Modeling and simulation of the microalgae derived hydrogen process in compact photobioreactors
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OUTLINE

1. Introduction
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5. Conclusions
6. Suggestions
The USA currently imports more than 60% of its petroleum.

2/3 of it go to transportation fuels

140 x 10^9 gallons of gasoline/year
44 x 10^9 gallons of diesel/year
WHAT ARE MICROALGAE?

MICROALGAE are the unicellular algae with great photosynthetic capability and rapid growth due to their simple structure.
MICROALGAE comprise the **phytoplankton** and are the basis of the aquatic food chain.

**AUTOTROPHIC** – are energy primary producers

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2
\]

Chlorophyll + mineral salts

Lipids

Proteins

DNA, RNA, etc
MICROALGAE METABOLISM

HETEROTROPHIC METABOLISM

CARBON SOURCE
- glycerol
- glucose
- acetate

H2O + CO2
PHOTOSYNTHESIS

MIXOTROPHIC METABOLISM

LIGHT SOURCE

AUTOTROPHIC METABOLISM

H2O + CO2
PHOTOSYNTHESIS

- glycerol
- glucose
- acetate
Biodiesel production

- Triglycerides are converted first to diglycerides, monoglycerides and then to glycerol.
- The equilibrium reaction requires 3 mol of alcohol per mol of triglyceride. Industrial processes use excess alcohol to ensure it is in the direction of the methyl esters.
- The reaction is catalyzed by using acids and alkali. Alkali catalyzed transesterification is 4000 times faster (sodium and potassium hydroxide). Sodium-methoxide.
- \( T = 60^\circ C \)
- Reaction takes place in about 90 minutes.
### EFFICIENCIES

<table>
<thead>
<tr>
<th>CROP</th>
<th>OIL (L/ha)</th>
<th>LAND AREA NEEDED (M ha)</th>
<th>PERCENT OF EXISTING US CROPPING AREA&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>172</td>
<td>1540</td>
<td>846</td>
</tr>
<tr>
<td>Soybean</td>
<td>446</td>
<td>594</td>
<td>326</td>
</tr>
<tr>
<td>Canola</td>
<td>1190</td>
<td>223</td>
<td>122</td>
</tr>
<tr>
<td>Coconut</td>
<td>2689</td>
<td>99</td>
<td>54</td>
</tr>
<tr>
<td>Palm oil</td>
<td>5950</td>
<td>45</td>
<td>24</td>
</tr>
</tbody>
</table>

<sup>a</sup> For meeting 50% of all transport needs of the US

(Chisti, 2007 e Chisti, 2009)
**Raceway ponds**

*Inexpensive operation*

*Simple construction*

- High losses via evaporation

- Problems of contamination

**Photobioreactors**

- More expensive construction (~10x)

- More engineering

- Less evaporation

- Better CO₂ use

- Better mixing

- Higher biomass concentration (easier harvesting)

- Volumetric biomass productivity (~13 x)
PROJECT LOCATION IN BRAZIL
CULTIVATION IN PHOTOBIOREACTORS

**Raceway Pond**
- Agitation paddle
- Harvesting
- Water, nutrients

**Modular Photo-Bioreactor**
- C, H, L dimensions

**Tubular and Horizontal Photobioreactors**
- Light exposed tubes
- Degasser
- Water, nutrients
- Harvesting
- O₂, Air / CO₂
Photoinhibition

Specific growth rate vs. Sunlight intensity

Photoinhibited region
Plant summary

H₂ for trigenerator

Industrial Emissions
2. BIBLIOGRAPHIC REVIEW

Hydrogen

<table>
<thead>
<tr>
<th>Combustível:</th>
<th>Valor do Poder Calorífico Superior (a 25ºC e 1 atm)</th>
<th>Valor do Poder Calorífico Inferior (a 25ºC e 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hidrogénio</td>
<td>141,86 KJ/g</td>
<td>119,93 KJ/g</td>
</tr>
<tr>
<td>Metano</td>
<td>55,53 KJ/g</td>
<td>50,02 KJ/g</td>
</tr>
<tr>
<td>Propano</td>
<td>50,36 KJ/g</td>
<td>45,6 KJ/g</td>
</tr>
<tr>
<td>Gasolina</td>
<td>47,5 KJ/g</td>
<td>44,5 KJ/g</td>
</tr>
<tr>
<td>Gasóleo</td>
<td>44,8 KJ/g</td>
<td>42,5 KJ/g</td>
</tr>
<tr>
<td>Metanol</td>
<td>19,96 KJ/g</td>
<td>18,05 KJ/g</td>
</tr>
</tbody>
</table>
Biohydrogen
1. Direct Biophotolysis
2. Indirect Biophotolysis
3. Photofermentation
4. Dark fermentation
5. Hybrid systems
2. BIBLIOGRAPHIC REVIEW

Indirect Biophotolysis

(stage 1 - aerobic)

\[ 12 \text{H}_2\text{O} + 6 \text{CO}_2 + \text{light energy} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 \quad (1) \]

(stage 2 - anaerobic)

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{H}_2\text{O} + \text{light energy} \rightarrow 12 \text{H}_2 + 6 \text{CO}_2 \quad (2) \]
Electron transport pathways related to hydrogenase in green algae. The electrons could originate in the water photolysis or in the plastoquinone through cellular substrates oxidation via glycolysis or in the Krebs cycle. (MELIS and HAPPE, 2001).
Challenges:
1. Low hydrogen generation rate
2. High cost
3. GMO
4. Engineering – PBR; contamination; purification, separation
5. Sensitivity to oxygen
6. Co-products (e.g., biodiesel)
7. Mathematical modeling
General objective: $\text{H}_2$ production mathematical modeling

Specific objectives:
1. Mathematical model
2. Low computational time
3. Experimental comparison
4. Case study
Mathematical modeling

3. MATERIALS AND METHODS

Mathematical modeling

Growth Reduction

Log phase

Stationary phase

Death (nutrients/self-shading)

Lag phase

Cell density (cel/ml x 10,000)

Cultivation time (days)
Mathematical modeling

Molina Grima, 1996

\[
\mu = \frac{\mu_{\text{max}} I_{\text{av}}}{b + \frac{c}{I_0} I_{\text{av}} + I_K \left(1 + \left(\frac{I_0}{K_i}\right)^a\right)}
\]
3. MATERIALS AND METHODS
3. MATERIALS AND METHODS

\[ V^{(j)} \frac{d\gamma_{\text{alg}a}^{(j)}}{dt} = \frac{\dot{m}}{\rho} \left( \gamma_{\text{alg}a}^{(j-1)} - \gamma_{\text{alg}a}^{(j)} \right) + V^{(j)} \gamma_{\text{alg}a}^{(j)} (\mu - \alpha) \]

\[ V^{(j)} \frac{d\gamma_{\text{CO}_2}^{(j)}}{dt} = \frac{\dot{m}}{\rho} \left( \gamma_{\text{CO}_2}^{(j-1)} - \gamma_{\text{CO}_2}^{(j)} \right) - V^{(j)} \gamma_{\text{alg}a}^{(j)} R_{y_{\text{CO}_2}/y_{\text{alg}a}} (\mu - \alpha) \]
3. MATERIALS AND METHODS

\[ V^{(j)} \frac{dy_{O_2}^{(j)}}{dt} = \frac{m}{\rho} \left(y_{O_2}^{(j-1)} - y_{O_2}^{(j)}\right) + V^{(j)} y_{alg a} R_{y_{O_2}} / y_{alg a} \left(\mu - \alpha\right) \]

algae *Scenedesmus almeriensis* (SÁNCHEZ et al., 2008)

\[
\mu = \left( A_1 e^{\left(-\frac{E_{a1}}{RT}\right)} - A_2 e^{\left(-\frac{E_{a2}}{RT}\right)} \right) I_{avg}^n
\]

\[
I_{avg} = I_0 \cdot e^{-d.C.K_a}
\]
3. MATERIALS AND METHODS

\[ V^{(j)} \frac{d y_{H_2}^{(j)}}{d t} = \frac{\dot{m}}{\rho} \left( y_{H_2}^{(j-1)} - y_{H_2}^{(j)} \right) + V^{(j)} y_{H_2}^{(j)} \left( \mu_{H_2} - \alpha_{H_2} \right) e^{-\frac{y_{O_2}}{y_{O_2,sat}}} \]

**Dilution**

\[ \mu_{H_2} = \frac{\mu_{\text{max}} I_{\text{avg}}}{I_k + I_{\text{avg}}} \]
3. MATERIALS AND METHODS

Martínez and Casas [26]

\[
\frac{dy_i}{dt} = \frac{27v_{meio}D_iu_i}{2gr_0^4} \left( y_{i,sat} - y_i \right)
\]

\[
y_i(t_d) = y_{i,sat}\left\{1 - \left(1 - e^{-Kt_d}\right)\right\}
\]

\[
K = \frac{27v_{medium}D_iu_i}{2gr_0^4} ; \quad t_d = \frac{L_{tdg}}{u_b} ; \quad u_b = \frac{2gr_0^2}{9v_{medium}} ; \quad A_{tdg} = \frac{\dot{m}_{CO_2} t_d}{y_{CO_2} \rho_{meio} L_{tdg}}
\]
3. MATERIALS AND METHODS

\[ pH = -\log \left( \frac{-k_a + \sqrt{k_a^2 + 4k_a[CO_2]}}{2} \right) \]

\[ T_\infty = T_{\text{min}} + \frac{\Delta T}{2} \left[ 1 - \frac{\Delta T}{2} \cos \left( \frac{\pi(t - t_0)}{43200} \right) \right] \]

\[ \varepsilon_{\text{mesh},i} = \frac{\|y_{i,mesh,j}\| - \|y_{i,mesh,j+1}\|}{\|y_{i,mesh,j}\|} \leq 0.01 \]
3. RESULTS AND DISCUSSION

A. Mesh and boundary conditions

The PBR measures \((5 \text{ m} \times 2 \text{ m} \times 8 \text{ m})\). The converged mesh according to Eq. (21) had a total of 6048 VEs.

The conditions for the cases considered in this work were:
1. Average sun irradiation: 500 W m\(^{-2}\) (day) and 0 W m\(^{-2}\) (night);
2. Side wind through one of the faces as desired. In this work, the wind flow was assumed from east to west: 5 m/s;
3. PBR temperature regime: between \(T_{\text{min}} = 283\) and \(T_{\text{max}} = 303\) K, and
4. Two simulation periods: 15 to 17 days, always beginning at 5 AM.
Fig. 5. Dry biomass versus cell number correlation.
Fig. 6. The comparison between numerical and experimental results for PBR microalgae growth.
Fig. 7. PBR microalgae mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.
Fig. 8. PBR CO$_2$ mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.
Fig. 9. PBR $O_2$ mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.
Fig. 10. PBR $\text{H}_2$ mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.
5. CONCLUSIONS

1. Indirect photolysis mathematical model has been developed
2. Low computational time application
3. Experimental validation for microalgae growth
4. Case study – expected trends have been observed
6. SUGGESTIONS

1. Prototype (HGP – “Hydrogen Generation Photobioreactor”)
2. Different green algae species for hydrogen generation
3. Complete characterization of the obtained fuel (e.g., purity)
4. Mathematical model improvement and experimental validation
5. Process thermodynamic optimization (numerical)
Thank you!!

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