13.15: Feedstocks and Reagents

Feedstocks

Feedstocks are the main ingredients that go into the production of chemical products. As discussed below, feedstocks may be acted upon by reagents, and often there is some overlap between the two categories of materials. Feedstocks are so important in the practice of green chemistry that much of Chapter 14, "Feeding the Anthrosphere: Utilizing Renewable and Biological Materials," is devoted to renewable feedstocks. Here they are introduced briefly as they relate to green chemistry and sustainability.

There are three major components of the process by which raw materials from a source are obtained in a form that can be utilized in a chemical synthesis, then converted to a product. The first of these is the **source** of the feedstock, an aspect that has a number of environmental and sustainability considerations. This may consist of a depleting resource, such as petroleum, in which case the lifetime of the resource and the environmental implications of obtaining it must be considered. From the standpoint of sustainability it is preferable to use recycled materials as feedstocks, although the availability of recycled materials suitable for this purpose is limited. A third source that is very desirable consists of renewable resources, particularly from materials made by photosynthesis and biological processes.

The second major aspect of converting feedstocks to final products is separation and isolation of the desired substance. An example of this step is the isolation of specific organic compounds from crude oil to provide a feedstock for organic chemical synthesis. It may be necessary to process raw materials from a source to convert it to the specific material used as a feedstock for a chemical process. Often most of the environmental harm in providing feedstocks comes during the isolation process, in large part because of the relatively large amount of waste material that often is generated in obtaining the needed feedstock.

The world chemical industry has been built primarily on fossil carbon feedstocks. Much of the impetus for the organic chemical industry was built during the late 1800s and early 1900s on the basis of organic chemicals isolated from the coal tar byproduct of coal coking. Later petroleum and natural gas became the basis of the petrochemicals industry which has produced enormous quantities of polymers, plastics, synthetic rubber, and thousands of other kinds of chemicals. Eventually this reliance on depleting fossil carbon resources must end. Therefore, one of the main goals of green chemistry has become a shift toward renewable feedstocks — biomass produced by photosynthesis — and to renewable reaction media, specifically water and supercritical and pressurized liquid carbon dioxide. In addition to being renewable, such feedstocks offer advantages over petroleum in that they are not toxic and they, and most of their products and intermediates, are biodegradable.

Biomass Feedstocks

The ongoing shift to a biobased economy offers the opportunity to design their processing and products on the basis of green chemistry and sustainability. Rather than petroleum refineries, biorefineries are used to process biobased feedstocks. Initially, the feedstocks used have been from grains of corn and oil seeds, such as soybeans. Cornstarch is hydrolyzed to sugars that are converted to alcohols by fermentation processes and to biodiesel fuel by esterification of the fatty acids in the oil seed lipids. Some commodity chemicals such as lactic acid are also made from grain sources. However, these are inefficient ways to utilize biomass, they compete with the consumption of grain for food, and the maximum production of grain requires intensive cultivation (often of marginal land), heavy use of fertilizer, and strong reliance on pesticides. A much more renewable approach is to utilize lignocellulose, the structural material of plants (such as wheat straw) either from dedicated crops or preferably from crop byproduct biomass or highly productive algae growing in water. Although attempts are being made to break down these lignocellulose materials with enzymes to produce fermentable sugars, a preferable pathway is the thermochemical route. This can be by pyrolysis of the biomass to produce a variety of organic liquids, some gas and a carbon residue that can be burned to provide heat for the pyrolysis. Alternatively, biomass can be reacted directly with hydrogen to produce liquid and gas products. Both pyrolysis and hydrogenation produce a large variety of liquids including oxygenated organics that can be run through a biorefinery. As discussed in Chapter 15 on energy, the best approach is thermochemical gasification of the biomass to produce a synthesis gas mixture of CO and H_2 that can be used with well known technology to synthesize gasoline, diesel fuel, aircraft fuel, alcohols, substitute natural gas, and various organic chemical feedstocks.

Genetic engineering can be very useful in producing biomass for feedstocks. One area in which there is much room for improvement is in enhanced efficiency of photosynthesis. Crops can be bred to increase the amount of byproduct biomass along with the grain they produce. Dedicated crops can be developed for the production of large quantities of biomass, alone. This has already been done using conventional plant breeding techniques to develop rapidly growing hybrid poplar trees that produce large quantities of lignocellulosic wood.

Carbohydrate Feedstocks

The most abundant biomass feedstocks are carbohydrates. It follows that one of the most promising pathways to obtaining useful raw materials and fuels from biomass is their synthesis directly from carbohydrates. As an example of a feedstock chemical that can be synthesized from fructose, a monosaccharide made in abundance from cornstarch and sucrose (common table sugar) is dimethylfuran (Figure 13.9) an oxygen-containing cyclic organic compound that has most of the desirable properties of hydrocarbons as a fuel and raw material. As shown in Figure 13.9, fructose and dimethylfuran have similar structural formulas and the conversion is largely a matter of removing oxygen from fructose by reaction with hydrogen. This synthesis and monosaccharide glucose as a feedstock are discussed in Chapter 14.

Green chemistry and the inevitable shift away from petroleum hydrocarbon feedstocks to biobased materials will cause a massive realignment of the chemical industry. Rather than manufacturing nondegradable materials using environmentally unfriendly technologies with depletable feedstocks, the new paradigm will employ green catalytic processes to convert biomass feedstocks to biocompatible (non-toxic, biodegradable) products.

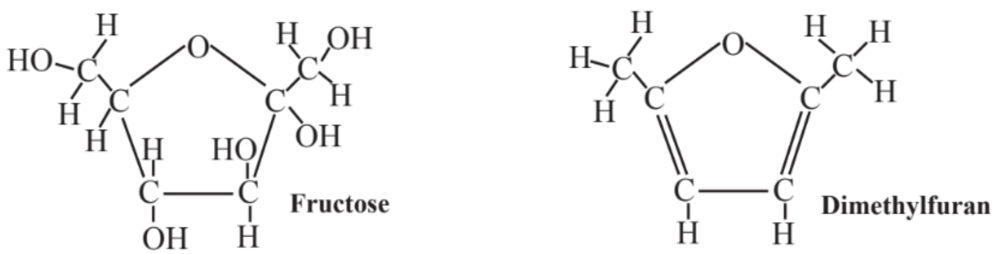


Figure 13.9. Fructose, a carbohydrate produced in abundance by plants, can be used to make dimethylfuran, a compound that resembles hydrocarbons in many of its properties and that can be used as a motor fuel and as a feedstock for organic synthesis.

Reagents

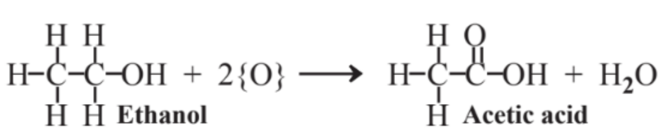
The term **reagents** is used here to describe the substances that act upon basic chemical feedstocks to convert them to new chemicals in synthetic processes. The kinds of reagents used have a very strong effect upon the acceptability of a chemical process with respect to green chemical aspects. Much of the work that has been done in developing and using green reagents has involved organic chemical processes, many of which are beyond the scope of this book. However, some of the general aspects of chemical reagents from a green chemical perspective are discussed here.

The most obvious characteristic required of a good chemical reagent is that it do what it is supposed to do completely and at an acceptable rate. A reagent with a high **product selectivity** produces a high percentage of the desired product with a low percentage of undesired byproducts. Another desirable characteristic of a good reagent is high **product yield** meaning that most of the feedstocks are converted to product. The use of reagents that provide high selectivity and yield means that less unreacted feedstock and byproduct material have to be handled, recycled, or disposed.

One of the most common measures taken in implementing green chemical processes is selection of alternative reagents. The criteria used in selecting a reagent include whether or not itis available, how efficient it is, and the effect that it has. Important considerations with the chemical transformation are whether it is stoichiometric or catalytic, the degree to which it is atom economical, and the quantities and characteristics of any wastes produced.

Reagents for Oxidation and Reduction

One of the main kinds of reactions for which reagents are used is **oxidation**, which usually consists of the addition of oxygen to a chemical compound or a functional group on a compound. (See Chapter 5, Section 5.7 for a discussion of oxidation and its accompanying phenomenon, reduction and section 13.8 regarding oxygen availability in oxidants and hydrogen availability in reductants.) An example of an oxidation reaction is the conversion of ethanol to acetic acid,



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where {O} is used to represent oxygen from some unspecified oxidant. Oxidation is one of the most common steps in chemical synthesis. A number of reagents are used as oxidants. Some of these reagents, such as potassium dichromate, $K_2Cr_2O_7$ are dangerous (dichromate salts are considered to be carcinogenic when inhaled for prolonged periods of time) and leave troublesome residues that require disposal.

Because of problems with oxidants that are commonly used, a major objective in the practice of green chemistry is to use more benign oxidants. Alternatives to the more traditional oxidant reagents include molecular oxygen (O2), ozone (O3), and hydrogen peroxide (H_2O_2), usually used with a suitable catalyst that enables the oxidation reaction to occur. Under the right conditions, hydrogen peroxide can be used as an alternative to elemental chlorine, Cl_2, a strong oxidant used to bleach colored materials, such as paper pulp and cloth. Since chlorine is toxic (it was used as a poison gas in World War I) and has a tendency to react with organic compounds to produce undesirable chlorinated organic compounds, hydrogen peroxide is a much preferable bleaching agent.

In contrast to the usually harsh conditions under which chemical oxidations are carried out, organisms carry out biochemical oxidations under mild conditions. In so doing, they use monooxygenase and peroxidase enzymes that catalyze the oxidizing action of molecular oxygen or hydrogen peroxide. An area of significant interest in green chemistry is to perform such oxidations in biological systems or to attempt the use of catalysts that mimic the action of enzymes in catalyzing oxidations with molecular oxygen or hydrogen peroxide.

Reduction, which consists of loss of O, gain of H, or gain of electrons by a chemical species is also a common operation in chemical synthesis. As is the case with oxidants, the reagents used to accomplish reduction can pose hazards and produce undesirable byproducts. Such reductants include lithium aluminum hydride ($LiAlH_4$) and tributyl tin hydride.

Electrons as Reagents for Oxidation and Reduction

As an alternative to the potentially troublesome oxidation and reduction procedures using reagents, **electrochemistry** provides a reagent-free means of doing oxidation and reduction. This is possible because an electrical current consists of moving electrons and oxidation consists of electron removal from a chemical species and reduction is addition of an electron. The passage of an electrical current between metal or carbon graphite electrodes through a solution resulting in oxidation and reduction reactions is called **electrolysis**. Consider the simplest possible case of electrolysis, that of water containing a non-reactive salt, such as Na_2SO_4, shown in Figure 13.10.

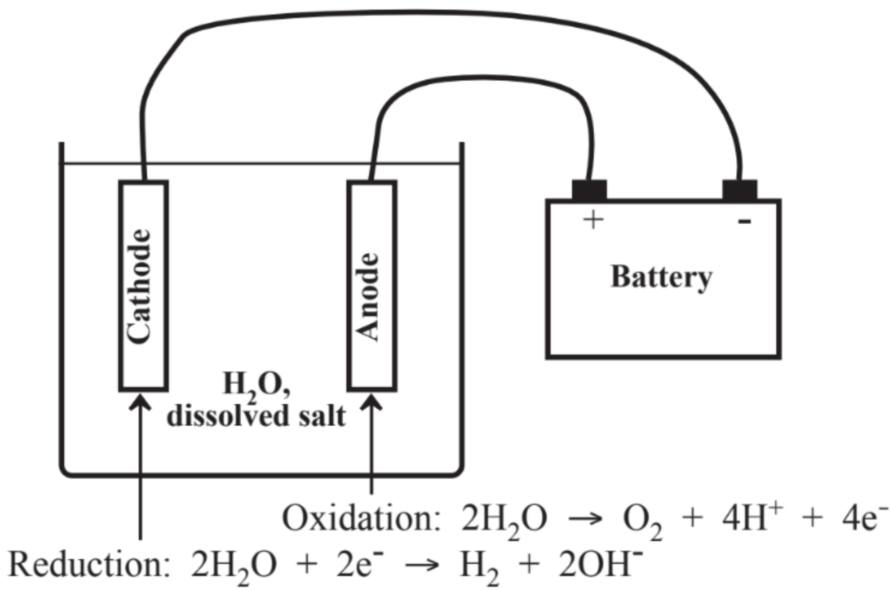


Figure 13.10. Apparatus for electrolysis in which a direct current of electricity is passed through a reaction medium, in this case water with a dissolved salt to make it electrically conducting. Reduction occurs when electrons are added to the medium at the cathode and oxidation when they are removed at the anode. Electrolysis is a reagent-free way of doing oxidation and reduction.

At the **cathode**, where electrons (e-) are pumped into the system and where reduction occurs, reduction of water occurs releasing H_2,

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{13.15.1}$$

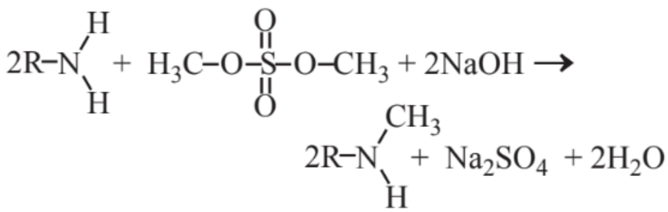
and at the **anode** where electrons are removed, O_2 is released as the water is oxidized:

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{13.15.2}$$

In the setup shown, H+ion generated at the anode OH-ion generated at the anode diffuse through the solution and react upon contact to produce water again. At the cathode, a dissolved chemical species could be reduced directly or the hydrogen generated could add to a species, reducing it. And at the anode another species could be oxidized directly by loss of electrons or the oxygen generated could add to a species, oxidizing it.

Miscellaneous Reactions with Reagents

Reactions other than oxidation and reduction are carried out by reagents. As an example of a commonly performed reaction that normally requires potentially troublesome reagents, consider **alkylation** with alkylating reagents in which an alkyl group, most frequently the -CH_3 (methyl) group, is added to an atom on an organic compound. The methylation reaction,



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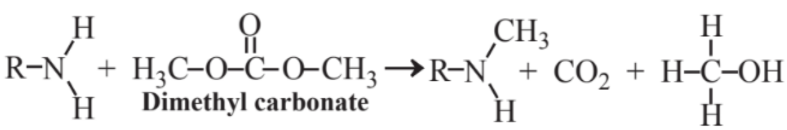
shows attachment of a methyl group to an amine group, -NH_2, that is part of an unspecified molecule represented “R.” Methylation of nitrogen is used in a number of chemical syntheses including preparation of analgesics such as Ibuprofen. The dimethyl sulfate reagent used to accomplish the methylation poses toxicity problems in that it is a suspect human carcinogen. The reaction also produces a byproduct of Na_2SO_4, which if contaminated with dimethyl sulfate reagent may pose disposal problems.

Dimethyl carbonate prepared by reacting methanol, CH_3OH, with carbon monoxide, CO, in the presence of elemental oxygen and a copper salt catalyst has been developed as a green alternative to dimethyl sulfate as a methylating reagent. When dimethyl carbonate acts as a methylating agent,



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methanol and innocuous carbon dioxide are generated as byproducts. The methanol can be recirculated through the system to generate additional dimethylcarbonate reagent.

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