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A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels

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ABSTRACT

The increasing global demand of biofuels for energy security and reduction in climate change effects generate the opportunity to explore new biomass sources. Algae is a very promising source of biomass in this context as it sequester a significant quantity of carbon from atmosphere and industrial gases and is also very efficient in utilizing the nutrients from industrial effluents and municipal wastewater. Therefore cultivation of algal biomass provide dual benefit, it provides biomass for the production of biofuels and also save our environment from air and water pollution. The life cycle assessment (LCA) of algal biofuels suggests them to be environmentally better than the fossil fuels but economically it is not yet so attractive.

1. Introduction

Renewable energy plays a crucial role in dealing with energy security, eco-friendliness and climate change issues at global and national levels [1–5]. Subhadra and Edwards [6] pointed out the three basic premises in current policy debates on energy, climate, and GHG emissions (i) strong requirement for cleaner energy production and conservation technologies on a global scale; (ii) the need for future mandates on emission reduction to be aligned with the clean energy production and energy conservation policies; (iii) the need to act with urgency.

The mass production of first-generation liquid biofuels has resulted in a series of problems related to food prices, land usage, and carbon emissions [7] and second generation biofuels production suffers with cost effectiveness, technological barriers, and feed stock collection networks [8]. Algal biofuels are an appealing choice [9] due to its rapid growth rate, high lipid content, comparatively low land usage and high carbon dioxide (CO_2) absorption and uptake rate [10–15]. Extensive research has been conducted to investigate the utilization of microalgae as an energy feedstock, with applications being developed for the production of biodiesel, bioethanol, and biohydrogen [16–18].

Algae represent a vast variety of photosynthetic species dwelling in diverse environments [8,19], they might be autotrophic or heterotrophic in nature [20]. The autotrophic algae use photosynthesis to harness sunlight and fix the inorganic carbon from atmospheric CO_2. There are many algal species which are heterotrophic and able to take up small organic molecules in the environment and turn them into the building blocks of their own, mainly fat and proteins. There are some algal species which can use either inorganic carbon from atmosphere or organic carbon from the environment and this process is called mixotrophy [20]. Via any of these processes algae can over a short period of time produce carbohydrates, lipids and proteins that can be processed to produce biofuels.

Using only sunlight and abundant and freely available raw materials (e.g. CO_2 and nutrients from wastewater) algae can synthesize and accumulate large quantities of neutral lipids and carbohydrates along with other valuable co-products (e.g. astaxanthin, omega three fatty acids, etc.). Algae can thus play a major role in the treatment/utilization of wastewater and reduce the environmental impact and disposal problems [6]. They can be grown on saline/coastal sea water and on non agricultural lands (desert, arid and semi-arid land) [11,21] and will not create a food–fuel competition. Compared to other advanced feedstock based on cellulose for biofuels production, algal genomics and basic research are more advanced and gaining in momentum [6]. This review is an overview of the pros and cons of various algal biofuels production pathways, their sustainability and life cycle assessment. In the following chapters the state of the art for different types of end-product biofuels from algae will be reviewed.

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2. Biodiesel

Recent interest in using oleaginous microalgae as a nonedible biodiesel feedstock has grown considerably, largely on the promise of high oil yields (5000–100,000 L ha^{-1} a^{-1}), the opportunity to capture waste CO_2, and the ability to cultivate algae on abandoned or unproductive land using brackish, salt, or wastewaters instead of freshwater [22]. Some microalgae respond to certain chemical and physical stimuli through the accumulation of intracellular triglycerides (TGs) [11]. Unlike terrestrial oilseeds, microalgae are cultivated in dilute aqueous suspensions that make lipid recovery complicated. Microalgae grown outdoors in open ponds typically have cell density and productivity ranging from 0.5 to 2 g dry biomass L^{-1} and 10–40 g m^{-2} d^{-1}, respectively [23]. Though higher biomass densities (5–200 g L^{-1}) can be achieved in thin-plate photobioreactors [24] and fermentors [25], dewatering and drying remain energy- and cost-intensive processes [26]. A biodiesel production process that obviates biomass drying and organic solvent use for oil extraction could lead to significant energy and cost savings. Attempts to combine extraction with acid catalyzed transesterification in one step have been successful with dry algal biomass, but the reaction is severely inhibited by water [27,28].

Levine et al. [22] have developed a two-step, catalyst-free biodiesel production process involving intracellular lipid hydrolysis coupled with supercritical in situ transesterification (SC-IST/E). In the first step, wet algal biomass (80% moisture) reacts at subcritical water conditions to hydrolyze intracellular lipids, conglomerate cells into an easily filterable solid that retains the lipids, and produce a sterile, potentially nutrient-rich aqueous phase. In the second step, the wet fatty acid (FA) rich solids are subjected to SC-IST/E with ethanol to produce biodiesel in the form of fatty acid ethyl esters (FAEEs). This process eliminates both biomass drying and triglyceride (TG) extraction (e.g., with an organic solvent such as n-hexane). They also identified several factors that motivate this approach, e.g. oil hydrolysis, supercritical esterification, etc. Oil hydrolysis is a well-known commercial process and can be carried out under mild subcritical water conditions [29]. Supercritical esterification can be performed at lower temperatures, in less time, and can achieve higher conversions compared to supercritical transesterification [30]. Amassing cells into a filterable solid accomplishes additional dewatering prior to transesterification with minimal costs; retention of FAs and remaining lipids in a solid matrix obviates difficulties with lipid recovery from aqueous systems. Nutrients (N and P) and glycerol from processed biomass can be captured and reused in a sterile aqueous phase free of catalyst. Finally, a well-engineered process to produce biodiesel through supercritical alcohol transesterification may reduce costs and energy expenditure relative to those of conventional catalytic methods [31,32].

Levine et al. [22] further manifested the feasibility of a two-step hydrolysis–solvolysis process to produce biodiesel from lipid-rich, wet algal biomass. The reactions of biomass and its components in liquid water are a focus of solvolysis [33] and results in micellar-like substructures of the biomass [34]. The hydrolysis–solvolysis process obviates biomass drying, organic solvent extraction, and catalysts, while providing a mechanism for nutrient recycling. A cursory experimental investigation of the influence of some key process variables led to crude biodiesel and FAEE yields as high as 100% and 66%, respectively, on the basis of lipids within the hydrolysis solids. Considering that about 80–90% of lipids in the original algal biomass were retained in the solids recovered after hydrolysis, the total process yield was somewhat lower [22]. The optimal time and temperature for hydrolysis must appropriately balance the desire for increased lipid hydrolysis with the likelihood of reduced lipid retention and solids yields at more severe conditions. In addition, it is imperative to improve the ester yield from SC-IST/E, which may have been limited by incomplete transesterification, decomposition/polymerization of unsaturated FA, hydrolysis of FAEE, or incomplete lipid extraction from the solid. A considerable benefit of the process described is the ability of its first step (hydrolysis) to create two sterile products: a relatively low moisture (<50% water), FA-rich solid and a nutrient-rich aqueous phase. Both are potentially amenable to a variety of downstream processes. Considering that the N and P required for producing algal biomass are nonrenewable resources, the ability to recycle these nutrients, together with a useful carbon source like glycerol, presents unique opportunities to further reduce the impact of algal biodiesel production [22]. This approach might be attractive if algal biomass is grown in wastewater (Significant part of this section has been directly quoted from Levine et al. [22]. Please refer Levine et al. [22] for more in-depth information on biodiesel).

3. Biogas

Algal biomass is rich in nutrients especially nitrogen and phosphorus, for which the use and potential loss may not be environmentally and economically sustainable [35]. A process to recycle nitrogen and phosphorus contained in algal waste after lipid extraction is therefore required in order to recover the nutrients that can be further utilized as fertilizers. Anaerobic digestion (AD) can be an answer to this problem, since this biotechnological process can mineralise algal waste containing organic nitrogen and phosphorus, resulting in a flux of ammonium and phosphate that can be used as a substrate for the microalgae [36]. The AD of algal waste not only recycles the nutrients but also provide biomethane, a renewable energy. AD involves the breakdown of organic matter to produce biogas [37]. AD process is appropriate for high moisture content (80–90% moisture) organic wastes [38], and can be useful for wet algal biomass. The AD process occurs in three sequential stages of hydrolysis, fermentation and methanogenesis. In hydrolysis the complex compounds are broken down into soluble sugars. Then, fermentative bacteria convert these into alcohols, acetic acid, volatile fatty acids (VFAs), and a gas containing H_2 and CO_2, which is metabolised into primarily CH_4 (60–70%) and CO_2 (30–40%) by methanogens [39].

Besides carbon, nitrogen and phosphorus which are major components in microalgae composition, oligo nutrients such as iron, cobalt, zinc are also found [40] and are known to stimulate methanogenesis [41]. The composition of algal biomass is species dependent having proteins (6–52%), lipids (7–23%) and carbohydrates (5–23%) [42]. When the composition of the organic matter is known, it is possible to evaluate the theoretical methane and ammonium yields that can be expected from the anaerobic digestion [43]. The theoretical methane potential increase with higher lipid content of the cell due to the high energetic content of lipids compared to carbohydrates and proteins [44,45], while hydrolysis of lipid is considered to be slower than protein and carbohydrate. Thus, Pavlostathis and Giraldo-Gomez [46] calculated the minimum values of limiting generation time for anaerobic treatment of various substrates and they found values of 0.18, 0.43 and 3.2 days for carbohydrates, proteins and lipids, respectively. Sialve et al. [35] calculated the methane potential and ammonia released during the anaerobic digestion of total biomass on the basis of composition of different algal species earlier given by Becker [47] (Table 1).

The biomass composition, pH, temperature, hydraulic and solid retention time (HRT and SRT) and loading rate determine the quantity and quality of biogas production during anaerobic digestion. The increase in temperature from 15 to 52 °C improves the methane conversion of *Spirulina maxima*, and the productivity together

Table 1
Composition of different algal species [47] and their theoretical methane potential and ammonia release during anaerobic digestion of the total biomass (adopted from Sialve et al. [48]).

Algal species	Protein (%)	Lipid (%)	Carbohydrate (%)	CH_4 ($L\ g^{-1}$ VS)	N–NH_3 ($mg\ g^{-1}$ VS)
Euglena gracilis	39–61	14–20	14–18	0.53–0.8	54.3–84.9
Chlamydomonas Reinhardtii	48	21	17	0.69	44.7
Chlorella Pyrenoidosa	57	2	26	0.8	53.1
Chlorella vulgaris	51–58	14–22	12–17	0.63–0.79	47.5–54.0
Dunaliella salina	57	6	32	0.68	53.1
Spirulina maxima	60–71	6–7	13–16	0.63–0.74	55.9–66.1
Spirulina platensis	46–63	4–9	8–14	0.47–0.69	42.8–58.7
Scenedesmus obliquus	50–56	12–14	10–17	0.59–0.69	46.6–42.2

with the volatile solids reduction is enhanced up to 35 °C [49]. HRT and SRT should be high enough to allow the active microbial populations to remain in the reactor, especially methanogens, and not to limit hydrolysis which is generally the limiting-step of the overall conversion of complex substrates to methane [35]. The optimal loading rates and HRT must be chosen depending on the type and composition of the algal biomass for maximum production of biomethane. When the cells are directly injected into the anaerobic process, accessibility of the intracellular content to the anaerobic microorganisms is limited by the resistance of the algal cell wall to hydrolysis. Thus, characteristics of algal species makes the difference for a given loading rate or HRT [50]. The most important factor impacting CH_4 proportion in the biogas is the pH, which controls the speciation of the carbonate system and the release of CO_2. At high pH, due to high alkalinity from NH_3 release the gas content will shift more to CH_4, resulting higher content of CH_4 in the produced biogas.

Anaerobic digestion of the protein rich (60%) cyanobacteria *S. maxima* releases an extremely high concentration of ammonia (up to 7000 mg L^{-1}) [49]. Sánchez Hernández and Travieso Córdoba [51] observed a strong concentration of volatile fatty acids as a consequence of the toxic effect of ammonia on the anaerobic flora. The acetoclastic methanogen bacteria are probably among the most sensitive to NH_3 [52,53]. Inhibiting concentrations vary in a wide range from 1.7 to 14 g L^{-1} and depend on several factors such as the acclimation period, the nature of substrate and inoculum together with operating conditions [53]. Thermophilic conditions enhance the inhibition effect [35]. High concentrations of ions such as Na^+, Ca^{2+} and Mg^{2+}, which increase alkalinity and decrease the fraction of unionized NH_3, can lower the inhibition effects [54]. Sodium ions are required by the anaerobic microorganisms for its metabolism in a range from 0.002 to 0.004 M, but above 0.14 M, they become strongly inhibitory [55–57], while marine microalgae require a culture medium with high sodium chloride content (0.5–1 M). However, it has been proved feasible to use salt-adapted microorganisms capable of withstanding high salinities. The selection of salt-tolerant microorganisms involves an adaptation of the sludge to high salt concentrations. As for NH_3 high temperature enhance the inhibition effect. The presence of other ions (Ca^{2+}, K^+, Mg^{2+}) can also play a significant, antagonistic or synergistic role on the potential toxicity of sodium [54].

Pre-treatment of a substrate prior to anaerobic digestion allows to significantly improve its biodegradability [35]. Separation techniques, concentration or dehydration, mobilize and maximize the proportion of organic matter in the fraction to be digested [58]. Chemical treatments (acids, bases, ozonation), thermal treatment and ultrasonic lysis improve the disintegration of the most refractory organic fractions [59,60]. These operations increase kinetics of production and/or methane yield. Co-digestion is a strategy to increase the performance of a digester by ensuring an optimal influent composition. Yen and Brune [61] reported a significant enhancement of the methane production with an addition of waste paper to algal sludge feedstock, the optimum C/N was observed to be between 20 and 25.

4. Bioethanol

Bioethanol can be produced from several different biomass feedstock. Nonetheless, the feasibility of using lignocellulosic biomass materials as a feedstock is often limited by the low yield and the high cost of the hydrolysis process based on the current technologies [20]. In this perspective, algal biomass is gaining wide attention as an alternative renewable feedstock for the production of bioethanol [8].

Algae have high photon conversion efficiency and can synthesize and accumulate large quantities of carbohydrate biomass for bioethanol production, from inexpensive raw materials [6,62]. Aquatic algal cells are buoyant, avoiding the need for structural biopolymers such as hemicellulose and lignin that are essential for higher plant growth in terrestrial environment. This simplifies the process of bioethanol production by eliminating the chemical and enzymatic pre-treatment steps [20]. Moreover, algal cells can be harvested within a short span of time as compared to other feedstock and hence can meet the increasing demand of feedstock for ethanol production [63].

Microalgae like *Chlorella, Dunaliella, Chlamydomonas, Scenedesmus,* and *Spirulina* are known to contain a large amount (>50% of the dry weight) of starch, cellulose and glycogen, which are raw materials for ethanol production [64,65]. Similarly, macro-algae (the large sized algae) can also be utilized for ethanol fermentation [66]. The absolute absence or near absence of lignin makes the enzymatic hydrolysis of algal cellulose simple. Macroalgal genera, such as, *Laminaria, Saccorhiza,* and *Alaria* are belonging to brown algal group and grows up to meters and their main energy storage materials are laminarin and mannitol [66,67]. The red algae such as *Gelidium amansii*, which is composed of cellulose, glucan and galactan, can also serve as a potential feedstock for ethanol production [68]. Macro-algae can be cultivated on nets or string, and can be seeded onto thin weighed strings suspended over a larger horizontal rope [66]. Oleaginous algal residue after extraction of oil also can be used for obtaining fermentable sugar for bioethanol synthesis [20].

Brennan and Owende [37] has listed the desirable characteristics of algal strains to be considered as candidates for biofuel production, such as (1) robust and able to survive the shear stresses common in photobioreactors; (2) able to dominate wild strains in open pond production systems; (3) high CO_2 sinking capacity; (4) limited nutrient requirements; (5) tolerant to a wide range in temperatures resulting from the diurnal cycle and seasonal variations; (6) potential to provide valuable co-products; (7) fast productivity cycle; (8) high photosynthetic efficiency, and (9) display self-flocculation characteristics.

Certain species of algae can produce ethanol from their photosynthates [20] during dark-anaerobic fermentation and thus serve as a direct source for ethanol production. Oleaginous microalgae generate biomass waste with high starch/cellulose content after oil extraction. This can be hydrolyzed to generate sugary syrup for ethanol production. Macro-algae are also harnessed as renewable source of biomass intended for ethanol production [20].

The microalgae store starch mainly in the cells and biomass can be harvested at regular intervals from photobioreactors or shallow raceway ponds. The starch can be extracted from the cells with the mechanical tools (e.g., ultrasonic, explosive disintegration, mechanical shear, etc.) or by dissolution of cell walls using enzymes [20]. The starch is then separated by extraction with water or an organic solvent and used for fermentation to yield bioethanol. Both saccharification and fermentation processes can be simultaneously carried out in a single step if an amylase producing strain can be used for ethanol fermentation. Utilization of starch degrading ethanol producers can preclude the cost incurred for acid or enzymatic saccharification of starch. Recently, Harun et al. [69] investigated the suitability of lipid extracted microalgal debris for fermentation with a yield of bioethanol about 4–10 g L^{-1} of the substrate. Besides starch, several algae, especially green algae can accumulate cellulose as the cell wall carbohydrate, which can also be used for ethanol production. The biomass from red alga can be depolymerised to yield mixed monosugars such as glucose and galactose [20].

Direct conversion of CO_2 to biofuel by photosynthesis would avoid the unnecessary expenditure of energy to create and destroy biopolymers normally used for cell structure or energy storage [70]. It is also certain that the dominant algal strains isolated from the local environmental conditions may not be the optimal for production of biofuel under controlled conditions therefore genetic engineering may be required [37]. The algal photosynthesis is mainly based on Calvin cycle in which ribulose-1,5-bisphosphate (RuBP) combines with CO_2 to produce two 3-phosphoglyceric acid (3-PGA) which is utilized for the synthesis of glucose and other metabolites [20]. Attempts were carried out to redirect 3-PGA to ethanol by introducing ethanol producing genes (pyruvate decarboxylase and alcohol dehydrogenase). An ethanogenic recombinant of *Rhodobacter* sp. was developed for carbon redirection from the Calvin cycle to ethanol [71]. The recombinant algal strain could produce ethanol in presence of light but required oxygen free condition as it was an anaerobe [20].

5. Biohydrogen

A new and unique process has been developed when substrates such as carbohydrates are fermented by a consortium of bacteria; they produce hydrogen and carbon dioxide [72]. Microalgae possess the necessary genetic, metabolic and enzymatic characteristics to photoproduce H_2 gas [73]. During photosynthesis, microalgae convert water molecules into hydrogen ions (H^+) and oxygen; the H^+ are then subsequently converted by hydrogenase enzymes into H_2 under anaerobic conditions [39]. Due to reversibility of the reaction, H_2 is either produced or consumed by the simple conversion of protons to H_2 [74]. Photosynthetic oxygen production causes rapid inhibition to the hydrogenase enzyme, and the photosynthetic H_2 production process is impeded [39,75,76]. Consequently, microalgae cultures for H_2 production must be subjected to anaerobic conditions [22].

There are two fundamental approaches for photosynthetic H_2 production from water. The first H_2 production process is a two-stage photosynthesis process where photosynthetic oxygen production and H_2 gas generation are spatially separated [73]. In the first stage, algae are grown photosynthetically in normal conditions. During the second stage, the algae are deprived of sulfur thereby inducing anaerobic conditions and stimulating consistent H_2 production [75]. This production process becomes limited with time, as H_2 yield will begin to level off after 60 h of production. The use of this production system does not generate toxic or environmentally harmful products but could give value added products as a result of biomass cultivation [21]. The second approach involves the simultaneous production of photosynthetic oxygen and H_2 gas. In this approach, electrons that are released upon photosynthetic H_2O oxidation are fed directly into the hydrogenase-mediated H_2-evolution process [73].

Anaerobic hydrogen production proceeds photofermentatively as well as without the presence of light. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen. The reactions involved in hydrogen production (Eqs. (1) and (2)) are rapid and these processes do not require solar radiation [72].

$$\text{Glucose} + 2H_2O \rightarrow 2\text{Acetate} + 2CO_2 + 4H_2 \tag{1}$$

$$\text{Glucose} \rightarrow \text{Butyrate} + 2CO_2 + 2H_2 \tag{2}$$

The H_2 productivity is theoretically superior to the two-stage photosynthetic process, but the simultaneous production process suffers severe hydrogenase inhibition after a very short period due to the photosynthetic production of oxygen [73]. Melis and Happe [21] found that using the two-stage photosynthesis process and H_2 production, a theoretical maximum yield of hydrogen by green algae could be about 198 kg H_2 ha^{-1} day^{-1}.

A new fermentation process that converts valueless organic waste streams into hydrogen-rich gas has been developed by Van Ginkel et al. [77]. The process employs mixed microbial cultures readily available in the nature, such as compost, anaerobic digester sludge, soil etc. to convert organic wastes into hydrogen-rich gas [72]. An enriched culture of hydrogen producing bacteria such as *Clostridia* was obtained by heat treatment, pH control and HRT control of the treatment system. Anaerobic fermentative microorganism, cyanobacteria and algae are suitable in biological production of hydrogen via hydrogenase due to reversible hydrogenases [78]. Cyanobacteria and algae can carry out photo-evolution of hydrogen catalyzed by hydrogenases. The reactions are similar to electrolysis involving splitting of water into oxygen and hydrogen [79].

6. Microalgae gasification

Generally in gasification process, the biomass reacts with oxygen and water (steam), partially oxidizing the biomass into a gas mixture known as syngas (a mixture of CO, H_2, CO_2, N, and CH_4) which is combustible at high temperatures (800–1000 °C) [37]. Nitrogen in the microalgae is reported to form ammonia during gasification. It can be recovered in the aqueous phase and then used as a source of nutrients for microalgae cultivation [80]. A low microalgae concentration is typically required, and the low supercritical temperature results in a gas rich in methane and carbon dioxide [81]. The nutrients, water, and carbon dioxide produced can be recycled Minowa and Sawayama [80]. In a gasification study of microalgae (*Chlorella vulgaris*) in supercritical water (SCW) using batch (quartz capillaries) and continuous flow reactors Chakinala et al. [82] reported that the dry gas from uncatalyzed gasification of algae in SCW were mainly composed by CO_2, CO, CH_4, H_2, and some C_2–C_3 compounds. Higher temperatures, low algae concentrations, and longer residence times favored the algae gasification efficiency. The addition of catalysts to the capillaries resulted in higher yields of hydrogen and lower CO yields via enhanced water–gas shift activity. Hirano et al. [83] partially oxidized *Spirulina* at temperatures ranging from 850 to 1000 °C, and determined the gas composition required to generate theoretical yield of methanol. They estimated that algal biomass gasification at 1000 °C produced the highest theoretical yield of 0.64 g methanol from 1 g of biomass. They also estimated an energy balance (ratio of methanol produced to the total required energy) of 1.1, which gives gasification a marginal positive energy balance, the low value being attributed to the use of an energy intensive centrifuge process during biomass harvesting.

The results obtained by Tsukahara et al. [84] indicated that *C. vulgaris* at a wide range of densities in the culture solution can be used directly for gasification and the recovered solution can be used for the cultivation of *C. vulgaris* over a wide range of dilution rates if additional nutrients (phosphate, magnesium ions and micro-elements) are added to the medium. In addition, ammonium ions in the recovered solution can be used as a nitrogen source.

7. Sustainability of algal biofuels

Microalgae can tolerate and utilize substantially higher levels of CO_2 than terrestrial plants hence they can utilize CO_2 emitted from petroleum-based power stations or other industrial sources which in turn can reduce emission of green house gas [8]. The whole algal biomass or algal oil extracts can be converted into different fuel forms, such as biogas, liquid and gaseous transportation fuel, kerosene, ethanol, aviation fuel, and biohydrogen through the implementation of processing technologies such as anaerobic digestion, pyrolysis, gasification, catalytic cracking, and enzymatic or chemical transesterification [85]. Algae can utilize nutrients such as nitrogen and phosphorous from a variety of waste water sources (e.g. agricultural run-off, concentrated animal feed operations, and industrial and municipal wastewater), thus providing a sustainable bioremediation of these wastewater for environmental and economic benefits [86]. The algal biofuels can also couple CO_2 neutral fuel production with CO_2 sequestration from other power industries, in turn generating carbon credits [87]. Presently most carbon capture and sequestration (CCS) discussions are about geological storage of CO_2. Whilst the oil and gas industry has successfully injected CO_2 into reservoirs, to date this has mainly been for increased yield of fossil hydrocarbon reserves and not for long-term storage. Even if this is proven safe, the biggest difficulty with this approach is the added cost of separation of the CO_2 from the emission streams. Carbon capture for biofuels is mitigating only in that it reduces new fossil reserves being released, by recycling carbon from the atmosphere [62].

There are many reports on the potential and bio-economics of algal biomass to generate fuels and most of these are based on the premise that one would utilize the CO_2 emitted from fossil-fuelled power stations or other industrial sources of CO_2 [88–92]. A number of features of algae make them attractive when compared to terrestrial feedstock crops. Although their growth requirements are similar to terrestrial plants, they use these resources very efficiently [93] and therefore have high productivity with comparatively low water use [94,95]. The algae absorb the extra CO_2 present, capturing it as biomass through increased growth. In relation to their potential for capture of CO_2 from fossil power plants microalgae offer additional benefits in that direct CO_2 capture processes are preferable to indirect ones. As microalgae grow in aqueous environments, directly passing flue gases through this medium is a very efficient way of capturing the CO_2 in those streams [89]. The application of CO_2 directly to terrestrial crops via enclosures is likely to be prohibitively expensive though indirect stimulation of land species by flue gases is an alternative approach, which may be cost-effective despite being very much less direct and less efficient [62]. *Botryococcus braunii*, a green colonial microalga, is an unusually rich renewable source of hydrocarbons. In a study Kita et al. [96] harvested wet microalgae, thermally pretreated to enhance hydrocarbon recovery using a solvent extraction process. Samples containing a mixture of *B. braunii* and water were kept below 100 °C for 10 min. The observed hydrocarbon recovery was 97.8% at 90 °C. The extraction results suggest that the energy-intensive concentration and drying processes of the harvest could be substituted by the less energy intensive heating.

A widely stated claim is that microalgae are capable of producing 30 times more oil per unit area of land than terrestrial oilseed crops [97]. The actual global oil production in 2007–2008 from oilseed crop was 0.592 t ha^{-1} for that year [98]. If one assumes an oil concentration in algae of ~42% [99], the 365 t ha^{-1} a^{-1} productivity in the AlgaeLink bioreactors equates to 153.3 t ha^{-1} a^{-1} oil produced, which is about 259 times better productivity than the actual terrestrial oilseed crops [62]. For open ponds, ~300 t ha^{-1} a^{-1} dry weight producing an algae containing 20–30% oil, production is 100–150 times greater and for continuous high rate ponds, assuming 20–30% oil content for the species that dominate them, 17–25 times. On average therefore the 30 times more productive claim is well justified with regard to oil production [62]. The production of algal biofuels seems very promising, efficient and sustainable as it can be produced from industrial wastewater and flue gases. Additionally, it sequester significant amounts of CO_2 with a lesser land use than terrestrial crops. For these reasons many believe that microalgae are the only economic route to biodiesel [10,100].

The major factors that will determine the impacts of biofuels include their contribution to land-use change, the feedstock used, and issues of technology and scale. Biofuels offer economic benefits, and in the right circumstances can reduce emissions and make a small contribution to energy security. The production of different biofuels has their own benefits, uncertainties and risks. In order to ensure net societal benefits of biofuel production, governments, researchers, and companies will need to work together to carry out comprehensive assessments, map suitable and unsuitable areas, and define and apply standards relevant to the different circumstances of each country [101]. Yan and Lin [102] revealed that the interactions among various sustainability issues make the assessment of biofuel development difficult and complicated. The complexity during the whole biofuel production chain generates significantly different results due to the differences in input data, methodologies applied, and local geographical conditions. A useful tool for addressing environmental sustainability issues is the LCA.

8. Life cycle assessment (LCA) of algal biofuels

The algal biomass can be utilized for the production of different biofuels, the different life cycle stages are presented in the Fig. 1. In an LCA study one valuation of alternative energy routes Rubio Rodríguez et al. [103] concluded that LCA based indicators might be an effective tool to compare alternative energy routes in terms of environmental impact and indirect natural resource costs towards different services and commodities. Yang et al. [1] examined the life-cycle water and nutrients usage of microalgae-based biodiesel production. This study quantified the water footprint and nutrients usages during microalgae biodiesel production. 3726 kg water is required to generate 1 kg microalgae biodiesel if freshwater is used without recycling. The results indicated that using seawater or wastewater can reduce the life-cycle freshwater usage by as much as 90%. However, a significant amount of freshwater (about 400 kg kg^{-1} biodiesel) must be used for culture no matter whether sea/wastewater serve as the culture medium or how much har-

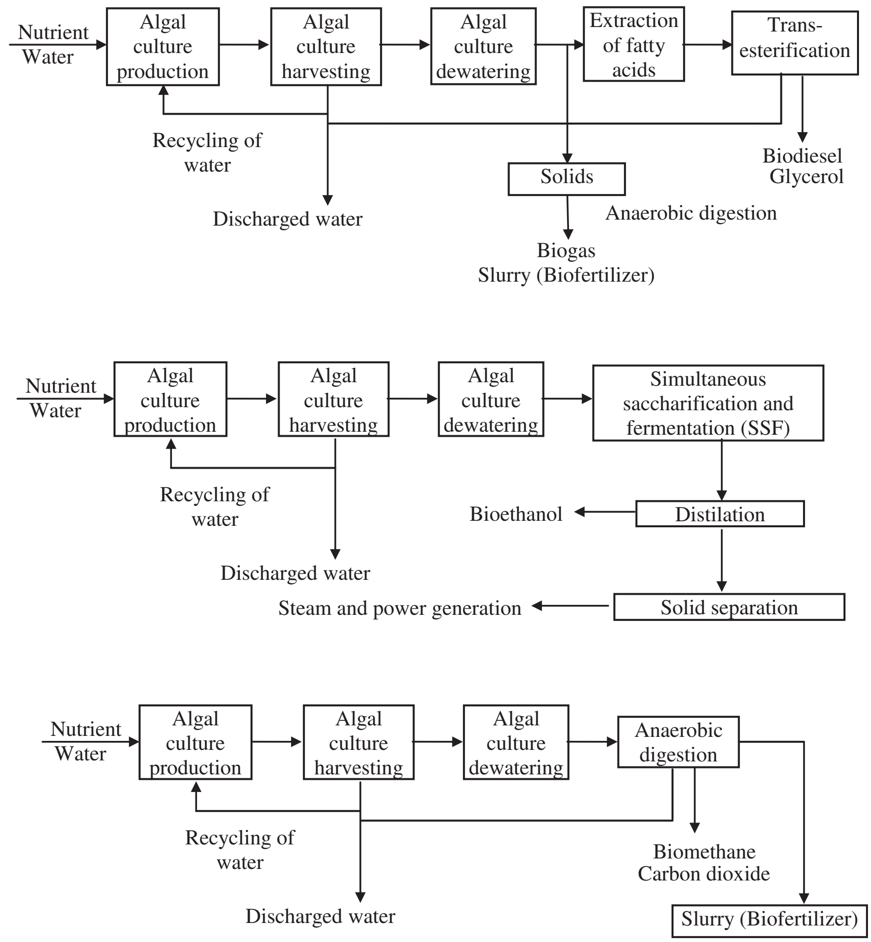

Fig. 1. The life cycle stages of biodiesel, bioethanol and biomethane production from algal biomass.

vested water is recycled. They also reported the life-cycle usages of nitrogen, phosphorous, potassium, magnesium, and sulfur are 0.33, 0.71, 0.58, 0.27, and 0.15 kg kg^{-1} biodiesel without harvest water recycling. However, when the harvest water is 100% recycled, the usage of these nutrients decreases by approximately 55%. Using sea/wastewater for algal culture can reduce nitrogen usage by 94% and eliminate the need of potassium, magnesium, and sulfur. Overall, the water footprint of microalgae-based biodiesel production gradually decreases from north to south as solar radiation and temperature increase.

The LCA study on utilization of macro-algae for enhanced CO_2 fixation and biofuels production performed by Aresta et al. [104] demonstrates that there is a potential energy benefit associated to recycling carbon by enhanced fixation of CO_2 by macro-algae, if it is associated with the use of effluent water as source of nutrients. The net energy gain depends on the conversion technology. In the best case considered so far, macro-algae can generate a net energy of the order of 11,000 MJ t^{-1} dry algae compared to 9500 MJ t^{-1} relevant to microalgae gasification.

"A recent life cycle assessment (LCA) of algal biodiesel production from *C. vulgaris* indicated that drying and hexane extraction accounted for up to 90% of the total process energy [105]. These data indicate that drying algal biomass and treating it as a substitute for terrestrial oilseeds in traditional solvent extraction and subsequent transesterification processes is not likely to be a net energy positive route toward sustainable biofuel production" [22].

An analysis of the energy life-cycle for production of biomass using the oil-rich microalgae *Nannochloropsis* sp. was performed by Jorquera et al. [13], which included raceway ponds, tubular and flat-plate photobioreactors (PBRs) for algal cultivation. The net energy ratio (NER) for each process was calculated. The results showed that the use of horizontal tubular PBRs is not economically feasible (NER < 1) and that the estimated NERs for flat-plate PBRs and raceway ponds is >1. The NER for ponds and flat-plate PBRs could be raised to significantly higher values if the lipid content of the biomass were increased to 60% dw/cwd. Recently, Campbell et al. [106] conducted a comparative LCA study of a notional production system designed for Australian conditions to compare biodiesel production from algae (with three different scenarios for carbon dioxide supplementation and two different production rates) with canola and ULS (ultra-low sulfur) diesel. Comparisons of greenhouse gas (GHG) emissions (g CO_2-eq per t km) and costs (¢ per t km) are given. Algae GHG emissions (27.6–18.2) compare very favorably with canola (35.9) and ULS diesel (81.2). Costs are not so favorable, with algae ranging from 2.2 to 4.8, compared with canola (4.2) and ULS diesel (3.8). This highlights the need for a high production rate to make algal biodiesel economically attractive. In an another study Collet et al. [107] conducted an LCA of biogas production from the microalgae *C. vulgaris* and the results are compared to algal biodiesel and to first generation biodiesels. These results suggest that the impacts generated by the production of methane from microalgae are strongly correlated with the electricity consumption. Progresses can be achieved by decreasing the mixing costs and circulation between different production steps, or by improving the efficiency of the anaerobic process under controlled conditions. A comparative LCA study of algal biodiesel facility has been undertaken by Lardon et al. [105] to assess the energetic balance and the potential environmental impacts of the whole process chain, from the biomass production to the biodiesel combustion. The outcome confirms the potential of microalgae as an energy source but highlights the imperative necessity of decreasing the energy and fertilizer consumption. Therefore control of nitrogen stress during the culture and optimization of wet extraction seem to be valuable options.

9. Conclusions

Algal biomass can be utilized for the production of various biofuels such as biodiesel, bioethanol, biogas, biohydrogen and syngas. The residual algal biomass generated in the lipid extraction for biodiesel can be appropriately utilized for the production of bioethanol or biomethane. However, significant improvements in the efficiency, cost structure and ability to scale up algal growth, lipid extraction, and biofuel production must be made to produce commercially viable biofuel. For this purpose a defined set of technology breakthroughs will be required to develop the optimum utilization of algal biomass for the commercial production of biofuel. If these technological breakthroughs occur, biofuels based on algal biomass will play a role in the future energy systems. At the current stage of development, it is still too early to comments on any preferred routes of biofuels production from algal biomass. Finally, comprehensive life cycle assessment of algal biofuels illustrating environmental benefits and impacts can and should be a tool for guiding technology development as well as for policy decisions.

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