Lecture 23, 2001

Photosynthetic Process

The conversion of solar energy into chemical energy.

The photosynthetic reaction is actually a mechanism of reactions.

Overall, the reaction converts CO_2 and H_2O into carbohydrate material and O_2.

Catalysts within the plant material play a big role in causing the reaction to proceed. These catalysts are molecules containing phosphorus and nitrogen.

The basic unit of the carbohydrate material is represed by

$[CH_2O]$

The overall reaction is

$$CO_2 + 4H_2O + 8h\nu \rightarrow [CH_2O] + O_2 + 3H_2O$$

($8h\nu$ = photons of visible light)

We could cancel 3 H_2O's on each side of the equation and write

$$CO_2 + H_2O + 8h\nu \rightarrow [CH_2O] + O_2$$

This would be stoichiometrically correct, however, it would not reflect the finding that it really takes 4 H_2O's to effect the photosynthetic reaction of one CO_2 molecule.

The reaction indicates 8 photons are required to effect the photosynthetic conversion of one CO_2 molecule. However, measurements indicate the actual number of photons required may be 10. Thus, there is some uncertainty.

What is the energy of the 8-10 photons used in the reaction?

A wavelength of 690 nm is assumed (based on the text). At this wavelength the energy of a photon is

$$h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ J\text{-}s)(3 \times 10^{8}\ m/s)}{(690 \times 10^{-9}\ m)(1.6 \times 10^{-19}\ J/eV)}$$

$= \underline{1.80\ eV}$ / photon

Thus, the solar energy used to effect one photosynthesis reaction (i.e., the conversion of one CO_2 molecule) is

$$1.8 \times (8 - 10) = \underline{14.4 - 18.0} \text{ eV}$$

eV = electron volt.

How does this energy compare to the chemical energy released when one unit of carbohydrate $[CH_2O]$ is burned.

The combustion reaction is

$$[CH_2O] + O_2 \rightarrow CO_2 + H_2O$$

[This is the reverse of our abbreviated photosynthesis reaction.]

Let's asume the H_2O is liquid.
The energies (i.e., enthalpies) of the reactants and products at scientific standard conditions of 25°C and 1 atm are

$[CH_2O]$	?
O_2	0
CO_2	$-393,522$ kJ/kmol
H_2O (liq)	$-285,838$ kJ/kmol

The energy released is the difference between the energy of the reactants and the products, i.e.

Energy Released = Energy of $[CH_2O]$
+ Energy of O_2
− Energy of CO_2
− Energy of $H_2O(l)$

Energy Released = Energy of $[CH_2O]$
$+ 0$
$- (-393{,}522)$
$- (-285{,}838)$

$=$ Energy of $[CH_2O]$
$+ 679{,}360$ kJ/kmol

This is the energy per kmol of material, i.e. $[CH_2O]$.
We divide by the number of molecules in a kmol to get Energy per molecule:

Energy Released = Energy of $[CH_2O]$
$$+ \frac{679{,}360 \text{ kJ/kmol}}{6.02 \times 10^{26} \text{ molecules/kmol}}$$

$=$ Energy of $[CH_2O]$
$$+ 1.13 \times 10^{-21} \frac{\text{kJ}}{\text{molecule}}$$

$=$ Energy of $[CH_2O]$
$$+ 1.13 \times 10^{-18} \frac{\text{J}}{\text{molecule}}$$

Converting to electron volts gives

$$\text{Energy Released} = \frac{\text{Energy of } [CH_2O] + 1.13\times10^{-18}\ \text{J/molecule}}{1.6\times10^{-19}\ \text{J/ev}}$$

$$= \text{Energy of } [CH_2O] + \underline{7.05}\ \text{ev/molecule}$$

This (i.e. 7.05 ev) is less than the 14.4 to 18.0 ev of photon energy absorbed per $[CH_2O]$ "molecule". Thus, not all of the photon energy ends up as the chemical energy of the carbohydrate

The measured value of the nominal chemical energy of the biomass, i.e. the energy released during perfect combustion, is <u>4.8</u> ev

This is called the heating value, actually the higher heating value (HHV) -- since liquid H_2O rather than vapor H_2O is taken as the product of combustion.

Thus HHV of [CH_2O] "molecule" $= \underline{4.8 \text{ eV}}$

Conversion to engineering units gives

$$4.8 \frac{\text{eV}}{\text{molecule}} \times 1.6 \times 10^{-19} \frac{\text{J}}{\text{eV}} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\times\ 6.02 \times 10^{26} \frac{\text{molecules}}{\text{kmol}}$$

$$= \mathbf{462{,}360} \text{ kJ/kmol}$$

Dividing by the molecular wt of [CH_2O] of 30 kg/kmol gives

HHV of biomass (dry)

$\cong$ 16,000 $\frac{KJ}{Kg}$

We can know backtrack and figure out the energy of $[CH_2O]$ in our calculation on pages 5 – 7.

By difference between 7.05 and 4.8 ev, the Energy of $[CH_2O]$ = – 2.25 eV

or $-2.25 \frac{eV}{molecule} \times 1.6 \times 10^{-19} \frac{J}{eV} \times \frac{1\ KJ}{1000 J}$

$\times 6.02 \times 10^{26} \frac{molecules}{Kmol}$

$= -216,720$ KJ/Kmol

This is the std state enthalpy of formation

Energy Efficiency

1) Some of sunlight is reflected or transmitted by plant, about 25%.
Leaves 75%.

2) About 50% of solar energy is insufficiently energtic ($\epsilon < 1.8$ ev), or in excess.
Leaves 37.5%.

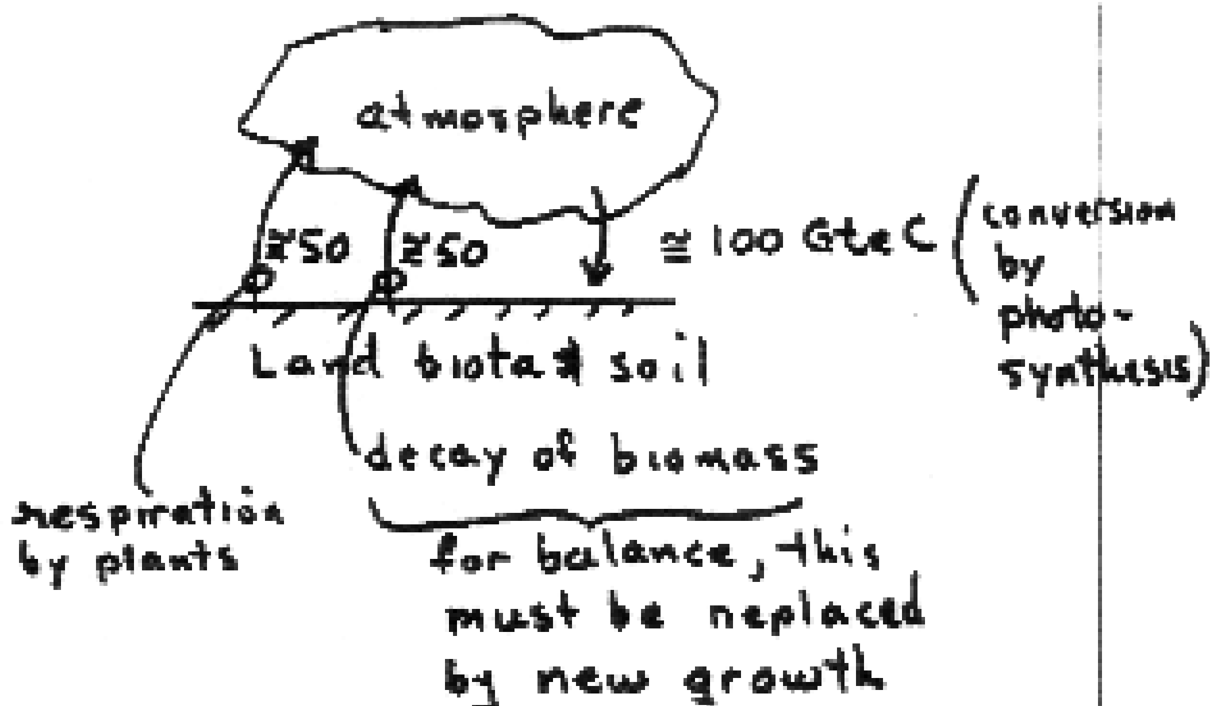
3)
$$\frac{\text{Chemical Energy of Carbohydrate}}{\text{Solar Energy used in Photosynthesis}} = \frac{4.8}{14.4 \rightarrow 18} = 33 \rightarrow 27\%$$

Leaves $12.5 \rightarrow 10\%$

4) Plants undergo respiration -- some of $[CH_2O]$ & O_2 used.

Carbon balance between earth & atmosphere

	C into atmosphere (GteC/yr)	C from atmosphere (GteC/yr)
Oceans	90	92
Fossil Fuel Burning	5	
Wildland Burning	2	
Land biota & soil	102	102



Thus, about 50 GteC biomass grown per year.

$$50 \times 10^{12} \frac{\text{kg C}}{\text{yr}} \times \frac{30 \text{ kg } CH_2O}{12 \text{ kg C}} \times \frac{16{,}000{,}000 \text{ J}}{\text{kg } CH_2O}$$

$$\times \frac{1}{3600 \frac{\text{s}}{\text{hr}} \times 24 \frac{\text{hr}}{\text{day}} \times 365 \frac{\text{day}}{\text{yr}}}$$

$$= 63 \times 10^{12} \text{ Watt} = 63 \text{ TW}$$

(text states 70 – 90 TW photosynthesis energy /sec)