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Biofuel potential production from the Orbetello lagoon macroalgae: A comparison with sunflower feedstock

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ABSTRACT

The diversification of different types and sources of biofuels has become an important energy issue in recent times. The aim of this work is to evaluate the use of two kinds of renewable feedstocks in order to produce biodiesel. We have analyzed the potential production of oil from two species of macroalgae considered as waste coming out from a lagoon system involved in eutrophication and from sunflower seeds. We have tested oil extraction yields of both feedstock. Furthermore, a comparison has been carried out based on the emergy approach, in order to evaluate the sustainability and environmental performance of both processes. The results show that, under present conditions, considering oil extraction yields, the production of oil from sunflower seeds is feasible, because of the lower value of transformity of the final product with respect to macroalgae. On the other hand, the results demonstrate that with improvements of oil extraction methodology, macroalgae could be considered a good residual biomass usable for biofuel production.

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1. Introduction

In the last 10 years many studies have been conducted on biofuels, pure or blends, for substituting a meaningful share of fossil fuels, in order to reduce GHG emissions and for achieving efficiency and a certain degree of sustainability [1]. The use of biomass to produce biofuels and their benefits are well known [2]. Biodiesel has gained considerable attention as the need to develop alternatives to traditional diesel fuel increases [3]. Biofuels have shown their best applications on the local scale; in fact, it is difficult to produce them for world supply, because of the excessive need for land. Indeed, a production from residual biomass is a feasible option in order to increase the sustainability if emergy-based analysis and other approaches indicate favorable results. The attention should be centered on the feedstocks (oilseed crops, vegetable

exhausted oil, animal fats) because of their differences in economic, energetic, and ecological costs [4–6]. In particular, the use of biomass that is not particularly useful for other purposes (food, fibers, etc.) should be pursued. The research should involve not only existing renewable sources available from land but also those coming from aquatic systems. During the last years there have been few attempts to study and estimate the real feasibility and sustainability of algal biomass utilization [7] in order to produce biodiesel. Some works focus on the use of different species of microalgae [8–10] because of their high oil yield with respect to oleaginous plants. After land-based biomass (sunflower, rapeseed), the possibility has been taken in consideration to use spontaneous macroalgae because they can be considered as a residual biomass ready to use for energy purposes. The aim of this work is to study and estimate the potentiality and

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sustainability of the use of two species of macroalgae in order to produce oil to generate biodiesel. A comparison between macroalgal oil production and one of the most common feedstocks (in land), sunflower, has been made on the basis of an energy evaluation in order to establish the relative level of sustainability of these two kinds of renewable feedstocks.

2. Materials and methods

2.1. Macroalgae system

Orbetello lagoon is located in southern Tuscany, Italy (42°25' and 42°29' lat. N and 11°10' and 11°17' long. E), covers a total area of 25.25 km² and is divided in two communicating basins [11] having 1 m average depth (Fig. 1). The system is an important site for fish-farming activities and since approximately 20 years ago the entire lagoon has been involved in an increased flow of nutrients (nitrogen, N and phosphorus, P) that have led the system to a certain level of eutrophication. N and P flows originate from domestic treatment plants, urban phytotreatments, land-based fishfarm outflows, eastern fish-farm phytotreatment outflows. In recent years there has been an excessive macroalgal growth [12–14] that has caused serious problems to the entire ecosystem. Two actions have been undertaken to reduce the ecological impact: the installation of 10 pumps in order to increase water exchanges between the sea and the lagoon, and the harvesting of macroalgal biomass. This last activity is executed every year from June to November by 4 boats collecting approximately 40 t per day of two dominant species: *Gracilariopsis longissima* (Rhodophyceae, 60%) and *Chaetomorpha linum* (Ulvophyceae, 40%). *G. longissima* (S.G. Gmelin) Steentoft, L. Irvine and Farnham occurs in European Atlantic coasts, from northern Iberian Peninsula to British Isles and in the Mediterranean Sea [15], is high up to 45 cm, consisting of subulate erect axes, slightly constricted basally, irregularly branched, sometimes proliferous from break zone, joined in a caespitose base. This red macrophyta contain in their cell walls and intercellular matrices one of the main gelling carbohydrate used in the hydrocolloid industry [16]. *G. longissima* is epilithic in the

lower eu littoral or in tide pool, often associated with sand cover, also present in drift materials. *C. linum* (O.F. Muller) Kutzing is a cosmopolitan species. The thalli of this green algae have a siphonocladous level of organization, with thick unbranched filaments made of multinucleate cells. The cell wall has an outer lamellar part mainly made of highly crystalline cellulose and an inner amorphous matrix made of a complex branched polymer of arabinose and galactose, with some xylose. It lives as unattached form in both estuarine systems and coastal lagoons subject to eutrophication [17].

The collection is estimated in 5000 t (wet basis 70% moisture content) per year of algae that are transported and confined in a landfill, with an annual cost of approximately €600,000 [18].

Attempts have been made to use these great quantities of biomass, such as the production of paper and agar, but both have failed because of low yield or quality of final products.

2.2. Macroalgae collection and oil extraction

Two samples of *C. linum* and *G. longissima* were collected in October 2006 and processed in laboratories in order to evaluate the lipid extraction yield. Triplicate samples were prepared for each algae species and lipids were extracted by a slightly modified Bligh and Dyer procedure (Fig. 2) [19]. Ground tissues were extracted with chloroform and methanol (2:1) for 20 min by orbital shaker and then chloroform and water (1:1) were added for 10 min in an orbital shaker; the first extracted phase was filtered by filter paper. The residue was extracted three times with chloroform and filtered. Organic phases were collected, evaporated to dry in pre-weighted vials, and the total lipid content was weighed. Results were expressed in mg g⁻¹ fresh weight. In order to report laboratory data at the industrial scale, we simulated a small plant (Fig. 3) for oil extraction, composed by three steel reactors working at ambient temperature and pressure, with solvent chemical extraction, separation, and with a solvent-recovery phase, taking into consideration the energy requirement. In this way,

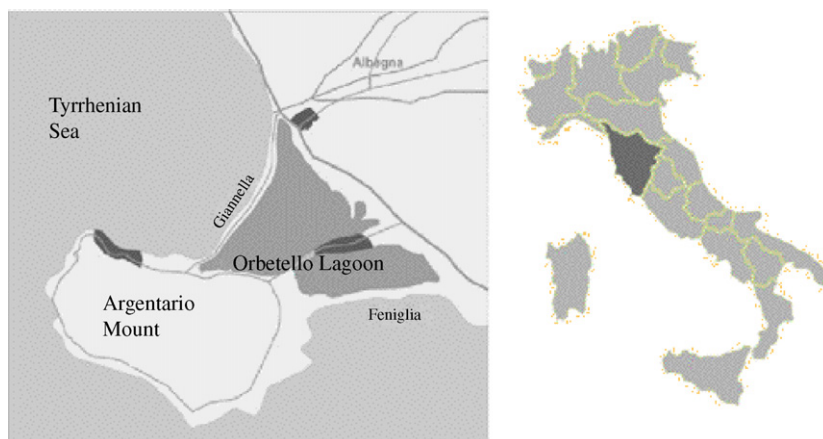


Fig. 1 – Localization of the Orbetello lagoon.

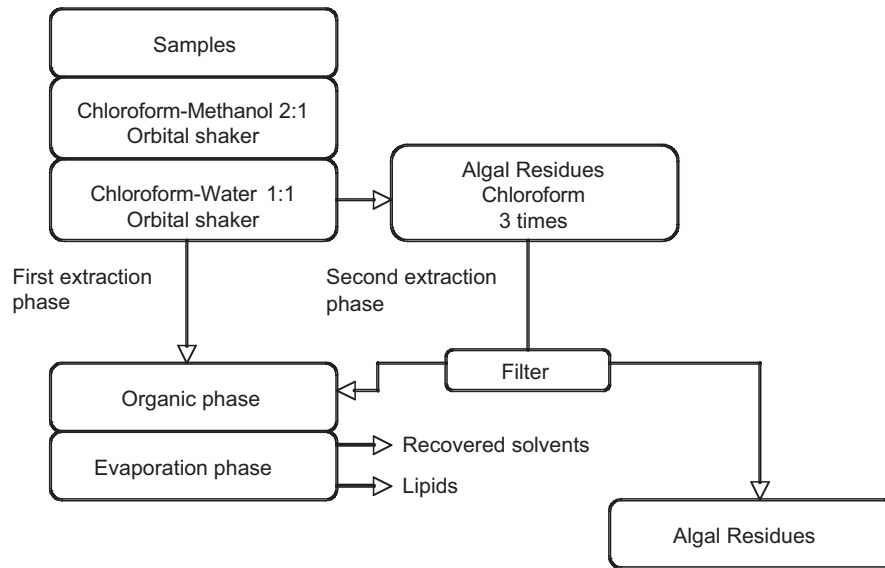


Fig. 2 – Chart of laboratory lipid extraction.

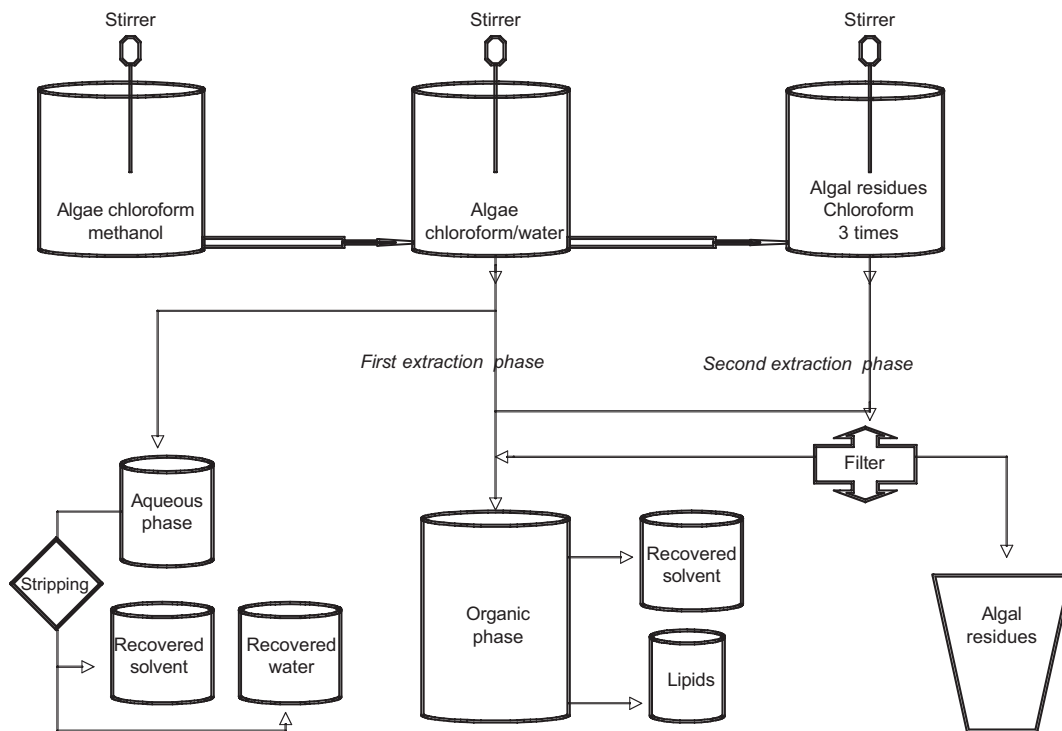


Fig. 3 – Simulated industrial plant for macroalgae.

all inputs were estimated for this phase and considered in the energy evaluation of the entire process.

2.3. Sunflower system

For sunflower (*Helianthus annuus*) oil production, a study conducted in a region of Italy (the Marche Region, main city Ancona 43°36'N and 13°31'E) was utilized as a Ref. [20]. It is a very complete and exhaustive report about sunflower cultivation that describes the entire process of the agricultural and

extraction phases of sunflower oil, with detailed definitions of inputs for sunflower crop (diesel fuels, fertilizers, field operations, machineries). The yield (kg ha^{-1}) of oilseed can vary depending on the field operations, fertilizers used, irrigation practices, and soil composition.

2.4. Sunflower cultivation and oil extraction

Total diesel consumption data for sunflower cultivation are estimated in $110 \text{ kg ha}^{-1} \text{ year}^{-1}$ [20] and reported in Table 1.

Table 1 – Diesel fuel consumption (kg ha⁻¹ year⁻¹) for sunflower cultivation

Ploughing	40
Sowing, herbicide	20
Fertilization	15
Harvesting	20
Transport	15
Total diesel consumption	110

For sunflower seeds yield a value of 1500 kg ha⁻¹ [20]; Kallivroussis et al. [21] report a raw oil yield of 32–38% for seed crushing. To calculate the yield of oil we considered the mean value fixed at 35%. Another important variable is the fertilizer input necessary for growing sunflowers. Data from the Marche study [20] indicate an average use of 100 kg ha⁻¹ of N fertilizer, 65 kg ha⁻¹ of P fertilizer, and 15 kg ha⁻¹ of potassium (K) fertilizer; we also report an average use of herbicide estimated in 3.5 kg ha⁻¹. With these conditions the oil yield of the sunflower system is approximately 525 kg ha⁻¹.

2.5. Emery evaluation

Emery is a well-known methodology introduced by Odum [22–24], and it represents the total amount of available energy (i.e. exergy), of one kind, generally solar energy, directly or indirectly required to make a product or to support a process. It is not a state function, since it depends on the pathway that the process follows. In fact, the emery of a product is related to the way it is produced. This methodology allows for the evaluation of a process on a common basis, the solar energy necessary to obtain a product (see Eq. (1)); the basis of emery evaluation is the conversion of all process inputs, including energy of different types and energy inherent in materials and services, into emery by means of a conversion factor called transformity.

Unlike emery, transformity is an intensive quantity, and is measured in sej J⁻¹ (emery per unit energy). It represents the inverse of an efficiency comparing two similar processes; a higher transformity means that more emery is needed to produce the some amount of output (see Eq. (2)).

$$Em_k = \sum_i Tr_i E_i, \quad (1)$$

$$Tr_k = \frac{Em_k}{E_k}. \quad (2)$$

The circularity of Eqs. (1) and (2) is avoided since, by definition, transformity of solar energy is 1 sej J⁻¹. In this way all inputs are converted into the solar equivalent energy needed to create those energy flows; each flow is summed and multiplied by its transformity, and the result is the measurement of total resources (renewable and non-renewable) that have been necessary in order to obtain a product or a process. A global emery flow base of 15.83E+24 sej year⁻¹ has been assumed; therefore, all calculated transformities, starting from the previously

used 9.44E+24 sej year⁻¹ standard, have been multiplied by 1.68 [25].

Emery has already been used in several works in order to establish a longer-term sustainability of biofuels production [1,26,27]. In the present study, this methodology is applied to compare two feedstocks and the evaluation considers the entire process until lipid extraction. The comparison does not consider the input for seeds and macroalgae transport to the processing plant and the storage phase for oil from both the feedstocks, but assumes that the extraction phase happens near the two systems; harvesting, collection, handling and storage of biomass can be a barrier due to economic and energetic costs. This problem can be overcome by developing locally applicable technologies to convert bulky raw materials (macroalgae) into energy-dense fuels. Input data and related calculations that appear in the following tables are carefully reported in Appendix A (sunflower system) and Appendix B (macroalgae system).

3. Results

3.1. Macroalgal lipid

Lipid concentrations were slightly lower in *G. longissima* (1.87 mg g⁻¹ fresh mass) than in *C. linum* (2.40 mg g⁻¹ fresh mass) and, generally, lipid contents of Orbetello lagoon's macroalgae are comparable with those reported in the literature for the same species or genus and extracted with comparable methodologies [28,29].

3.2. Macroalgae system

To describe the flows of energy and matter in the studied systems, a modelling language, called Energy System Diagram, has been developed. Fig. 4 reports the emery diagram of the macroalgae system and shows the relations between natural resources and final product, accounting for all energy and material flows involved in macroalgae oil production.

The following table (Table 2) reports all inputs (expressed in joules or grams) referred to each component entering in the productive process.

The macroalgae system (Fig. 4) starts from the growth and the harvesting phase. There are several inputs that contribute to the growth of macroalgae, both non-renewable (fossil based) and renewable (solar radiation, rain, wind, geothermal heat), but only those having the greater value of emery flow, that is rain and geothermal heat, were considered. The higher emery inputs, from non-renewable resources, are N and P flows, which feed the macroalgae bloom; the other higher inputs are steel for the harvesting boats (4 boats) and the electricity used by the 10 pumps in order to increase water exchanges between the sea and the lagoon and to improve the oxygen concentration of the aquatic system. The emery flow for this phase of the macroalgae system (Table 2) is 6.09E+18 sej year⁻¹. For the industrial phase, that is the oil extraction from macroalgae, there is a great consumption of non-renewable inputs like chemicals (chloroform and methanol) for the extraction procedure, which with the electricity used in the simulated extraction plant are the

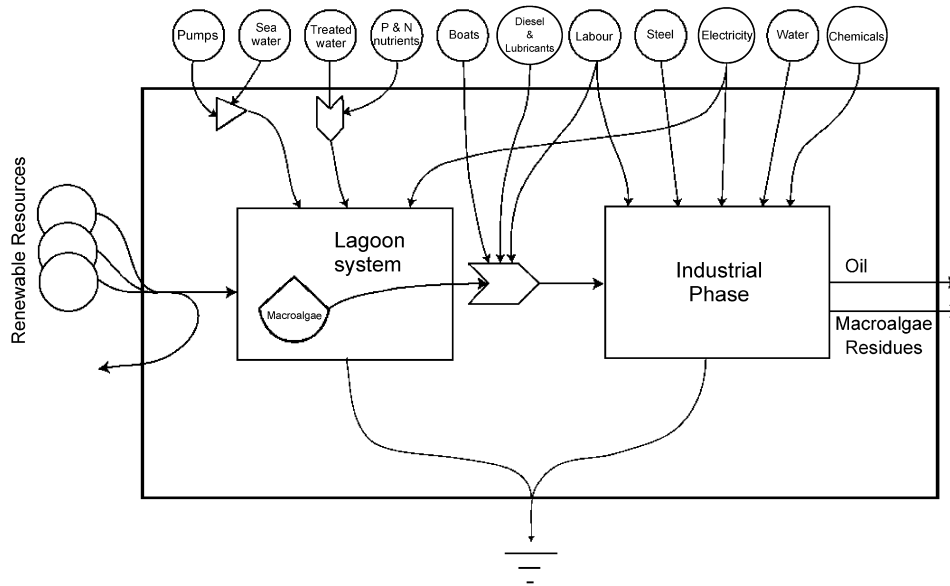


Fig. 4 – Emergy diagram of the macroalgae system. (For sake of clarity the inputs on the top are not in increasing order of transformity.)

Table 2 – Emergy inputs for macroalgae oil system

Input	Unit per year	Amount	Emergy per unit (sej unit ⁻¹)	Solar emergy (sej year ⁻¹)	Ref. for transformities
<i>Growth and harvesting phase</i>					
1. Solar radiation	J	1.11E+17	1	1.11E+17	[36]
2. Rain	g	1.70E+13	1.51E+05	2.57E+18	[36]
3. Wind	J	2.21E+11	2.52E+03	5.56E+14	[36]
4. Geothermal heat	J	1.20E+14	4.28E+03	5.12E+17	[36]
5. Nitrogen input	g	1.08E+08	2.41E+10	2.60E+18	[37]
6. Phosphorus input	g	6.00E+06	2.02E+10	1.21E+17	[37]
7. Diesel oil	J	1.00E+08	1.10E+05	1.10E+13	[25]
8. Lubricants	J	2.01E+10	1.10E+05	2.21E+15	[25]
9. Steel	g	4.40E+06	1.13E+10	4.97E+16	[37]
10. Human labor	J	1.95E+09	1.24E+07	2.41E+16	[37]
11. Steel	g	6.00E+05	1.13E+10	6.78E+15	[37]
12. Electricity	J	1.04E+12	2.00E+05	2.08E+17	[37]
Total energy flow for growth and harvesting phase				6.09E+18	
Output: collected macroalgae	g	5.00E+09	1.22E+09		
<i>Industrial phase (oil extraction)</i>					
13. Steel	g	2.50E+06	1.13E+10	2.83E+16	[37]
14. Human labour	J	1.95E+09	1.24E+07	2.41E+16	[37]
15. Electricity	J	6.71E+12	2.00E+05	1.34E+18	[37]
16. Water	g	2.50E+09	1.25E+06	3.13E+15	[37]
17a and b. Chemicals	g	4.52E+09	3.80E+08	1.72E+18	[37]
Total energy flow of extraction phase				3.11E+18	
Total process energy flow				9.21E+18	
Output: macroalgae oil	g	1.04E+07	8.85E+11		
Output: macroalgae oil	J	3.49E+11	2.64E+07		

highest inputs. To estimate this value we assumed that 80% of both solvents was recovered in the process, with an energy expense of 157 kWh (565 MJ) t⁻¹ of recovered solvent [30]. For the plant, we have simulated a scheme of macroalgae

treatment as reported in Fig. 3. In the industrial phase of macroalgae the emergy flow is 3.11E+18 sej year⁻¹. The total emergy flow required by the entire process of the macroalgae system is 9.21E+18 sej year⁻¹. Also in this case we divided the

value of energy flow for the energetic content of the total quantity of macroalgae oil output (10.04 t) of oil equivalent to 349 GJ; the energetic content of algae expressed as net calorific value or low heating value generally ranges between $32\text{--}35\text{ MJ kg}^{-1}$ [17,31,32], and we have chosen an average value of 33.5 MJ kg^{-1} as value. We obtained the value for the transformity, which is $2.64\text{E}+07\text{ sejJ}^{-1}$.

3.3. Sunflower system

Fig. 5 reports the emergy diagram of the sunflower system, showing the relations between natural resources and final product, accounting all energy and material flows involved in sunflower oil production.

Starting from the agricultural phase of the sunflower system, it can be noted that in order to obtain an output of 1500 kg of seeds, from which 6 kg are subtracted as input for the following year, the major inputs, among those non-renewable, invested in the process are fertilizers (N, P, K, fertilizers) followed by diesel oil and soil erosion (Table 3). This reflects the situation of modern agriculture, industrialized especially in monocultures, that is the major cause of natural non-renewable resource exploitations. In the industrial phase of the sunflower system, that is oil extraction, it can be noticed that electricity is the major input to reach a final oil extraction of 525 kg; once again it is evidenced that the weight of non-renewable inputs is due to their high transformities, justified by the great quantity of solar energy involved in their formation processes.

The final value of emergy flow necessary to sustain the entire process of the sunflower system and the relative oil output, from 1 ha, is $4.89\text{E}+15\text{ sej year}^{-1}$. Dividing the value of emergy flow by the energetic content of the total quantity of oil output ($1.76\text{E}+10\text{ J}$ per 525 kg of oil) we have the value of the transformity, which is $2.78\text{E}+05\text{ sejJ}^{-1}$.

4. Discussion

Comparing the transformities of the final oil output from both feedstock, the sunflower system, with a transformity of $2.78\text{E}+05\text{ sejJ}^{-1}$, shows a much higher efficiency than the macroalgae one (transformity of $2.64\text{E}+07\text{ sejJ}^{-1}$). This means that the macroalgae oil extraction process uses up 95 times of natural resources. This difference between the two systems is due to the great quantity of N and P inputs that annually reach the Orbetello lagoon and that cause the growth of macroalgae blooms. Moreover, in the industrial phase as well, there is a great amount of energy in chemicals used in the extraction (methanol and chloroform) and in the electricity used up by the simulated plant. This is due to a difference in the kind of oil extraction: mechanical in sunflower and chemical in the macroalgae system.

It is important to highlight that macroalgae are considered residual biomass; the harvesting process of macroalgae is a way to reduce the problem in the Orbetello lagoon, and it would be carried out independently from the oil extraction. For this reason, inputs involved in the growth and harvesting phase should not be considered. Therefore, we applied the emergy investment [33] in which only the inputs involved in the oil extraction phase have to be taken into account, as reported in the lower part of Table 2. The total emergy flow necessary for the processing of macroalgae is $3.11\text{E}+18\text{ sej year}^{-1}$ and the emergy investment for unit product (similar to a transformity) of final oil output is $8.93\text{E}+06\text{ sejJ}^{-1}$. Comparing this last value with the transformity of sunflower oil, it can be noticed that the exploitation of natural resources is still approximately 30 times higher for macroalgal biomass. This is due to the use of chemicals for extraction and to the great amount of energy used to recover the solvents. At this stage oil output yield from macroalgae is about 10 t year^{-1} ,

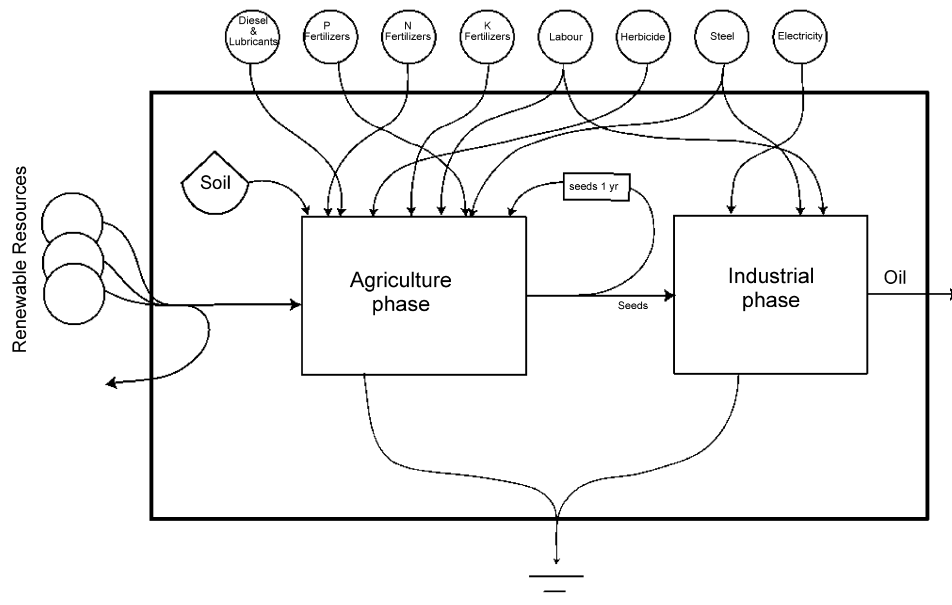


Fig. 5 – Emery diagram of the sunflower system. (For sake of clarity the inputs on the top are not in increasing order of transformity.)

Table 3 – Emery inputs for the sunflower oil seed system (1 ha)

Input	Unit per year	Amount	Emery per unit (sej unit ⁻¹)	Solar emery (sej year ⁻¹)	Ref. for transformities
<i>Agricultural phase</i>					
1. Solar radiation	J	4.59E+13	1	4.59E+13	[36]
2. Rain	g	8.26E+09	1.51E+05	1.25E+15	[36]
3. Wind	J	8.82E+10	2.52E+03	2.22E+14	[36]
4. Geothermal heat	J	3.15E+10	4.28E+03	1.35E+14	[36]
5. N fertilizers	g	1.00E+05	2.41E+10	2.41E+15	[37]
6. K fertilizers	g	6.50E+04	1.74E+09	1.13E+14	[37]
7. P fertilizers	g	1.50E+04	2.02E+10	3.03E+14	[37]
8. Herbicide	g	3.50E+03	3.80E+08	1.33E+12	[25]
9. Seeds	g	6.00E+03	3.23E+09	1.87E+13	Our calculations
10. Soil erosion	J	4.88E+08	1.24E+05	6.05E+13	[36]
11. Diesel oil	J	4.77E+09	1.10E+05	5.25E+14	[25]
12. Lubricants	J	4.02E+07	1.10E+05	4.42E+12	[25]
13. Steel	g	1.25E+03	1.13E+10	1.41E+13	[36]
14. Human labour	J	3.92E+05	1.24E+07	4.87E+12	[36]
Total emery flow of agricultural phase				4.84E+15	
Output: sunflower seeds	g	1.50E+06	3.23E+09		
<i>Industrial phase (oil extraction)</i>					
15. Steel	g	1.50E+02	1.13E+10	1.70E+12	[37]
16. Electricity	J	1.73E+08	2.00E+05	3.46E+13	[37]
17. Human labour	J	1.18E+06	1.24E+07	1.46E+13	[37]
Total emery flow of extraction phase				2.15E+15	
Total process emery flow				4.89E+15	
Output: sunflower oil	g	5.25E+05	9.31E+09		
Output: sunflower oil	J	1.76E+10	2.78E+05		

and with a typical transesterification process [34] a similar quantity of biodiesel usable pure or in blends (BD100, 100% biodiesel, BD50, 50% petroleum diesel and 50% biodiesel) can be obtained. The fuel supply coming out from the Orbetello lagoon could be used to cover the fossil diesel consumptions used for algae transport from the lagoon to the landfill. In fact, the annual diesel consumption of trucks is about 11 mt [18]. This can also bring about a reduction in carbon dioxide emissions; the difference between petroleum diesel and biodiesel is the time necessary for carbon dioxide fixation: for fossil diesel, the process occurs in geological time, whereas for biofuels from biomass the carbon dioxide released into the atmosphere was recently fixed [35]. Nonetheless if we compare the energy expenditure and the output of the industrial process, we see that the former is higher than the latter. This means that in the present situation there is no energy advantage in building up such a system. From the point of view of renewability of resources, the non-renewable percentage of the emery flow to the macroalgae system is about 66% with respect to 78% of the sunflower system. This means that if we want to have a more sustainable process to produce oil from macroalgae, it is fundamental to find other procedures that allow increasing the oil extraction yield. This could also make the process more favorable from an energy viewpoint.

The attempt to use a new kind of feedstock is a good approach to finding alternative processes, in order to increase

the yield of oil extraction and to reach a potential production that would cover all the fuel needs of lagoon practices.

5. Conclusion

The sunflower system showed a higher environmental efficiency (lower transformity) with respect to the macroalgae system. This is due to higher inputs of mostly non-renewable resources, such as chemicals and electricity in the macroalgae system. Moreover, an emery investment approach has been applied to take in account only the inputs involved in the macroalgae oil extraction phase, in order to exclude those inputs of the growth and harvesting phases that would exist independently from the production of oil. Nevertheless, in this case as well, the value of the transformity remains higher with respect to that of sunflower oil ($8.93E+06 \text{ sejJ}^{-1}$ versus $2.78E+05 \text{ sejJ}^{-1}$, respectively). From the point of view of natural resource exploitation and energy requirements, macroalgae oil extraction is not profitable on the basis of the actual oil yield extraction. Nevertheless, biodiesel potential production from macroalgae oil output yield could be used to cover at least the fossil diesel consumption for macroalgae truck transportation from the lagoon to the landfill. This work applied a methodology to extract oil from a new kind of feedstock, and represents a good approach for finding alternative methodologies that will increase the yield

of oil extraction and decrease non-renewable resources, in order to render feasible the use of macroalgae as residual biomass for renewable energy production.

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Appendix A. Sunflower oil

See Table A1.

Table A1 – Input data and related calculations in sunflower system

Agricultural phase		
1. Solar energy		Ref. [38]
Cultivated area	1.00E+00	ha
Solar radiation	5.7	GJ ha ⁻¹
Albedo land	2.00E-01	(% given as decimal)
Energy = Area × Isolation × 1-albedo	4.59	GJ ha ⁻¹ year ⁻¹
	4.59E+13	J ha ⁻¹ year ⁻¹
2. Rain		Ref. [38]
Rain (average)	8.26E-01	m year ⁻¹
Water density	1.00E+03	Kg m ⁻²
Quantity = Area × Rain × Water density	8.26E+09	g year ⁻¹
	8.26E+09	g ha ⁻¹ year ⁻¹
3. Wind		Ref. [38]
Area	1.00E+00	ha
Energy on land	2.45E+04	kWh year ⁻¹ ha ⁻¹
Conversion factor	3.60E+06	J kWh ⁻¹
Energy = Energy on land × Area × 3.6E+06	8.82E+10	J year ⁻¹
	8.82E+10	J ha ⁻¹ year ⁻¹
4. Geothermal heat		Ref. [38]
Heat flow per area	3.15E+06	J m ⁻² year ⁻¹
Energy = Area × Heat flow per area	3.15E+10	J year ⁻¹
	3.15E+10	J ha ⁻¹ year ⁻¹
5. Soil erosion		Ref. [38]
Erosion rate	9.00E+00	gm ⁻² year ⁻¹
% Organic in soil	2.40E-01	Given as %
Energy content/g organic	2.26E+04	J g ⁻¹
Net loss = Area × Erosion rate	9.00E+04	g year ⁻¹
Energy of net loss = Net loss × % Organic × Energy content/g organic	4.88E+08	J year ⁻¹
	4.88E+08	J ha ⁻¹ year ⁻¹
6. Fertilizers quantity		Ref. [20]
Nitrogen (N)	1.00E+05	g ha ⁻¹ year ⁻¹
Phosphorus (P)	1.50E+04	g ha ⁻¹ year ⁻¹
Potassium (K)	6.50E+04	g ha ⁻¹ year ⁻¹
7. Herbicide		Ref. [20]
Quantity	3.50E+03	g ha ⁻¹ year ⁻¹
8. Sunflower seeds		Ref. [20]
Quantity	6.00E+03	g ha ⁻¹ year ⁻¹

Table A1. (continued)

9. Diesel		Our calculations
Quantity	1.10E+05	g ha ⁻¹ year ⁻¹
Energy content	4.34E+04	J g ⁻¹
Energy = Quantity × Energetic content	4.77E+09	J ha ⁻¹ year ⁻¹
10. Lubricants		Our calculations
Quantity	1.00E+03	g ha ⁻¹ year ⁻¹
Energy content	4.02E+04	J g ⁻¹
Energy = Quantity × Energetic content	4.02E+07	J ha ⁻¹ year ⁻¹
11. Human work		Our calculations
Labor hours	7.50E-01	h ha ⁻¹ year ⁻¹
Metabolic man-daily energy	1.26E+07	J day ⁻¹
Metabolic energy man-hour	5.23E+05	J h ⁻¹
Total energy = Energy of metabolism × Work hours	3.92E+05	J
12. Steel machinery (threshing machine)		Ref. [39]
Total machinery amount	2.50E+07	g
Machinery amount per ha	2.50E+04	g ha ⁻¹
Life time	2.00E+01	years
Quantity	1.25E+03	g years ⁻¹ ha ⁻¹
13 Sunflower seeds	1.50E+06	g ha ⁻¹
Industrial phase (oil extraction)		
14 Steel machinery (press)		Ref. [20]
Press	3.00E+06	g
Life time	1.00E+01	years
Quantity per year (8760 h)	3.00E+05	g year ⁻¹
Theoretical time use (12 h per 250 days per year)	3.00E+03	h
Quantity used per input from 1 ha (quantity per year/theoretical time use)	1.50E+02	g
15 Electricity		Ref. [20]
Consumption (1.00E+06 seed crushing)	3.20E+01	kWh
Consumption (1.5E+06 seed crushing)	4.80E+01	kWh
Total consumption	1.73E+08	J
16 Human labor		Our calculations
Labor hours (1.5E+06 seed crushing)	1.50E+00	
Metabolic man-daily energy	1.26E+07	J day ⁻¹
Metabolic energy man-hour	5.23E+05	J h ⁻¹
Metabolic energy (1.5E+06 seed crushing)	7.87E+05	J
Total energy = Energy of metabolism × Work hours	1.18E+06	J ha ⁻¹ year ⁻¹
17 Sunflower oil		Our calculations
Product quantity	5.25E+05	g ha ⁻¹ year ⁻¹
Energy content	3.35E+04	J g ⁻¹
Product quantity = Quantity × Energetic content	1.76E+10	J ha ⁻¹ year ⁻¹

Appendix B. Macroalgae oil

See Table A2.

Table A2 – Input data and related calculations in macroalgae system

<i>Growth and harvesting phase</i>		
1. Solar energy		Ref. [40]
Area	2.53E+01	km ²
Solar radiation	1.38E+02	GJ year ⁻¹
Albedo	2.00E-01	(% given as decimal)
Energy = Area × Insolation × 1–Albedo	1.11E+08	GJ year ⁻¹
Total energy	1.11E+17	J year ⁻¹
2. Rain		Ref. [41]
Rain (average)	6.72E-01	m year ⁻¹
Water density	1.00E+03	kg m ⁻²
Quantity = Area × Rain × Water density	1.70E+13	g year ⁻¹
3. Wind		Ref. [41]
Area	1.00E+00	ha
Energy on land	2.45E+04	kWh year ⁻¹
Conversion factor	3.60E+06	J kWh ⁻¹
Energy = Energy on land × Area × 3.6E+06	2.23E+14	J year ⁻¹
4. Geothermal heat		Our calculations
Heat flow per area	1.50E+02	mW m ⁻²
Energy = Area × Heat flow per area	1.20E+14	J year ⁻¹
	4.73E+12	J year ⁻¹
5 and 6. Indirect fertilizers input		Ref. [14]
Quantity		
Nitrogen (N)	1.08E+08	g year ⁻¹
Phosphorus (P)	6.00E+06	g year ⁻¹
7. Diesel		Ref. [18]
Quantity	1.00E+08	g year ⁻¹
Energy content	4.34E+04	J g ⁻¹
Energy = Quantity × Energetic content	4.34E+12	J year ⁻¹
8. Lubricants		Ref. [18]
Quantity	5.00E+05	g year ⁻¹
Energy content	4.02E+04	J g ⁻¹
Energy = Quantity × Energetic content	2.01E+10	J year ⁻¹
9. Steel harvesting boats		Ref. [18]
Total machinery amount (22 t per boat)	8.80E+07	g
Life time	2.00E+01	years
Quantity	4.40E+06	g years ⁻¹
10. Human labor		Our calculations
Labor hours	3.72E+03	h year ⁻¹
Metabolic man-daily energy	1.26E+07	J day ⁻¹
Metabolic energy man-hour	5.23E+05	J h ⁻¹
Total energy = Energy of metabolism × Work hours	1.95E+09	J
11. Steel pumps		Ref. [18]
Total machinery amount (10 pumps)	3.00E+06	g
Life time	5.00E+00	years
Quantity	6.00E+05	g years ⁻¹
12. Electricity		Ref. [18]
Energy consumption	32	kWh
Total consumption (900 h per 10 pumps)	2.88E+05	kWh
Total consumption	1.04E+12	J
Output macroalgae	5.00E+09	g year ⁻¹
13. Steel extraction		Our calculations

Table A2. (continued)

Reactor plant	2.50E+07	g
Life time	1.00E+01	years
Quantity	2.50E+06	g year ⁻¹
14. Human labor		Our calculations
Labor hours	3.72E+03	h year ⁻¹
Metabolic man-daily energy	1.26E+07	J day ⁻¹
Metabolic energy man-hour	5.23E+05	J h ⁻¹
Total energy = Energy of metabolism × Work hours	1.95E+09	J
15a. Electricity		Ref. [30], our calculations (on the basis of evaporation energy 1227 J g ⁻¹)
Consumption (1 mt methanol recovered)	5.65E+08	J
Consumption (80% methanol recovery)	3.60E+12	J
Total consumption	3.60E+12	J
15b. Electricity		Ref. [30], our calculations (on the basis of evaporation energy 264 J g ⁻¹)
Consumption (1 metric ton chloroform recovered)	2.64E+08	J
Consumption (80% chloroform recovery)	3.10E+12	J
Total consumption	3.10E+12	J
Total consumption	6.71E+12	J
methanol+chloroform recovery		
16. Water		Our calculations
Quantity (input per 5000 t of macroalgae)	5.00E+09	g
Quantity (input per 5000 t of macroalgae with 50% recovery)	2.50E+09	g
Actual used	2.50E+09	g
17a. Chemicals		Our calculations
Methanol		
Quantity (input per 5000 t of macroalgae)	7.90E+09	g
Quantity (input per 5000 t of macroalgae with 80% recovery)	6.32E+09	g
Actual used	1.58E+09	g
17b. Chemicals		Our calculations
Chloroform		
Quantity (input per 5000 t of macroalgae)	1.47E+10	g
Quantity (input per 5000 t of macroalgae with 80% recovery)	1.18E+10	g
Actual used	2.94E+09	g
Macroalgal oil		Our calculations
Product quantity	1.04E+07	g year ⁻¹
Energy content	3.35E+04	J g ⁻¹
Product	3.49E+11	J year ⁻¹
quantity = Quantity × Energetic content		

REFERENCES

- [1] Bastianoni S, Marchettini N. Ethanol production from biomass: analysis of process efficiency and sustainability. *Biomass & Bioenergy* 1996;11:411–8.
- [2] Subramanian KA, Singal SK. Utilization of liquid biofuels in automotive diesel engines: an Indian perspective. *Biomass & Bioenergy* 2005;29:65–72.
- [3] European Parliament, Directive2003/30/CE, <europa.eu.int/eurlex/pri/it/oj/dat/2003/l123/l_12320030517it00420046.pdf>.
- [4] Zheng S, Kates M, Dubé MA, McLean DD. Acid-catalyzed production of biodiesel from waste frying oil. *Biomass & Bioenergy* 2006;30:267–72.
- [5] Kalam MA, Masjuki HH. Biodiesel from palmoil: an analysis of its properties and potential. *Biomass & Bioenergy* 2002;23:471–9.
- [6] Canakci M. The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresource Technology* 2007;98:183–90.
- [7] Sheehan J, Dunahay T, Benemann J, Roessler P. A look back at the US Department of Energy's aquatic species. Program Biodiesel from Algae. Report of National Renewable Energy Laboratory TP-580-24190 (NREL), July 1998.
- [8] Yusuf C. Biodiesel from microalgae. *Biotechnology Advances* 2007;25:294–306.
- [9] Han X, Xiaoling M, Qingyu W. High quality biodiesel production from a microalga *Chlorella protothecoides* by heterotrophic growth in fermenters. *Journal of Biotechnology* 2006;126:499–507.
- [10] Xiaoling M, Qingyu W. Biodiesel production from heterotrophic microalgal oil. *Bioresource Technology* 2006;97:841–6.
- [11] Travaglia C, Lorenzini M. Monitoring algae growth by digital analysis of LANDSAT data: the Orbetello lagoon case study. In: RSC Series. Rome: FAO;1985. p. 19.
- [12] Lenzi M. Experiences for the management of Orbetello lagoon: eutrophication and fishing. *Science of the Total Environment* 1992;5:1189–98.
- [13] Bombelli V, Lenzi M, editors. The Orbetello lagoon and the Tuscany coast. In: Schramm, Nienhuis, editors. *Marine Benthic Vegetation. Ecological Studies* 1996;123:331–7.
- [14] Lenzi M, Palmieri R, Porrello S. Restoration of the eutrophic Orbetello lagoon (Tyrrhenian Sea, Italy): water quality management. *Marine Pollution Bulletin* 2003;46:1540–8.
- [15] Gurgel CFD, Liao LM, Fredericq S, Hommersand MH. Systematics of *Gracilariopsis* (Gracilariales, Rhodophyta) based on *rbcL* sequence analyses and morphological evidence. *Journal of Phycology* 2003;39:1–19.
- [16] Mollet JC, Rahanoui A, Lemonie Y. Yield, chemical composition and gel strength of agarocolloids of *Gracilaria gracilis*, *Gracilariopsis longissima* and the newly reported *Gracilaria cf. vermiculophylla* from Roscoff (Brittany, France). *Journal of Applied Phycology* 1998;10:59–66.
- [17] Aresta M, Dibenedetto A, Carone M, Colonna T, Fragale C. Production of biodiesel from macroalgae by supercritical CO₂ extraction and thermochemical liquefaction. *Environmental Chemistry Letters* 2005;3:136–9.
- [18] Personal communication from Lenzi M, Lealab of the Orbetello lagoon, October 2006.
- [19] Bligh EG, Dyer WJ. A rapid method for total lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology* 1959;37:911–7.
- [20] Riva G, Pedretti E, Toscano G, Cerioni R, Duca D. *Agroenergie: Filiere per la produzione di energia elettrica da girasole*. Regione Marche, Italy: Comitato Termotecnico Italiano (CTI); 2006.
- [21] Kallivroussis L, Natsis A, Papadakis G. The energy balance of sunflower production for biodiesel in Greece. *Biosystems Engineering* 2002;81:347–54.
- [22] Odum HT. Self organisation, transformity and information. *Science* 1988;242:1132–9.
- [23] Odum HT. *Environmental accounting. Emery and environmental decision making*. New York: Wiley; 1996.
- [24] <<http://www.emergysystems.org/index.php>>, June 2007.
- [25] Odum HT, Brown MT, Brandt-Williams S. *Introduction and global budget, Handbook of emery evaluation*. Gainesville, USA: Center for Environmental Policy, University of Florida; 2000. Folio no. 1.
- [26] Nilsson D. Energy, exergy and emery analysis of using straw as fuel in district heating plants. *Biomass & Bioenergy* 1997;13:67–73.
- [27] Carraretto C, Macor A, Mirandola A, Stoppato A, Tonon S. Biodiesel as an alternative fuel: experimental analysis and energetic evaluations. *Energy* 2004;29:2195–211.
- [28] Khotimchenko SV. Lipids from the marine alga *Gracilaria verrucosa*. *Chemistry of Natural Compounds* 2005;41:285–8.
- [29] Devi Prasad PV. A seasonal study of the red seaweeds *Soliera tenera* and three species of *Gracilaria* from Jamaica. *Hydrobiologia* 1986;140:167–71.
- [30] Process for recovering methanol. United States Patent no. 20060135826, 2004 <<http://www.freepatentsonline.com/20060135826.html>>. June 2007.
- [31] Yang YF, Feng CP, Inamori Y, Maekawa T. Analysis of energy conversion characteristics in liquefaction of algae. *Resources Conservation & Recycling* 2004;43:21–33.
- [32] Han X, Xiaoling M, Qingyu W. High quality biodiesel production from a microalga *Chlorella protothecoides* by heterotrophic growth in fermenters. *Journal of Biotechnology* 2006;126:499–507.
- [33] Marchettini N, Ridolfi R, Rusici M. An environmental analysis for comparing waste management options and strategies. *Waste Management* 2007;27:562–71.
- [34] Ma F, Hanna MA. Biodiesel production: a review. *Bioresource Technology* 1999;70:1–15.
- [35] Tiezzi E. *The end of time*. Southampton: WIT Press; 2002.
- [36] Odum HT. *Emery of global processes. Handbook of emery evaluation*. University of Florida, Gainesville, USA: Center for Environmental Policy. *Environmental Engineering Sciences*; 2000. Folio no. 2.
- [37] Brandt-Williams S. *Emery of Florida agriculture. Handbook of emery evaluation*. Gainesville, USA: Center for Environmental Policy, University of Florida; 2002. Folio no. 4.
- [38] Tiezzi E. *Analisi di sostenibilità ambientale della Provincia di Siena, Provincia di Siena. Progetto SPINECO*. 2001/2004. Siena, Italy: Università di Siena.
- [39] <http://www.franz-kleine.com/en/sf10-2_daten.php>, June 2007.
- [40] <<http://clisun.casaccia.enea.it/Pagine/TabellaRadiazione.htm>>.
- [41] <<http://www.rete.toscana.it/sett/agric/foreste/ricerche/99-180.pdf>>, June 2007.