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SCIENCE & TECHNOGY

ENERGY FROM AQUATIC BIOMASS

Aquatic biomass is considered as a second (or third) generation option for the production of biofuels. The best utilization for energy purposes is not its direct combustion. Several technologies are available for the extraction of compounds that may find application for the production of gaseous fuels (biogas, dihydrogen) or liquid fuels (ethanol, biooil, biodiesel).

The world energy demand is increasing at a rate never experienced before: during the next 30 years an increase of 20-66 PWh is foreseen from the actual 16 PWh, with a two- or five-fold increase of the consumed energy. Emerging economies will use over 60% of the total energy with respect to actual less than 40%. In a couple of years, for the first time since ever, China will use more energy than the USA and will remain the first consumer for the next decades. As fossil C-based fuels provide over 80% of the used energy today and the accumulation of CO_2 into the atmosphere is causing serious worries for its potential effect on climate change, the need to take measures for controlling the CO_2 production has become a must. So, several technologies have been developed able to control the CO_2 accumulation into the atmosphere, as categorised in Tab. 1.

The use of renewable energies such as biomass has attracted much attention in these days. Mainly two sources have been so far exploited: cereals, that afford ethanol by fermentation, and seeds, used for the extraction of bio-oil. The use of cereals for the production of ethanol for energy purposes has caused the rise of their price and, as a consequence, of the price of floor and, thus, of bread and other floor-derived food products. The concern about the possible scarcity of food in favour of energy products and the observed increase of prices has pushed to find alternative routes to biofuels avoiding the use of food raw materials.

The need to decouple energy issues from both land use and food production is so pushing away from the first generation biofuels or crop-derived-biofuels towards second and third generation biofuels. Besides the utilization of cellulosic materials and lignine, the

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exploitation of aquatic biomass (microalgae, macrolagae, plants, any other vegetal biomass) is a strategy that may contribute to produce large volumes of biofuels and help EU countries to meet the target of 20% substitution of transport fossil fuels with bio-fuels by 2020.

The interest towards aquatic biomass for energy uses has considerably increased worldwide as witnessed by the industrial investments (see Algae World 08 [1, 2]) in such area and by the number of major international events recently organised and aimed at defining the potential of aquatic biomass for the production of biofuels, and setting the most advanced discoveries about the way to circumvent constraints in cultivation, harvesting and processing. It is interesting to note that aquatic biomass may have a large utilization: it has been, in fact, estimated (Colorado State University and New Hampshire University, [5]) that the amount of biofuels that may be produced from aquatic biomass in USA may cover the needs of the entire transportation sector. Nevertheless, several barriers and technical challenges are on the way to a large commercialization of biofuels from aquatic biomass. Critical issues are:

Fig. 1 - Example of an Algae Farm

i) to implant a sustainable culture that may produce for years;
ii) the high capital and operational costs of a pond;
iii) the collection costs.

Also, the extraction technology and the conversion of bio-oil needs to be optimized.

The start of a production of aquatic biomass for energy production may be a risky operation, considered the large fluctuation of the price of fossil oil today: with fossil-oil below 100 US$/barrel, hardly biodiesel may become competitive with diesel from fossil fuels. But, with oil above 100 US$ per barrel the biodiesel from aquatic biomass may be economic [3, 4]. On the other hand, aquatic biomass as well has a good potential of being used as a source of specialty chemicals and, finally, some components have value as animal feeding or fertilizers. The integration of the use of aquatic biomass for chemicals-use and for fuels-production may eventually make economic the production of biofuels. All together, it is possible to infer from existing open- and patent-literature data that aquatic biomass has a potential for application of the concept of

Tab. 1 - Technologies for the control of the accumulation of CO2 in the atmosphere

Technology	Example	Application	Effect
Efficiency	Production of electric energy	Innovative combustion technologies	Reduction of CO_2 emission
	Use of energy	Responsible use of energy	Reduction of CO_2 emission
Fuel shift	Substitution of coal and oil with gas	Less use of the most abundant fossil-C	Reduction of CO_2 emission
Innovative technologies for electric energy production	IGCC	The decarbonisation of fossil carbon helps to concentrate the emission of CO_2	Reduction of the sparse emission of CO_2
Non-carbon based fuels	Nuclear energy	Application in intensive energy demand such as industry and electrified transport	Reduction of the use of fossil-C
Perennial energies	Solar, wind, hydro, geothermal	Depending on the geo-position of countries	No fossil-C extracted
CCS	Capture and disposal of CO_2	Energy intensive	More fossil-C used
CO_2 utilisation	CO_2 is recycled mimicking Nature	Chemical, Technological, Enhanced-biological use: economic use of CO_2.	Less fossil-C extracted
Renewables	Biomass utilisation	Terrestrial and aquatic biomass	CO_2 is recycled

biorefinery for the production of chemicals and energy as well as for water treatment for re-use, but no examples are available that certify the real benefit of the *value chain* exploitation.

The use of internal desert environments (Fig. 1) or marginal coastal areas for biomass production may rise great economic benefits for less rich regions and communities. Natural or artificial basins can be considered for exploitation or resources recovery. Fisheries are interesting candidates for coupling water treatment and aquatic biomass growing.

Also, municipal and process waters can be used, with the additional benefit of water treatment and better resource utilization. Interestingly, aquatic biomass can be also grown offshore. Bioreactors and photobioreactors (Fig. 2) also represent a great opportunity for decoupling the algae cultivation from climate.

On the basis of these considerations, it is possible to say that it is not a problem to find a placement for a plant for growing aquatic biomass: aquatic biomass can be grown everywhere but at different costs.

Aquatic biomass has several benefits over terrestrial, as summarized in Tab. 2 and 3.

It is evident, on the basis of the data reported in Tab. 2 and 3, that aquatic biomass has a much higher potential than terrestrial biomass for the production of biofuels. In fact, not only biodiesel can be produced, but also biogas, bioethanol, biohydrogen, depending on the type of aquatic biomass used and its composition.

Microalgae, macroalgae and plants have a different composition and can be used for different purposes.

Tubular photobioreactor (source: www.genitronsviluppo.com <http://www.genitronsviluppo.com>)

So far, aquatic biomass has been considered within the EU mainly for animal (mammalian or fish) feeding or the extraction of specialty chemicals such as astaxanthine. Projects were mainly funded to investigate the cultivation technologies (bioreactors) of micro-algae used for fish feed.[5] Almost no attention has been paid to the potential of use of micro-algae as energy source, in spite of the fact that micro-algae can be very rich in lipids (up to 70% dry weight, with a good average standard of 30-40%) and particularly suited for biodiesel production. Tab. 4 shows some data about the capacity of lipid production of a number of strains.

The content of lipids may vary over a large range, making the strains more or less suitable for energy production. It is interesting to note that microalgae,

Tab. 2 - Comparison of the properties of terrestrial and aquatic biomass

Terrestrial Biomass	Aquatic Biomass
• Light efficiency 1.5-2.2%	• Light efficiency 6-8% (or higher when irradiated bioreactors are used)
• Requires land and water	• May not require land for cultivation (coastal, offshore)
• Productivity depends on soil quality (for a given plant)	• Low lignocellulose content
• Soil additives may be required (environmental and economic costs)	• Richer in water
• Biomass is generally rich in ligno-cellulosic components	• Lipid/protein/polysaccharide content can be adjusted
• Seed plants are most used	• Easy to grow in bioreactors (light-temperature adjustment): decoupling from climatic conditions
• Open area more than greenhouse cultivation	

Tab. 3 - Comparison of different sources for the production of the biodiesel needed in the transport sector in the USA

Crop	Oil yield (L/ha)[a]	Land area needed	Percent of existing US cropping area[a]
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil Palm	5950	45	24
Microalgae[b]	136900	2	1.1
Microalgae[c]	58700	4.5	2.5

[a]For meeting 50% of all transport fuel needs of the United States;
[b]70% oil (by wt) in biomass,
[c]30% oil (by wt) in biomass

Tab. 4 - Lipid content of various strains of microalgae

Microalgae	Oil content (% dry wt)
Botryococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp	20-35
Nannochloropsis sp.	31-68
Nannochloris oleabundans	35-54
Nitzschia sp.	45-47
Phaeodactylum tricornutum	20-30
Schzochytrium sp	50-70
Tetraselmis sueica	15-23

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Tab. 5 - Distribution of fatty acids in lipids present in some macro-algae

Fatty acid	**Species and relative percentage of organic compounds**			
Number of carbon atoms/Number of unsaturated bonds	*Ulva lactuca*	*Enteromorpha compressa*	*Padiva pavonica*	*Laurencia obtuse*
Saturated $C_{12} \rightarrow C_{20}$	15.0%	19.6%	23.4%	30.15
Mono-unsaturated $C_{14} \rightarrow C_{20}$	18.7%	12.3%	25.8%	9%
Poly-unsaturated $C_{16/2} \rightarrow C_{16/4}$ $C_{18/2} \rightarrow C_{18/4}$, $C_{20/2}$	66.3%	68.1%	50.8%	60.9%

Tab. 6 - Influence of the CO_2 concentration on the distribution of FAs in the same organism cultured at ambient conditions and under a high concentration of CO_2

Content g/100 g yield extract											
FAMEs	14:0	16:0	16:1	18:0	18:1	18:2	20:0	20:4	20:5	Total FAMEs	Phytols
Control	5.2±1.7	9.4±1.6	0.9±0.2	0.5±0.2	5.9±1.8	5.9±1.2	0.2±0.1	0.5±0.2	0.6±0.2	29.1±4.3	26.2±4.6
10% CO_2	5.0±1.1	***16.2±2.0***	0.8±0.1	0.5±0.3	***11.0±1.6***	***19.2±2.5***	0.3±0.2	***1.1±0.2***	***1.6±0.4***	55.5±3.7	43.2±4.4

being monocellular organisms, can be easily manipulated and their lipid content, as well as the protein content, can be adjusted either by genetic manipulation or by physical stress manipulation, by regulating the N or C content of the cultures.

A point to be considered is that rarely the algal bio-oil is constituted by a single type fatty-acid, most frequently the lipid fraction of algae (both micro- and macro-algae) contains a large variety of FA, as shown in Tab. 5. Nevertheless, such distribution can be driven, as shown in Tab. 6, for example by controlling the CO_2 concentration.

Macro-algae (seaweeds) have so far attracted attention only with respect to bioremediation and waste water treatment, and partly as source of chemicals [6], and their potential for energy production has only marginally been explored [7-11]. As Tab. 7 shows, macro-algae have in average a lower content of lipids and the best performance reaches 21% of lipids. Anyway, the lower growing and harvesting costs, make them much interesting with respect to micro-algae as a energy or chemicals source.

Both micro- and macro-algae are rich in chemicals that can be extracted by using a series of different technologies, as shown in Tab. 8. Compounds that can be extracted from micro- and macro-algae are:

- coloring substances and antioxidants;
- enzymes (superoxidedismutase, restriction enzymes, phosphoglycerate kinase, luciferase and luciferin);
- polymers (polysaccharides, starch, poly-beta-hydroxybutiric acid);
- peptides, toxins, aminoacids, steroids, essential oils such as geraniol-geranyl formate or acetate- cytronellol-nonanol-eucalyptol;
- pigments, such as chlorophylls, carotenoids, xantophylls;
- amines, inorganic compounds.

The high product distribution entropy makes sometimes not economically convenient the extraction of a product. Noteworthy, the ability of algal organisms to concentrate a type of substance upon stress may help to reduce the entropy and to increase the concentration of a product in the biomass. As a mater of fact, it is possible to grow selected farms of algae for the production of, for example, astaxanthine. Several of the substances listed above have a high added value that makes economically possible their production using this approach.

The implementation of the cascade of technologies helps to extract substances with a complex structure using the most appropriate technology besides the use of the biomass for the production of simple molecules.

Tab. 9 shows the differences between macro- and micro-algae. The former may afford a much larger productivity and require very simple growing technologies. Their harvesting is also very simple and low-cost. All together, such positive aspects may compensate the lower lipid productivity typical of macro- with respect to micro-algae.

Tab. 8 - Use of a cascade of technologies for a full use of biomass

Very soft ***Non-destructive technologies***	**Soft** ***Semi-destructive technologies***	**Hard** ***Destructive technologies***
Extraction of molecules with a complex molecular structure: molecular and polymeric compounds	Breaking of complex structures Production of energy products or simple chemicals	Breaking of natural complex structures and production of very simple chemicals ($CO-H_2$) that can be used for making again new complex molecular compounds (chemicals and fuels)

Tab. 7 - Lipid content of some macro-algae

Species	**Lipid content**
Palmaria Palmata	0.3
Fucus serratus	2.1
Codium harveyi	8.8-12.1
Codium duthiae	12.2-20.7
Codium fragile	21.1
Cladophora	12-20

Tab. 9 - Performance of Micro- and Macro-Algae

Parameters	**Microalgae**	**Macroalgae**
Growing season	250-280 d	210-240 d
Productivity, dw	33-50 t ha^{-1}	10-70 t ha^{-1}
Lipid content	20-75 % dw	0.3-32 % dw
Production cost	100/5,000 US$ t^{-1} dw	100 $ t^{-1} dw
Heat value GJ t-1	21 GJ t^{-1} dw	12.2-20 GJ t^{-1} dw
Energy cost	0.56 $ MJ^{-1}	0.05-0.6 $ MJ^{-1}

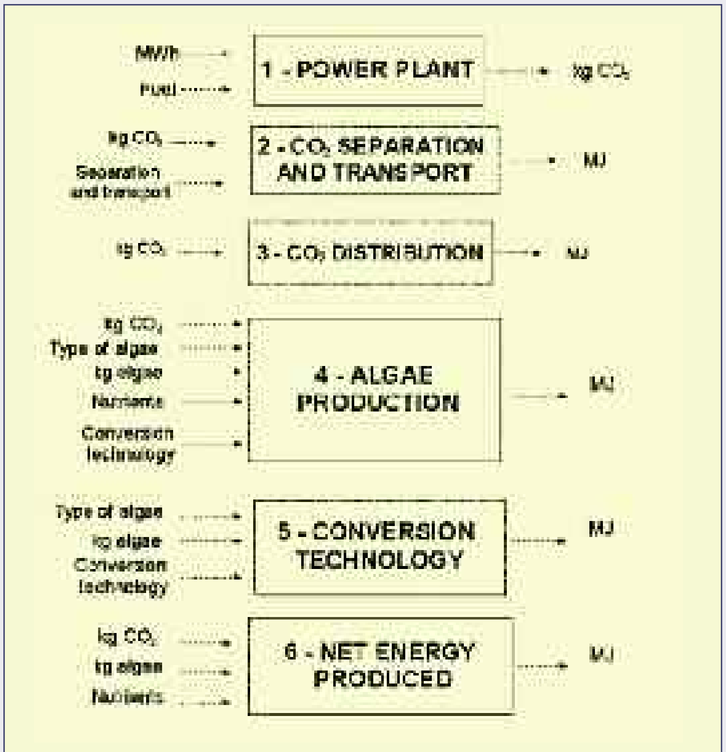

Fig. 3 - Life cycle assessment

In summary, aquatic biomass represents a much larger variety of raw materials with respect to fossil fuels and their full potential needs to be correctly exploited by defining the most appropriate transformation routes and the most adequate technologies.

In order to make the most advantageous use of aquatic biomass it is necessary to make an integration of the existing expertise in the area of aquatic biomass cultivation, with nanotechnologies, process intensification and new nanosized materials production in a single process. The biorefinery approach is the most sound for the real exploitation of the aquatic biomass: this attitude is now entering into operation around the world.

The way to evaluate the real energetic or economic potential of aquatic biomass is the application of LCA [12-14] following the scheme represented in Fig. 3.

This allows to calculate the energy and substances flows in the entire process and to establish the real potential of biomass for chemicals and energy production.

All together aquatic biomass is an interesting source for chemicals and energy that requires an accurate investigation for discovering its real potential.

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RIASSUNTO

Energia da biomassa acquatica

La biomassa acquatica (da acque dolci o saline) può assumere un ruolo importante nella produzione di combustibili per trasporto (biogas, etanolo, biodiesel) evitando ogni conflitto di uso come fuel o alimento. Essa può essere cresciuta in zone desertiche, poco adatte alla agricoltura, e in acque reflue (da scarichi municipali o da selezionate attività produttive quali l'acquacoltura). La produttività di biofuel per ettaro è oltre dieci volte quella della biomassa terrestre a causa della maggiore efficienza di utilizzo dell'energia luminosa solare e della maggiore capacità di accumulo di lipidi rispetto alle piante terrestri.