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Thermochemical conversion of microalgae: challenges and opportunities

David Chiaramonti[a]*, Matteo Prussi[a], Marco Buffi[a], David Casini[a], Andrea Maria Rizzo[a]

[a]*Renewable Energy COnsortium for R&D, RE-CORD c/o Department of Industrial Engineering, School of Engineering University of Florence, Viale Morgagni 40, I-50134 Florence, Italy*

Abstract

Research in Advanced Biofuels steadily developed during recent years. A number of highly innovative technologies have been explored at various scale: among these, lignocellulosic ethanol and CTO (Crude Tall Oil)-biofuel technologies already achieved the early-commercial status, while hydrotreating of vegetable oils (HVO, or HEFA) can be considered today fully commercial. However, despite the level of innovation in each specific technological process under consideration, the feedstock maintains a central role in making a biofuel chain really sustainable. In this context, microalgae grown in salt-water and arid areas offers a considerable opportunity for advanced biofuel production: at the same time, however, they also represent a considerable challenge. Processing microalgae in an economic way into a viable and sustainable liquid biofuel (a low-cost mass-produced product) is not trivial. So far, the main attention has been given to cultivating the microorganism, accumulating lipids, extracting the oil, valorising co-products, and treating the algae oil into biodiesel (through esterification) or HEFA (Hydrotreated Esthers and Fatty Acids), this second one representing a very high quality biofuels, almost a drop-in fuel (suitable either for road transport or for aviation), which production exceed 2 Mt y-1 today.

However, extracting the algae oil at low cost and at industrial scale is not yet a full industrial mature process, and the still limited market size of algae-to-biofuels makes difficult the development of industrial-scale systems. Nevertheless, another option can be considered, i.e. processing the whole algae into dedicated thermochemical reactors, thus approaching the downstream processing of algae in a completely different way from separation.

The present work examines the possible routes for thermochemical conversion of microalgae, distinguishing between dry-processes (namely pyrolysis and gasification) and wet-processes (near critical water hydrothermal liquefaction and hydrothermal gasification). Typical expected elementary composition of major products is given. Main peculiarities of batch versus continuous processing are also discussed from an engineering point of view.

Major engineering advantages and challenges in thermochemically conversion of algae are identified and discussed, in view of the production of a transport biofuel. Finally, future perspectives for each route are given in terms of current and expected technological readiness level.

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* Corresponding author. *E-mail address:* david.chiramonti@re-cord.org

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1. Introduction

A large number of scientific works demonstrate that microalgal biofuels are technically feasible [1] but positive economical and energetic balances have still to be demonstrated [2],[3],[4]. Microalgae represent a niche technology, with currently still only limited commercial applications: nutraceuticals and feed supplements, aquaculture, pigments, polyunsaturated fatty acids, diagnostic and fine chemicals; among these the biofuels sector has still to express its real potential. A global turnover above 5,000 million US$ can be estimated for other high value products, such as: functional food, feed additive, aquaculture, DHA and β-Carotene markets [5]. The main factor limiting the development of the markets, and especially those of algae biofuels and food, is the production costs. The actual cost is related to the complexity of the cultivation phase and the downstream processes required to extract the high-value products. Despite the today costs and the real efficiency of conversion of light, although not higher than that of plants [6], microalgae grown in salt-water and arid areas offers a considerable opportunity for advanced biofuel production: at the same time, however, they also represent a considerable challenge. The development of a commercially viable microalgae production is still representing a major challenge, both from a strictly technical point of view as well as from an economic one. Despite their high production potential, many research activities shown that the energy consumption within production of biofuels from algae, which includes harvesting and extraction, is a limiting factor for the economics balance. Sander (2010) [7] estimated that a two stages harvesting process can contribute to the 88÷92% of the entire energy input of the LCA and 20%÷30% of the total production cost [8]. Algae downstream process is strongly connected with the harvesting phase. Harvesting aims at separating these small cells (1-50 μm), at low density (0.5-3 gr l^{-1}) from the medium. There is not yet a unique commercial solution for algae harvesting, as each algae strain, downstream process and product destination can set different technical specifications for this phase. Shape of algal cells, cell wall structure and oil composition vary from one algal strain to another, even two different cultures of the same strain are not similar in nature. Several harvesting strategies like centrifugation, sedimentation, flocculation, flotation, electrophoresis and micro-filtration, and any combination of these can have been proposed to harvest microalgae. The harvesting solution has thus to be coupled with the downstream process.

The downstream processes can be divided in two main pathways:

- the extraction of the lipid and/or carbohydrates and high value compounds;
- process the whole algae stream obtaining a bioliquid or an intermediate towards biofuels.

Carbohydrates are interesting for ethanol production, but currently the lipid production for biodiesel has shown higher performance: according to Rodolfi et al. [9] and Studt et al. [10], the potential oil yield of microalgae cultures is 5 to 20 times higher that of palm oil (ton ha^{-1} yr^{-1}).

Specific cultivation techniques, such as starvation, can improve the oil quantity and quality toward downstream transesterification to biodiesel. Removing nutrients such as nitrogen from the growth medium, slows down the cell division and induces a "stress" behavior in which cell size increases and neutral lipid as observed in Chlorella vulgaris [11] and Nannochloropsis. Bondioli [12] showed that Nannochloropsis sp. F&M-M24 has a large potential as a renewable biofuel feedstock for: algae accumulated neutral lipids up to 50% of the dry biomass, with triglycerides representing the most abundant component (C16-C18), producing an oil that, with the exception of a high PUFA content, fulfills biodiesel feedstock chemical requirements (results of the Italian MAMBO project). The lipids contained in microalgae are intracellular, this makes the oil extraction usually more complex than the extraction from terrestrial crops, such as sunflower or olive: for instance, the mechanical pressing is usually not applicable to microalgae [13]. After harvesting, the biomass paste can still contains more that 80% (on wet basis) of moisture and this is a key factor for the definition of the downstream extraction methods. Several oily fruits have similar characteristic and so wet extraction can be taken into account, in order to save the biomass drying stage [14], [15].

Dry extraction routes are today technologically more mature and they allow for saving residues, usually of high interest for the general economical balance of the plant. Chemical solvent extraction is the most common method used to extract lipids from oily seeds. For algae feedstock, the real efficiency of the solvent extraction is strongly related to algae strain [16].

Wet extraction has the big advantage of avoiding the drying. In wet pathways, cell disruption can be based on mechanical approaches (microwave, ultrasonication, high pressure stresses, etc.), biological approaches (use of enzyme for cell disruption, etc.) or thermochemical (Hydro Thermal Liquefaction).
Biological methods are based on cell degradation by means of enzymes. Although there are other biological methods such as autolysis, most investigations of biological cell disruption utilize enzymes. The advantages of enzymatic route are the mild reaction conditions and the high selectivity. The cell envelope of microalgae, such as Chlorella, has very resistant layers, but these can be degraded by a mixture of enzymes [17]. Compared with mechanical methods, the enzymatic methods exhibited very competitive results [18]. The critical downfall of this method is the high cost of the enzymes.
Once the oil is extracted from the cells, the most common ways to produce biofuel is the transesterification process. The transesterification process allows obtaining biodiesel that is a mixture of fatty acid methyl esters (FAME).

The wide use of traditional biodiesel has highlight many limits of this product such as the not complete compatibility with existing engine, low oxidation stability, poor characteristic at low temperatures, etc. To overcame this limit the hydroconversion of vegetable oil is today used. The hydroprocessing of triglycerides are realized by the hydrogenation of the double bonds of the oil chains and the removal of oxygen by the use of a proper catalyst. This process leads to the production of a mixture of C15-C18 hydrocarbons, usually commonly called HEFA, "green diesel", "renewable diesel" or "bio-hydrogenated diesel", with more similar characterizes of petro-diesel than biodiesel [19] and today representing a very high quality biofuels, almost a drop-in fuel (suitable either for road transport or for aviation), which production exceed 2 Mt y^{-1} today. The hydrogenation process allows also obtaining lighter fraction within the boiling point range of jet fuel or gasoline, increasing the market potential of the algae oils [20], [21]. The main critical issue of this technological pathway is the implementation at very large scale and competitive costs, especially considering the low specific value of the biofuels. The biorefinery concept has also to tackle the issue of the differences in the market size: fuels/food/feed/chemicals/energy.

An alternative approach can be to process the whole algae stream. Thermochemical processes are available both on dry as well as on wet phase. Nevertheless the pyrolysis and HTL are largely investigated of lignocellulosic materials with different technological issues than algae biomass processing.

2. Algae pyrolysis

The pyrolysis process occurs in the range of 400-600 °C in absence of oxygen. A complex Bio Crude Oil can be obtained in various percentage: between 30-70%, depending on the process conditions [22]. Dry matter is needed to feed to the reactor and this stage can require a large amount of energy. Fast pyrolysis allows obtaining high oil yield using a heating rate (°C min^{-1}) and short vapors residence time. The oil obtained can be considered as intermediate for a biorefinery plant, as further treatments are required to obtain a biofuel.

In figure 1 is shown a potential schema for coupling microalgae production and pyrolysis process. The gas phase produced during the pyrolysis can be used to dry the algae paste and CO_2 can be recovered for algae production. Biomass can be fractionated to obtain high added value products before pyrolysis.

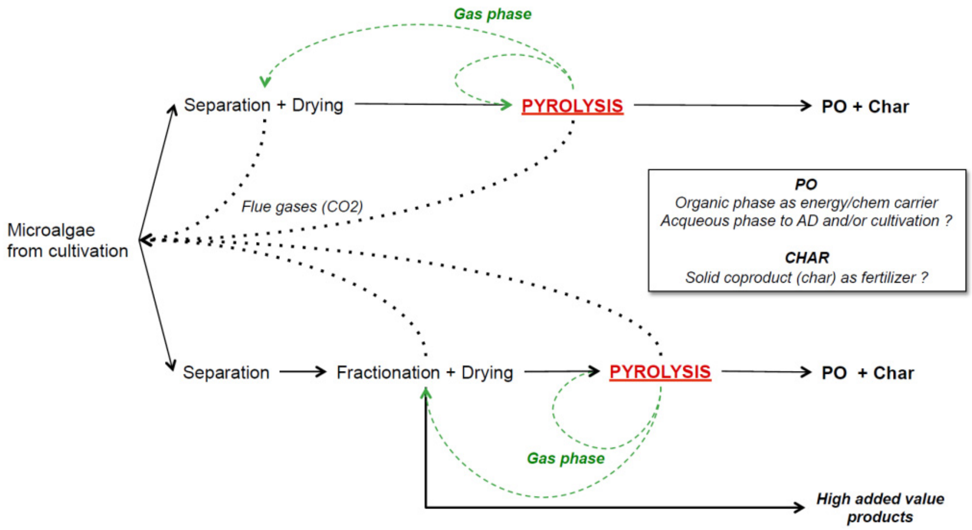

Figure 1: schematic of the microalgae pyrolysis process.

Experiences carried out in algae pyrolysis showed the feasibility of biooil production from this feedstock [23]. Slow pyrolysis process has been tested in several recent works; Grierson et al. [24] tested six microalgae species with slow pyrolysis. The oil yields ranges between 24 and 43%wt and a char yields ranging from 34 to 63%wt. Pan et al. [25] studied the influence of temperature and catalyst on of Nannochloropsis sp in slow pyrolysis conditions. In their work the oil yield ranges from 19%wt with catalyst up to 31%wt in presence of HZSM-5. Advantages of the use of catalytic was found also in terms of higher heating value (32.7 MJ kg−1).

Fast pyrolysis has been investigated in order to maximize the algae bio crude oil yield. Miao et al. [26], [27] studied the fast pyrolysis of several microalgae species: C. pro-tothecoides and M. aeruginosa, obtaining an oil yield ranging from 17.5 to 23.7% wt and reaching the 57.9%wt for heterotrophic Chlorella protothecoides. Elliot et al. (2013) [28] processed Chlorella protothecoides and Microcystis aeruginosa at 500-600°C min^{-1} with a residence time of 2-3 s with an oil yield 18-24%wt. Similar results were obtained for Spirulina platensis. In the work the effect of the temperature was also investigated, demonstrating that for this kind of feedstock a reduction of temperature leads to an increase in oil yield: the maximum oil production was $57\%_{wt}$ with a process temperature of 450°C.

3. Algae HTL (Hydrothermal liquefaction)

Hydrothermal liquefaction (HTL) can directly convert wet biomass into a liquid biocrude oil either with or without the use of a catalyst [29]. The reaction can take place on wet biomass in water at critical conditions: process temperatures and pressures of 280-370 °C, 10-25 Mpa (< 2 MPa: HTC) [28]. The conversion efficiency of microalgae HTL depends on various parameters including reaction temperature, retention time and the composition of feedstock. Biocrude oil production from microalgae through HTL has therefore received increasing attention in recent years [30]. Distinguished from the routine algae-to-biodiesel approach, which largely depends on lipid contents, HTL can convert not only lipids but also other organic components such as proteins and carbohydrates [31]. The chemical properties of biocrude oil are highly dependent on the feedstock composition including proteins, carbohydrates, and lipids [32]. Biocrude oil contains the 10–20%wt of Oxygen and Nitrogen with an energy density in the range of 30–37 MJ kg^{-1}[33].

Hydrothermal liquefaction of microalgae appears to be a very promising technology for biofuel production, but still in a very early stage of development [34] and mainly batch reactors are used for testing.

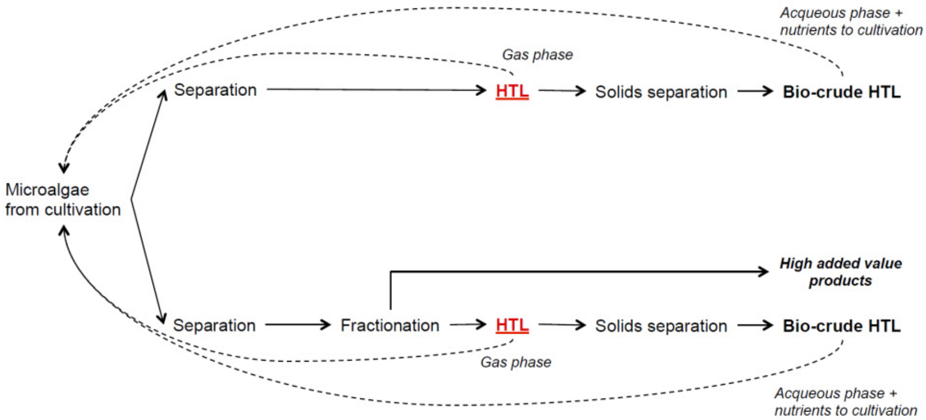

Figure 2: schematic of the microalgae HTL process.

The typical HTL biocrude yields resulted from many studies to be close to 50-60%wt [31] depending also on the use of homogeneous and heterogeneous catalysts. Minowa et al. [35] published some first reports on microalgae HTL (Botryococcus braunii and Dunaliella tertiolecta) in a batch reactor fed by high concentration algae mass: 50% wt.- 78.4% wt. At 300 °C the oil yield was between 37 % wt. and 64%wt depending on the algae processed. More recent works presented results for microalgae, such as: Chlorella vulgaris and C. pyrenoidosa, Nannochloropsis occulata, Scenedesmus dimorphus, Porphyridium cruentum, Desmodesmus sp. as well as Chlorogloeopsis fritschii and Spirulina cyanobacteria. These works demonstrate that a wide range of microalgae can be processed in HTL reactors, obtaining a mixture of oxygenated hydrocarbons with a high mass yield [36], [32], [29], [37]. Zhou et al. [38] investigated HTL of microalgae, combined with wastewater treatment, demonstrating that low-lipid high-protein *Nannochloropsis* sp. (B) and high-lipid low-protein *Chlorella* sp. (Y) were efficiently converted to biocrude oil. The highest biocrude yields were 55.0% (B) and 82.9% (Y). The hydrocarbon content in biocrude was 6.7–29.8% (B) and 4.7–17.9% (Y). Elliott et al. [28] reached in their study high conversions yields even with high slurry concentrations: up to 35% wt. of dry solids. Elliott et al effectively applied catalytic hydrotreating for hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization of the biocrude. An important result of this study was that catalytic hydrothermal gasification was effectively applied for HTL byproduct water clean-up, in order to allow nutrients recycle in algae growth ponds.

From the studies available in literature is clear that the continuous reactors are more interesting for an industrial point of view but their use tends to reduce the allowed feeding concentration and introduce many technological challenges. Jazrawy et al, 2013 [39] worked with Chlorella and Spirulina with a loading factor between 1–10 %wt biomass, at 250–350°C, for 3–5 min residence time and 150–200 bar. The maximum biocrude yield was 41.7 %wt. The key elements for the development of microalgae HTL reactors are today mainly related to the feeding stage, especially in terms of aggregation state and load concentration, temperature, residence time, use of catalysts and product separation and water recirculation (figure 2).

4. Processes comparison

Comparing the two processes for treating the microalgae highlight some critical issues for the pyrolysis. The drying stage, required to enter in a pyrolysis reactor, is always a critical point that is particularly relevant for microalgae feedstock due to the low concentration of the algae in the cultivation medium: typically ranging from 10-20% even after harvesting.

Pyrolysis oil shows some advantages such as the lower viscosity, comparable with the vegetable oil one, but in terms of yield, Nitrogen and Oxygen content and thus heating value, the HTL appears a more interesting technology.

The specificity of the feedstock introduces critical issues for the reactor itself. The technologies designed so far are based on the experience carried out in lignocellulosic materials, while algae have higher inorganic and ashes content, peculiar state of aggregation depending on the harvesting and pretreatment occurred, etc. The use of salty water for algae cultivation increases the problem related to corrosion and solid deposition, especially for HTL due to the more critical pressure and temperature operation conditions.

Trying to define the technology readiness level of the processes, the pyrolysis appears to be the more mature one, close to demonstration scale as the prototype scale plant are already operating. HTL of microalgae is moving from the applied research stage to a small scale prototyping. The upgrading of the oil is at an applied scale for both pyro and HTL oils and thus it results the most critical aspect of the thermochemical downstream of the microalgae.

6. Conclusions

A large number of scientific works demonstrate that microalgae based biofuels is technically feasible but economical and energetic positive balances have still to be demonstrated. In terms of technological pathways, the results available indicate that pyrolysis oil quality and energy yield shows minor advantages with respect to HTL and thus at the present stage HTL appears a more interesting technology. Nevertheless pyrolysis appears to be today more mature, close to demonstration scale, while HTL of microalgae is moving from the applied research stage to a small scale prototyping. The specificity of the feedstock introduces critical issues for the reactor and actual technologies are designed on the based on the experience carried out in lignocellulosic materials. Critical aspects for considering pyrolysis and HTL a suitable technological downstream pathways for microalgae sector are related to the oil upgrading that, at the present stage, still requires to move forward from the applied research scale.

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