A BRIEF THERMODYNAMIC ANALYSIS OF THE PHOTOSYNTHESIS PROCESS

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Summary

Increased atmospheric carbon dioxide concentration has led to a global environmental focus on methods to capture and reduce this gas. One route is to consider biological systems, since they are capable of reducing carbon dioxide by photosynthesis. The benefit of this process is its reliance on light energy from the sun – a "free", long-lasting energy source. The photosynthetic reaction is analysed thermodynamically, at ambient temperature, to establish photon requirements relative to carbon dioxide uptake and carbohydrate production. By looking at the energy and entropy balances, and the change in Gibbs Free Energy across this reaction (ΔG_{rxn}), necessary photon amounts are calculated at different wavelengths.

Keywords

CO2 capture, utilization and sequestration

Introduction

The increase in carbon dioxide in the atmosphere poses a contributing factor to undesirable climate change. The photosynthetic process used by plants presents itself as an effective method of carbon dioxide reduction. The aim of this paper is to theoretically analyse the thermodynamics of the photosynthetic process in the hope of being able to quantify the light energy requirements for reducing atmospheric carbon dioxide. Petela[1] mentions that a thermodynamic analysis provides different views of the same process; the first law of thermodynamics provides a better understanding of the process and highlights areas of it that can be optimised.

The basic photosynthetic process involves the reaction of water and carbon dioxide, with light energy (photons), to form oxygen and carbohydrates. For the purposes of this paper, glucose is the selected carbohydrate. This can be justified by its role as one of the simplest organic "building blocks" in nature, and thus its relevancy to many plant forms, including algae. Pimentel[2] has said that there is a need for laboratory and field research for the production of algae and bio-oil. The photosynthetic reaction is shown below in Eq. (1.1):

$$CO_2 + H_2O \xrightarrow{\text{LIGHT}} \frac{1}{6}C_6H_{12}O_6 + O_2 \quad (1.1)$$

The approach of thermodynamic analysis used in this paper is that used by Patel *et al*[3]. This involves only looking at the overall process mass balance, namely a "black box" approach. Figure 1 illustrates this method; the thermodynamic properties of the input and output streams are the focus of the analysis.

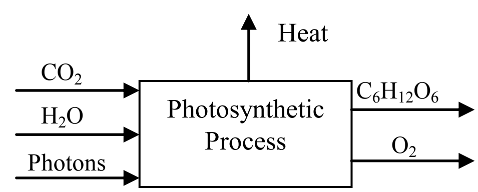

Figure 1: Black box overview of the process

Analysis and Results

The energy balance over the process can be considered as the following:

$$H_{in} + E_{photons}(\lambda) = H_{out} + Q \quad (1.2)$$

It should be noted that the heat, or energy transfer between the system and surroundings, Q, is assumed to be exothermic. Thus some energy is lost to the surroundings by the plant or biological system in the process. The energy of the photon is described by the Plank relation:

$$E_{photons} = N_A \frac{nhc}{\lambda} \quad (1.3)$$

Where n represents the number of moles of photons, h is Plank's constant, N_A is Avogadro's number, c is the speed of light and λ is the photon wavelength. The entropy balance relating to the photosynthetic process can be considered as:

$$S_{in} + S_{gen} + S_{photons} = S_{out} + \frac{Q}{T} \quad (1.4)$$

The internal entropy generation term, S_{gen}, can be considered negligible if it is assumed that the process is nearly reversible. Gibbs Free Energy is defined as follows and is applied to the input and output streams:

$$G = H - TS \quad (1.5)$$

By rearranging and substituting, the following is derived:

$$G_{out} - G_{in} + TS_{photons} = E_{photons} \quad (1.6)$$

Kirwan Jr.[5] suggests that the intrinsic entropy of photons is negligible, while Gudkov[6] takes the viewpoint that "light is a form of high grade energy which carries no thermodynamic entropy." Thus the inherent entropy of the photons is thus assumed to be zero in this paper, giving:

$$\Delta G_{rxn} = E_{photons} = N_A \frac{nhc}{\lambda} \quad (1.7)$$

Since ΔG_{rxn} can easily be acquired from formation data, the moles of photons, n, required per mole of reactant consumed or product formed can be determined at different wavelengths. Figure 2 below shows the moles of photons required as a function of wavelength to reduce one mole of carbon dioxide.

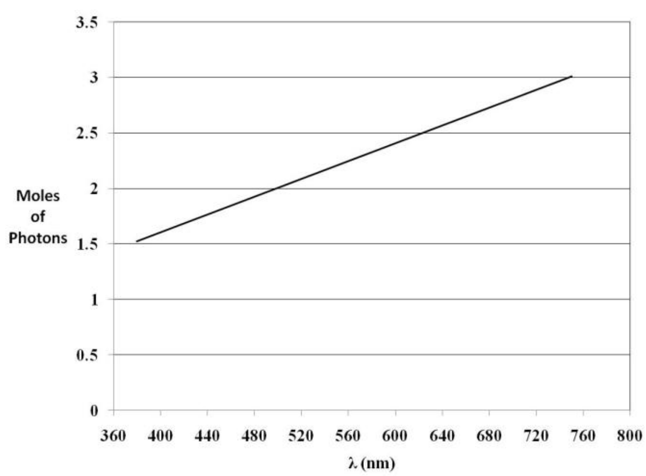

Figure 2: Moles of photons required, at a particular wavelength within the visible light range, to reduce 1 mole of carbon dioxide.

Hall and Rao[4] state that the main chlorophyll types found in most plant forms, including algae, are chlorophyll *a* and chlorophyll *b*. The absorption peaks are 420 and 660 nm for chlorophyll *a*, and for chlorophyll *b* the absorption peaks occur at 435 and 643 nm. At these wavelengths, the chlorophyll species are most receptive to photons and thus more readily photo-excited. The moles of photons required at these wavelengths are obtained from Figure 2, and vary between 1.69 and 2.65.

Discussion

In all these figures, however, it is assumed that photon absorption efficiency is 100%, which is not the case in nature due to plant photo-receptor characteristics. Thus, it can be expected that in reality, more than the theoretically predicted amounts of photons will be required. This, however, is subject matter for an entirely new discussion and will not be dealt with here. For comparative purposes, Radmer and Kok[7] cited that 10 photons are required for liberating 1 mol O_2 or consuming 1 mol CO_2 for the growth of algae. Raven and Johnston[8] calculated the number of photons needed for different RUBISCO enzymes in plants. They computed that 8 photons are needed per CO_2 for general RUBISCO but 15.2 photons are needed for the algal RUBISCO however Raven and Geider[9] stated that algal photosynthesis requires 8 photons.

Conclusions

It has been shown how to theoretically calculate the photon yield of photosynthetically converting carbon dioxide and water into glucose. This has been compared to values that have been estimated as being needed to activate the appropriate enzymes. The much lower theoretical values suggest that there might be room for genetically improving the photosynthesis process.

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