

## Chapter 8: Photosynthesis: Energy From the Sun

### I Identifying Photosynthetic Reactants and Products.

- In the 1800's, it was known that there were three principle ingredients for photosynthesis: water, carbon dioxide, and light.
- There were two products: carbohydrates and oxygen.
- The water, which came from the soil, was transported through the roots.
- The CO<sub>2</sub> and oxygen were taken up from the air.
- Light was an absolute necessity in order to produce oxygen and carbohydrates.
- By 1804, scientists summarized photosynthesis:  $\text{CO}_2 + \text{H}_2\text{O} + \text{light energy} \rightarrow \text{sugar} + \text{O}_2$ . (See Figure 8.1)
- More recently, using radioactive isotopes, it has been determined that the actual reaction is:  $6\text{CO}_2 + 12\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6 \text{H}_2\text{O}$ .
- Water appears on both sides of the equation because water is both used as a reactant and released as a product. (See Figure 8.2)

### II The Two Pathways of Photosynthesis: An Overview

- Photosynthesis occurs as a result of many and not just a single step.
- When looked at as a whole, it can be separated into two different pathways.
  - The first pathway is called the *light reaction*, and is driven by light. It produces ATP and the reduced electron carrier, NADPH+H<sup>+</sup>.
  - The second pathway, called the Calvin-Benson cycle, does not use light directly. It uses ATP, NADPH+H<sup>+</sup> and CO<sub>2</sub> to produce sugar.
- The light reactions are mediated by molecular assemblies called photosystems.
  - These systems pass electrons from one molecule to another and some of this flow is coupled to synthesis of ATP.
  - The pathway is referred to as photophosphorylation. Both NADPH + H<sup>+</sup> and ATP are produced by the light reactions.
- The second path is the *Calvin-Benson Cycle*, which uses the energy stored in NADPH + H<sup>+</sup> and ATP to fix CO<sub>2</sub> into carbohydrates.

### III Properties of Light Pigments

*Light is the source of the energy required to drive photosynthesis*

#### A. Light comes in packets called photons

- Visible light is part of the electromagnetic radiation spectrum. It comes in discrete packets called photons.
- Light also behaves as if it were a wave. The wavelength of light is the distance between one of the peaks and the next peak of the waves. (See Figure 8.4)

- Visible light fits into the overall electromagnetic spectrum between ultraviolet and infrared radiation. (*See figure 8.5*).
- Humans perceive light as having distinct colors. The colors relate to the wavelength of the light as shown in *Figure 8.5*.
- The frequency of light is inversely related to its wavelength.
  - The shorter the wavelength the higher the frequency, the longer the wavelength the lower the frequency.
  - The amount of energy contained in a single photon is directly proportional to its frequency.
  - The shorter the wavelength, the greater the energy of the photon.
  - A photon of red light has a wavelength of 660nm, and has less energy than a photon of blue light, which has a wavelength of 430 nm.
- Brightness is a measure of the photons striking an area per unit time, such as one cm<sup>2</sup> per second. Light intensity is often expressed in energy units, such as calories per square centimeter per second.

#### **B. Absorption of a photon puts a pigment in an excited state**

- When a photon and a pigment molecule meet, one of three things happens:
  - The photon may bounce off the molecule. This is reflection.
  - The photon may pass through the molecule. This is transmission.
  - If neither of these outcomes occur, the photon is absorbed by the molecule. This is excitation.
- If absorbed, the photon disappears, but the energy it possessed can be neither created nor destroyed and is therefore absorbed by the electron.
  - The electron is raised from its ground state to an excited state of higher energy.
  - The difference between the excited and the ground state is precisely equal to the energy of the absorbed photon. (*See Figure 8.6*)
- All molecules absorb electromagnetic radiation, but differ in the specific wavelengths absorbed.
- Molecules that absorb wavelengths in the visible range are called pigments.
- When a beam of white light shines on an object, and the object appears to be red in color, it is because it has absorbed other colors from the white light *except* for the color red.
- In the case of chlorophyll, plants look green because they absorb green less effectively than the other colors found in sunlight.

#### **C. Light absorption and biological activity vary with wavelength**

- A given type of molecule can absorb radiant energy of only certain wavelengths.
- If we plot the absorption of the compound as a function of wavelength, the result is an absorption spectrum. (*See Figure 8.7*)

- Absorption spectrums are good fingerprints of compounds. Sometimes an absorption spectrum contains enough information to enable us to identify an unknown compound.
- If absorption results in an activity of some sort, then a plot of the effectiveness of the light as a function of wavelength is called an action spectrum. *Figure 8.8* shows the action spectrum of photosynthesis by *Anacharis*, a freshwater plant.

#### **D. Photosynthesis uses chlorophylls and accessory pigments**

- Chlorophylls are important pigments in photosynthesis.
- Plants have two predominant chlorophylls: chlorophyll A and chlorophyll B. These molecules differ slightly in their structure.
  - Both have a similar ring structure.
  - In the center of the chlorophyll ring is a magnesium atom. At the peripheral location of the ring is a long hydrocarbon tail that can associate with the hydrophobic region of the thylakoid membrane. (*See Figure 8.9*)
- These chlorophylls absorb blue and red wavelengths, which are near the ends of the spectrum.
- Other accessory pigments absorb photons that are intermediate in energy, between the red and blue wavelengths, and then transfer a portion of that energy to chlorophylls.
- Examples of accessory pigments are the carotenoids such as beta carotene, which absorb photons in the blue and blue-green wavelength, and appear deep yellow in color.

### **IV Light reactions:**

#### **A. Light absorption**

- A pigment molecule enters an excited state when it absorbs a photon.
- The excited state is unstable. One of two things will happen.
- The molecule might return to ground state, emitting a photon of light. This is called fluorescence. (*See Figure 8.6*)
  - When the molecule fluoresces, it emits a photon of a longer wavelength. (*See Figure 8.10*)
  - This is because of the second law of thermodynamics, which says that during an energy transfer, not all the energy is available to do work.
- The molecule might pass some of the absorbed energy to other pigment molecules.
  - Pigments in the photosynthetic organisms arrange into energy absorbing antennae systems.
  - In these systems, complex proteins hold the molecules in the correct orientation to enable the transfer of energy.

- The excited electrons are passed to the reaction center of the antenna complex.
- The pigment molecule in the center is always a molecule of chlorophyll A.
- There are other chlorophyll A molecules in the antenna, but they absorb light at shorter wavelength.

### **B. Excited chlorophyll acts as a reducing agent**

- The ground state chlorophyll, symbolized by Chl, is not much of a reducing agent, but excited Chl\* is a good one.
- The reducing capability of Chl\* is because excited molecules have electrons zipping around further away from the nucleus. (*See Figure 8.11*)
- Less tightly held, the electron is more likely to be passed on in a redox reaction to an oxidizing agent.
- Chl\* can react with an oxidizing agent in a reaction like  $\text{Chl}^* + \text{A} \rightarrow \text{Chl}^+ + \text{A}^-$ .
- This is the first biochemical consequence of light; chlorophyll becomes a reducing agent after having absorbed a photon.
- The electron is passed on to an oxidizing agent. Chlorophyll then becomes a positively charged ion, which is missing an electron.

## **V Electron Flow Phosphorylation and Reductions**

- The passing of an electron from chlorophyll to an electron acceptor begins an electron flow.
  - The electrons flow through a series of carriers, where redox reactions occur, one after another, and the energy of these redox reactions is used to pump protons.
  - The process is referred to as photophosphorylation.
- Another high energy product that is generated is  $\text{NADPH} + \text{H}^+$ . Similar to the NAD found in cellular respiration,  $\text{NADP}^+$  is nicotinamide adenine dinucleotide phosphate.
- There are two different systems for flow of electrons in photosynthesis.
- The noncyclic electron flow produces  $\text{NADPH} + \text{H}^+$  and ATP. (*See Figure 8.12*)
- Noncyclic electron flow also produces the oxygen that we find in the atmosphere.
- Cyclic electron flow produces just ATP.

### **The oxygen we breathe:**

- All the oxygen in the atmosphere is generated by *non-cyclic* photophosphorylation.
- When the excited electron is passed from chlorophyll P680 (photosystem II), it leaves the chlorophyll molecule oxidized and charged,  $\text{Chl}^+$ .
- The electrons to restore the chlorophyll come from water.
- $\text{H}_2\text{O} \rightarrow 2\text{e}^- + 2\text{H}^+ + 1/2\text{O}_2$
- The oxidized chlorophyll A is reduced by an electron from a manganese containing protein called protein Z.

- Protein Z regains its lost electron by oxidizing a water molecule.
- The protons ( $H^+$ ) generated are released into the thylakoid lumen, where it helps to build the proton gradient.

#### A. Noncyclic Events summary:

- Photons are absorbed by chlorophyll P680 molecules.
- The P680 excited electrons transfer to the electron transport chain.
- The P680 is reduced by Protein Z and electrons from the hydrogen atoms of water.
- Free energy of P680 electrons power proton ( $H^+$ ) transport from stroma to lumen of chloroplast.
- Absorption of photons by P700 of photosystem I occur.
- The P700 electrons are replaced by those flowing from P680.
- Electrons from P700 are transferred to the electron transport chain.
- The P700 electrons and free protons from the stroma are used to reduce  $NADP^+$  to  $NADPH + H^+$ .
- See Figure 8.12 for details.

#### B. Cyclic electron flow produces ATP but no NADPH

- Photosystem I acts on its own. (*See Figure 8.13*)
- Cyclic refers to the circular pathway of P700 electrons.
- Energy produced must be stored in ATP and  $NADPH+H^+$  to drive the Calvin-Benson cycle. This cycle uses more ATP than  $NADPH+H^+$ .
  - To keep balance, cyclic electron flow makes ATP without making  $NADPH+H^+$ .
  - No photolysis of water occurs during cyclic events.
  - No oxygen is generated by the cyclic events.
- The P700 molecule, the reaction center chlorophyll, starts at ground state.
  - It absorbs a photon and becomes  $P700^*$ .
  - The  $P700^*$  molecule reduces ferredoxin ( $Fd^{red}$ )
  - In contrast to non-cyclic photophosphorylation where  $Fd^{red}$  reduces  $NADP^+$ ,  $Fd^{red}$  passes its electron to plastoquinone (PQ).
  - The PQ molecule passes the electron to the cytochrome complex.
  - The electron continues down a redox chain, pumping protons as it goes.
  - The  $P700^+$ , the chlorophyll that lost an electron, gets it back again at the end of the chain.

#### C. Chemiosmosis is the source of ATP

- The ATP molecules are produced by a mechanism similar to what is described in Chapter 7 for mitochondria.
- The same type of chemiosmotic mechanism operates in photosynthesis, but is called photophosphorylation. (*See Figure 8.14*)

- High-energy electrons move through a series of redox reactions releasing energy, which is used to transport protons across the membrane.
- Active proton transport results in the proton motive force: a difference in pH and electrical charge across the membrane.
  - In chloroplasts the electron carriers in the thylakoid membrane are oriented so as to move protons into the interior of the thylakoid, and the inside becomes acidic in respect to the outside.
  - The ratio of H<sup>+</sup> inside versus outside a thylakoid is usually 10,000 to 1, which is a difference of 4 pH units.
  - This difference in pH leads to the diffusion of H<sup>+</sup> out of the thylakoid through specific protein channels, ATP synthases, that couple the formation of ATP to proton diffusion.
- Photosynthetic pathways are the products of evolution.
  - The first photosynthesis organisms were probably anaerobic bacteria that used hydrogen sulfide rather than water for a source of electrons:  $\text{CO}_2 + 2\text{H}_2\text{S} \rightarrow (\text{CH}_2\text{O}) + 2\text{S} + \text{H}_2\text{O}$ .
  - Many bacteria still use a system which releases sulfur rather than oxygen.
- Around three billion years ago, a new pigment and other enzymes, allowed the extraction of electrons from water, the reduction of NADP<sup>+</sup> and the production of O<sub>2</sub> as a byproduct.
- Over hundreds of millions of years these *Cyanobacteria* would have poured oxygen into the atmosphere, which made the evolution of cellular respiration possible.

## VI Making Sugar from CO<sub>2</sub>: The Calvin-Benson Cycle

- Most of the enzymes used to make sugar from CO<sub>2</sub> are found dissolved in the stroma of the chloroplast.
  - The cycle created by these enzymes do not use sunlight directly, they use the energy generated from photosynthesis in the form of ATP and NADPH.
- A. Isotope labeling experiments reveal the steps of the Calvin-Benson cycle.**
- Radioactively labeled carbon in CO<sub>2</sub> was used to identify the products generated by photosynthesis. (*See Figure 8.15*)
    - After a 30 second exposure to <sup>14</sup>CO<sub>2</sub>, the cells were killed and carbohydrates and amino acids were extracted.
    - Many compounds, including monosaccharides and amino acids, contained <sup>14</sup>C.
  - Then they shorten the exposure time to <sup>14</sup>CO<sub>2</sub> to just 3 seconds.
    - Only one compound was found labeled with <sup>14</sup>C.
    - The compound was a 3 carbon sugar called 3 phosphoglycerate (3PG).
  - Other products of the cycle were found by increasing the length of time of exposure in a stepwise manner until the whole pathway was revealed.

- Finding a labeled 3-carbon sugar was unexpected. Additional research discovered that the real first product is a 6 carbon sugar:
  - The initial reaction of the Calvin-Benson cycle fixes one CO<sub>2</sub> into a 5 carbon compound ribulose 1,5-bisphosphate (RuBP).
  - An intermediate 6-carbon compound forms, which is unstable and breaks down to form two 3-carbon molecules of 3PG, which is the sugar that Calvin discovered.
  - The enzyme that catalyzes the fixation of carbon dioxide is ribulose bisphosphate carboxylase/oxygenase, called *rubisco*, which is the most abundant protein in the world, comprising 20% of all the proteins in a leaf. (See Figure 8.16)

**B. The Calvin-Benson cycle is composed of 3 processes:**

- They are 1) Fixation of CO<sub>2</sub>, 2) Conversion of fixed CO<sub>2</sub> into carbohydrates, and 3) Regeneration of the CO<sub>2</sub> acceptor RuBP.
- The end product of the cycle is glyceraldehyde 3-phosphate, G3P, which is a three carbon sugar-phosphate, also called triose phosphate. (See Figure 8.17)
- There are two fates for the G3P:
  - A third ends up as starch, which is stored in the chloroplast and serves as a source of glucose.
  - Two-thirds of the G3P is converted to the disaccharide, sucrose, which is transported out of the leaf to other organs, where it is hydrolyzed into glucose and fructose to provide a source of energy.
- Most of the stored energy is released by glycolysis and cellular respiration by the plant itself, during growth, development and reproduction.
- Some of this material is consumed by heterotrophs, where glycolysis and respiration releases the stored energy. (See Figure 8.3 for an overview of the process of photosynthesis.)

**VII Photorespiration and Its Evolutionary Consequences**

*Rubisco sometimes fixes O<sub>2</sub> instead of CO<sub>2</sub>, lowering the overall rate of CO<sub>2</sub> fixation and limiting plant growth. (See Figure 8.19)*

**A. RuBP reacts with O<sub>2</sub> in photorespiration**

- Rubisco is a carboxylase, adding CO<sub>2</sub> to an acceptor molecule RuBP, as well as an oxygenase, adding O<sub>2</sub> to RuBP.
- These two reactions compete with each other. When RuBP and oxygen react, one of the products is a two compound, glycolate. RuBP + O<sub>2</sub> → glycolate.
  - The glycolate diffuses into membrane enclosed organelles called peroxisomes.
  - In the peroxisomes, a series of reactions convert glycolate into glycine.

- The glycine diffuses into the mitochondria where two glycine molecules are converted into another amino acid serine.
- This pathway is called photorespiration.
- It uses the ATP and NADPH produced in the light reaction.
- The net effect of photorespiration is that it undoes what the Calvin-Benson cycle accomplishes.
- CO<sub>2</sub> is released instead of being fixed into a carbohydrate.
- In many plants, photorespiration reduces the amount of carbon fixed by 25%.
- Rubisco acts as an oxygenase if the CO<sub>2</sub> levels are very low and the oxygen levels are very high.
- Oxygen levels become very high when stomata are closed to prevent water loss, when the weather is hot and dry.
- CO<sub>2</sub> is consumed and oxygen is generated and finally the oxygen concentration becomes sufficiently high and the oxygenase activity proceeds.

#### **B. Some plants have evolved systems to bypass photorespiration**

- A solution to the problem has been achieved by some plants.
  - The concentration of oxygen in the atmosphere is 21% and the concentration of CO<sub>2</sub> is 0.036%.
  - The rubisco enzyme prefers CO<sub>2</sub>, but at very high oxygen concentrations, the oxygenase activity begins.
- Many plants are called C<sub>3</sub> plants. They are called C<sub>3</sub> plants because the CO<sub>2</sub> is first fixed into the 3-carbon molecule as already described.
- In corn, sugarcane and other tropical grasses, chloroplasts with abundant rubisco are in layers in the interior of the leaf. (*See Figure 8.19*)
  - Like C<sub>3</sub> plants, these plants close stomata on hot, dry days, but their rate of photosynthesis neither falls off, nor does photorespiration occur. They are called C<sub>4</sub> plants.
  - The C<sub>4</sub> plants perform normal Calvin-Benson cycles, but they have an additional early reaction that fixes CO<sub>2</sub> without losing carbon to photorespiration.
  - The C<sub>4</sub> plants have two separate enzymes for CO<sub>2</sub> fixation in different chloroplasts, in two different locations in the leaf.
  - One type is present in the mesophyll cells near the surface of the leaf.
  - They fix CO<sub>2</sub> into a 3-carbon acceptor compound, phosphoenolpyruvate, to form a 4-carbon fixation product, oxaloacetate.
  - The enzyme that does this is PEP carboxylase. (*See Figure 8.20*)
  - PEP carboxylase does not have oxygenase activity.
  - It fixes CO<sub>2</sub> even when the level of CO<sub>2</sub> is extremely low.
  - The four carbon compounds diffuse out of the mesophyll cells into the bundled sheaths in the interior of the leaf.
  - The chloroplasts of these cells contain abundant rubisco.

- The 4-carbon compounds are decarboxylated, losing CO<sub>2</sub> and regenerating the 3-carbon acceptors, which then diffuse back to the mesophyll cells. The C<sub>4</sub> cells appeared about 12 million years ago.
- A hundred million years ago, the concentration of CO<sub>2</sub> was four times that of what it is now. As the CO<sub>2</sub> levels declined, more efficient C<sub>4</sub> plants would have had an advantage over C<sub>3</sub> counterparts.

### C. CAM plants also use PEP carboxylase

- Other plants besides C<sub>4</sub> species use PEP carboxylase to fix and accumulate CO<sub>2</sub>, while their stomata are closed. (*See Figure 8.21*)
- Such plants include succulents, such as cacti and pineapple, and also, several kinds of flowering plants.
- These plants conserve water by keeping stomata closed during the daylight hours and open at night.
- The CO<sub>2</sub> metabolism in these plants is called the crassulacean acid metabolism or CAM, after the succulents where it was discovered.
  - In CAM plants, CO<sub>2</sub> is fixed initially in the mesophyll cells to form a 4-carbon compound, oxaloacetate, which is then converted to malic acid.
  - The fixation occurs during the night, when less water is lost through the open stomata.
  - The stomata close during the day, and the accumulated malic acid is shipped to the chloroplast, where decarboxylation occurs to supply CO<sub>2</sub> for the operation of the Calvin-Benson cycle.

## VIII Metabolic Pathways in Plants

- Green plants are autotrophs, and can synthesize all their molecules from three simple starting materials: CO<sub>2</sub>, H<sub>2</sub>O, and NH<sub>4</sub>.
- Plants use ATP and NADPH for a number of processes besides the Calvin-Benson cycle, but ATP is also needed in organs that don't photosynthesize, and during times when the sun is not shining.
- To satisfy their need for ATP, plants like all organisms carry out cellular respiration. Aerobic respiration and fermentation both occur in plants, although respiration is more common.
- Cellular respiration takes place both in the dark and in the light.
- Photosynthesis and respiration are closely linked by the Calvin-Benson cycle.
  - The 3PG from the Calvin-Benson cycle can be converted into pyruvate, the end product of glycolysis .
  - The G3P from the Calvin-Benson cycle can be converted into hexophosphates, such as glucose 1-phosphate, which can enter glycolysis.
- Once carbon skeletons from the Calvin-Benson cycle enter glycolysis and the citric acid cycle, they can be used anabolically to make lipids, proteins, and other carbohydrates. (*See Figure 8.22*)

- Energy flows from the sunlight to reduce carbons in photosynthesis.
- Energy can be stored in macromolecules such as polysaccharides and lipids.
- For plants to grow, energy storage must exceed energy released. Overall, fixed carbon must exceed that used for respiration.