UTILIZATION OF MACRO-ALGAE FOR ENHANCED CO_2 FIXATION AND ENERGY PRODUCTION

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Introduction

The aquatic biomass represents a very interesting source of energy as it has a higher photosynthetic activity with respect to terrestrial plants, an easy adaptability to grow in different conditions, the possibility of growing either in fresh- or marine waters, avoiding the use of land. Either marine micro-algae or sea-weeds could be used as energy source also if the micro-algae have received much attention with respect to the macro-algae.

In this paper we discuss the use of selected Mediterranean macro-algae as source of biofuel. The extraction of oils and biofuel has been carried out using different technologies under mild energetic conditions. Supercritical-carbon dioxide and solvent extraction has been used efficiently to extract the fuel. The SC-CO_2 extraction is quite advantageous. SC-CO_2 is not toxic and, as its critic temperature is quite close to room temperature, it could be also used for the extraction of thermo-labile compounds. A preliminary balance, energetic and economic, will be also presented.

Particular attention has been dedicated to the preparation of samples for extraction in order to ameliorate the efficiency of the process, and to the characterization of the lipidic content.

Results and Discussion

The key step of this work has been the selection of some algae typical of the Adriatic or Jonian sea. In particular, the study has been carried out on two algae, the Chaetomorpha linum (O.F. Müller) Kützing (Cladophorales, Cladophoraceae) and the Pterocladiella capillacea (S.G. Gmelin) Santelices et Hommersand) (Gelidiales, Rhodophyta). Chaetomorpha linum is the dominant species in the bentopleustophytic population of Mar Piccolo in Taranto (Jonian sea), the latter being very much present in the estuary of the Galeso river where it can reach a density of 3 600 g/m^2. P. capillacea, a very good agarophyte, can be found on the rocky substrates in the South Adriatic sea close to Bari and can reach a density of 1 500 g/m^2. Going 150 km further south in the Adriatic sea, it is still present, but in lower amount.

The two species have been selected because of their easy availability and low cost harvesting technology, presence and vegetation all the year long, growth on a large scale in an artificial environment, high percent of compounds that have a potential use as biodiesel.[1]

The effect of several parameters such as biomass production in presence of nitrogen sources, ratio biomass/volume, salinity, temperature and irradiance have been also considered.[1]

In this work, a methodology has been developed for the extraction of biodiesel from algae. Supercritical carbon dioxide has revealed to be particularly suited as extraction solvent. A quali-quanti-tative comparison of the extracts obtained by using this technique with those obtained using the organic solvent extraction has been carried out. The scCO_2 technique revealed to be more efficient and less costly. By using scCO_2 (40-50 °C, 25-30 MPa) in a SITEC apparatus operated in a continuous mode, the extraction of oil from algae has been carried out using either scCO_2 alone or added with methanol (1 mL) as co-solvent.

In order to have an efficient extraction it is necessary to pre-treat the algae. In fact if they are used as collected, no oil is extracted. Among the various techniques, grounding of the dried (at 35 °C) algae in liquid nitrogen is the most effective. The very fine solid obtained, can be extracted under the conditions specified above. Per each sample the amount of extracted oil has been determined per kg of dry matter. The oil content varied from 7 to 20 %. Then the oil has been analysed by CG-MS and its composition determined. Almost all products in the GC were identified so far (96 % of the total) and the mass spectrum of each product was compared with that of an authentic sample used as standard. This has allowed to identify the components of the oil and to calculate the heat content expressed as MJ/kg oil. Such value has been checked through a combustion test. Such studies have shown that the morphological difference of the two algae is associated to a different lipid content, both quantitative and qualitative. In fact, in C. linum methyl myristate, methyl palmitate, methyl linoleate and methyl oleate were found, while P. capillacea was shown to contain besides methyl myristate and methyl palmitate, methyl arachidonate and methyl-all-cis-5,8,11,14,17 eicosanpentaenoate as major components (see Table 1).

Table 1. Principal compound of the oil

Algae	Pressure (bar)	T (°C)	Esters (methyl)	Lipidic content (%)
Chaetomorpha linum	240	50	myristate, palmitate, linoleate, oleate	15
Pterocladiella capillacea	265	50	myristate, palmitate, arachidonate, all-cis-5,8,11,14,17 eicosanpentaenoate	7.5

Studies are still in progress for the complete characterisation of the extract.

A life cycle assessment study has been initiated for the evaluation of the potential of macro-algae for fuel production. Below we discuss the main compounds of the LCA flow-sheet.

Macro-algae need nutrients (N, P, microelements) to which the energy Enu is associated. The cultivation energy is indicated as Ec. A variance analysis has shown that if the energy of nutrients is taken into consideration, the energetic balance may be negative. Therefore, in order to avoid such huge amount of energy input, either effluent water from aquaculture plants should be used, or some selected municipal waters. Algae work as a purifying agent and treated water can be either re-circulated to the fish-pond or immitted into natural basins without paying any penalties. Such use of effluent water, by the way, generates a credit to the process that may be ultimately taken into account. With respect to micro-algae, macro-algae do not need a vigorous stirring. This difference introduces a credit for the macro-algae system when compared to micro-algae. At the end, algae must be harvested, Er. As macro-algae grow either on a solid substrate or free-floating in water, in the former case it is necessary to cut the algae, Eh. The collection is quite easy as it is possible to install a net that when risen allows to collect algae and to let excess water run-off. Also this step is less energy requiring for macro-algae than for micro-algae, that need filtration for their separation. The drying is made by using solar energy or recovered heat, so that the only requested energy is the transfer and mixing, Ee. Once the algae are dried, they need to be pre-treated for the extraction, Epr. Alternatively, algae can be directly used without drying, by using the anaerobic fermentation. As extraction techniques, here the extraction with scCO_2 (Esc) or organic solvents (Eos) have been considered. The utilization of scCO_2 as solvent for the extraction appears quite interesting, as recovered carbon dioxide can be used, making the whole process solvent-free. Comparing the two extraction techniques, it comes out that the energy required for the sc technique is the compression of

CO_2 and heating to 40-50 °C. Therefore the thermal energy input is much lower than using the extraction with solvents. Moreover, by using organic solvents it comes out that the isolation of the oil at the end of the extraction, is much more energy requiring than using scf. In the latter case, it is enough to decompress the gas for isolating the oil. As the scf technique uses a continuous extraction apparatus with recovery of gas, this method appears to be characterized by a lower energy than the organic solvent extraction, and to be more environmentally friendly than the use of solvents. In order to be able to make a correct energetic balance, the extracted oil has been fully (over 96% of the components) characterized for its components. The energetic content has been estimated by using an equation that considers the nature of the components and their heat of combustion, so that the net energy produced by the oil can be calculated (Eq. 1).

$$\Delta H = 3500 + 650\,\Delta n + (a) \quad \text{kJ mol}^{-1} \qquad (1)$$

This value has been checked using a combustion bomb. The global balance of the process takes into account all the energy inputs and the produced energy. (Eq. 2)

(Eric)+Eb+Ers-Ets-Esa (Escr)-Ed (Ed')-Ec-Enu-Er-Eh-Ee-Epr-Esc(Eso)-Ees=Enet
(2)

Enet indicates the net energy recovered. In Equation 2 the first three terms represent the recovered energy, while others are spent energy. The first term is eventually the energy recovered from the hot flue gases that arrive to the algae pond may be very low. Eb is the energy associated to the solid residue (cellulose). Ets is the energy needed for transportation of the gas from the source, Esa is the energy for separation using monoethanolamine (Escr is the separation energy using the cryogenic technology), Ed is the energy of distribution of gas (Ed' is the energy of distribution in case of non separated flue gas). Ec is the energy of cultivation and other terms have the same meaning as in the text. Such contribution is not included in calculations.

General considerations and process data.

So far, all energetic quantities listed above have been collected. Moreover, data relevant to alternative processes for algae treatment have been gathered, these are reported below for a comparison of technologies. Micro-algae have growing costs much higher than macro-algae. In this study CO_2 is recovered using MEA, we assume that nutrients have not to be added, that the pond is at a maximum distance of 5 km from the source, that treated water from fish ponds is re-circulated to the fish pond. Algae from Jonian or Adriatic sea have been used.

The following balance is possible:
Biofuel energy 22-35 MJ/kg dw
Total energy produced 16-20 MJ/kg dw
Total energy spent for the production and harvesting 11-15 MJ/kg dw
Net energy recovered 5-9MJ/kg dw.
Comparison system
Such data can be compared with some literature data
Gasification of micro-algae: energetic input 10.48 MJ/kg dw; energy produced 17.77 MJ/kg dw; net energy 6.29 MJ/kg dw
Combustion of algae: 3.55 MJ/kg dw

The combustion is the technology that generates less energy, also if it is the most direct. Therefore, it looks like the cultivation of macro-algae for the production of biofuel is a technology that has to be taken into consideration for energy production and carbon recycling. Such data are only the first output and need revision and all steps need optimisation and an up-scaling of the process is necessary. For such study both a longer time and a higher investment are necessary. The treated aspects are very interesting if coupled with aquaculture activities that are very common in Italy.

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References

(1) Final Report, Project CNRC008EBF - CNR AGENZIA 2000.