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Mass transfer modeling and maximization of hydrogen rhythmic production from genetically modified microalgae biomass

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ABSTRACT

A transient mathematical model for managing microalgae derived hydrogen production as a source of renewable energy is developed for a well stirred photobioreactor. The model allows for the determination of microalgae and hydrogen mass fractions produced by the photobioreactor with respect to time. A Michaelis–Menten type expression is proposed for modeling the rate of hydrogen production, which introduces a mathematical expression to calculate the resulting effect on H_2 production rate after genetically modifying the microalgae species. The so called indirect biophotolysis process was used. Therefore, a singular opportunity was identified to optimize the aerobic (t_1), to anaerobic (t_2), stages time ratio of the cycle for maximum H_2 production rate, i.e., the process rhythm. A system thermodynamic optimization is conducted through the complete model equations to find accurately the optimal system operating rhythm for maximum hydrogen production rate, and how wild and genetically modified species compare to each other. The maxima found are sharp, showing up to a ~60% variation in hydrogen production rate for $t_{2,opt} \pm 1$ day, which highlights the importance of system operation in optimal rhythm. Therefore, the model is expected to be useful for design, control and optimization of hydrogen production as a source of renewable energy.

1. Introduction

Microalgae derived hydrogen has been considered one possible environmentally correct alternative to supply a so called hydrogen economy. However, H_2 production has been demonstrated only at the laboratory scale, and the yield of H_2 is still low for commercial application. Therefore, the optimization of design and operating parameters for maximum H_2 production is a possible direction to address the issue of increasing hydrogen production rate.

A fully optimized system to produce hydrogen as a clean fuel, in an economically viable way, is still a dream. However, no matter how far from reach that goal is, many efforts are being conducted to achieve it. The first challenge is the production, which needs to depict a favorable cost-benefit relation. Next challenges are storage and distribution. Biological production of hydrogen technologies provide a wide range of approaches to generate hydrogen, including direct or indirect biophotolysis, photo or dark fermentations (or a process combining both) and hybrid biological hydrogen production by electrochemical processes [1–3]. Several microorganisms are able to produce biofuels like hydrogen, but recent studies have targeted cyanobacteria and green microalgae [1,4–8].

The indirect biophotolysis is a biological process to produce hydrogen. In this approach, hydrogen is produced from water using a system of microalgae photosynthesis to convert solar energy into chemical energy in the form of hydrogen through several steps: (i) biomass production by photosynthesis, (ii) biomass concentration, (iii) dark aerobic fermentation produces 4 mols of hydrogen/mol fo glucose in the algal cells, together with 2 mols of acetate, and (iv) conversion of 2 mols of acetate into hydrogen [1]. The process is divided in three reactions, two of which depend on the light and the other is light independent. These reactions are written as follows [9]:

(stage 1 – aerobic)

$$6H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

(stage 2 – anaerobic)

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \quad (2)$$

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Nomenclature

A	constant, Eq. (20)
A_1, A_2	frequency factors or pre-exponential values, h^{-1}
B	constant, Eq. (21)
b_0, b_1, b_2	coefficients for each algae species
C	mass concentration, $kg\ m^{-3}$
E_{a1}, E_{a2}	activation energy, $kJ\ mol^{-1}$
GMO	genetically modified organism
I	specific specular radiation, $W\ m^{-2}$ or $\mu E\ m^{-2}\ s^{-1}$
I'_k	Constant representing the affinity of algae to light, $W\ m^{-2}$ or $\mu E\ m^{-2}\ s^{-1}$
K_1, K_2	constants, Eq. (6)
K_a	extinction coefficient, $m^2\ kg^{-1}$
n	constant exponent for the microalgae species
n_{mod}	total number of genetic modifications
P_{decay}	percent decay per day of the O_2 mass fraction
PAR	photosynthetically active radiation, $W\ m^{-2}$ or $\mu E\ m^{-2}\ s^{-1}$
r	radius, m
R	universal gas constant, 8.317 $kJ\ kmol^{-1}\ K^{-1}$
$R_{a/b}$	stoichiometric coefficient for generating species a as species b is produced
t	time, s
T	medium temperature, K
y	mass fraction, kg of component/kg of medium
Y_b, Y_p	specific coefficients for each algae species

Greek Letters

α	specific maintenance rate, s^{-1}
γ	microalgae biomass consumption rate, s^{-1}
η	H_2 mass production efficiency, Eq. (15)
μ	specific production rate, s^{-1}
ξ	genetic modification factor
ρ	density, $kg\ m^{-3}$

Subscripts

avg	average
alga	microalgae biomass
aerobic	aerobic stage
anaerobic	anaerobic stage
f	final
GMO	genetically modified organism
i	species type; type of genetic modification
k	affinity with solar radiation
max	maximum
medium	cultivation medium
opt	optimal
others	all other substances that compose the medium besides microalgae and H_2
sun	sun
tot, *T*	total
tt	photobioreactor transparent tube
wild	wild species
0	initial condition; photobioreactor tube surface
1	aerobic stage
2	anaerobic stage

$$2CH_3COOH + 4H_2O + \text{light} \rightarrow 8H_2 + 4CO_2 \quad (3)$$

Adding Eqs. (1)–(3), the overall reaction results as follows:

$$12H_2O + \text{light} \rightarrow 12H_2 + 6O_2 \quad (4)$$

The hydrogen production reactions are simple, but depend on a series of simultaneous factors to happen within the microalgae chloroplasts so that H_2 is indeed produced. Such conditions (or factors) need to be optimal for maximum H_2 production. The optimization basically depends on the microalgae strain, the available growth condition (e.g.: medium CO_2, $SO_4^=$ and O_2 content; nutrients; photobioreactor type). Predictive mathematical models could be used in simulations that point to the ideal combination of such factors. Computational simulations allow for the reduction in the trial times, which would have much lower costs as compared to the execution of experiments on a real system. Simulation techniques also provide good visualization of the results (e.g., graphs, tables); possibility of multiple executions of a model, and flexibility for achieving desirable characteristic changes in the studied systems, generating goals of supporting information to decision-making. Since models are most useful when directed at a clearly specified and well-defined problem, the crucial first step in modeling is to precisely define the question(s) to be addressed. The nature of the problem is likely to determine what are the most appropriate modeling techniques to use [10,11].

Research groups are bioprospecting microalgae in nature aiming at H_2 production [12]. However, are the microalgae available in nature good enough? Since the most primitive use of natural resources for human life in the planet, the best available resources have been sought. Ancient civilizations confined cattle and selected the best breeders to obtain the best possible offspring, i.e., genetic improvement has been developed continuously by humans, even before genetics has become a research area in Biology. The potential of microalgae genetic improvement for hydrogen production has just started to be assessed, and is likely to achieve the productivity needed to make the process economically viable. There are many ongoing efforts in this direction, and in recent decades many advances have been achieved. The tools of genetic engineering available have been adapted to microalgae [13] and an almost unlimited number of genetic improvement alternatives can be performed currently. Strategies including increasing the number of gene copies, increase or decrease gene expression (up- or down-regulation), and even the expression of heterologous genes from other species are possible by cloning the DNA of interest in vectors which are meant to be inserted in microalgae, followed by selection of transformants through selective media [13].

The knowledge generated by the genome sequencing of some microalgae species, such as *Chlamydomonas reinhardtii* [14], a leading producer of hydrogen [15], and also considered a model organism in biology [16], allows for further knowledge of complex biological processes [17], including those that regulate the chemical reactions shown in Eqs. (1)–(4). Some target genes were identified and selected for genetic improvement [18], but other genes related with hydrogen production are still unknown [19]. All three genomes (chloroplast, mitochondrial and nuclear) can be transformed in *Chlamydomonas*, and each has distinct transcriptional, translational and post-translational properties that make them distinct [13]. In addition, the advantage of having a well known, controllable and rapid (about two weeks) sexual cycle, permits the combination of favorable mutations in one strain of *Chlamydomonas*, through classical genetic methodology. Dubini and Ghirardi [18] suggested that the combination of specific mutations