LEARNING OUTCOMES

Students, after mastering the lecture materials of course, should be able to:

1. explain the situation of food supply by 2050.
2. explain radiation use efficiency in relation to the effort to increase food crop production.
3. explain what has been obtained in the past during green revolution to increase food crop production.
4. explain light absorption by plants.
5. explain photosynthetic pigments implicated in the light absorption.
6. explain electron excitation with the light absorption.
7. explain fluorescence as a consequence of electron excitation.
8. Electron transfer following electron excitation.
LECTURE OUTLINE

I. INTRODUCTION
   1. Food Crop Production
   2. Radiation Use Efficiency
   3. Green Revolution

II. ELECTRON TRANSPORT
   1. Light Absorption
   2. Photosynthetic Pigments
   3. Electron Excitation
   4. Fluorescence
   5. Electron Transfer

1. INTRODUCTION

1. Food Crop Production
   - It is questioned whether a sufficient food supply can be met by 2050 with the global human population rising from ~7 billion now to 9–10 billion by 2050.
   - This is due partly to the present problems:
     1. the limited arable land for an extension of food crop area,
     2. a massive change of food crop area to other uses,
     3. the worldwide trend towards a more meat-rich human diet,
     4. the loss of harvest and grazing land, and
     5. the negative effects of global warming on crop production.
2. Radiation Use Efficiency

- The efficient use of solar irradiation energy across the growing season is the ultimately main factor determining crop yields.

- Photosynthesis, a process that all life on earth depends on, is the process converting solar energy to be chemical energy used for the assimilation of CO$_2$.

- More than $10^9$ metric tons (10 billions ton) of atmospheric CO$_2$ are assimilated and converted into biomass per year.

- Photosynthesis can be looked at from different perspectives: (i) light reactions and carbon assimilation, (ii) leaves and canopy structure, and (ii) source-sink relationships.

Fig. 1. The process of photosynthesis viewed from different perspectives. Source: Flügge et al. (2016)
- Montheith equation shows that

\[ \text{Crop Yield} = 0.487 \times S_t \times \varepsilon_i \times \varepsilon_c \times \varepsilon_p \]

\( S_t \), available solar irradiance
\( \varepsilon_i \), efficiency of radiation interception
\( \varepsilon_c \), conversion efficiency of intercepted solar energy
\( \varepsilon_p \), partition of biomass to yield (harvest index)

- A simple equation was developed as a practical approach to estimate radiation use efficiency as follows:

\[ \text{BM} = \text{RUE} \times \text{PAR} \]

\( \text{BM} \), cumulative total (above) plant biomass
\( \text{RUE} \), radiation use efficiency
\( \text{PAR} \), cumulative PAR intercepted

Fig. Cumulative total biomass of peanut as a function of cumulative total PAR intercepted
3. Green Revolution

- The Green Revolution raised the yield potential of the major grain crops mainly by increasing the harvest index, which is now about 0.6.
- Breeders were also able to improve the light interception efficiency, which in modern cultivars is up to about 0.8–0.9.
- All available evidence suggests that additional grain yields by further increasing the harvest index or optimizing light interception are rather unlikely; they appear to be close to their biological limits already.
- In contrast, the best light conversion efficiency (LCE, $\varepsilon_c$) observed in field experiments is far below the theoretical maxima.

Fig. HI in relation to grain yield of twenty rice genotypes in Chile. Quezada et al. (2013)
Table 7.1 Latest facts and figures about rice in Australia (2013–2014)

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Cultivated area</td>
<td>52,000 ha</td>
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<tr>
<td>Annual production</td>
<td>819,000 tons</td>
</tr>
<tr>
<td>Consumption (per capita/year)</td>
<td>10 kg</td>
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<tr>
<td>Domestic use</td>
<td>15 %*</td>
</tr>
<tr>
<td>Export</td>
<td>85 %*</td>
</tr>
<tr>
<td>Average national yield</td>
<td>10.7 t ha(^{-1})</td>
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<tr>
<td>Farm gate value of industry</td>
<td>A$ 350 million</td>
</tr>
<tr>
<td>Total value including exports</td>
<td>A$ 800 million</td>
</tr>
<tr>
<td>Rank in Australian exported grains</td>
<td>Third</td>
</tr>
<tr>
<td>Rank in Australian exported agricultural commodities</td>
<td>Ninth</td>
</tr>
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Adopted from Bajwa & Chauhan (2017)

- The best LCE (\(\varepsilon_c\)) is 0.24 in C3 and 0.37 in C4-crops while the theoretical maxima of LCE is 0.46 in C3- and 0.6 in C4-plants, and thus not yet close to its biological limit.
- Therefore, a prime target when aiming to increase crop yield is to enhance, and in the long term to redesign, photosynthesis with respect to light energy conversion efficiency.
- Light energy conversion efficiency comprise the efficiency of:
  - electron transport to produce chemical energy (NADPH & ATP),
  - chemical energy use in the assimilation of CO\(_2\) to be organic molecules, and
  - metabolism to synthesize cell components or plant biomass.
2. ELECTRON TRANSPORT

1. Light Absorption
   - Light absorption in the photosynthetic process is the conversion of light energy into chemical energy.
   - The rate of light absorption is first determined by the rate of light interception.

\[ R = R_0 e^{-kL} \quad R = R_0 L^{-a} \]

Sorghum (Radialek, 2018 unpublished)
- The absorption of light energy is the use of light energy to excite electrons from ground orbit to singlet state.
- In order to utilize the energy of a photon in a thermodynamic sense, this energy must be at least as high as the Gibbs free energy of the photochemical reaction involved.

\[ E = h\nu = \frac{hc}{\lambda} \]

where \( h \) is the Planck constant \((6.6 \times 10^{-34} \text{ J s})\) and \( c \) the velocity of the light \((3 \times 10^8 \text{ m s}^{-1})\). \( \lambda \) is the wavelength of light.
- The mole (abbreviated to \( \text{mol} \)) is used as a chemical measure for the amount of molecules and the amount of photons corresponding to \( 6 \times 10^{23} \) molecules or photons (Avogadro number \( \text{NA} \)).
• The energy of one mol photons amounts to:
  \[ E = \left( \frac{hc}{\lambda} \right) N_A \]
• In fact, much energy is lost during energy conversion, with the consequence that the energy of the photon must be higher than the Gibbs free energy of the corresponding reaction. We can equate the Gibbs free energy \( \Delta G \) with the energy of the absorbed light:
  \[ \Delta G = E = \left( \frac{hc}{\lambda} \right) N_A \]
• The introduction of numerical values of the constants \( h, c, \) and \( N_A \) yields:
• The energy of one mol photons amounts to:
  \[ E = \left( \frac{hc}{\lambda} \right) N_A \]
  \[ \Delta G = \left[ 6.6 \times 10^{-34} \text{ (Js)} \right] \left( 3 \times 10^8 \text{ m/s} \right) \left( \lambda \text{ m} \right) \left( 6 \times 10^{23} \text{ mol} \right) \]
  \[ \Delta G = 119000 / (\lambda, \text{nm}) \text{ [kJ/mol photons]} \]

2. Photosynthetic Pigments
• Chlorophyll is the main photosynthetic pigment that undergoes electron excitation after light absorption.
• The basic structure of chlorophyll is a ring made of four pyrroles, a tetrapyrrole, which is also named porphyrin.
• Mg\(^{++}\) is present in the center of the ring as the central atom, and covalently bound with two N atoms and coordinately bound to the other two atoms of the tetrapyrrole ring.

A pyrrole

Chlorophyll a

Chlorophyll b

Phytol side chain

Hydrophobic membrane anchor
• When a photon with a certain wavelength hits a chromophore molecule that absorbs light of this wavelength, the energy of the photon excites electrons and transfers them to a higher energy level.

• A general property of chromophores is that they contain many **conjugated double bonds**, 10 in the case of the tetrapyrrole ring of chl-a. These double bonds are delocalized.

![Resonance structures of chlorophyll-a](image)

Fig. 2.5 Resonance structures of chlorophyll-a. In the region marked red, the double bonds are not localized; the $\pi$ electrons are distributed over the entire conjugated system. The formyl residue of chlorophyll-b attracts electrons and thus affects the $\pi$ electrons of the conjugated system.

3. **Electron Excitation**

• After absorption of energy, an electron of the conjugated system is elevated to a higher orbit. This excitation state is termed **singlet**.

• As a rule, the higher the number of double bonds in the conjugated system, the lower the amount of energy required to produce a first singlet state.

• For the excitation of chlorophyll, dark red light is sufficient, whereas butadiene ($\text{CH}_2=\text{CH}_2$), with only two conjugated double bonds, requires energy-rich ultraviolet light for excitation.
The released excitation energy is converted to (i) photochemical work, (ii) fluorescent or (iii) phosphorescent light, or (iv) dissipated into heat.

Fig. 2.6 Schematic presentation of the excitation states of chlorophyll-a and their return to the ground state. Source: adapted from Heldt & Piechulla (2010)

4. Fluorescence

- Light energy absorbed by chlorophyll molecules in a leaf can undergo one of three fates:
  (i) it can be used to drive photosynthesis (photochemistry),
  (ii) excess energy can be dissipated as heat or
  (iii) it can be re-emitted as light—chlorophyll fluorescence.

- Once PSII absorbs light and $Q_A$ has accepted an electron, it is not able to accept another until it has passed the first onto a subsequent electron carrier ($Q_B$).
- During this period, the reaction centre is said to be ‘closed’.
- When a leaf is transferred from darkness into light, PSII reaction centres are progressively closed. This gives rise (during the first second or so of illumination) to an increase in the yield of chlorophyll fluorescence.
Fluorescence. The competition between these processes allows us to resolve the efficiency of PSII.

Fig. A schematic figure showing electron transport within the PSII reaction centre complex. Energy absorbed by chlorophyll within the light-harvesting complex can be dissipated via **photochemistry**, by **heat** (non-photochemical quenching), or as **fluorescence**. The competition between these processes allows us to resolve the efficiency of PSII.

1. The measuring beam (MB) excites chlorophyll but is not of a sufficient intensity to induce electron transport through PSII (i.e. 'charge separation' when Pheo is reduced). This gives $F_o$, the minimal level of fluorescence, and reaction centres are said to be open.

2. A brief saturating pulse (SP) of light results in the formation of the maximum possible yield of fluorescence, $F_m$. During this pulse reaction centres are effectively closed.
A schematic figure explaining the transfer of energy and electrons within PSII that result in open and closed centres and the formation of $F_0$ and $F_m$ states, respectively. The excited state $P_{680}^+$ and subsequent transfer of an electron to the primary acceptor $Q_A$ gives rise to a closed centre. $Q_A^-$ cannot accept another electron until it has passed its electron onto the next electron acceptor, $Q_B$.

- Following on from this, however, the fluorescence level typically starts to fall again, over a time-scale of a few minutes.
- A typical fluorescence trace made on dark-adapted leaf material showing how $F_0$ and $F_m^0$ are formed.
  - Quantum yield of PSII: 
    \[
    \Phi_{PSII} = \frac{(F_m^0 - F_t)}{F_m^0} 
    \]
  - Photochemical quenching: 
    \[
    qP = \frac{(F_m^0 - F_t)}{F_m^0} 
    \]
  - Non-photochemical quenching: 
    \[
    NPQ = \frac{(F_m^0 - F_m)}{F_m} 
    \]

\[ J = \Phi_{PSII} \times PFDa \times (0.5) \]
5. Electron Transfer

- Photosynthetic electron flow is driven by two photochemical reactions catalyzed by PSII and PSI, which are linked in series by the electron transport chain (Fig. 1).

![Fig. 1. Electron transport pathways of oxygenic photosynthesis. Electron transport pathways are shown by dotted lines.](image)

- Following excitation of the special chlorophylls in the reaction center, the P680+Pheo− radical pair is established quickly, within a few tens of picoseconds.
- The PSII reaction center complex binds two quinones (plastoquinones, PQs), denoted Q_A and Q_B.
- Q_A is bound tightly to the PSII reaction center and functions as the first relatively stable electron acceptor.
- Q_B, which is bound more loosely, functions as a secondary electron acceptor.
- Reduction of the two quinones proceeds through a five-step process:
  1. The first electron is released from P680 and transferred to Q_A to produce a plastosemiquinone, Q_A^−.
Fig. Schematic diagram of the reaction center core of monomeric PSII. The D1 and D2 proteins bind most of the cofactors involved in charge separation and electron transport. Electrons are transferred from P680 to pheophytin (Pheo) and subsequently to two plastoquinone molecules, QA and QB. The nonheme iron (Fe) does not have a direct role in electron transfer.

P680$^+$ is reduced by Z, a tyrosine residue in the D1 subunit. Also indicated is the oxidation of water by the Mn cluster, which is bound to the luminal side of the complex and stabilized by a peripheral protein, PsbO (labeled as MSP). CP43 and CP47 are chlorophyll a-binding core antenna proteins. D1 is susceptible to photooxidative damage and undergoes active turnover.

- $Q_B$, which is bound more loosely, functions as a secondary electron acceptor. Reduction of the two quinones proceeds through a five-step process:
  1. The first electron is released from P680 and transferred to QA to produce a plastosemiquinone, QA$^\cdot$.
  2. This electron is then transferred to QB to yield the semiquinone QA$^\cdot$. The loss of the electron returns QA$^\cdot$ to QA$^-$. A second electron is then transferred from P680 to QA to produce a second QA$^\cdot$.
  3. The second electron is subsequently transferred from QA$^\cdot$ to QB$^\cdot$ to produce a fully reduced QB$^{2\cdot}$ molecule. Again, QA$^\cdot$ reverts to QA$^-$. Finally, the fully reduced QB$^{2\cdot}$ takes up two protons from the stromal side of the membrane, yielding a plastoquinol, QBH$_2$.
- P680, the reaction center chlorophyll of PSII, undergoes light-induced oxidation to produce the strong oxidant, P680$^+$, which can oxidize water (H$_2$O).
The oxidation of $2\text{H}_2\text{O}$ releases $4\text{e}^-$, $4\text{H}^+$ and $\text{O}_2$ as shown in the following reaction.

$$2\text{H}_2\text{O} \rightarrow 4\text{e}^- + 4\text{H}^+ + \text{O}_2$$

The electrons are then used by the PSII reaction center for the reduction of the primary electron acceptors of PSII, $Q_A$ and $Q_B$, on the stromal side of the membrane.

Once it has accepted two electrons, $Q_B$ is released from PSII into the plastoquinone pool and reduced plastoquinol docks to the $Q_o$ site of Cyt$b_6f$.

This complex acts as a proton pump in a $Q$-cycle-like process.

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**Q-Cycle of Cyt$b_6f$**

Fig. Plastoquinone (PQ) is reduced to plastoquinol (PQH$_2$) with electrons from photosystem II (PSII) and the $Q_n$ site in the cytochrome $b_6/f$ complex (Cyt $b_6/f$). Then, PQH$_2$ is oxidized at the $Q_p$ site in Cyt $b_6/f$. Source: Shimakawa et al. (2018)
4. NADH and ATP

- The absorption of four quanta by PSII and four by PSI extracts four electrons from two molecules of water, releasing four protons and oxygen into the thylakoid lumen.
- Linear transport of these four electrons from PSII to PSI can reduce two NADP⁺ and pump eight protons into the thylakoid lumen through the action of the Q cycle (Sacksteder et al., 2000).
- On the basis of the rotational catalysis model with the chloroplast integral membrane portion (CFO) of the ATP synthase having 14 c-subunits (which form a ring structure in the FO subcomplex), 14 protons are required to synthesize three ATP (4.67 H+/ATP; Seelert et al., 2000; Vollmar et al., 2009).

Consequently, eight quanta absorbed for linear electron flow can generate two NADPH and 2.57 ATP (12 protons x 3 ATP/14 protons).

- This was observed experimentally with spinach (Spinacia oleracea) thylakoids supplied with NADP (Furman and Badger, 1983).
- However, other estimates of only four H⁺/ATP (Steigmiller et al., 2008) have been observed, which would yield three ATP/two NADPH.
- The production of 3 ATP/2 NADPH exactly matches consumption by the Calvin-Benson cycle.
- Whereas 2.57 ATP/2 NADPH requires a mechanism to supply additional ATP (Allen, 2002; Kramer et al., 2004; Amthor, 2010).
THANK YOU

Спасибо

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