

# Modeling the Kinetics of Photosynthetic Chemistry

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Osoka E.C.

**Abstract**— In this work, the chemical kinetics of photosynthesis was extensively explored. Kinetic models were established. Existing data from the internet were used for the validation of the models. It was observed that the models are real and natural as they follow the growth profile nature of photosynthetic release, together with the uptake of oxygen and carbon dioxide respectively. The models actually conform to what was found in literature. Therefore photosynthetic activities could be studied using natural growth models, in conjunction with the specificities of photosynthetic phenomena. This work can be employed in the growth study of plants in agriculture, carbon cycle, and perhaps ozone layer depletion or carbon sequestration.

**Index Terms**— Carbon dioxide, heat, kinetics, modeling, oxygen, photosynthetic chemistry.

## I. INTRODUCTION

Photosynthesis is a process used by plants and other organisms to convert light energy normally from the sun into chemical energy that can be inter-released as fuel, and for other organism's activities. This chemical energy is stored in carbohydrate molecules such as sugars which are synthesis of carbon dioxide and water; hence the name photosynthesis from the Greek words photo-'light' and synthesis of 'putting together'[1]. Photosynthesis is simply the manufacture of organic material from water and carbon dioxide by green plant in the light [2].

Early life – history stages of many organisms lack circulatory system but are small enough to achieve adequate gas exchange through diffusion. The risk of hypoxia is magnified for larger embryos [3].

Internal partial pressure of oxygen in egg masses of amphibians and marine invertebrates are associated with increase in embryonic mortality or with developmental delays. The causal relationship between low oxygen and these developmental risks have been demonstrated by rescuing embedded embryos with additional oxygen bubbled into the external medium.

The consequences of local photosynthesis oxygen for marine invertebrates egg masses are, by comparison, poorly known and have concerned only association between egg masses and unicellular algae [4, 5].

When the air  $CO_2$  content rises, nearly all of earths plants experience increased rates of photosynthesis, and because photosynthesis convert carbon dioxide into sugar, elevated levels of atmospheric  $CO_2$  practically always stimulate the production of non-structural carbohydrates. In turns, with greater non-structural carbohydrates,  $CO_2$  enriched plants have more raw materials at their disposal for facilitating

increased growth and development [6]. Elevated  $CO_2$  has also been shown to enhance nonstructural carbohydrate concentration in the leaves of various trees. For example, observed 30 to 100%  $CO_2$ -induced increase in sugar and starch concentration with leaves of four semi-deciduous tropical forest species in response to a doubling of the atmosphere  $CO_2$  content. Similar  $CO_2$ -induced increase in leaf nonstructural carbohydrate concentrations have been reported in spruce [7].

Before scientists understood the process of photosynthesis, they were at a loss to explain how plant could grow and increase their mass while others assumed that water alone gave plants their heft. None of these explanations, however, held up when tested experimentally. In test after test, mass lost by soil, water and even carbon dioxide didn't measure up to the mass gained by a growing plant [8].

Regulation properties of biological process can be determined by their hierarchical organization in space and time

The type of regulation that will take place in a system depends on time-space hierarchy of the processes and on the character of the influencing factors. From kinetic view point, the existence of regulation in a system means that models parameters (usually the rate constant of reactions) change in response to the action; internal or external factors of model of primary photosynthetic process is compartmentalized and describes the events taking place in the three main compartments of the chloroplast;stroma, thylakoid membrane and thylakoid lumen [5, 9].

Illumination initiates electron transfer along the electron transport chain with coupled trans-membrane protons translocation from the chloroplast stroma into thylakoid lumen, where by an electrochemical proton gradient is created across the thylakoid membrane.Generation of chemical proton gradients involve highly specialized pigment-protein complexes of photo-system I and II as well as the cytochrome complex. The electron chemical gradient is utilized in ATP synthesis by ATP Synthase [10].

The problem is how to capture an accurate model that can X-ray the complex activities in photosynthetic process. Since there are multiple activities or reactions during electron transfer; it is important to obtain a model that will explain this transfer.

It is important to study the electron transfer phenomenon in photosynthesis so that the actual mechanism of the photosynthesis can be exploited in other area.

The objective of this work is to mathematically model variations in parameters with time as photosynthetic activities continue. The variable parameters are regarded as metabolites.

This work is to model the metabolite variation with time and to explain some of the intricate mechanisms in photosynthesis only. It does not give the details of electron transfer within the three compartments.

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II. LITERATURE

Many spectra of absorptance (the absolute value of light absorption) measured with integrating spheres have shown clearly that ordinary green leaves of land plants absorb a substantial fraction of green light [2]. It is known that green light once absorbed by the leaves drives photosynthesis with high efficiency [11, 12]. On an absorbed quantum basis, the efficiency or photosynthesis quantum yield of green light is comparable with red light and greater than that of blue light. The difference between the quantum yields of green and blue light is particularly large in woody plants grown out doors in high light.

As an optical system, the leaf differs from a pigments solution in two aspects: the concentration of pigments in chloroplasts and the diffusive nature of plant tissues. The first factor decreases the opportunity for light to encounter pigment and generally decrease light absorption, and has been called the sieve or flattening effect. Once light that is strongly absorbed by chlorophylls, such as blue or red, encounters a chloroplast, most of the light is absorbed [11, 13].

The second point that distinguishes leaves from a simple pigments solution is that leaf tissues are diffusive. This is due to the fact that the leaf consist of cells and intercellular air spaces. The diffusive nature of leaf tissues increases the light path length (devour effect) and thereby the opportunity of light to encounter chloroplast leading to the increase in absorptance. On the other hands, the diffusive nature of the leaf tissues inevitably increases the reflectance of the leaf to some extent [14, 15].

The micro fiber optic method is the most efficient in measuring the flux of light within a leaf. Because the viewing angle of the optical fiber is narrow, the angular distribution of the lights flux, including backward scattering, is measured by inserting the fiber into the leaf from various directions. To analyze the light environment within the leaf in relation to photosynthesis, it is necessary to know the light absorption profile, not the light fluxes present. This is because only, those photons absorbed by pigments can work photochemically [12]. Our absorptance data agree well with a previous calculation of light absorption gradient, which was based purely on the experimental data [16]. When compared on a unit chlorophyll bases, the chloroplast in the lower part of the leaf absorbs (10% of those in the uppermost part, even at a wavelength of 550nm at which the absorption gradient is most moderate). For wave length with strong absorption, such as red and blue, the fractions are much smaller [2].

The differences in photosynthetic properties found between the chloroplasts in the upper and lower parts of the leaf are essentially identical to those found between the sun and shade plants [13].

The most efficient situation is realized when the profile of light absorption and the profile of photosynthesis capacity are

perfectly matched, and all chloroplast in the leaf behave synchronously with respect to photosynthetic light saturation. When leaves are irradiated from the upper side, therefore there will be a situation in which the upper chloroplasts are height saturated while the chloroplasts in the lower parts still need additional height to reach saturation. In other words the quantum yield of photosynthesis differs within the heart being less in the uppermost part [7, 9]. It has long been known that the sharpest height response curve are obtained when these leaves are irradiated equally from both sides. If a plant's capacity to utilize carbon is limited (Sink limited), any increase in photosynthesis cannot be sustained and will curtailed through feedback process [3, 16]. Hence, the concentration of photosynthetic enzyme is usually lower in plants grown under elevated CO<sub>2</sub>. It has been hypothesized that drought plants are under carbon starvation and their growth under carbon limitation.

Accumulation under water deficit has been reported in several species of various plants parts, and for different carbon forms. Soluble carbohydrate concentration increases under water deficit in the leaves of plants [8]. Carbohydrates also accumulate in stems as well as in the roots. Accumulation occurs both after rapid osmotic shocks and during slowly developing water deficit [11].

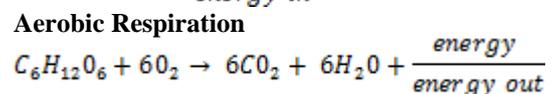
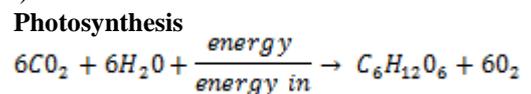
The impact of water deficit on carbon metabolism has been the matter of numerous studies. Some report that in some cases the enzymes involved show signs of down-regulation but more often support the view of increased metabolic activity [6].

III. ENERGY INPUT AND DEVELOPMENT OF KINETIC MODELS

Energy input into ecosystems

The Theory of Photosynthesis versus Respiration

In the green plants both photosynthesis and respiration occur. In relatively bright light photosynthesis is the dominant process (meaning that the plant produces more food than it uses). At night, or in the absence of light, photosynthesis essentially ceases, and respiration is the dominant process; the plant consumes food (for growth and other metabolic processes).



The two processes are shown in the simplified equation above. Photosynthesis absorbs energy (from sunlight) whereas aerobic respiration yields energy (as a result of the oxidation of glucose, the carbohydrate molecule shown here).

Table1: Stoichiometric table for photosynthesis reaction

| Species                                       | Symbol | Initially       | Change                | Remaining                             | Concentration                         | Concentration         |
|---|--------|-----------------|-----------------------|---------------------------------------|---------------------------------------|-----------------------|
| CO <sub>2</sub>                               | A      | N <sub>A0</sub> | -N <sub>A0</sub> X    | N <sub>A0</sub> (1-x)                 | C <sub>A0</sub> (1-x)                 | C <sub>A0</sub> (1-x) |
| H <sub>2</sub> O                              | B      | N <sub>B0</sub> | -N <sub>A0</sub> X    | N <sub>A0</sub> (θ <sub>B</sub> -x)   | C <sub>A0</sub> (θ <sub>B</sub> -x)   | C <sub>A0</sub> (1-x) |
| C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> | C      | N <sub>A0</sub> | 1/6 N <sub>A0</sub> X | N <sub>A0</sub> (θ <sub>C</sub> +x/6) | C <sub>A0</sub> (θ <sub>C</sub> +x/6) | C <sub>A0</sub> x/6   |
| O <sub>2</sub>                                | D      | N <sub>D0</sub> | N <sub>A0</sub> X     | N <sub>A0</sub> (θ <sub>D</sub> +x)   | C <sub>A0</sub> (θ <sub>D</sub> +x)   | C <sub>A0</sub> x     |
| Inert   |        | N <sub>I0</sub> |                       | N <sub>I0</sub>                       | C <sub>I0</sub>                       | C <sub>I0</sub>       |

Note that these are essentially “competing” processes: one producing glucose (photosynthesis) and the other consuming glucose (respiration).

When such an experiment is actually performed it is found that increasing the brightness (intensity) of light increases the rate of photosynthesis, but only to a certain point, beyond which increasing the brightness of light has little or no effect on the rate of photosynthesis.

Conversely, reducing the brightness of the light causes a decrease in photosynthetic activity.

The light intensity, at which the net amount of oxygen produced is exactly zero, is called the compensation point for light. At this point the consumption of oxygen by the plant due to cellular respiration is equal to the rate at which oxygen is produced by photosynthesis.

The compensation point for light intensity varies according to the type of plant, but it is typically 40 to 60W/m<sup>2</sup> for sunlight. The compensation point for light can be reduced (somewhat) by increasing the amount of carbon dioxide available to the plant, allowing the plant to grow under conditions of lower illumination.

### Compensation point for carbon dioxide

Under conditions of constant and uniform illumination the rate of photosynthesis can be increased by simply increasing the amount of carbon dioxide (i.e. increasing the atmospheric partial pressure) available to plants.

As before, one can measure the rate of photosynthesis as a function of carbon dioxide pressure by placing a green plant in a sealed container and measuring the rate at which oxygen is produced.

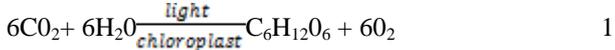
As the partial pressure of carbon dioxide increases there is an almost linear increase in the rate of oxygen production, which implies an identical increase in the rate of photosynthesis.

This increase eventually levels off, and further increases in the concentration of carbon dioxide have no further effect.

Conversely, reducing the carbon dioxide concentration reduces the rate of photosynthetic activity. The level at which the oxygen production rate drops to zero is called the compensation point for carbon dioxide.

### Development of Kinetic Models

The kinetic model was developed, following the metabolite behavior in the photosynthetic system. This was done using the stoichiometry of the simplest of photosynthetic reaction as shown below



$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \text{ or } \frac{r_A}{-6} = \frac{r_B}{-6} = \frac{r_C}{1} = \frac{r_D}{1} \quad 4$$

**Table1: Stoichiometric table for photosynthesis reaction**

Note:  $\theta_B = \frac{N_{B0}}{N_{A0}} = \frac{1}{1} = 1$ ;  $\theta_C = \frac{N_{C0}}{N_{A0}} = \frac{0}{1} = 0$ ;  $\theta_D = \frac{N_{D0}}{N_{A0}} = \frac{0}{1} = 0$

### Computation of reaction orders and rate constant

$$\text{If } -r_A = -\frac{dC_A}{dt} = KC_A^\alpha C_B^\beta \quad 5$$

$$\text{Taking log, } \ln(-r_A) = \ln K + \alpha \ln C_A + \beta \ln C_B \quad 6$$

$$Y = a_0 + \alpha x_1 + \beta x_2 \quad 7$$

$$\text{So that } S = \sum(Y - a_0 - \alpha x_1 - \beta x_2)^2 \quad 8$$

$$\text{For } \frac{\partial S}{\partial a} = 0, \sum Y - na_0 - \alpha \sum x_1 - \beta \sum x_2 = 0 \quad 9a$$

$$\text{For } \frac{\partial S}{\partial \alpha} = 0, \sum Y x_1 - a_0 \sum x_1 - \alpha \sum x_1^2 - \beta \sum x_1 x_2 = 0 \quad 9b$$

$$\text{For } \frac{\partial S}{\partial \beta} = 0, \sum Y x_2 - a_0 \sum x_2 - \alpha \sum x_1 x_2 - \beta \sum x_2^2 = 0 \quad 9c$$

Solving equations 9a to 9c gives:

$$\beta = 2.1954, \quad \alpha = 0.2373, \quad a_0 = -12.6545$$

$$\gamma = \alpha + \beta = 2.433$$

### Computation of photosynthesis transient relationship

From stoichiometry, Table 1 and equation (3.5)

$$-r_A = -\frac{dC_A}{dt} = -C_{A0} \frac{d(1-x_A)}{dt} = K[C_{A0}(1-x)]^\alpha [C_{A0}(1-x)]^\beta$$

$$C_{A0} \frac{dx}{dt} = KC_{A0}^{\alpha+\beta} (1-x)^{\alpha+\beta}$$

$$\frac{dx}{dt} = K^i (1-x)^\gamma$$

Where  $K^i = KC_{A0}^{\alpha+\beta-1}$  and  $\gamma = \alpha + \beta$

Separating variables,  $(1-x)^{-\gamma} dx = K^i dt$

And putting  $u = (1-x), du = -dx$ ;

we have,  $-u^{-\gamma} du = K^i dt$

$$\text{Integrating, } \frac{u^{-\gamma+1}}{-\gamma+1} = \frac{(1-x)^{1-\gamma}}{1-\gamma} \int_{x_0}^x = -K^i t \int_0^t$$

$$\frac{(1-x)^{1-\gamma} - (1-x_0)^{1-\gamma}}{1-\gamma} = -K^i t$$

$$x = 1 - \left[ \frac{(1-x_0)^{1-\gamma} - (1-\gamma)K^i t}{1-\gamma} \right]^{\frac{1}{1-\gamma}} \quad 10$$

$$CO_2, H_2O: C_{A0}(1-x) = C_{A0} \left[ \frac{(1-x_0)^{1-\gamma} - (1-\gamma)K^i t}{1-\gamma} \right]^{\frac{1}{1-\gamma}} \quad 11$$

$$\text{Carbohydrate: } C_{A0} \left( \theta_C + \frac{x}{6} \right) = C_{A0} \left( \theta_C + \frac{1}{6} \left( 1 - \left[ \frac{(1-x_0)^{1-\gamma} - (1-\gamma)K^i t}{1-\gamma} \right]^{\frac{1}{1-\gamma}} \right) \right) \quad 12$$

$$\text{Oxygen: } C_{A0}(\theta_D + X) = C_{A0} \left( \theta_D + \left( 1 - \left[ \frac{(1-x_0)^{1-\gamma} - (1-\gamma)K^i t}{1-\gamma} \right]^{\frac{1}{1-\gamma}} \right) \right) \quad 13$$

If there was water before the production of water (steam) of reaction; then from stoichiometry and equation (3.5), becomes

$$-r_A = -\frac{dC_A}{dt} = -C_{A0} \frac{d(1-x)}{dt} = K[C_{A0}(1-x)]^\alpha [C_{A0}(\theta_B - x)]^\beta$$

$$C_{A0} \frac{dx}{dt} = KC_{A0}^{\alpha+\beta} (1-x)^\alpha (\theta_B - x)^\beta$$

$$\frac{dx}{dt} = K^i (1-x)^\alpha (\theta_B - x)^\beta$$

$$K^i = KC_{A0}^{\alpha+\beta-1}$$

$$K^i dt = \frac{dx}{(1-x)^\alpha (\theta_B - x)^\beta} \equiv \frac{A}{(1-x)^\alpha} + \frac{B}{(\theta_B - x)^\beta}$$

$$\text{So that } 1 \equiv A(\theta_B - x)^\beta + B(1-x)^\alpha$$

$$\text{If } x = \theta_B; 1 = B(1-\theta_B)^\alpha, B = \frac{1}{(1-\theta_B)^\alpha}$$

$$\text{If } x = 1; 1 = A(\theta_B - 1)^\beta, A = \frac{1}{(\theta_B - 1)^\beta}$$

$$K^i t = \frac{1}{(\theta_B - 1)^\beta} \int \frac{dx}{(1-x)^\alpha} + \frac{1}{1} \int \frac{dx}{(\theta_B - x)^\beta}$$

$$-K^i t = \frac{1}{(\theta_B - 1)^\beta} \left[ \frac{(1-x)^{1-\alpha}}{1-\alpha} \right]_{x_0}^x + \frac{1}{1} \left[ \frac{(\theta_B - x)^{1-\beta}}{1-\beta} \right]_{x_0}^x$$

$$K^I t = \frac{1}{(\theta_B - 1)^\beta} \left[ \frac{(1-x_0)^{1-\alpha} (1-x)^{1-\alpha}}{1-\alpha} \right] + \frac{1}{(1-\theta_B)^\alpha} \left[ \frac{(\theta_B - x_0)^{1-\beta} - (\theta_B - x)^{1-\beta}}{1-\beta} \right]$$

14

The equilibrium constant of redox reaction are determine from the experimental data or midpoint redox potential [10].

$$K_{eq} = \exp \left[ \frac{\Delta Em}{RT/nF} \right]$$

Where F is faraday,  $\Delta Em$  is the difference of midpoint redox potential measured relative to a standard hydrogen electrode and n is the number of electrons transferred in the course of the redox reaction. Conversion of solar energy into chemical energy through the utilization of inorganic materials by photo catalytic  $CO_2$  reduction, which is also known as artificial photosynthesis, is the next change for sustainable development.[2]. In the present “state of the act of artificial photosynthesis processes, nature is so far mimicked only to the extent that  $CO_2$  is reduced by water to variable”.

**The variation of rate of photosynthesis and time**

Like all natural growth rate, photosynthesis is not left out in their behaviour. The change in rate is partially proportional to the rate and partially proportional to the square of rate which act as an inhibitor, i.e. photosynthesis with respect to carbon dioxide.

$$\frac{dy}{dx} = K_1 Y - K_1 B Y^2$$

15

The 2<sup>nd</sup> term assumes that the inhibition is proportional to the square of the rate, and, this equation, on integration, yields the logistic analytical solution.

$$Y = \frac{Y_0 e^{K_1 x}}{1 - b Y_0 (1 - e^{K_1 x})}$$

16

If the so-call compensation point is brought in, we will have

$$Y = \frac{Y_0 e^{K_1 (x_0 - x)}}{1 - b Y_0 (1 - e^{K_1 (x_0 - x)})}$$

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**Data collection**

The data for the validation of this work are obtained from previous research works in the net, since such experiments are not possible in our laboratory.

$Y_0$  represent ( $H_2O$  &  $CO_2$ ),  $Y_1$  represent ( $O_2$ ),  $Y_{12}$  represent ( $C_{12}H_{22}O_{11}$ )

**Curve Fitting**

MATLAB package 7.9 was used in curve-fitting the data. Scatter diagram of the collected data was plotted and mathematical model was super-imposed on it to see the goodness of fit of the model to the raw collected data.

**Table 2: Concentrations of carbon dioxide, water, oxygen and carbohydrate during daily photosynthesis at the back of a leaf (Dey et al., 2004).**

| Time(days) | $Y_0$ | $Y_1$ | $Y_{12}$ |
|------------|-------|-------|----------|
| 0          | 4.196 | 1.804 | 0.301    |
| 1          | 1.354 | 4.646 | 0.774    |
| 2          | 0.808 | 5.193 | 0.865    |
| 3          | 0.575 | 5.425 | 0.904    |
| 4          | 0.449 | 5.553 | 0.926    |
| 5          | 0.365 | 5.635 | 0.939    |

$Y_0$  represent ( $H_2O$  &  $CO_2$ ),  $Y_1$  represent ( $O_2$ ),  $Y_{12}$  represent ( $C_{12}H_{22}O_{11}$ )

**Table 3: Amount of  $CO_2$  and  $O_2$  absorbed during photosynthesis in a day (Indracanti et al., 2009).**

|               |    |    |    |     |      |     |     |      |      |    |    |    |
|---------------|----|----|----|-----|------|-----|-----|------|------|----|----|----|
| $CO_2$ (ppmv) | 2  | 10 | 20 | 27  | 36.5 | 40  | 38  | 32.5 | 22   | 12 | 7  | 3  |
| $O_2$ (ppmv)  | 34 | 30 | 15 | 2.5 | 8    | 4.5 | 7.5 | 12.5 | 17.5 | 25 | 30 | 34 |
| Time (hr)     | 6  | 7  | 9  | 10  | 11   | 12  | 13  | 14   | 15   | 16 | 17 | 18 |

**Table 4: Net rate of photosynthesis versus concentration absorbed (Diwan, 2009).**

|  |      |     |     |      |     |     |      |      |      |
|--|------|-----|-----|------|-----|-----|------|------|------|
| Rate of photosynthesis ( $\mu mol/m^2 s$ ) | 0    | 13  | 20  | 26.5 | 31  | 34  | 36.6 | 37.5 | 37.5 |
| $CO_2$ PPMV                                | 73.8 | 200 | 300 | 400  | 500 | 600 | 700  | 800  | 900  |

**Table 5: Cumulative concentration of  $CO_2$  during photosynthesis versus time (Evans and Vogelmann, 2003).**

|                   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $CO_2$ Conc (ppm) | 300 | 300 | 305 | 310 | 320 | 325 | 340 | 350 | 375 | 410 | 450 | 520 | 575 | 635 | 750 | 850 | 975 |
| Time (hr)         | 0   | 12  | 25  | 38  | 50  | 75  | 90  | 100 | 113 | 125 | 138 | 150 | 163 | 185 | 197 | 200 | 213 |

**Table 6: Change in Gibbs free energy versus molecular weight of hydrocarbon and oxygen (Bahdrand Deniz, 2012).**

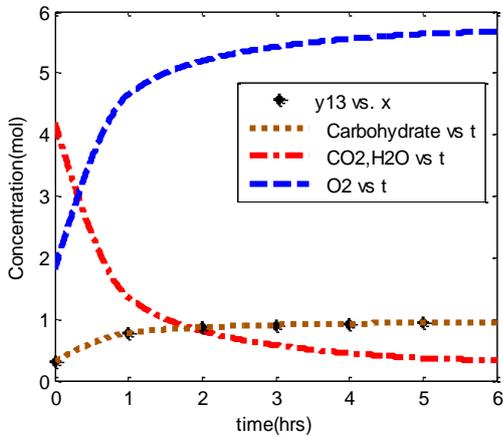
| MW  | $\Delta G_F / H_C$ product | $\Delta G_F / O_2$ |
|-----|----------------------------|--------------------|
| 16  | 801.0                      | 400.5              |
| 24  | 689.2                      | 459.5              |
| 38  | 1306.6                     | 435.5              |
| 132 | 288.0                      | 480.0              |

**Table 7: The rate of photosynthesis versus reaction temperature. (Evans and Vegelmann, 2006).**

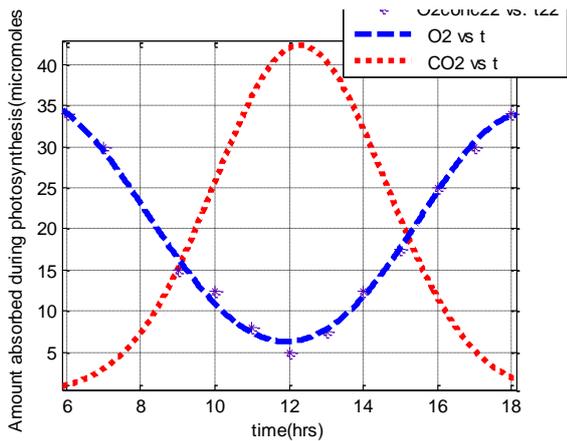
|  |    |    |    |      |     |       |     |       |      |      |
|--|----|----|----|------|-----|-------|-----|-------|------|------|
| Rate of photosynthesis ( $\mu mol/m^2 s$ ) | 25 | 37 | 50 | 87.5 | 129 | 187.5 | 200 | 187.5 | 87.5 | 0    |
| Temperature ( $^0C$ )                      | 0  | 5  | 10 | 15   | 20  | 25    | 30  | 35    | 36.5 | 38.5 |

IV. RESULTS AND DISCUSSION

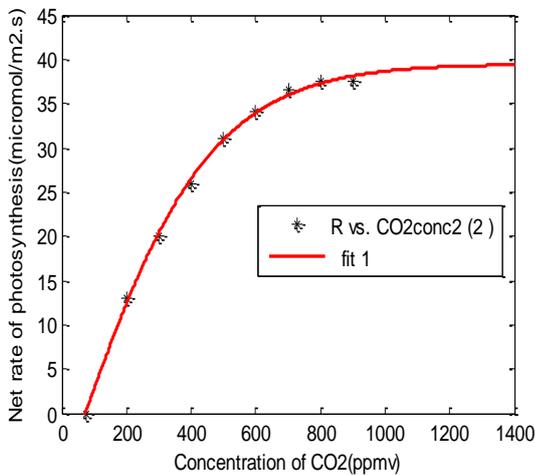
The results of the computations which are done in the previous section are as shown below in figures 1, 2, 3a, 3b, 4, 5, 6 and 7 respectively



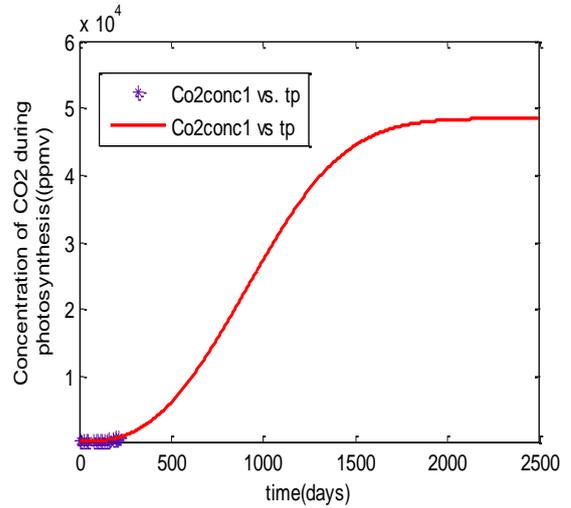
**Fig 1:** Concentration of CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub> and carbohydrate versus time during daily photosynthesis in the back of a leaf



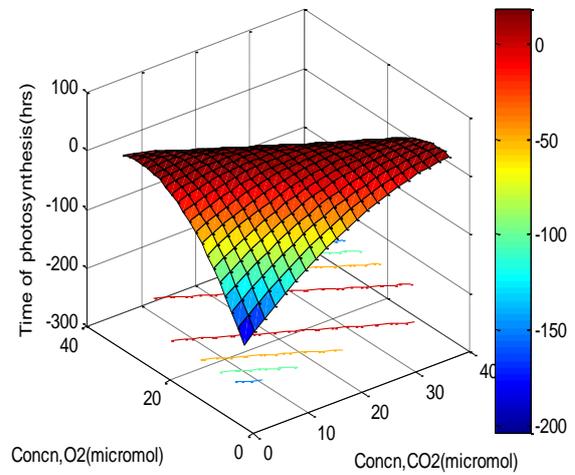
**Fig 2:** Amount of CO<sub>2</sub> and O<sub>2</sub> absorbed during photosynthesis in a day



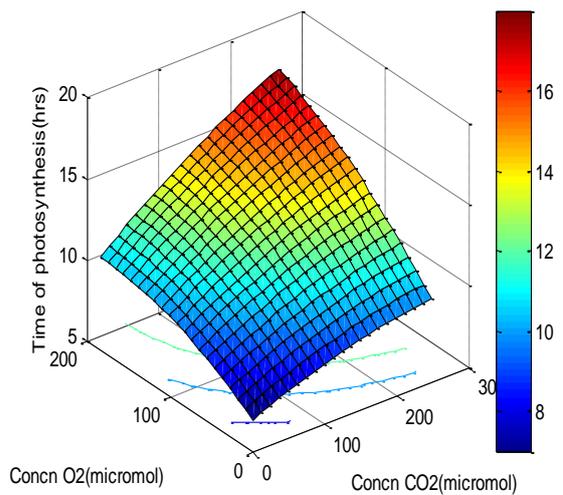
**Fig 3a:** Net rate of photosynthesis versus concentration of CO<sub>2</sub> absorbed



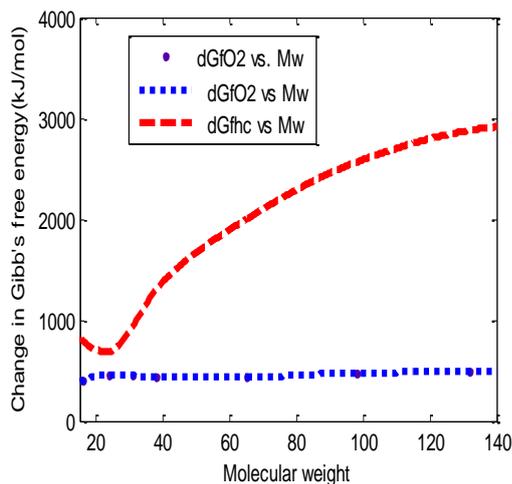
**Fig 3b:** Concentration of CO<sub>2</sub> during photosynthesis versus time



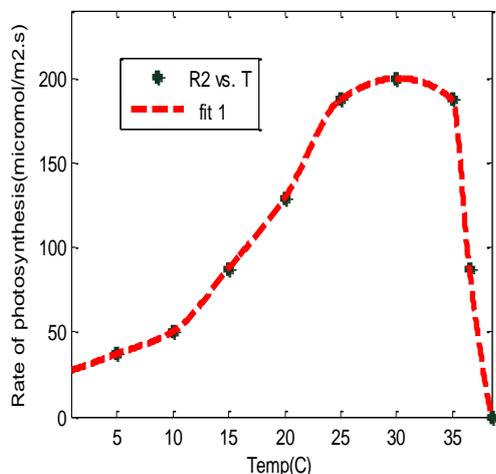
**Fig 4:** 3-D surface response plot of time of photosynthesis versus Concentrations of CO<sub>2</sub> and O<sub>2</sub> (absorbed by the leaf)



**Fig 5:** 3-D surface response plot of time of photosynthesis versus Concentrations of CO<sub>2</sub> (taken in) and O<sub>2</sub> (given out) in the reaction



**Fig 6:** Change in Gibbs free energy versus molecular weight of hydrocarbons and oxygen



**Fig 7:** Rate of photosynthesis versus

V. DISCUSSION

Figure 1 is a plot of the model equations 11, 12, & 13 using Table 2. The figure shows that oxygen is increasing while carbon dioxide and water are decreasing with time during daily photosynthesis at the back of a leaf. The carbohydrate (food) that is made increases slightly and remains at a concentration of one mole as time increases.

Figure 2 which is a plot of Table 3 shows the interchange of oxygen and carbon dioxide absorbed during daily photosynthesis. Around mid-day, carbon dioxide is produced highest and oxygen is reduced lowest. This solution changes in about next six hours and so on.

Figure 3a is a plot of net rate of photosynthesis versus concentration of carbon dioxide absorbed cumulatively using model equation 15. We can notice from Table 4 that the figure has compensation point (the point at which the net rate is zero). In this case notice also that the curve is made up of two sections, the first part of the slope (limitations by CO<sub>2</sub> diffusion) and the second part of the slope characterized by biochemical limitation and of course (the x-axis represent the internal CO<sub>2</sub> concentration (PPMV) in the leaf).

In figure 3b, model equation 14 was superimposed on Table 5 scatter diagram to produce figure 3b, where X-axis is not CO<sub>2</sub> but time (in days) and Y-axis is not net rate but just

concentration of CO<sub>2</sub> during photosynthesis. Observe that there is no compensation point and that the cumulative sigmoidal curve is a growth profile having ultimate values at some time in the future.

In figure 4, the algorithm section was followed in making the 3-D surface response plot of time of photosynthesis against concentrations of CO<sub>2</sub> and O<sub>2</sub> absorbed by the leaf. The lines on the floor show that there is reciprocal of interaction between concentrations of O<sub>2</sub> and CO<sub>2</sub>. When the lines on the floor are parallel to any of the axes on the floor, there will be no interaction between them. Otherwise the two axes on the floor could be directly proportional, inversely proportional, or with very serious interaction when there are curves.

Again in figure 5, the algorithm section was followed in making this plot. But the interaction between the two axes on the floor shows that there is serious reciprocal interaction.

Figure 6 is a shape preserving interpolant plot of Table 6. The figure shows that the Gibbs free energy of hydrocarbon rises so fast while that of energy is almost constant as the molecular weight of hydrocarbon increases.

In figure 7, another shape preserving interpolant plot, the rate of photosynthesis rises slowly like a growth profile with increase in photosynthetic reaction temperature to a table peak, stay for about 190 micro mol/m<sup>2</sup>s and drops sharply to zero rate at 40°C. It will be observed that this highest temperature is ambient in regions of African Sahara.

VI. CONCLUSION

In this work, chemical kinetics of photosynthesis were extensively explored. Kinetic models were established. Data from internet were invoked in and used for validation of the models. It was observed that the models are real and natural as they follow the growth profile nature of photosynthetic release and uptake of oxygen and carbon dioxide respectively. The models actually conform to what is found in the literatures. Therefore photosynthetic activities could be studied using natural growth models in conjunction with specificities of photosynthetic phenomena.

This work can be used in studying growth of plant in agriculture, carbon cycle and perhaps ozone layer depletion or carbon sequestration.

REFERENCES

- [1] Humman (1805).Catalysis.The Art of splitting water nature Vol. 211, No. 718, pp.778-779, ISSN 0028-0836.
- [2] Bahdr and Deniz.(2012) Photosynthetic O<sub>2</sub> formation tracked by time-resolved X-ray Experiments.Science.Vol. 310, No. 5750 (November 2012), pp. 1019-1021, ISS 0036-8075.
- [3] Des marais (1994). Photosynthesis 5<sup>th</sup> edition studies in biology Cambridge university press 1994, p 45-51.
- [4] Ellemore S. and Vogel. (1983). The mechanism of photosynthesis. American Elsevier pub. Co., ISBN 978044195584, New York.
- [5] Dey G. R., Belapurkar A. D and Kishore K. (2004). Photo-Catalytic Reduction of Carbon Dioxide to Methane using TiO<sub>2</sub> as suspension in water, journal of photochemistry and photobiology a – chemistry, Vol. 163, No. 3, pp. 503-508, 1010 – 6030.
- [6] Jitaru M. (2007). Electrochemical carbon dioxide reduction in liquid media. M.Sc. Thesis, chemical Engineering Department middle East Technical University Ankara Turkey Foyer A. (1984) photobiochem., photobiophy, Vol. 9 pp. 79-87.
- [7] Indracanti V. P., Schobert H. H and Kubrick J.D. (2009). Quantum mechanical modeling of CO<sub>2</sub> with irradiated stoichiometric and oxygen-deficient Anatine TiO<sub>2</sub> surface. Implications for the photocatalytic reduct ion of CO<sub>2</sub> energy & fuels, vol. 23, (October 2009), P.P 5247-5247-5256,ISSN 08870624.

- [8] Hill R. and Bendall F. (1960). Function of the two cytochrome components in chloroplasts: A working hypothesis. Nature, vol. 186, No. 4719, pp. 136-137, ISSN 0028-0836.
- [9] Blankenship (2002). Biochem Biophys. Act, Vol. 1318 pp. 322-373.
- [10] Lebedeva G.V., Belyeva N. E., Ruzichenko G. Y. and Demin O. V. (2002). BioThermoKinetics in the post genomic Era, Larsson C., Pahlman I. and Gustafsson I., Eds., Gotborg Ghalmers Reproservice, 1998, pp. 196-199.
- [11] Haumann M., Liebisch P., Muller C., Barra M., Grabolle M. and Dau H. (2005). Photosynthetic O<sub>2</sub> Formation TRAPPED by Time – Resolved X – ray Experiments Science, Vol.310, No. 5750, (November 2005), pp. 1019 – 1021, ISSN 0036-8075.
- [12] Crosby M. (1997). Photochemphotobio B. Biology (1997) Holt physiol plant mol. Bio 1991, Vol 42, pp. 313 – 349.
- [13] Diwan J. J. (2009). Calvin Cycle-Photosynthetic Dark Reactions, In: Rensselaer Polytechnic Institute, 27.03.2001, Available from <http://www.rpi.edu/dept/bcbp/molbiochem/MBWeb/mb2/part1/dark.htm>
- [14] Evans J. R. and Vogelmann T. C. (2003). Profiles of <sup>14</sup>C fixation through spinach leaves in relation to light absorption and photosynthetic capacity. Plant Cell Environ. 26:547-560.
- [15] Evans J. R. and Vogelmann T. C. (2006). Photosynthesis within isobilateral Eucalyptus pauciflora leaves. New phytol. 171:771-782.
- [16] Anpo M., Yamashita H., Ikue K., Fujii Y., Zhang S. G., Ichihashi Y., Park D. R., Suzuki Y., Koyano K. and Tatsumi T. (1998). Photocatalytic reduction of CO<sub>2</sub> & H<sub>2</sub>O on Ti-MCM-41 and Ti-MCM-48 Mesoporous zeolite catalysts. Catalysis today, VOL.44, no 1-4, pp. 322, ISSN 09020-5861.



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