsequent pickling step the acidity of the hides are adjusted by treatment with a brine solution and sulphuric acid.

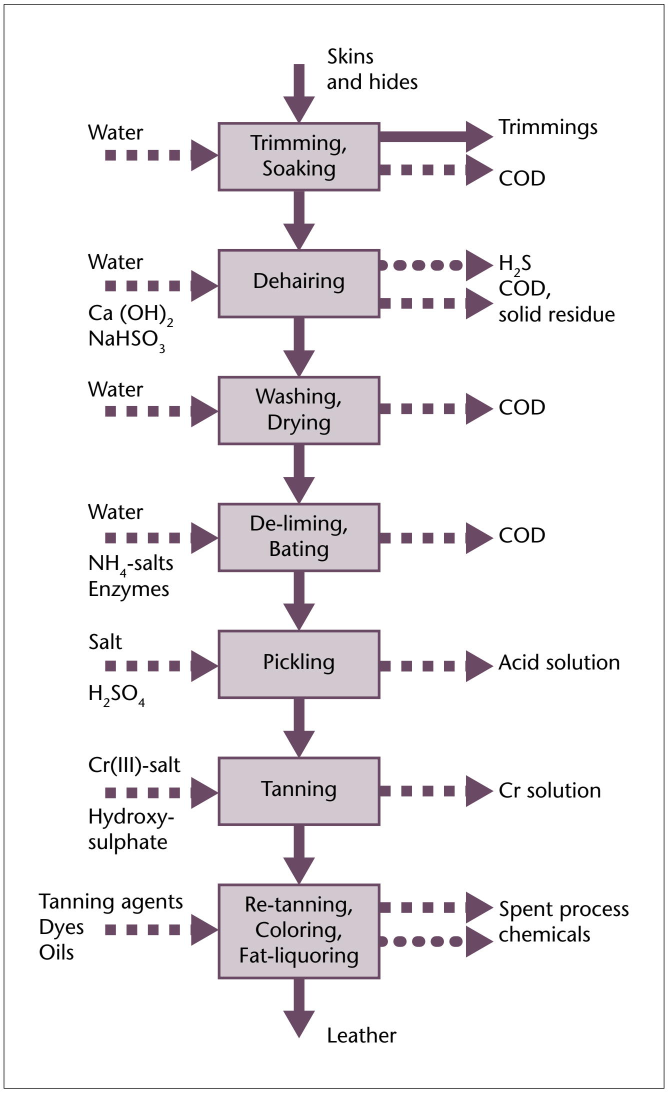


Figure 12.3 *Process flow diagram of leather tanning using chromium III as the tanning agent [UNEP, 1996].*

In the chromium tanning step chromium (III) hydroxysulphate reacts with the collagen in the hides, thereby preserving it from deterioration.

Another series of wet operations gives the leather the colour and other properties desired in the finished material. The tanned hides are placed into another drum for re-tanning, colouring, and fat-liquoring. Re-tanning is a second, shorter tanning operation normally using a tanning agent other than chromium, such as vegetable or synthetic tannins, formaldehyde or iron and zirconium salts. After the re-tanning, a pigment is added in order to dye the leather to the desired colour, after which the hides are taken out and wrung to remove excess moisture. Next a mixture of oils is added. This operation, called fat-liquoring, helps to produce the desired softness. Finally the leather is dried and physically conditioned.

12.5.4 Use of Enzymes for Leather Tanning

Several of the process steps in the traditional tanning process can be improved by replacing chemicals used with enzymes [Kamini, 2005]. In the tanning process the formation of hazardous pollutants is significantly greater in the pre-tanning stages than in the post-tanning ones. The chemicals mainly responsible for pollution in the pre-tanning are lime, sodium sulphide, and caustic soda as well as salt and de-greasing solvents. By introducing enzymatic treatment of the hides in the pre-tanning stages substantial reduction of hazardous pollutants is achieved. The type of enzymes used is proteolytic enzymes, proteases. By careful selection of specific strains of enzymes for the different pre-tanning stages, it is possible to produce non-polluting, easily biodegradable effluents. In the dehairing step the use of proteolytic enzymes instead of chemical treatment with lime and sodium sulphide will only digest the cells of the root section of the hairs, leaving the keratinised (hornified) parts unaffected, thereby enabling the recovery of hair with good quality and strength. Enzymatically dehaired skins also show better strength properties and greater surface area. The enzymatic action during dehairing, to some degree, also digests non-leather forming proteins as albumins, globulin and mucoids, and split collagen fibres. Because of this, separate bating and de-liming steps will be superfluous or at least greatly simplified.

Soft leathers such as glove and clothing leathers have to be de-greased. The traditionally used detergents and hazardous chlorinated organic solvents as perchloroethylene and trichloroethylene can be substituted with water-soluble enzyme lipases. The advantages of using enzymes for de-greasing are the elimination of solvents, reduction in surfactants, and possible recovery of valuable by-products.

In the tanning process, Chromium (III) is the most common tanning agent. In traditional chrome tanning the utilisation factor of Chromium is only about 66%. By introduction of high-exhaustion tanning and in-process chromium recycling the utilisation factor can be increased up to 98%. High-exhaustion tanning is achieved by increasing the reactivity of the collagen and increasing the penetration of chrome tannin's introduction of reactive groups into the chrome tannin complexes, so called masking, This is achieved by using additives or auxiliary preparations such as dicarboxylic acids, polycarboxylates, polyamids, oxazolidine, and others, together with optimisation of process parameters such as chrome concentration in the tanning liquid, temperature, pH, and reaction time.

The spent tanning liquid can be directly recycled in the process, either for pre-tanning or, after filtering, for preparation of fresh tanning liquid, thereby further reducing the amount of chromium emitted from the process.

Study Questions

1. Describe briefly the notion of green chemistry and list the original four IUPAC principles of green chemistry.
2. List and explain as many as possible of the 12 generally adopted principles of green chemistry.
3. How do you select raw materials in green chemistry? Give examples of "green" raw materials.
4. Explain why hydrogen is a particularly suitable energy carrier in green chemistry, and how it may be produced from non-fossil resources.
5. Compare the fuel cell and the combustion motor from an environmental perspective.
6. Give examples of how toxic heavy metals have been replaced by redesigning chemical processes.
7. Give some important principles used to find improved alternatives to chemical reactions.
8. Explain how mass efficiencies and atom efficiencies can be improved in a chemical process, and why it is important.
9. Give examples of how green chemistry based chemical reactions improve the economy, resource management, and environmental performance or of a reaction.
10. What is included in biotechnological processes? Describe and give examples of the three main technologies used.

Abbreviations

CFCs	ChloroFluoroCarbons.
DC	Direct Current electricity.
IUPAC	International Union of Pure and Applied Chemistry.
MIC	Methyl Iso Cyanate.
OECD	Organisation for Economic Cooperation and Development.
PEM	Proton Exchange Membrane fuel cells.
PFTE	Poly Tetra Fluoro Ethylene (common trade name Teflon).
PV	PhotoVoltaic cells.
R&D	Research and Development.
RoHS	Restriction of Hazardous Substances (EU directive).
SOFC	Solid Oxide Fuel Cells.
TRI	Toxic Release Inventory.
VOCs	Volatile Organic Compounds.
WEEE	Waste Electrical and Electronic Equipment (EU directive).

Internet Resources

Organisation for Economic Cooperation and Development (OECD) – Environment Directorate/Chemical Safety
http://www.oecd.org/ehs/

Green & Sustainable Chemistry Network
http://www.gscn.net/

U.S. Environmental Protection Agency (EPA)
– Green Chemistry
http://www.epa.gov/greenchemistry/

American Chemical Society (ACS)
http://www.chemistry.org/

The Royal Society of Chemistry (RSC)
– Green Chemistry Network
http://www.chemsoc.org/networks/gcn/

Interuniversity National Consortium
"Chemistry for Environment" (INCA)
http://venus.unive.it/inca/

International Union of Pure and Applied Chemistry (IUPAC)
http://www.iupac.org

First International IUPAC Conference on Green Chemistry, September 2006.
http://www.chemistry-conferences.com/2006/09/10%20-%2015%20IUPAC%20Conference%20on%20Green%20Chemistry%20(Dresden%20-%20DE).htm

Greenchem
– A research programme at Lund University, Sweden
http://www.greenchem.lu.se/