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Spectral optical properties of selected photosynthetic microalgae producing biofuels

Euntaek Lee, Ri-Liang Heng, Laurent Pilon *

Mechanical and Aerospace Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, 420 Westwood Plaza, Eng. IV 37-132, Los Angeles, CA 90095, USA

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ABSTRACT

This paper presents the spectral complex index of refraction of biofuel producing photosynthetic microalgae between 400 and 750 nm. They were retrieved from their experimentally measured average absorption and scattering cross-sections. The microalgae were treated as homogeneous polydisperse spheres with equivalent diameter such that their surface area was identical to that of their actual spheroidal shape. An inverse method was developed combining Lorentz–Mie theory as the forward method and genetic algorithm. The unicellular green algae *Chlamydomonas reinhardtii* strain CC125 and its truncated chlorophyll antenna transformants *tla1*, *tlaX*, and *tla1-CW*$^{+}$ as well as *Botryococcus braunii*, *Chlorella sp.*, and *Chlorococcum littorale* were investigated. These species were selected for their ability to produce either hydrogen gas or lipids for liquid fuel production. Their retrieved real and imaginary parts of the complex index of refraction were continuous functions of wavelength with absorption peaks corresponding to those of *in vivo* Chlorophylls *a* and *b*. The T-matrix method was also found to accurately predict the experimental measurements by treating the microalgae as axisymmetric spheroids with the experimentally measured major and minor diameter distributions and the retrieved spectral complex index of refraction. Finally, pigment mass fractions were also estimated from the retrieved absorption index. The method and/or the reported optical properties can be used in various applications from ocean remote sensing, carbon cycle study, as well as photobiological carbon dioxide mitigation and biofuel production.

1. Introduction

Photobiological carbon dioxide (CO_2) fixation and biofuel production have received major academic and industrial interest in recent years due to rising concerns over global warming, fossil fuel cost, as well as energy security. The technology consists of providing CO_2 and sunlight to selected species of microorganisms grown in photobioreactors. These microorganisms, in turn, grow and may produce (i) gases such as methane and hydrogen or (ii) lipids which can be converted to liquid fuels, depending on the species and growth conditions.

Solar radiation is the energy source driving the metabolic activity of photosynthetic microorganisms. As light penetrates into the photobioreactor, it is absorbed and scattered by the microorganisms. Light transfer in photobioreactors is governed by the radiative transfer equation (RTE). The latter is an energy balance on the radiative energy traveling along a particular direction $\hat{s}$. The absorption and scattering coefficients of microalgae along with the scattering phase function are major parameters needed to solve the RTE for simulating, designing, scaling-up, optimizing, and controlling photobioreactors [1].

* Corresponding author. Tel.: +1 310 206 5598; fax: +1 310 206 2302.
E-mail address: pilon@seas.ucla.edu (L. Pilon).

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These characteristics are strongly dependent on wavelength and vary from one species to another. They can be determined either experimentally [2,3] or based on electromagnetic wave theory [4]. This latter approach often assumes that the scatterers have relatively simple shape (e.g., spherical) and ignore their heterogeneous nature by attributing them a uniform effective complex index of refraction [5,6]. Pottier et al. [4] recognized that for complex microorganisms shapes (e.g., cylinders and spheroids), advanced numerical tools are required to predict their absorption and scattering coefficients and scattering phase function collectively called radiation characteristics. On the other hand, experimental measurements account for the actual shape, morphology, and size distribution of the microorganisms. However, experimental setups can be expensive and measurements are time consuming.

In order to design, optimize, and operate photobioreactors for CO_2 fixation and biofuel production, it would be convenient to have the ability to predict the radiation characteristics of microalgae from first principles instead of carrying out costly and time consuming experiments. If the effective spectral real and imaginary parts of the complex index of refraction as well as the microorganisms shape and size distribution are known to within an acceptable level of uncertainties, the absorption and scattering coefficients can be predicted by Lorentz–Mie theory [7], if the microalgae are spherical, or by the T-matrix method [8], if the particles have more complex shapes.

The present study aims to retrieve the spectral real part (or refraction index) and imaginary part (absorption index) of the complex index of refraction of microalgae from experimentally measured size distribution as well as absorption and scattering cross-sections [3,9]. The green algae *Chlamydomonas reinhardtii* strain CC125 and its truncated chlorophyll antenna transformants *tla1*, *tlaX*, and *tla1-CW*$^+$ [3] as well as *Botryococcus braunii*, *Chlorella sp.*, and *Chlorococcum littorale* [9] were considered in this study. Finally, the results were used to retrieve the microalgae pigment concentrations and gain insight into their composition.

2. Background

2.1. Microbial light harvesting pigments

Photosynthesis begins with the absorption of photons by the photosynthetic apparatus which consists of three major components (i) the reaction center, (ii) the core antenna, and (iii) the peripheral antenna. Photochemical charge separation and electron transport take place in the reaction center [10]. The core antenna contains the photosynthetic pigments chlorophylls or bacteriochlorophylls. It is surrounded by the peripheral antenna which is an assembly of chlorophylls, bacteriochlorophylls, and other accessory pigments such as carotenoids and phycobiliproteins. The peripheral antenna is particularly important in channeling additional photon energy to the reaction center at small light intensities. In microalgae and cyanobacteria, the photosynthetic apparatus is located on the photosynthetic membrane called thylakoid [11].

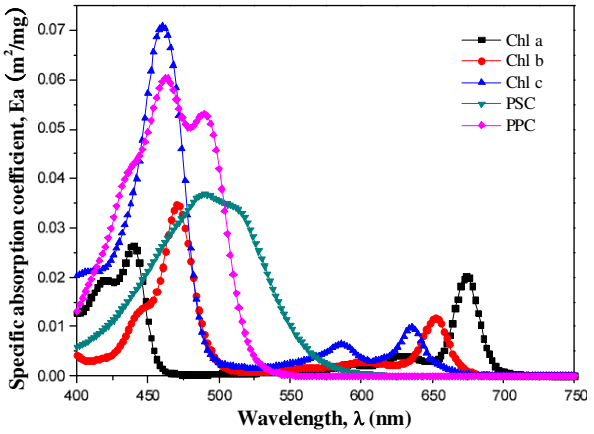

Fig. 1. *In vivo* specific absorption coefficient *Ea* (in m^2/mg) of primary pigments chlorophylls *a*, *b*, and *c* and photosynthetic carotenoids (PSC), and photoprotective carotenoids (PPC) over the spectral region from 400 to 750 nm [12].

Different pigment molecules absorb over different spectral bands of the visible and near infrared parts of the spectrum enabling more efficient utilization of solar energy. Fig. 1 shows the *in vivo* specific absorption coefficient *Ea* (in m^2/mg) of primary pigments chlorophylls *a*, *b*, and *c* as well as accessory pigments such as photosynthetic carotenoids (PSC), and photoprotective carotenoids (PPC) measured over the spectral region from 400 to 750 nm [12]. It indicates that Chlorophyll *a* (Chl *a*) absorbs around 435 and 676 nm while Chlorophyll *b* (Chl *b*) absorbs around 475 and 650 nm. Since they do not absorb green light ($\lambda \approx 520-570$ nm) significantly, these microalgae appear green to the human eye. On the other hand, carotenoids are accessory pigments found in all photosynthetic microorganisms. They absorb mainly in the blue part of the spectrum (400 nm $\lesssim \lambda \lesssim$ 550 nm) [10]. Carotenoids serve two major functions (i) shielding the photosynthetic apparatus from photo-oxidation under large light intensities and (ii) increasing the solar light utilization efficiency by expanding the absorption spectrum of the microorganism.

The intracellular pigments such as chlorophylls and carotenoids are typically extracted by using organic solvents which penetrate through the cell membrane and dissolves the lipids to extract pigments [13,14]. Methanol, acetone, and ethanol are usually used as the organic solvents in the pigments extraction process [15,16]. Overall, measuring the pigment concentration can be very time consuming and suffers from various and sometimes large experimental uncertainties [13].

C. reinhardtii contains Chl *a* and Chl *b* and photoprotective carotenoids (PPC) [4]. Pottier et al. [4] measured their mass fraction by acetone extraction and optical density measurements as 1.4 wt.%, 0.7 wt.%, and 0.45 wt.%, respectively. Berberoğlu et al. [9] measured the mass concentrations (in g/kg of dry weight) of Chl *a* and Chl *b* for microalgae *C. littorale*, *B. braunii*, and *Chlorella sp.* using ethanol extraction method [11]. Unfortunately, their