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1 Thermochemical conversion of microalgae: challenges and
2 opportunitiesDavid Chiramonti^{a*}, Matteo Prussi^a, Marco Buffi^a, David Casini^a, Andrea Maria Rizzo^a3 ^aRenewable Energy Consortium for R&D, RE-CORD c/o Department of Industrial Engineering, School of Engineering University
4 of Florence, Viale Morgagni 40, I-50134 Florence, Italy5 **Abstract**

6 Research in Advanced Biofuels steadily developed during recent years. A number of highly innovative technologies
7 have been explored at various scale: among these, lignocellulosic ethanol and CTO (Crude Tall Oil)-biofuel
8 technologies already achieved the early-commercial status, while hydrotreating of vegetable oils (HVO, or HEFA)
9 can be considered today fully commercial. However, despite the level of innovation in each specific technological
10 process under consideration, the feedstock maintains a central role in making a biofuel chain really sustainable. In
11 this context, microalgae grown in salt-water and arid areas offers a considerable opportunity for advanced biofuel
12 production: at the same time, however, they also represent a considerable challenge. Processing microalgae in an
13 economic way into a viable and sustainable liquid biofuel (a low-cost mass-produced product) is not trivial. So far,
14 the main attention has been given to cultivating the microorganism, accumulating lipids, extracting the oil, valorising
15 co-products, and treating the algae oil into biodiesel (through esterification) or HEFA (Hydrotreated Esters and
16 Fatty Acids), this second one representing a very high quality biofuels, almost a drop-in fuel (suitable either for road
17 transport or for aviation), which production exceed 2 Mt y⁻¹ today.
18 However, extracting the algae oil at low cost and at industrial scale is not yet a full industrial mature process, and the
19 still limited market size of algae-to-biofuels makes difficult the development of industrial-scale systems.
20 Nevertheless, another option can be considered, i.e. processing the whole algae into dedicated thermochemical
21 reactors, thus approaching the downstream processing of algae in a completely different way from separation.
22 The present work examines the possible routes for thermochemical conversion of microalgae, distinguishing between
23 dry-processes (namely pyrolysis and gasification) and wet-processes (near critical water hydrothermal liquefaction
24 and hydrothermal gasification). Typical expected elementary composition of major products is given. Main
25 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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28 1. Introduction

29 A large number of scientific works demonstrate that microalgal biofuels are technically feasible [1]
30 but positive economical and energetic balances have still to be demonstrated [2],[3],[4]. Microalgae
31 represent a niche technology, with currently still only limited commercial applications: nutraceuticals and
32 feed supplements, aquaculture, pigments, polyunsaturated fatty acids, diagnostic and fine chemicals;
33 among these the biofuels sector has still to express its real potential. A global turnover above 5,000
34 million US\$ can be estimated for other high value products, such as: functional food, feed additive,
35 aquaculture, DHA and β -Carotene markets [5]. The main factor limiting the development of the markets,
36 and especially those of algae biofuels and food, is the production costs. The actual cost is related to the
37 complexity of the cultivation phase and the downstream processes required to extract the high-value
38 products. Despite the today costs and the real efficiency of conversion of light, although not higher than
39 that of plants [6], microalgae grown in salt-water and arid areas offers a considerable opportunity for
40 advanced biofuel production: at the same time, however, they also represent a considerable challenge.
41 The development of a commercially viable microalgae production is still representing a major challenge,
42 both from a strictly technical point of view as well as from an economic one. Despite their high
43 production potential, many research activities shown that the energy consumption within production of
44 biofuels from algae, which includes harvesting and extraction, is a limiting factor for the economics
45 balance. Sander (2010) [7] estimated that a two stages harvesting process can contribute to the 88÷92% of
46 the entire energy input of the LCA and 20%÷30% of the total production cost [8]. Algae downstream
47 process is strongly connected with the harvesting phase. Harvesting aims at separating these small cells
48 (1-50 μm), at low density (0.5-3 gr l^{-1}) from the medium. There is not yet a unique commercial solution
49 for algae harvesting, as each algae strain, downstream process and product destination can set different
50 technical specifications for this phase. Shape of algal cells, cell wall structure and oil composition vary
51 from one algal strain to another, even two different cultures of the same strain are not similar in nature.
52 Several harvesting strategies like centrifugation, sedimentation, flocculation, flotation, electrophoresis
53 and micro-filtration, and any combination of these can have been proposed to harvest microalgae. The
54 harvesting solution has thus to be coupled with the downstream process.

55 The downstream processes can be divided in two main pathways:

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

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

61 Specific cultivation techniques, such as starvation, can improve the oil quantity and quality toward
62 downstream transesterification to biodiesel. Removing nutrients such as nitrogen from the growth
63 medium, slows down the cell division and induces a “stress” behavior in which cell size increases and
64 neutral lipid as observed in *Chlorella vulgaris* [11] and *Nannochloropsis*. Bondioli [12] showed that
65 *Nannochloropsis* sp. F&M-M24 has a large potential as a renewable biofuel feedstock for: algae
66 accumulated neutral lipids up to 50% of the dry biomass, with triglycerides representing the most
67 abundant component (C16-C18), producing an oil that, with the exception of a high PUFA content,

68 fulfills biodiesel feedstock chemical requirements (results of the Italian MAMBO project). The lipids
69 contained in microalgae are intracellular, this makes the oil extraction usually more complex than the
70 extraction from terrestrial crops, such as sunflower or olive: for instance, the mechanical pressing is
71 usually not applicable to microalgae [13]. After harvesting, the biomass paste can still contains more that
72 80% (on wet basis) of moisture and this is a key factor for the definition of the downstream extraction
73 methods. Several oily fruits have similar characteristic and so wet extraction can be taken into account, in
74 order to save the biomass drying stage [14], [15].

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

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

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

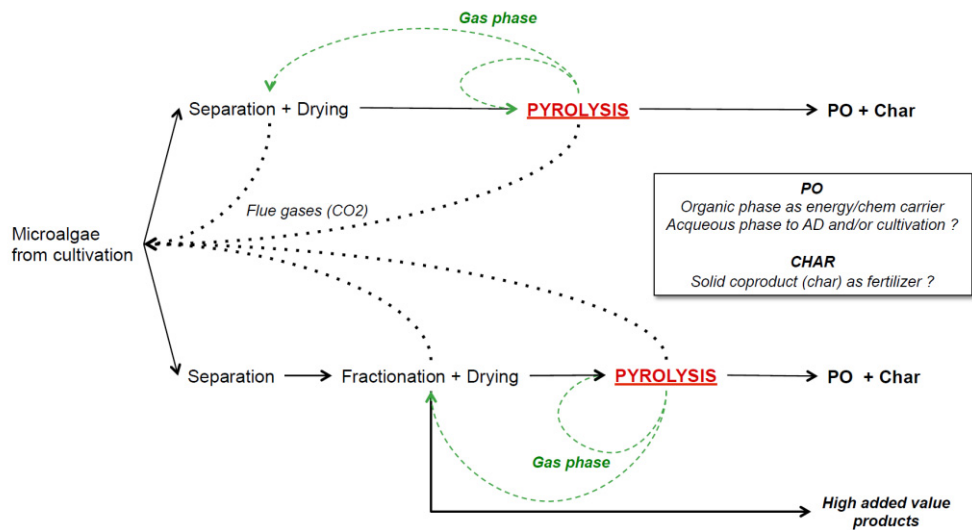
105 An alternative approach can be to process the whole algae stream. Thermochemical processes are
106 available both on dry as well as on wet phase. Nevertheless the pyrolysis and HTL are largely
107 investigated of lignocellulosic materials with different technological issues than algae biomass
108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

109 2. Algae pyrolysis

110 The pyrolysis process occurs in the range of 400-600 °C in absence of oxygen. A complex Bio Crude
111 Oil can be obtained in various percentage: between 30-70%, depending on the process conditions [22].
112 Dry matter is needed to feed to the reactor and this stage can require a large amount of energy. Fast

113 pyrolysis allows obtaining high oil yield using a heating rate ($^{\circ}\text{C min}^{-1}$) and short vapors residence time.
 114 The oil obtained can be considered as intermediate for a biorefinery plant, as further treatments are
 115 required to obtain a biofuel.

116 In figure 1 is shown a potential schema for coupling microalgae production and pyrolysis process. The
 117 gas phase produced during the pyrolysis can be used to dry the algae paste and CO_2 can be recovered for
 118 algae production. Biomass can be fractionated to obtain high added value products before pyrolysis.
 119



120
 121

122

Figure 1: schematic of the microalgae pyrolysis process.

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

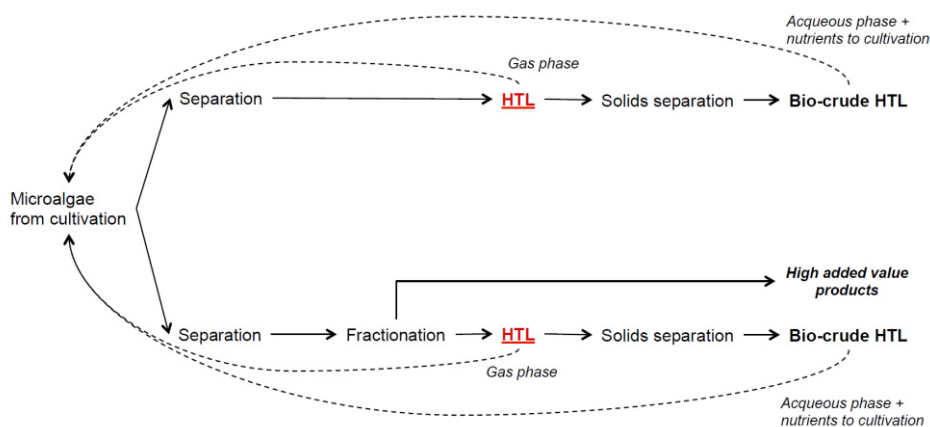
130 Fast pyrolysis has been investigated in order to maximize the algae bio crude oil yield. Miao et al.
 131 [26], [27] studied the fast pyrolysis of several microalgae species: *C. pro-tothecoides* and *M. aeruginosa*,
 132 obtaining an oil yield ranging from 17.5 to 23.7% wt and reaching the 57.9%wt for heterotrophic
 133 *Chlorella protothecoides*. Elliot et al. (2013) [28] processed *Chlorella protothecoides* and *Microcystis*
 134 *aeruginosa* at $500\text{-}600^{\circ}\text{C min}^{-1}$ with a residence time of 2-3 s with an oil yield 18-24%wt. Similar results
 135 were obtained for *Spirulina platensis*. In the work the effect of the temperature was also investigated,
 136 demonstrating that for this kind of feedstock a reduction of temperature leads to an increase in oil yield:
 137 the maximum oil production was 57%_{wt} with a process temperature of 450°C .

138 3. Algae HTL (Hydrothermal liquefaction)

139 Hydrothermal liquefaction (HTL) can directly convert wet biomass into a liquid biocrude oil either
 140 with or without the use of a catalyst [29]. The reaction can take place on wet biomass in water at critical

141 conditions: process temperatures and pressures of 280-370 °C, 10-25 Mpa (< 2 MPa: HTC) [28]. The
 142 conversion efficiency of microalgae HTL depends on various parameters including reaction temperature,
 143 retention time and the composition of feedstock. Biocrude oil production from microalgae through HTL
 144 has therefore received increasing attention in recent years [30]. Distinguished from the routine algae-to-
 145 biodiesel approach, which largely depends on lipid contents, HTL can convert not only lipids but also
 146 other organic components such as proteins and carbohydrates [31]. The chemical properties of biocrude
 147 oil are highly dependent on the feedstock composition including proteins, carbohydrates, and lipids [32].
 148 Biocrude oil contains the 10–20%wt of Oxygen and Nitrogen with an energy density in the range of 30–
 149 37 MJ kg⁻¹[33].

150 Hydrothermal liquefaction of microalgae appears to be a very promising technology for biofuel
 151 production, but still in a very early stage of development [34] and mainly batch reactors are used for
 152 testing.
 153



154

155

Figure 2: schematic of the microalgae HTL process.

156 The typical HTL biocrude yields resulted from many studies to be close to 50-60%wt [31] depending
 157 also on the use of homogeneous and heterogeneous catalysts. Minowa et al. [35] published some first
 158 reports on microalgae HTL (*Botryococcus braunii* and *Dunaliella tertiolecta*) in a batch reactor fed by
 159 high concentration algae mass: 50% wt.- 78.4% wt. At 300 °C the oil yield was between 37 % wt. and
 160 64%wt depending on the algae processed. More recent works presented results for microalgae, such as:
 161 *Chlorella vulgaris* and *C. pyrenoidosa*, *Nannochloropsis oculata*, *Scenedesmus dimorphus*,
 162 *Porphyridium cruentum*, *Desmodesmus sp.* as well as *Chlorogloeopsis fritschii* and *Spirulina*
 163 cyanobacteria. These works demonstrate that a wide range of microalgae can be processed in HTL
 164 reactors, obtaining a mixture of oxygenated hydrocarbons with a high mass yield [36], [32], [29], [37].
 165 Zhou et al. [38] investigated HTL of microalgae, combined with wastewater treatment, demonstrating that
 166 low-lipid high-protein *Nannochloropsis sp.* (B) and high-lipid low-protein *Chlorella sp.* (Y) were
 167 efficiently converted to biocrude oil. The highest biocrude yields were 55.0% (B) and 82.9% (Y). The
 168 hydrocarbon content in biocrude was 6.7–29.8% (B) and 4.7–17.9% (Y). Elliott et al. [28] reached in their
 169 study high conversions yields even with high slurry concentrations: up to 35% wt. of dry solids. Elliott et
 170 al effectively applied catalytic hydrotreating for hydrodeoxygenation, hydrodenitrogenation, and
 171 hydrodesulfurization of the biocrude. An important result of this study was that catalytic hydrothermal

172 gasification was effectively applied for HTL byproduct water clean-up, in order to allow nutrients recycle
173 in algae growth ponds.

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

182 **4. Processes comparison**

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

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

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

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

201 **6. Conclusions**

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

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