

*Figure 1.10* The light and dark reactions of oxygenic photosynthesis. The light-driven production of oxygen occurs in reaction centres embedded in the thylakoid membrane. The electrons from this process reduce NADP to NADPH, and also enable the production of ATP from ADP and inorganic phosphate ( $\text{P}_i$ ). The dark carbon fixation cycle occurring in the stroma is driven by NADPH and ATP.

first ‘stable’ product of  $\text{CO}_2$  reduction is a three-carbon compound) is the commonest mechanism, operating in algae and most plants. Some plants, especially those indigenous to hot climates, such as corn (maize) and sugar cane, operate the  $\text{C}_4$  cycle. Edwards and Walker discuss these and other carbon fixation cycles such as the CAM cycle in Chapter 4; Blankenship (2002) provides a full account.

#### 1.4 Energy-storage efficiency of photosynthesis

Photosynthesis is the only natural process able to store a significant amount of solar energy as chemical energy in biomass: terrestrial plants, particularly trees, are the main repositories. However, nature has not entered photosynthesis for any energy efficiency awards—the imperative for any photosynthetic organism is replication, not the accretion of biomass. Nonetheless, if the energy-storage process were not adequately efficient, it would not serve this primary purpose.

In our context, the energy-storage efficiency of photosynthesis is of course of great interest. It determines the flux of energy into the biosphere, the land area required to produce a given number of food calories, and the biomass yield from a

given area of an energy crop plantation. In this section, we first look at the structures of the carbohydrates that are the main energy-storage compounds of photosynthesis, and then the maximum gross and net efficiencies permitted by the characteristics of the photosynthesis reaction, and finally the energy-storage efficiencies actually achieved in the wild and in cultivated crops.

#### *1.4.1 Carbohydrates*

The immediate end product of photosynthesis is the monosaccharide D-glucose. Fig. 1.11a shows its structure in its usual cyclic form. Both plants and animals break down this simple sugar to obtain energy via the metabolic process known as glycolysis. The end product of this depends on the nature of the organism and whether oxygen is present. In green plants in normal, aerobic conditions, glycolysis proceeds (via the citric acid cycle) to form the fully oxidised products  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and the energy released by this process, when coupled with respiratory electron flow, drives the synthesis of 36 molecules of ATP (adenosine triphosphate), the energy-carrying molecule that is found in the cells of all living organisms.

Glucose that is not immediately required by a photosynthetic organism is polymerised, to provide both the oligosaccharides often associated with lipids and proteins and the polysaccharides that constitute the main structural materials and nutritional reservoirs of plants. Cellulose (Fig. 1.11b) is the most abundant structural material, constituting about half the cell-wall material of wood and higher plants, and accounting for over half of all the fixed carbon in the biosphere. It is a linear polymer of up to 15,000 D-glucose residues held by hydrogen bonds in a rigid assembly of great strength. Glycogen (Fig. 1.11c), the chief food reserve of photosynthetic bacteria and animals, is a branched polymer of D-glucose residues. Starch, which is the main food reserve of plants as well as a major nutrient for herbivorous animals, is a mixture of the two polysaccharides  $\alpha$ -amylose (an isomer of cellulose) and amylopectin (similar to, but more highly branched than, glycogen).

#### *1.4.2 Gross efficiency ignoring respiration*

Green plants contain carbon in a reduced state, mainly as carbohydrates. The chemical energy stored in these compounds is released when they are metabolised in the living plant, or when the plant biomass is burned or otherwise oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Since plant biomass is mainly comprised of D-glucose polymers, the energy

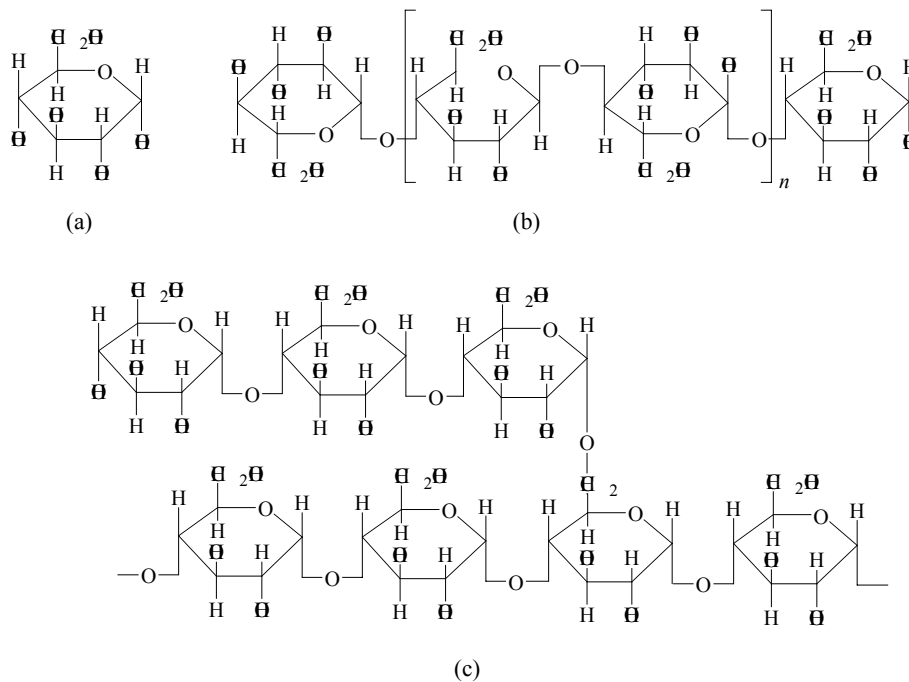
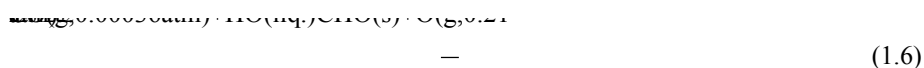


Figure 1.11 Structures of the energy-storing carbohydrates of photosynthesis: (a) D-glucose, in its common cyclic form  $\alpha$ -D-glucopyranose; (b) the linear polymer of D-glucose residues that is the primary structure of cellulose; (c) glycogen, a highly branched polymer of D-glucose residues.

released when biomass is oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is roughly equal to the enthalpy of synthesis of D-glucose from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Under normal atmospheric conditions, we can write this reaction as



where  $\text{C}_6\text{H}_{12}\text{O}_6$  is D-glucose. For this reaction,  $\Delta H = 467 \text{ kJ}$  and  $\Delta G = 496 \text{ kJ}$  at 298 K; the standard values are  $\Delta H^\circ = 467 \text{ kJ}$  and  $\Delta G^\circ = 480 \text{ kJ}$  (Bolton, 1979).

Neglecting for the moment the inevitable loss of some biomass in a living plant by the process of respiration, we can define the photosynthetic energy (enthalpy) storage efficiency  $\eta_{\text{PS}}$  of a green plant, acting as a photoconverter of solar energy, as

$$\eta_{\text{PS}} = \frac{\text{Energy stored in biomass}}{\text{Solar energy incident on the plant}} \quad (1.7)$$

To calculate  $\eta_{PS}$  for sunlight of a given spectral distribution, Schneider (1973) and Bolton (1979) rewrote eq. 1.7 as

$$\eta_{PS} = \frac{N_A \int_{\lambda_{min}}^{\lambda_{max}} \phi_{\lambda} \alpha_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_{\lambda} d\lambda} \quad (1.8)$$

where  $N_A$  is the Avogadro constant and, for the wavelength band  $\lambda$  to  $\lambda + d\lambda$ ,  $I_{\lambda}$  is the incident solar spectral photon flux (photons  $m^{-2} s^{-1} nm^{-1}$ ),  $I$  ( $W m^{-2} nm^{-1}$ ) is the incident solar spectral irradiance  $\alpha_{\lambda}$  is the spectral absorptivity (fraction of light absorbed by the plant),  $\phi_{\lambda}$  is the quantum yield for the production of  $O_2$  or consumption of  $CO_2$ ,  $\Delta H$  is the enthalpy of the photosynthesis reaction, and  $\lambda_{min}$  and  $\lambda_{max}$  are the minimum and maximum wavelengths that effect the reaction.

Using experimental data at 10 nm intervals for  $\alpha_{\lambda}$ ,  $I$ , and  $\phi_{\lambda}$ , Bolton (1979) calculated  $\eta_{PS}$  from eq. 1.8 and obtained a value of  $(9.2 \pm 0.8)\%$ . This is the upper bound on the gross efficiency of energy storage in a healthy growing leaf, ignoring respiration. In using experimental values of  $\alpha_{\lambda}$  and  $\phi_{\lambda}$ , it takes account of the dip in  $\alpha_{\lambda}$  values in the green and  $\phi_{\lambda}$  values towards the red. If  $\phi_{\lambda}$  were to maintain the 'ideal' value of 0.125 (or 8 photons per  $O_2$  molecule evolved) from 360 nm to 700 nm and then drop off as the experimental values from 700 nm to 720 nm, the gross efficiency would rise even higher, to 13.3%.

#### 1.4.3 Net efficiency allowing for respiration

The calculated gross energy-storage efficiency of ~9% of a green plant can never be achieved in real life because all photosynthetic organisms must constantly consume a portion of their stored energy in the process of respiration to obtain the energy to stay alive. Respiration effectively reverses oxygenic photosynthesis, and so reduces the energy-storage efficiency to a net value below the gross value.

There are two types of respiration—dark respiration and photorespiration, the latter occurring only in the light. The rate of dark respiration in green leaves lies in the range 0.5–4.0  $mg CO_2 dm^{-2} hr^{-1}$  at 25 C (Zelitch, 1971). This has only a small effect on the efficiency in bright sunlight, subtracting perhaps ~0.2% from the gross efficiency. Photorespiration, on the other hand, is responsible for a much more serious loss of fixed carbon. In plants using the normal  $C_3$  carbon fixation cycle, photorespiration occurs at such a rate that some 30% (at 25 C) to 40% (at 35 C) of the gross yield of photosynthesis is lost. Plants using the  $C_4$  cycle lose rather less.

The combination of dark respiration and photorespiration reduces the calculated maximum net efficiency of photosynthesis to a value between 5.3% at 35 C and 6.2% at 25 C (Bolton, 1979). This agrees well with other estimates: 5.3% (Bassham, 1976); 5.5% (Hall, 1977); 5% (Boardman and Larkum, 1975). This is the expected instantaneous maximum efficiency for a healthy leaf growing in optimal conditions. There are a number of factors, explored in the next section, that reduce time-average values well below this, although short-term values can approach 5%.

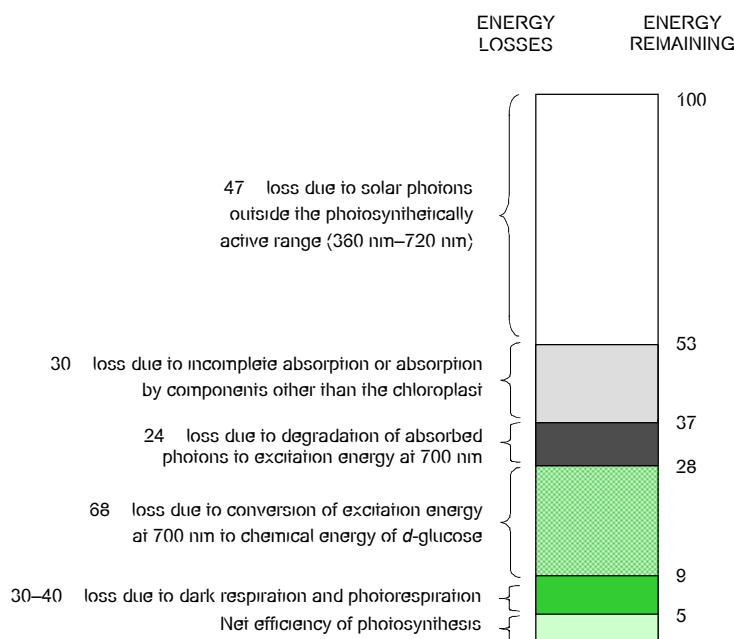


Figure 1.12 Energy losses in photosynthesis.

Figure 1.12 shows in another way how the upper bound of ~5% on the energy-storage efficiency of a green plant comes about. Nearly half (47%) of the solar energy incident on a plant is lost because it lies outside the photosynthetically active range of 400–700 nm. A further 16% is lost by incomplete absorption of PAR (Photosynthetically Active Radiation) or by its absorption by components other than the chloroplast. A further 9% is lost by thermalisation—the degradation to heat of the ‘excess’ energy of absorbed photons of wavelength below 700 nm, that is, energy above 1.77 eV, which is the threshold or ‘bandgap’ energy  $U_g$  of P700. A further substantial loss of 19% arises because the synthesis of D-glucose stores only the

fraction ( $H/8U_g$ ) of the energy of eight thermalised P700\* states. That leaves only ~5% of the incident solar energy to be stored as chemical energy. This is still a formidable value; the instantaneous energy-storage capability of a green leaf in the Sun leaves most artificial molecular photoconverters of solar energy in the shade.

#### 1.4.4 Efficiencies achieved in wild and cultivated crops

The time-average energy-storage efficiency of green-plant photosynthesis is much lower than the instantaneous maximum values of ~5% calculated in the previous section, for a number of obvious reasons. For example, the growing season is limited, the plant canopy does not intercept all incident sunlight, light levels may be too low or too high for maximum photosynthetic efficiency, and plant growth may be inhibited by factors such as water or thermal stress.

The global energy-storage efficiency of photosynthesis can be calculated from knowledge of net primary production (NPP), the mass of carbon fixed annually by photosynthesis. Global NPP is ~100 GtC yr<sup>-1</sup>, about half on land and half in the oceans (see Section 6.5). The molar free energy of the photosynthesis reaction (eq. 1.6) is 496 kJ mol<sup>-1</sup>, which corresponds to a specific energy-storage capacity of 41.3 kJ g<sup>-1</sup> fixed carbon. Global NPP of 100 GtC yr<sup>-1</sup> thus corresponds to ~4 × 10<sup>21</sup> J of chemical energy stored in photosynthetic biomass per year.

The total solar energy received at the Earth's surface is 2.75 × 10<sup>24</sup> J yr<sup>-1</sup>. Thus the net efficiency of photosynthesis averaged over Earth's surface (land and oceans) is ~0.15%. About half of the incoming solar energy is in the PAR range of 360–720 nm, so the energy efficiency of PAR utilisation is ~0.3%. Modest as these efficiencies are, the amount of energy stored annually by photosynthesis is about ten times greater than current world energy consumption.

Agriculture—the cultivation of plants for food—arose in the Fertile Crescent about 10,500 years ago. Traditional methods of plant breeding by the selection and crossing of species with favourable characteristics (for example, hardiness and plant size) have hugely improved food crop yields since then. Energy-storage efficiencies of 0.5–1.0% on an annual basis are typical in modern food crops, and short-term yields can be as high as ~4%. C<sub>4</sub> plants, with their modified CO<sub>2</sub> fixation pathway, have considerably higher efficiencies than C<sub>3</sub> plants, especially in tropical and sub-tropical areas where their growth rate is less likely to saturate under high light levels. In future, global warming may extend the geographic range of some crops and trees to higher latitudes, and increased CO<sub>2</sub> levels may increase growth rates.

It is not widely appreciated that traditional plant-breeding techniques were effectively an imprecise form of genetic engineering: plants that have favourable characteristics and are therefore selected for breeding have favourable genotypes, which are therefore selectively replicated in future generations of plants. About half of past improvements in yields of rice, wheat and maize is due to genetic inputs. Recently, plant-breeding methods have been extended by two new 'genetic' techniques: tissue culture, which allows the crossing of favourable genotypes at cellular level to form new cultivars, and genetic modification, which involves the incorporation of individual genes directly into plant genomes. Despite the current outcry about GMOs (genetically modified organisms), a significant part of future improvement is likely to come from transgenically improved plants. Denis Murphy describes the enormous potential of 'agbiotech'—the application of genetic techniques to improve food and non-food crop traits and yields in Chapter 13.

### **1.5 Energy and chemicals from biomass**

Biomass was one of humanity's earliest energy sources, and it remains an important resource today and for the future. Traditional plant biomass, particularly fuelwood, currently supplies a significant part of the energy needs of the developing world. Used and regrown sustainably, such energy sources could become an important component in a future CO<sub>2</sub>-neutral energy economy. In the USA, biomass provides nearly 4% of final energy consumption. In the EU, biomass provided 7% of total primary production in 1997. Methane produced by landfill wastes is used to generate electricity as a matter of good practice in many countries.

Plant biomass resources include wood and wood wastes, agricultural crops and their residues, and aquatic plants and algae. Energy can be derived from biomass in three main ways:

- by direct combustion to provide heat and light as such, or to raise steam and hence generate electricity;
- by gasification to provide 'biogas', a combustible gas mixture predominantly consisting of H<sub>2</sub>, CO and CO<sub>2</sub>, that can be used for heating or electricity generation or converted to useful chemicals such as methanol;
- by fast pyrolysis at temperatures around 480–550 C, giving a high yield of 'bio-oil', an espresso-coffee-like liquid that can substitute for conventional fuel oil in transport and static applications.