Evaluation of energy consumption and CO_2 emissions in the production of biohydrogen from microalgae feedstock

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Introduction - The 2003/30/EC European Directive aims to promote the use of biofuels and other renewable fuels instead of oil derivatives for transport purposes. In long term this is expected to contribute to the fulfillment of European climate change agreements. Therefore, hydrogen appears as a promising alternative fuel and "energy carrier". Hydrogen can be produced from renewable sources, namely biomass [1], and more particularly by the photobiological process and dark fermentation [2], being designated as "biohydrogen" (bioH_2) [3]. Simple sugars such as glucose, sucrose and lactose are readily metabolized and are thus preferred as substrates for hydrogen production. However, the costs for pure carbohydrate sources are high for practical-scale hydrogen production, which can only be viable when based on renewable and low cost sources [4]. Carbohydrates are the main potential fermentable substrates for producing bioH_2, *e.g.* potato peels, sugarcane and microalgae biomass. The high productivity of microalgae, the potential for CO_2 sequestration from atmosphere and the capacity of several species to accumulate sugars in high concentrations make this type of biomass attractive for bioconversion purposes. Understanding the energy and environmental burdens of bioH_2 production allows insights into its sustainability. This research aims at evaluating the energy demands and CO_2 emissions of producing bioH_2 from microalgae. Life Cycle Assessment (LCA) methodology is partially followed according to the principles of ISO 14040 [5]: inventory (LCI) of laboratorial data, scale-up considerations, identification of bottlenecks and possible improvements on the production chain.

2. Experimental – The LCI covers the fundamental processes concerning the microalgae-based bioH_2 production. The data of photoautotrophic and fermentative hydrogen production by *Anabaena* sp. [6], fermentative hydrogen production by *Clostridium butyricum* from a hydrolyzate of *Scenedesmus obliquus* [7] and from *Sc. obliquus* and *Nannochloropsis* sp. biomass [8], integrated on a biorefinery scheme, were obtained in experiments performed at the National Laboratory of Energy and Geology, LNEG, in the city of Lisbon, located on the western coast of Portugal (38º 42′ N, 9º 11′ W). The hydrolyzate of *Sc. obliquus* contained approximately 10–17% of sugars (dry weight, DW), while the *Sc. obliquus* biomass attained about 30% of sugars (DW). *Nannochloropsis sp.* contained approximately 17 % of sugars (DW).

The bioH_2 production chain included several unit processes, starting from the growth of microalgal biomass that in its turn needs nutrients, CO_2 gas, and artificial/natural light. Only operational processes were accounted for in this study, *i.e.* machinery production, vehicle production, storage, and residues treatment were not included. The SimaPro 7.1 software [9], adapted for the average Portuguese electricity generation mix, was used as database for the calculation of energy consumptions in nutrients, water and gas requirements.

Electricity is the main energy input for the assessed biorefineries. However, to produce the electricity, the conversion of raw materials into energy is subjugated to the conversion processes efficiency. Then, the electricity production is admitted as a unit process of bioH_2 production. Energy efficiency and CO_2 emissions regarding the electricity used in bioH_2 production pathways and the energy expended in electricity production were considered according to the respective electricity generation mix and losses in the respective years, 2008 to 2011 (Table I). Namely, it corresponds to the overall energy consumption and emissions. The final energy and CO_2 emission ratios were estimated by Eqs. 1 and 2:

Table I. Electricity mix characterization for Portugal in terms of year, mix, efficiency and CO_2 per power station, electricity losses.

Year	Non-renewable energy (%)	Renewable energy (%)	Primary energy requirement (MJ/MJ_{el})	Efficiency of the grid mix (%)	Emission factor of grid mix (gCO_2/MJ_{el})
2008	68	32	1.30	43.5	128.3
2009	65	35	1.27	44.1	95.1
2010	49	51	1.02	49.5	87.2
2011	54	46	1.17	46.1	76.3

$$CO_2 = \sum CO_{2_{eachprocess}} \Big/ (LHV \times m_{H_2})\ (Eq.\ 1)$$

$$Energy = \sum Energy_{eachprocess} \Big/ (LHV \times m_{H_2})\ (Eq.\ 2)$$

where *LHV* is the low heating value of hydrogen and m_{H2} is the mass of hydrogen produced.

The fundamental processes considered in the microalgae-based bioH_2 production are described in Figures 1-4.

In the case of bioH_2 production by the cyanobacteria *Anabaena* sp. two pathways were performed: exclusively photoautotrophically and *via* both photoautotrophic production and fermentation of the residual biomass. The processes considered are presented in Figure 1: indoor cyanobacteria culture with artificial lightning; harvesting; drying and bioH_2 production (photoautotrophic and fermentation).

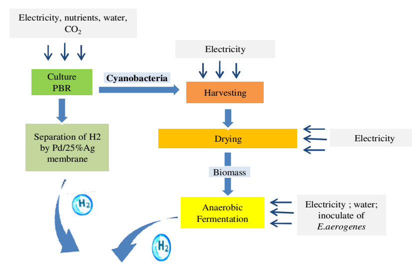

Figura 1. Biohydrogen production by *Anabaena* sp. cyanobacteria and by dark fermentation from residual biomass. [7]

Figure 2 shows each process considered in the production of bioH_2 in the fermentation of a hydrolyzate of *Sc. obliquus* by *C. butyricum*: microalgal growth with artificial lightning, harvesting and drying; hydrolysis of the biomass, preparation of the fermentation medium (basal medium, BM1) and pre-inoculum; degasifications and fermentation process.

In the referred bioH_2 production chains all energy consumptions estimated for the inputs in nutrients of the fermentation media, N_2 gas, and operational equipment were affected by the Portuguese electricity, E_{e-}, which has a resulting associated uncertainty, see Eqs. 3 and 4:

$$E_{nutrients,water,gas} = E_{Simapro} \times E_{e^-}\ (Eq.\ 3)$$

$$E_{equipment} = P_{equipment} \times \Delta t \times cf \times E_{e^-}\ (Eq.\ 4)$$

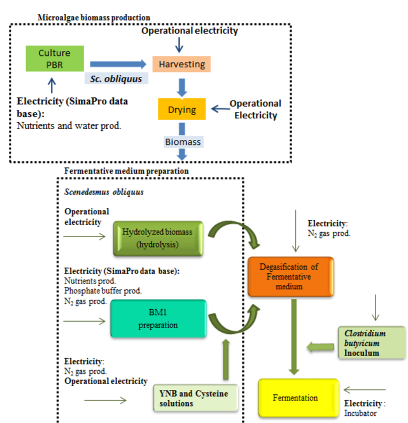

Figura 2. Scheme of hydrogen production in the fermentation of sugars *of Sc. obliquus* hydrolyzate by *C. butyricum.* [8]

where Δt are the working hours and *cf* is the capacity factor of the equipment if $\neq 0$. For *Nannochloropsis* sp. and *Sc. obliquus* biomass, the inputs of equipment's were measured and the respective energy required was determined according to Eq. 5:

$$E_{equip}^{\ measurement}(MJ) = \tilde{A} \times V \times \Delta t \times \left(1 \times 10^{-06}\right) \times cf \times E_{e^-} \quad (Eq.\ 5)$$

where Ã is the alternate electric current (A), V is the electric tension (V) and Δt is the working time (s).

In the case of *Nannochloropsis* sp. three pathways were considered: hydrogen production from the whole biomass by dark fermentation (bioH_2 *via* whole biomass); hydrogen production by dark fermentation from the leftover biomass after soxhlet extraction (bioH_2 *via* SE – biorefinery 1) and hydrogen production by dark fermentation from the leftover biomass after Supercritical Fluid Extraction (bioH_2 *via* SFE – biorefinery 2). Figure 3 shows the complete scheme of these processes chain.

Some process improvements were analyzed in the case of *Sc. obliquus* biomass. The microalga was grown in open raceway ponds with sun light instead of artificial light. *Sc. obliquus* was used as dried biomass to produce bioH_2, without previous hydrolysis. Beyond the microalga culture, the preparation of pre-inoculum and fermentative medium, and the fermentation process were considered (Figure 4). The first scale-up attempt was made regarding two scenarios: the optimized scenario (pilot scale) and the best scenario (industrial scale).

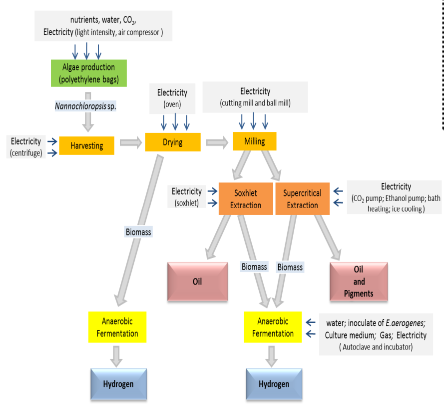

Figura 3. Scheme of energy inputs of the biorefinery for oil, pigment and biohydrogen production from *Nannochloropsis* sp. biomass. [9]

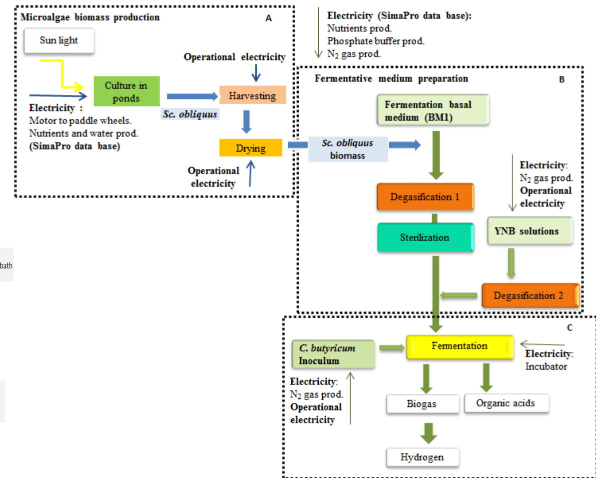

Figura 4. Scheme of the experimental stages of biomass production and the whole fermentation process, and corresponding inputs/outputs: (A) *Sc. obliquus* biomass production, (B) Fermentative medium preparation, (C) Fermentation.

The energy consumption and CO_2 emissions evaluation of bioH_2 production by and from cyanobacteria, and from microalgae biomass was attempted, in order to identify technological bottlenecks and possible improvements. This study also exploits the application of bioH_2 in the road transport sector, in opposition to natural gas reforming and electrolysis pathways, and conventional gasoline use.

3. Results e Discussion – Table I resumes the obtained values of energy consumption and CO_2 emissions for each bioH_2 production process considered.

Table I. Energy consumption and CO_2 emissions for each bioH_2 production process.

BioH_2 chain	Energy (MJ/MJ_{H2})	Min	Max	CO_2 (g/MJ_{H2})	Min	Max
BioH_2 from dried *Sc. obliquus* - best scenario	7.20	5.72	8.23	470.5	413.2	516.8
BioH_2 from dried *Sc. obliquus* - optimized scenario	12.48	8.30	12.52	818.7	710.4	920.7
BioH_2 as by-product from dried *Sc. obliquus*	33.28	27.28	37.26	2172.0	1935.1	2331.6
BioH_2 from dried *Sc. obliquus*	88.00	70.31	99.49	5776.0	5118.4	6268.0
BioH_2 as by-product from bioref 1 *Nannochloropsis* sp.	147.00	119.00	164.00	9665.0	8645.0	10369.0
BioH_2 as by-product from bioref 2 *Nannochloropsis* sp.	168.00	136.00	187.00	11020.0	9858.0	11820.0
BioH_2 as by-product from *Sc. Obliquus* hydrolyzate	364.30	281.20	404.90	27198.0	24149.0	29218.0
BioH_2 by *Anabaena* sp. (Photoautotrophic)	1538.00	1184.00	1715.00	114641.0	101476.0	123587.0
BioH_2 by *Anabaena* sp. cyanobacteria (Photoauto.+Ferm.)	1723.00	1327.00	1919.00	128502.0	113825.0	266887.0
BioH_2 from *Sc. obliquus* hydrolyzate	8884.14	7614.14	9866.14	758743.8	673892.4	813576.4
BioH_2 from *Nannochloropsis* sp.	9058.00	7285.00	10123.00	591112.0	527022.0	634402.0

The laboratorial photoautotrophic bioH_2 production by *Anabaena* sp. consumed 1538 MJ/MJ_{H2} of energy and emitted 115 kg CO_2/MJ_{H2}. The use of the residual *Anabaena* sp. biomass as substrate in a subsequent dark-fermentation process increased those values by 12.0%.
BioH_2 production by *C. butyricum* from a hydrolyzate of *Sc. obliquus* showed one of the higher values of energy consumption and CO_2 emission.
In the bioH_2 production by fermentation of the *Nannochloropsis* sp. leftover biomass, the scheme identified as *Biorefinery 1* (biodiesel SE + hydrogen), presented the lowest results, 172-239 MJ/$MJ_{produced}$ and 12.5-15.0 kg CO_2/$MJ_{produced}$. However, the scheme *Biorefinery 2* (biodiesel SFE + hydrogen) attained similar results, with the advantage of including the extraction of high-value pigments, by SFE, and of being a clean technology that doesn't use toxic organic solvents. *Biorefinery 2* represents the best energy and CO_2 compromise. Hydrogen as co-product may be advantageous in terms of process yield and profit.
Pilot studies should complement this work in order to achieve sustainable feasible processes at an industrial scale. In the case of bioH_2 production by and from *Anabaena* sp., from a hydrolyzate of *Sc. obliquus* and from *Nannochloropsis* sp. biomass, scale-up possibilities of process optimization were identified for future implementation [6-8].
In the case of *Sc. obliquus* dried biomass, the improvements made presented an improved efficiency in energy production. Biological hydrogen production by *C. butyricum* from *Sc. obliquus* dried biomass attained 7.3 g_{H2}/$kg_{biomass}$. This H_2 yield was obtained at the expense of 71-100 MJ/MJ_{H2} of energy consumption and 5-6 kg CO_2/MJ_{H2} of CO_2 emissions, considering the whole production process. The obtained results show a great potential of biological hydrogen production by *C. butyricum* from *Sc. obliquus* dried biomass for process scale-up. In optimized scale-up scenarios built up from the laboratorial results of the former study, bioH_2 production can be considered competitive comparing with conventional production by electrolysis (3.43-3.81 MJ/MJ_{H2} and 200.4-217.5 gCO_2/MJ_{H2} [10]). In terms of energy consumption, the biological process may attain 6-8 MJ/MJ_{H2} and it may become especially advantageous in terms of CO_2 balance, with values of CO_2 absorption of 1130 gCO_2/MJ_{H2}, decreasing total values of emissions for (-716) to (-613) gCO_2/MJ_{H2}.
In terms of scale-up based on laboratorial results of bioH_2 production from microalgal biomass, the best industrial scale scenario proposed in this work would produce sufficient hydrogen to replace 7 % of an urban taxi fleet at the expense 100 ha of soil occupation and 6-8 MJ of energy consumption per MJ of hydrogen produced.

4. Conclusions - With the results upon which this study was based, it was possible to identify the most critical steps of microalgae culture and biofuel production and which therefore require mandatory optimization before further pilot and industrial upscale, to make biohydrogen production a viable and sustainable application in the future. The results are expected to fill gaps in current fuel cradle-to-gate databases, to open the possibility of considering this biofuel in future demonstration projects and to give indications on the worthiness of considering cyanobacteria/microalgae as potential feedstock for bioH_2. When considering CO_2 balances at the scaled up level, bioH_2 production from microalgal biomass is particularly advantageous due to the CO_2 absorbing capacity of the microalgae. Finally, this analysis shows that the biological production of hydrogen must be further investigated to make microalgae biofuels production energy and environmentally relevant.

5. References

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