Efficiency of solar energy conversion as a function of light intensity*

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Abstract: The kinetic model has been developed for disserting the efficiency of solar energy conversion as a function of light intensity. A comparison of theory with experimental results shows that the model provides a satisfactory agreement. We have estimated the essential parameters of photosynthetic systems (the size of the photosynthetic antenna, the rate of electron transport, the correlation between photosynthesis and respiration) that are responsible for reaching the maximum efficiency at "one sun" and "one hundred suns" light illumination intensities. Recommendations for the improvement of photosynthetic system parameters using genetic engineering methods are also provided.

Keywords: solar energy conversion; photosynthesis; chemical kinetics; electron transport; biological membrane.

INTRODUCTION

The crucial characteristic of any method of energy conversion is the efficiency of energy transformation. This characteristic is essential when solar energy conversion technologies are discussed. The efficiency of transformation of solar energy into electricity (photovoltaic conversion) or into biofuels (photosynthetic production of biomass) determines the volume of energy production and, finally, the economics and acceptance of the developing energy technology [1–6].

The particularity of any method of solar energy conversion is the complex character of transformation efficiency as a function of light intensity. In a general case, the efficiency of light energy transformation increases at low light intensities, reaches the maximum, and drops down at high fluxes of light. Such behavior is typical, and the nature of this phenomenon demands description and understanding.

In this research, the kinetic approach was used for analysis of this phenomenon, and the photosynthetic production of biomass was analyzed as a typical important case of solar energy conversion system.

The objectives of the present study were

- to develop a simple and reliable kinetic model for describing the efficiency of energy conversion in photosynthesis and
- to reveal proceeding from an analysis of the model, to identify the possible directions for "improvement" of the photosynthesis energetic parameters, and to estimate the parameters of systems capable of operating with maximum efficiency at light intensities of "one sun" and "one hundred suns".

EFFICIENCY AND PRODUCTIVITY OF PHOTOSYNTHETIC SYSTEMS

Illumination of photosynthetic apparatus located within biological membranes of plants and microalgae leads to a continuous electron flow. According to the Z-scheme of photosynthesis, the photosynthetic apparatus expends two photons for transporting one electron [7,8].

$$A_1 \xrightarrow[h\nu]{k(I)} A_2 \xrightarrow{k_e} A_3 \xrightarrow{k_{CO_2}} A_1 \tag{1}$$

The states of a photosynthetic unit can be represented approximately by kinetic scheme 1. State A_1 is characterized by the capacity of absorbing a quantum (or quanta) of light with primary charge separation. The intensities of the process can be described by the rate constant and the reaction frequency $k(I)$, which depends on the light intensity. State A_2 with separated charges undergoes a transformation as a result of electron transport via the protein electron transport chain. The slowest, limiting step of the process can be represented by the rate constant of the first-order k_e. Finally, the electron transport to CO_2, with the reduction of the acceptor to carbohydrate completes the electron transport cycle (dark stages of photosynthesis). The process which depends on CO_2 concentration may be characterized approximately by the limiting rate constant of the second-order k_{CO_2}. The kinetics, the productivity of the systems, and the efficiency of energy conversion will be determined by one or another step of scheme 1, depending on the conditions and relations between the rate constants of different steps.

One can determine the energy conversion coefficient in the photosynthesis mechanism as a ratio of the flux of product generation and the value of the absorbed light energy

$$\eta = \eta_1 \times \eta_2 \times \eta_3 \times J_p/I \tag{2}$$

where J_p is the fluxed generated product, expressed in units of stored chemical energy, and I is the absorbed light intensity, with coefficients η_1, η_2, η_3 set by the particularities of photosynthetic mechanism.

Owing to the spectral properties of its pigments, the photosynthetic apparatus can absorb only a certain part of solar energy over the whole solar spectrum (coefficient η_1). In accordance with [7], the photosynthetic pigments absorb about half of the solar energy ($\eta_1 \sim 0.45$).

Coefficient η_2 describes a two-quantum electron transport mechanism. The value of coefficient η_2 estimated by accumulation of the inner energy will be 41.8 %, and the one estimated by accumulation of free energy is 34.7 %. Coefficient η_3 characterizes the reflecting capacity of the system. For most of the systems, this coefficient is equal to 0.8–1.0.

In accordance with kinetic scheme 1, the flux of the product of the photosynthetic reaction in the steady-state regime may be expressed by the equation

$$J_p = \{k(I) \times A_0/[1 + k(I)/k_e + k(I)/k_{CO_2} \times CO_2]\} - \beta A_0 \tag{3}$$

where A_0 is the total concentration of photosynthetic units per unit of the surface.

Equation 3 describes the steady-state rate of the product generation in the system (biomass, oxygen). The additional process ($-\beta A_0$) involves the consumption of the energy accumulated in the system. The rate of this process is approximately proportional to the total amount of the biomass in the system (the number of cells, reaction center, etc.). The coefficient of proportionality is set by β. It can express the rate constant of the limiting step of energy consumption, for example, the limiting rate constant of a certain elementary process of the respiration mechanism.

From eq. 3, an important characteristic of the photosynthetic process follows. Namely, the dependence of the flux of the photosynthetic products (oxygen or biomass) on the light intensity or the terminal electron acceptor (CO_2) concentration is expressed by the functions with "saturation".

For high CO_2 concentration, we have

$$J_p = \{k_e \times k(I)/[k_e + k(I)]\} \times A_0 - \beta A_0 \tag{4}$$

And for high intensities of the absorbed light

$$J_p = [k_{CO_2} \times k_e \times CO_2/(k_{CO_2} \times CO_2 + k_e)] \times A_0 - \beta A_0 \tag{5}$$

When one uses "saturated" intensities and concentrations of CO_2, the productivity of the system is determined by the difference between the rates of the limiting steps of the protein electron transport (k_e) and the limiting step of energy consumption (β)

$$J_p = (k_e - \beta) \times A_0 \tag{6}$$

$$I \rightarrow \infty$$

$$CO_2 \rightarrow \infty$$

The energy conversion coefficient in the photosynthesis mechanism is a function of the absorbed light intensities. The dark steps of the process, for instance, the protein electron transport, become limiting factors at high light intensities, and the productivity of photosynthesis remains constant even with a further increase of the input light energy flux.

For "saturated" CO_2 concentrations [$k_{CO_2} \times CO_2 \gg k(I)$], in accordance with eqs. 2 and 3, the efficiency of the system will be described by the equation

$$\eta = \eta_1 \times \eta_2 \times \eta_3 \{(k(I) \times k_e \times A_0/[k(I) + k_e]I\} - \beta A_0/I \tag{7}$$

A_0 can be set by the value of the absorbed light optical density. When the optical density value equals 1, $A_0 = (n\varepsilon_x)^{-1}$, where n is the number of chlorophyll molecules per reaction center, ε_x is the extinction coefficient.

The function $k(I)$ can be represented by various forms, depending on the mechanism of primary processes. We can consider the simplest case. The rate constant of light absorbtion by the system is a linear function of the adsorbed light intensity

$$k(I) = \alpha \times I, \ \alpha = n\varepsilon_x \tag{8}$$

In this case, the rate constant of the light energy absorption is defined by the number of pigment molecules and the extinction coefficient of its absorption

$$k(I) = n\varepsilon_x I \tag{9}$$

From eqs. 7 and 9, it follows that the dependence of the efficiency of energy conversion on the light intensity is determined by the following equation:

$$\eta/\eta_1 \times \eta_2 \times \eta_3 = [1/(1 + \alpha I/k_e) - \beta/\alpha I] \tag{10}$$

The function of the efficiency of the energy conversion by the photosynthetic system is determined by two parameters: ratio k_e/α and dimensionless ratio k_e/β. The ratio k_e/α has a meaning of intensity expressed either in energy or molecular units.

The nature of the limiting stage in the electron transport chain and the value of the limiting rate constant k_e are of key significance. To determine the order of k_e/α one can assume that the number of pigment molecules per reaction center equals 10^2, "an average" extinction coefficient ε_x equals 10^4 $M^{-1} \times cm^{-1}$ and $k_e = 50$ s^{-1}. The latter was estimated by statistic analysis of the rate constants of the limiting steps in enzymatic catalysis [9].

If it is assumed that the value of "an average" quantum of photosynthetically active radiation equals 50 kcal $\times$ Einstein^{-1}, then the value of k_e/α for the photosynthetic process assumed parameters will be about 110 W/m^2.

The functional dependence of $\eta/\eta_1 \times \eta_2 \times \eta_3$ on the light intensity has two peculiarities.

(1)   There is a threshold light intensity I_0 below which no energy is stored in the system ($\eta/\eta_1 \times \eta_2 \times \eta_3 \leq 0$).

$$I_0 = k_e/\alpha \times 1/(k_e/\beta - 1) \tag{11}$$

The value of this threshold intensity is determined by the two above-mentioned parameters k_e/α and k_e/β.

(2)   The dependence of the energy conversion coefficient on the light intensity is a function with a maximum determined by the equation

$$(\eta/\eta_1 \times \eta_2 \times \eta_3)_m = (k_e/\beta - 1)^2/[k_e/\beta + (k_e/\beta)^{1/2}]^2 \tag{12}$$

The value of intensity which corresponds to extremum is described by the formula

$$I_m = k_e/\alpha \times [1 + (k_e/\beta)^{1/2}]/(k_e/\beta - 1) \tag{13}$$

It is of interest to note that a maximum value of the energy conversion coefficient is determined only by the ratio of the limiting rate constant of electron transport and the corresponding constant of energy consumption.

The maximum value of the energy conversion coefficient in the photosynthesis mechanism for conditions of solar spectrum type is equal to $\eta_1 \times \eta_2 \times \eta_3 \sim 0.15$. It is a sufficiently high value.

It would be of interest to estimate maximum fluxes of photosynthesis proceeding from the knowledge of the electron transport limiting rate. The maximum flux of photosynthesis depends on a concentration of the reaction centers which absorb the whole light flow. We can consider the maximum possible flux of the reaction which can occur if light absorbtion is carried out only by the reaction centers. If "an average" molar absorbtion is coefficient equal to about 10^4 $M^{-1} \times cm^{-1}$, the surface concentration of reaction centers will be 10^{-3} mol $\times m^{-2}$. For such conditions, the maximum flux of product generation will be equal to 5×10^{-2} electron equivalent per second (at $k_e \gg \beta$) (the limiting step of electron transport is characterized by rate constant of about 50 s^{-1}; see above). After 12 h of illumination, the oxygen productivity of 1 m^2 of the surface would be about 270 mol $\times m^{-2} \times day^{-1}$. If the basic equation of photosynthesis is

$$CO_2 + H_2O \rightarrow O_2 + (CH_2O)_n \tag{14}$$

The stoichiometric relations will give a value of 8.1 kg $\times m^{-2} \times day^{-1}$ for the maximum biomass productivity of photosynthesis.

It is a very high productivity which could be realized only at saturated intensities of light, at saturated CO_2 concentrations, and in the absence of the photosynthetic antenna (one molecule of pigment per reaction center).

THEORY AND EXPERIMENT

A comparison of eq. 10 with the experimental results shows that the model under consideration provides a satisfactory description of the experimental dependences of the energy conversion coefficient on absorbed light intensity.

Figure 1 presents the dependence of $\eta/\eta_1 \times \eta_2 \times \eta_3$ taken from the experimental results of [10] and theoretical dependence followed from eq. 10 at $k_e/\alpha = 120$ W/m^2, $k_e/\beta = 6$. (According to [10], the value of the conversion coefficient $\eta = \eta_2 \times J_p/I$. The data of the work [10] have been reassessed on the basis of $\eta_2 = 0.34$, see above). One should regard as satisfactory the coincidence of the theoretical and experimental dependences.

An additional assessment of the results of the kinetic model has been made on the basis of experimental data of the study [11].
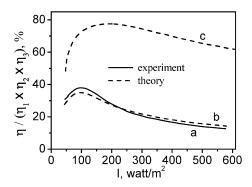
Fig. 1 Microalga *Chlorella* energy conversion coefficient vs. light intensity. Curve a: experimental data of [10]; curve b: theoretical estimation in accordance with eq. 11 ($k_e/\alpha = 120$ W/m^2, $k_e/\beta = 6$); curve c: theoretical estimation in accordance with eq. 11 for $k_e/\alpha = 120$ W/m^2, $k_e/\beta = 58$, defined from results of Fig. 2.

In accordance with the developed model, the productivity of the system (the flux of product per unit of surface) is described by eq. 4. Our analysis shows that the equation gives a quantitative description of the experimental dependences of the system's productivity on CO_2 concentration and intensity of absorbed light. It can be illustrated by experimental results of the study [11] which examined in detail the characteristics of biomass growth of thermophilic strain *Chlorella sp. K* at different CO_2 concentrations and light intensities. The estimates show that the contribution of energy consumption process (CO_2 formation via respiration) is not large ($\beta A_0 = 6\, l\, CO_2$ m^{-2} day^{-1}). According to eq. 4, the dependence of $(J_p + \beta A_0)^{-1}$ on the inverse concentration of CO_2 for different CO_2 concentrations should be presented as a series of parallel straight lines

$$(J_p + \beta A_0)^{-1} = 1/\alpha \times I \times A_0 + 1/k_e \times A_0 + 1/k_{CO_2} \times A_0 \times CO_2 \tag{15}$$

The intercepts should exhibit a hyperbolic dependence on the inverse intensity of absorbed radiation energy. Figure 2 demonstrates that such dependences do occur. At high concentrations of CO_2 and light intensities, photosynthesis becomes "saturated". The maximum productivity of the system takes place at infinite CO_2 concentrations and light intensities. It is estimated in accordance with eq. 15 from Fig. 2B and equals $\bar{k}_e \times A_0 = 350 \pm 50\, l\, CO_2 \times$ m^{-2} day^{-1}. The values of all basic photosynthetic parameters at "saturated" CO_2 concentrations, namely: $k_e/\alpha = 120$ W $\times$ m^{-2}, $k_e/\beta = 58$ follow from the data on Fig. 2. In accordance with eqs. 11–15, the parameters of the light curve: $I_0 = 20$ W $\times$ m^{-2}, $I_m = 170$ W $\times$ m^{-2} and $\eta_m = 11.5$ % can be calculated. Thus, the calculations based on the experimental results of the work [11] show that thermophilic strain *Chlorella* operates with a maximum energy conversion efficiency of 11.5 % over the solar spectrum at intensity of 170 W/m^2.

With the aid of k_e/α and k_e/β, we can estimate the energy conversion coefficient values at any light intensity. These data presented in Fig. 1 (curve c). The same figure shows both the data of the work [10] on the productivity of mesophilic strain *Chlorella* and the curve plotted on the basis of the kinetic model described above (eq. 10).

Thus, the kinetic model furnishes a sufficiently satisfactory description of the most typical properties of biomass accumulation by cultures of microalgae. It should be noted that the model is the simplest one. Its further development allows a quantitative description of phenomena with complex effects such as the inhibition by high light intensities or high CO_2 concentration.

It is essential to elucidate the following questions:

What are the parameters of the photosynthetic apparatus (the size of the photosynthetic antenna, the rate of electron transport, the correlation between photosynthesis and respiration) to approximate the system's productivity to the maximum possible one and to correlate the maximum of efficiency to "an average" solar light intensity ($I_m = 400$ W/m^2)?
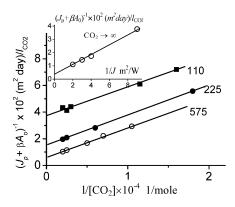
Fig. 2 Productivity of thermophilic *Chlorella sp. K* vs. CO_2 concentration and light intensity (see inset) (experimental data of [11] transformed in the coordinates of eq. 15). The numbers of the lines given at the main figure correspond to the absorbed light intensity (W/m^2).

What are the parameters of a photosynthetic system capable of operating at concentrated solar light, for instance, at light intensity of "one hundred suns" (I_m = 40 kW/m^2)?

OPTIMUM PHOTOSYNTHESIS AT "ONE SUN"

Imagine a photosynthetic system with "average" parameters, for example, *Chlorella*. Its energy conversion coefficient is shown in Fig. 1 (curves a, b). At light intensities of "one sun" (400 W $\times$ m^{-2}), the solar energy conversion coefficient is equal only to 2.6 %. Presuming that several apparatus characteristics (the size of the photosynthetic antenna, the ratio of photosynthesis rate and respiration) remain constant, we shall study photosynthesis systems at different temperatures. It is obvious that the coefficient of system light energy consumption $k(I)$ should not, in fact, depend on the temperature, while the rate constants of limiting enzymatic processes (k_e and k_{co_2}) increase appreciably with the growth of temperature. At "saturated" CO_2 concentrations, the changes in photosynthesis efficiency due to electron transport rate alteration at various temperatures can be analyzed.

The dependence of electron transport rates on the temperature has been studied within the range of 10–60 °C. The activation energy values of the process have been shown to be 10–15 kcal $\times$ mol^{-1} for a number of systems. Such values are typical of the majority of chemical and enzymatic processes. For example, the activation energy of electron transport to an electron acceptor in isolated chloroplasts was found to be 12.5 $\pm$ 1.0 kcal $\times$ mol^{-1} [4]. Starting from the value, the value of k_e at any temperature can be estimated. We also can study how the change of k_e/α would affect the shape of light curves and the efficiency for photosynthetic systems at various temperatures.

Figure 3 shows the results of numerous calculations of the photosynthetic system both at 20 °C (k_e/α = 120 W $\times$ m^{-2}, k_e/β = 6, these parameters correspond to experimental data in Fig. 1), and at 60 °C (k_e/α = 1560 W $\times$ m^{-2}), at 40 °C (k_e/α = 480 W $\times$ m^{-2}), at 80 °C (k_e/α = 4536 W $\times$ m^{-2}).

The ratio of k_e/β equals 6 and is constant for every system (both k_e and β are supposed to exhibit a similar dependence on temperature).

It is clear that use of thermophilic systems (if the other parameters are constant) must raise photosynthesis productivity, and shift the maximum energy conversion coefficients to the range of the highest light intensities.
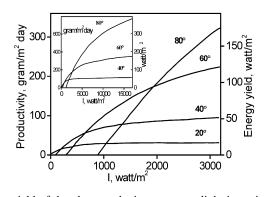
Fig. 3 Productivity and energy yield of the photosynthetic system vs. light intensity at various temperatures (the numbers on the curves). For all the cases, $k_e/\beta = 6$. The curve at 20 °C corresponds to experimental data in Fig. 3. The values of k_e/α (W/m^2) at various temperatures are: 20 °C: 20; 40 °C: 480; 60 °C: 1560; 80 °C" 4536, respectively.

If it is assumed that maximum of efficiency corresponds to a solar light intensity of $I_m = 400$ W × m^{-2} and $k_e/\beta = 6$, then k_e/α should be equal to 580 W × m^{-2} for optimum photosynthesis at "one sun". Its value corresponds to a system working at 45 or 20 °C, but with the photosynthetic antenna decreasing 4.8-fold (the number of pigment molecules per reaction center are to be decreased 4.8-fold). The parameters of optimal system are presented in Fig. 4.

Curves 1 and 1' express the productivity and energy conversion coefficient for "usual" strain *Chlorella* at 20 °C (curve 1 is also given on Fig. 1). Curves 2 and 2' fit the same system provided it functions at 45 °C. One can see that the energy conversion coefficient and the system's productivity are to increase significantly.
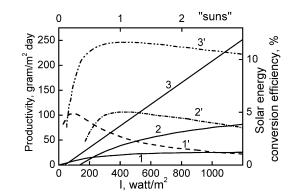

Fig. 4 Optimum photosynthesis at "one sun", $I_m = 400$ W/m^2. Curves 1 and 1': the initial system's biomass productivity and the energy conversion coefficient, respectively, for *Chlorella* (experimental data of Fig. 3); Curves 2 and 2': biomass productivity and energy conversion coefficient for optimum photosynthesis ($k_e/\alpha = 5860$ W/m^2, $k_e/\beta = 6$); Curves 3 and 3': biomass productivity and energy conversion coefficient for optimum photosynthesis ($k_e/\alpha = 3600$ W/m^2, $k_e/\beta = 100$).

Curves 3 and 3' express parameters of an "improved" strain with the maximum of efficiency at "one sun" and an appreciable increase of the ratio of k_e/β ($k_e/\beta = 100$). The value of k_e/α needs to be equal to 36 000. It corresponds to photosynthesis at 60 °C with a 2.3-fold photosynthetic antenna decrease or at 46 °C with a 6.2-fold antenna decrease.

Thus, thermophilic photosynthesis is a way of increasing the productivity. The data in Fig. 1, which show the dependences of energy conversion coefficient for mesophilic and thermophilic strains of *Chlorella*, also illustrate this point.

Thermophilic microalgae are shown to be able to "work" actively at 50–60 °C, but cyanobacteria do it at the highest temperatures.

OPTIMUM EFFICIENCY AT LIGHT INTENSITY OF "ONE HUNDRED SUNS"

A large-scale solar energy conversion is impeded by high construction costs. If it were possible to intensify the process at least 100-fold, cut the size of the systems, and reduce the working surfaces production, the solution would become much more feasible. Simple technological installations capable of 10–100-fold solar light concentration are being designed.

This theory makes it possible to answer the question: what are the parameters of the system capable for operating with maximum efficiency at solar light intensity of "one hundred suns" ($I_m = 40 \text{ kW} \times \text{m}^{-2}$)?

Figure 5 indicates parameters of an "optimum" system capable of working at light intensity of "one hundred suns". Curves 1 and 1' fit the productivity and efficiency at $I_m = 40 \text{ kW} \times \text{m}^{-2}$. Parameters k_e/α must be equal to 54 000 (for $k_e/\beta = 6$). It corresponds to system at 70 °C with the pigment antenna decreasing 20-fold (10–20 pigment molecules per reaction center). The same Fig. 5 shows calculated data for the system with $k_e/\alpha = 54\,000$, but with a markedly decreased respiration intensity ($k_e/\beta = 100$). The maximum efficiency for the latter system corresponds to the intensity of absorbed light at 10 "suns".
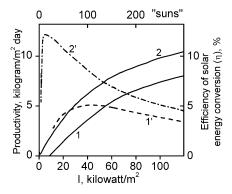

Fig. 5 Optimum photosynthesis at light intensity of "one hundred suns". Curves 1 and 1': the biomass productivity and energy conversion coefficient for the system with $k_e/\alpha = 54.0 \text{ kW/m}^2$, $k_e/\beta = 6$, $I_m = 40 \text{ kW/m}^{2)}$; Curves 2 and 2': the biomass productivity and energy conversion coefficient for the system with $k_e/\alpha = 54.0 \text{ kW/m}^2$ and $k_e/\beta = 100$, respectively.

To achieve that, it is necessary to perform the process at high temperatures (60–80 °C) and substantially reduce the size of the pigment antenna.

Thus, one can infer a method for increasing the productivity in conjunction with the maximum efficiency of photosynthesis: (1) the use of thermophilic cultures, (2) reduction of the photosynthetic antenna, and (3) a relative decrease in the respiration intensity. We may suggest that with the help of selection, genetics, and genetic engineering, it is possible to build a thermophilic system enriched by reaction centers with respect to the pigment. The above results define the trends of further improvement of the primary productivity of systems for obtaining maximum energy conversion.

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