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Algae-based biorefinery concept: an LCI analysis for a theoretical plant

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Abstract

Both micro and macro algae have a potential to be a valuable feedstock for biorefineries. The theoretical impact assessment of this kind of plant can be carried out through an LCA, which is a key tool in order to evaluate the potential environmental impact of a process throughout its entire life cycle. Hence, it is a priority to perform an LCI with the aim of gathering all the data and simulating all the unit process of a theoretical biorefinery. The Inventory ensures to obtain a simple and immediate way to represent several aspects of a biorefinery, e.g. productivity, environmental pressures, required resources in terms of raw materials and energy. One of the main aspects clearly shown in this study is the significant environmental pressures due to the cultivation and harvesting steps, for which it is desirable to consider a biomass collection from the environment, especially from areas where eutrophication phenomena are particularly recurrent. Another conclusion drawn from the study is that the total plant production per year appears very limited, if compared to any conventional refinery. The following approach can also provide a starting data set to perform a first approximate economic analysis of the costs/gains of the outlined project, and it could be used as a first concept design for the project development of a real plant.

Keywords: biorefinery; biofuels; micro and macroalgae; LCI; LCA

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1. Introduction

The reaching of the oil pick demand has promoted research on 2nd and 3rd generation of biofuels. Within this perspective the use of algae, both – micro and macro, become a key opportunity for selecting alternative feedstocks [1, 2]. Nevertheless, the overall sustainability of the entire production process and its economically feasibility is still a key research question [3]. Research findings highlighted the need of addressing attention to biofuel as promising substitute to fossil-based fuels addressed to a more secure energy sector [1]. During the last decades' biodiesel and bioethanol production from algae and terrestrial plants have become attractive at world level as alternative to fossil-based pathways. Nevertheless there are constraints on the use of biological feedstock and its availability [4] and in connection to the dilemma of "food versus fuel" directly undermining the overall sustainability [5].

Biofuel production from algae represents implementable methods to provide positive effects within the share of the global demand for transport fuels [6]. There are several studies that show algae-based biofuels chains as economically and environmentally sustainable concepts [7]. This is in first instance related to the high efficiency that algae-based systems have on the transformation of biomass leftovers and wastes to valuable energy carriers (i.e. biomethane, bioethanol and biodiesel) [8]. Algae can also be a nutritional supplements [8], displacing environmental burdens if used as interface for solving environmental pollution issues. In this context seaweed biorefinery framework represents a conceptual model for high value added product production along with production of biofuels either fluid or gaseous. This in turn reduces the cost of fuel production with maximum utilization of the biomass [9]. More in specific with the term "biorefinery" is thus described a close cycle of production of biofuels in combination with high value co-products from biomasses though the sue biotechnologies in a favourable and sustainable way (i.e. environmentally and economicacally) [10]. Both macroalgae and microalgae represent high-value biological feedstock pharmaceutical products, feed/food supplements, and pigments [11] not related only to the biofuels conversion pathways. An algae-based biorefinery can be defined as [12] integrated technologies favouring algae-to-biofuels systems and prior the all conversion technologies starting from the biomass production to the extraction of useful co-products.

This paper provides an LCI of the biorefinery concept of a theoretical specifically addressed to the production of biodiesel, bioethanol and biomethane using a micro- and macro-algae feedstock. Specifically, the focus is based on the design of a hypothetical biofuel and biochemical production system, making a proper distinction between two different algal feedstocks, conversion processes and obtainable end products. Through integration of green chemistry into biorefineries and the use of low environmental impact technologies, future sustainable production chains of biofuels and high value chemicals from biomass can be established. The biorefinery concept embraces a wide range of technologies able to separate biomass resources into carbohydrates, proteins, triglycerides, which can be converted into value added products, biofuels and chemicals. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals. This concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. The aim of this bio-industry is to be competitive on market and lead to the gradual replacement of oil refinery products [13].

The theoretical impact assessment of a biorefinery can be carried out through a Life Cycle Assessment (LCA), which is a useful tool to evaluate the potential environmental impact of a product, process or activity throughout its entire life cycle. The aim of this study is to minimize the impact of the process on human life conditions and environment, both in terms of used resources and pollution, by studying all the different production phases in order to optimize the most critical ones. Hence, at the same time, a Life Cycle Inventory (LCI) must be performed to gather all the data and to simulate all the process nodes of the hypothetical biorefinery. This paper focuses on this type of inventory. The present LCI has been structured around the main steps of the biorefinery process:

- Algal biomass production and harvesting (pre-treatments);
- Transformation processes;
- Downstream processes.

In addition to pre-existing data gathering [14], the final results have been obtained by introducing some simplifying assumptions.

2. Main hypothesis

To obtain a range of end products that could be the widest possible, two different feedstocks were selected (i.e. micro- and macro-algae); each of them intended to follow its own production path in an integrated process, with a view to collecting the resulting products from both the parallel lines and managing them together. Specifically, micro and macro algal biomass were selected as raw materials as described in the following:

- Standard microalgae (raw composition: $CH_{1.83}O_{0.48}N_{0.11}P_{0.01}$ [15]) were considered as the starting material to produce biodiesel, biogas and glycerol;
- *Zostera Marina* [16] was identified as the raw material for the production of bioethanol and biogas.

The study was developed also considering: the theoretical plant built in center-south of Italy, an in-situ cultivation site of microalgae while the macroalgae were assumed to be imported from the Baltic Sea (taking into account the transportation impact). For the use of water was considered a recirculation system in order to avoid further use of this resource. In the study the avoided water was considered pure-like water and it was hypothesized to be mainly return back to the system in the cultivation phase.

For the microalgae production two scenarios were analyzed: pond cultivation (100 ha in size) and cultivation in photo-bioreactors, taking into accounts the different productive yields and energy consumptions.

Some factors were introduced to scale-up the performance of a pilot plants data to a hypothetical industrial facility, because the state of the art on this technology is currently still experimental [17].

2.1. Process structure design

Two production lines were structured for the upstream process, both converging into only one downstream post-treatment line.

In all unit processes, the main input and output streams of energy and matter were identified and balanced, considering all the possible recycling and re-circulation options in order to minimize the impacts. To reflect the difficulties of a real industrial process, for many of the process steps (particularly in the separation phase) a safety factor was introduced (0.7–0.98 depending on the nature of the step itself [14, 18]). The concept design of the main reactors and tanks was performed in order to quantify the structural materials and the initial impact of the plant construction was calculated. The impact of the structural materials was evaluated considering a 10-year maximum life time for the plant. The process lines will be separately described below.

2.2. Microalgae line

The line is composed of five main unit processes: cultivation, harvesting and pre-treatments, acid transesterification, product separation and anaerobic digestion. The table below represents the explained process (Fig. 1).

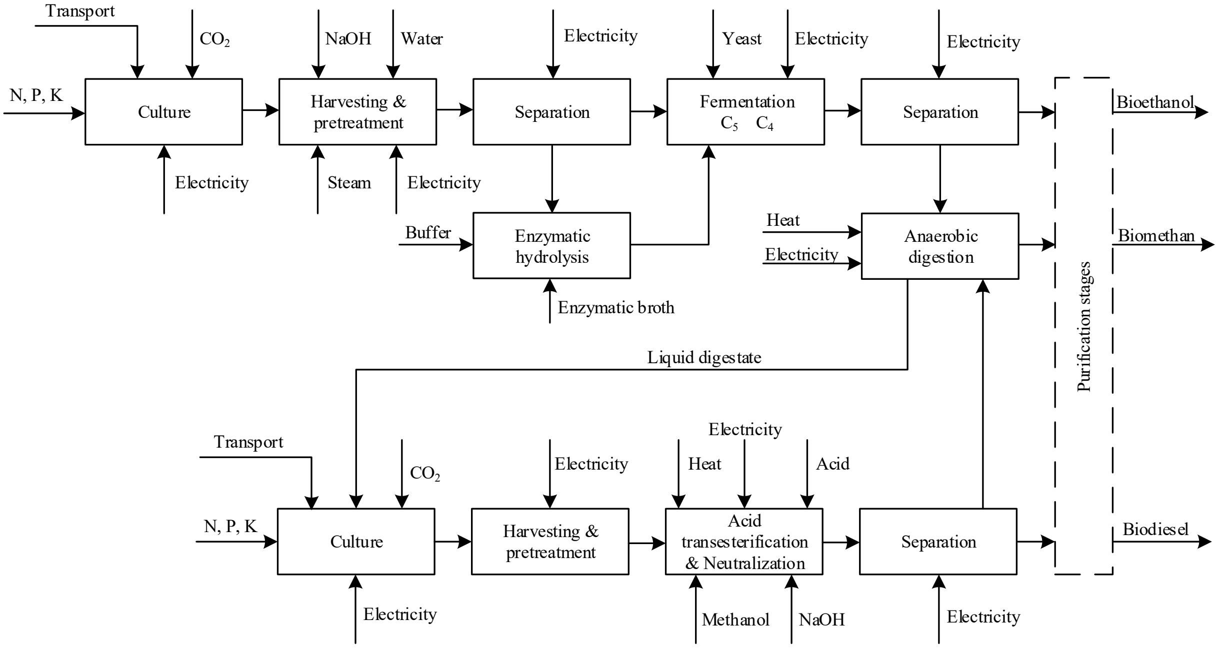

Fig. 1. Plant design.

2.3. Macroalgae line

This line is composed of six main unit processes: cultivation, harvesting and pre-treatments (including extractive process), enzymes production and enzymatic hydrolysis, product separation, parallel alcoholic fermentations, anaerobic digestion. The process is slightly more complex than the microalgae one as the same feedstock is converted in different product streams on which some steps occur in parallel, and then the resulting by-products are treated together. The table below is representative of this higher complexity (Fig. 1).

2.4. Downstream

The downstream processes include biodiesel washing, bioethanol distillation to increase its concentration, anaerobic digestion products blending, recovery and purification. Glycerol purification was not included in the present study; the raw glycerol can be considered a final co-product without undergoing any downstream process.

Biodiesel washing is performed using water with a 1:1 volumetric ratio [19].

Anaerobic digestion generates biogas, solid and liquid digestate. These streams are produced at different concentrations depending on the feeding materials thus the two productive lines give different results. The analogue product streams from the two lines are blended and then a final treatment is performed on these mixed streams.

Biogas (CH_4 plus CO_2 in variable proportions) purification to obtain bio-methane (97.7 % CH_4) is accomplished after blending, through a PSA upgrading process [20]. The total removed carbon dioxide is recycled into the microalgae cultivation step to contribute to the algal CO_2 requirements. In addition, the liquid digestate is dried to remove toxic liquid compounds and recirculated to the microalgae cultivation step as a fertilizer (N and P recovery) [21]. The solid digestate, instead, has been used as a fertilizer.

2.5. LCI data reporting

The main data calculated in this work are reported below considering a 10-year maximum life time for the plant.

Table 1. Microalgae LCI.

Step	Value process	Units	Notes
Cultivation & Harvesting [22]			
Input			
Nitrogen	0.221	t/die	
Phosphorus & Potassium	0.096	t/die	
CO_2	29.30	t/die	
Water (make-up)	822	t/die	
Culture & harvesting Electricity	166817	kWh/die	
Concrete (pond construction)	31650	t	
Output			
Algae dry	25	t/die	50 % w/w of solid
Water	25	t/die	
Pure water (avoided)	4950	t/die	
Transesterification in situ & Neutralization			
Input			
Algae dry (50 % w/w of solid)	25	t/die	T = 65 °C
Water	25	t/die	
Methanol	47.60	t/die	
H_2SO_4	0.37	t/die	308:1 (solvent: oil)
NaOH	0.30	t/die	Cat. 0.678:1 (mol/mol)
Steel reactor construction	0.96	t	
Electricity & Heat	373.16	kWh/die	
Output			
Water	25.14	t/die	
Na_2SO_4	0.54	t/die	$H_2SO_4 + 2\ NaOH \rightarrow 2\ H_2O + Na_2SO_4$
Methanol	47.14	t/die	
Glycerol & Waste	0.44	t/die	
Biodiesel	4.32	t/die	
Lipids & cake	20.70	t/die	Lipid molecular weight = 890
Anaerobic Digestion			
Input			
Solution to Anaerobic Digestion	117.30	t/die	
Cake	20.70	t/die	17.65 % w/w solid
Electricity & Heat	5.52	kWh/die	
Steel reactor construction	6.64	t	
Output			
Biogas	4.01	t/die	
Solid digestate	21.88	t/die	
Liquid digestate	112.11	t/die	

Table 2. Macroalgae LCI.

Steps	Value process	Units	Notes
Cultivation & Harvesting			
Input			
Nitrogen	0.38	t/die	
Phosphorus & Potassium	0.06	t/die	
CO_2	15.45	t/die	
Water (make-up)	0	t/die	Sea cultivation
Electricity for cultivation and harvesting	8860	kWh/die	
Output			
Total Suspension Mass	25.3	t/die	
Algae dry	12.65	t_{DAF}/die	50 % p/p dry matter
Water	12.65	t/die	
Steam-Explosion Pretreatment			
Input			
Total Suspension Mass	25.30	t/die	
Algae dry	12.65	tDAF/die	Residence time = 300 s
Water	12.65	t/die	
Steam HP	12.65	t/die	T = 180 °C P = 14 bar (1 kg/dry kg)
Acid	0.52	t/die	Acid catalyst (2 % of tot mass)
Electricity & Heat	3889.78	kWh/die	
Steel (reactor construction)	273.21	kg	D: 0.7 m, H: 2.8 m, s: 5 mm
Washing water	37.74	t/die	
Output			
Emicellulose solution (SM)	34.06	t/die	89 % water
Washed fibers (IM)	35.90	t/die	76 % water
Steam	6.21	t/die	
Enzymatic hydrolysis			
Input			
Washed fibers (IM)	34.11	t/die	
Buffer	9.21	t/die	
Enzymatic broth	13.26	t/die	Produced from inoculum, C5 syrup and 5 % of deluded IM
Steel (reactor construction)	2084.47	kg	
Output			
Monomeric sugar in C6 syrup after Enzymatic hydrolysis	2.90	t_{DAF}/die	
Hydrolyzed	56.58	t/die	
L/S Separations			
Input			
Hydrolyzed	56.58	t/die	T = 40 °C
Emicellulose solution (SM)	34.06	t/die	
Steam BP	3.03	t/die	

Electricity	254.94	kWh/die	
Output			
Syrup of C6	52.28	t/die	
Syrup of C5	31.03	t/die	
Water condensed	3.03	t/die	
Steam Removed	3.03	t/die	
Semi-solid Cake	4.30	t/die	To Anaerobic Digestion
Alcoholic Fermentation of C5			Residence time: 48 h, X_{brodo} = 1.1 kg/L
Input			
Syrup of C5	29.48	t/die	Reduced for use in Enzymatic broth production
Yeast	0.35	t/die	Yeast 12 g/L of the syrup
Electricity mixing/pumping	1.20	kWh/die	
Steel (reactor construction)	0.38	t	D: 1.26 m, H: 7.56 m, s: 3 mm
Output			
Bioethanol from C5	0.28	t/die	
Vinasse C5	29.42	t/die	
CO_2	0.13	t/die	
Alcoholic Fermentation of C6			
Input			
Syrup of C6	52.28	t/die	
Yeast	0.63	t/die	
Electricity mixing/pumping	66.48	kWh/die	
Steel (reactor construction)	6.41	t	D: 3.11 m, H: 18.66 m, s: 3 mm
Output			
Bioethanol from C6	1.32	t/die	
Vinasse C6	50.96	t/die	
CO_2	0.63	t/die	
Anaerobic Digestion			
Input			
Residual waters	80.49	t/die	
Sugar C5 in Vinasse C5	0.07	t/die	
Sugar C6 in Vinasse C6	0.29	t/die	
Semi-solid Cake	4.30	t/die	5.34 % w/w solid
Electricity	66.48	kWh/die	
Steel reactor construction	41.40	t	
Output			
Biogas	2.05	t/die	
Solid digestate	3.18	t/die	
Liquid digestate	79.91	t/die	

Table 3. Downstream biogas purification phase LCI.

Biogas Purification	Value process	Units	Notes
Input			
Total feed of biogas	6061.90	kg	From microalgae and macroalgae line
Biomethane input to depuration	3953.82	$kgCH_4$/die	CH_4 content of the total feed of biogas
Methane fraction in input	0.65		Mean molecular weight 25.74
Electricity	5552.15	MJ/die	
Activated carbon filter	721.03	kg	D: 0.8 m, L: 3.5 m, ε_b: 0.41, X_b: 695 kg/m^3
Output			
Purified Biomethane	3628.86	kg/die	97.7 % CH_4
CO_2	2433.05	kg CO_2	

Table 4. Downstream bioethanol distillation phase LCI.

Bioethanol Distillation	Value process	Units	Notes
Input			
Total Bioethanol	1.60	t/die	Input bioethanol fraction: 0.008
Total Vinasse	80.38	t/die	
Heat	61.06	MWh/die	
Electricity	132.96	kWh/die	
Output			
Concentrated Bioethanol	1.49	t/die	($X_{bioethanol}$ = 0.789 kg/L)
Residual waters & Vinasse	80.49	t/die	

Table 5. Downstream biodiesel washing phase LCI.

Biodiesel washing	Value process	Units	Notes
Input			
Biodiesel	4.32	t/die	
Water	4.36	t/die	
Output			
Biodiesel	3.81	t/die	Efficiency factors: 0.9 centrifugation; 0.98 settler
Water	4.87	t/die	
Electricity	0.05	kWh/die	

3. Results and discussion

The final results were found in accordance with the current literature data: the total amount of dry microalgal biomass required to produce 1 kg of biodiesel is 6.56 kg [15], while the amount of dry macroalgal biomass needed to obtain 1 kg of bioethanol is 8.48 kg [14].

Regarding microalgae cultivation, two different scenarios were studied; pond cultivation and photo-bioreactors were simulated and, once fixed the massive algae production, results could be compared to evaluate the land use in the two cases: the utilization of photo-bioreactors allows a space saving of 60 %.

The environmental burdens deriving from the "cultivation and harvesting" processes are significant (Table 1). This step needs a lot of energy, raw materials and land use to be accomplished. It would therefore be desirable to hypothesize a different way to obtain the biomass, collecting it from the environment, in areas where eutrophication phenomena are particularly recurrent. Another interesting aspect is the production of raw glycerol from biomass: due to the nature of the process, the produced glycerol contains a certain quantity of salt.

In this study, the produced salt is Na_2SO_4, but this output can be modified whether it is used in basic or acid catalysis within the transesterification process, or if an alternative neutralizer is used. The choice of the combination of catalyst and neutralizer can be driven by different reasons: if the raw glycerol cannot easily be placed on the market, it must be separated from the salt, which can be used as algal fertilizer; consequently, the pure glycerol is sold on market. If, otherwise, raw glycerol can be considered a high value co-product, the catalyst and neutralizer choice should be based on the costs of these compounds and on the effectiveness of their production in the process.

The environmental pressures deriving from the "transesterification" process is very high due to the use of chemical agents that have a long and impacting supply chain (Table 1). The latter option is the one explored in this study, given that raw glycerol can be considered a high value added biochemical product of the biorefinery.

4. Conclusions

The presented LCI provides an important preliminary attempt to evaluate several aspects of a biorefinery concept now focused on the biofuel production, e.g. productivity, environmental pressures and required resources in terms of matter and energy. The data are now presented as Life Cycle Inventory but not fully analysed, for this reason interpretations and discussion are still not on their final stage: for example, the total plant production per year appears very limited, if compared to any conventional fossil refinery. However, productivity should also be evaluated in relation to the environmental impact of the two alternative refineries, through a comparative LCA and introducing a normalization of the inputs and outputs against an analogue end use.

More than this, the previous approach can also provide a starting data set to perform a first approximate economic analysis of the costs/gains of the outlined project, and it could be used as a first concept design for the project development of a real plant.

Of course, the described data have been extrapolated from literature, using scale-up factors: this study should be integrated by experimental data large scale trials to be suitable to support a real project [20]. Therefore, the next step will be a LCIA, supported by a LCC in order to drive attention also to the real economic impact of this type of plant.

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