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Review Article

Algae Fuels as an Alternative to Petroleum

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Abstract

Here we examine the scale of petroleum consumption and the current lack of scalable petroleum alternatives. We highlight the contribution that macroalgae and microalgae can collectively make as feedstocks in the future energy mix, discuss recent advancements and current development pathways, and consider the potential and the limitations of these production systems for economic and environmental sustainability moving towards a scale of 10-20% of global petroleum consumption.

Keywords: Macroalgae; Microalgae; Fossil fuel; Biofuels; Bioproducts; Feedstock

Introduction

The scale of global fossil fuel consumption is massive. In 2011 almost 11,000 million tons of oil equivalent (Mtoe) were consumed in the form of oil, gas, and coal-based fossil fuels [1]. While fossil fuel consumption continues to increase (\sim 32% increase from 2000 to 2011) to sustain our growing population and the advancement of developing nations (e.g. China and India), most of this increase in consumption comes from coal (\sim 57% increase 2000-2011) and natural gas (\sim 34% increase 2000-2011). Coal and gas production rates are currently increasing faster than consumption rates (figure 1) [1]. For petroleum oil however, consumption (\sim 14% increase 2000-2011) has grown faster than oil production (\sim 10% increase 2000-2011) [1] in the same period largely due to the plateau in production of conventional oil; a harbinger of some major challenges and changes to the future energy mix.

The petroleum industry can exploit a range of feedstocks for the production, processing and transformation of liquid hydrocarbons, of which conventional oil has, until recently, been the cheapest and most readily accessible. Currently, we are witnessing a necessary transition to a more diverse mix of feedstocks. A significant factor in the choice of future feedstocks will be the impact on global CO₂ emissions [2] for which targets have been set by many governments suggesting a trend that is likely to increase. If effective, these targets would impose a market premium increasingly favouring CO₂-neutral feedstocks, including fuels derived from algae. The technology of producing biocrude and more specific oils from algae has recently made significant progress in addressing economic obstacles and the scalability of photoautotrophic algae production is arguably high (up to ~10-20% of global fuel consumption), when water and nutrient recycling strategies are employed. Here we discuss how algae can contribute to the renewable production of biofuels and bioproducts relative to other sources.

Global Fuel Consumption

Hydrocarbon based fuels represent ~80% of our global energy consumption [1,3]. In comparison, biofuel technologies promoted as a means to address fuel security and climate change concerns, currently represent only ~0.6% of global fuel consumption [1]. Supply of first generation biofuels such as corn ethanol and rapeseed derived biodiesel have increased substantially, but this has been accompanied by a *food versus fuel* debate [4,5] which has now manifested as real world concerns, as biofuel production volumes from such sources

are already threatening global food security [6,7]. Petroleum derived oil represents ~56% of global fuel consumption and the scale of this enormous consumption (~ $4.1x10^9$ T in 2011) [1] presents an issue of scalability to advocates of biofuel and bioenergy technologies. Global production of the main food products in 2010 totalled ~7.6x10⁹ T [8] yet the embodied energy of our global food harvest is dwarfed by the energy we consume from petroleum (Figure 2) which is around three times greater. Combined with the energy losses associated with processing biomass into energy dense fuels, any attempt to generate a globally significant contribution to petroleum alternatives with food crops or with systems that divert energy from food production, will incur significant economic and social impacts that must be properly evaluated and planned for.

The extraction of petroleum oil is becoming more costly and problematic [9,10] as easily extracted reservoirs are depleted. Ironically, the unprecedented prospect of complete arctic ice loss in the summer [11] is opening up new opportunities for oil exploitation, as well as other deep sea prospects (now ~70% of new oil discoveries are in the deep sea [10]). The technical challenges of liberating unconventional petroleum resources and the prospect of increasing oil prices (predicted rises to ~US\$120-140 bbl-1 by 2035 [12,13]) are indeed stimulating technology development in response. It remains controversial as to whether conventional oil production has peaked (largely depending on how "conventional oil" is defined). Predictions range from optimistic estimates of continued increases in production (e.g. [12,13]) through to more polarised debates such as those summarised by Kerr [14-17]. At some point, it is assumed that climate change related effects, particularly temperature rise and precipitation changes (with corresponding effects on food production), must heighten concerns not only over the effects of climate change but its real economic cost

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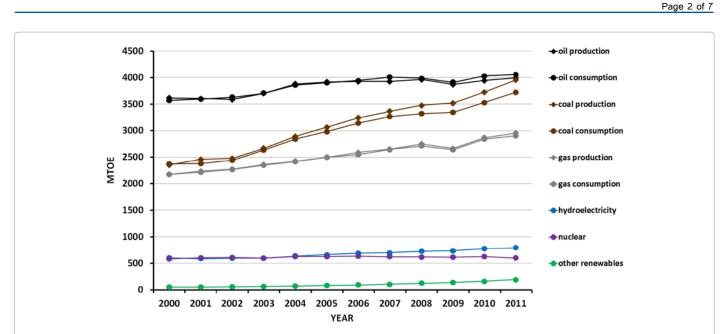


Figure 1: Energy production/consumption since 2000. Data from BP Statistical Review of World Energy 2012 [1]. It should be noted that production values for hydroelectricity, nuclear, and other renewables (which are generally direct electricity generating technologies) are represented by BP data as Mtoe values through the application of a 38% thermal efficiency conversion factor.

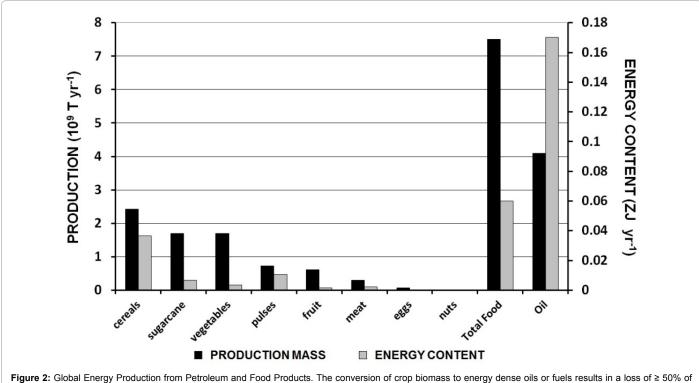


Figure 2: Global Energy Production from Petroleum and Food Products. The conversion of crop biomass to energy dense oils or fuels results in a loss of ≥ 50% of embodied energy. Food crops cannot therefore replace a globally significant proportion of energy as oil, without dramatically increasing pressure upon food security. The data presented for oil is sourced from BP Statistical Review of World Energy 2012 [1] and for food data is sourced from FAOSTAT [8], with general food calorific values calculated as previously by Stephens et al. [43].

e.g. costs of reduced crop yields, damage from extreme weather events and adaptation of communities [18,19]. Subsequently, an obvious social response will be an increasingly vocal promotion of legislative action to limit CO_2 emissions, in part by shifting to renewable fuels and renewable electricity generation. The two non-renewable options for alleviating this pressure are effective and economical CO_2 capture and sequestration technologies, and a massive expansion of nuclear power, neither of which appears to be making dramatic progress at present. In the absence of such progress, claims that the majority of fossil fuels must be left in the ground rather than combusted [20] are indeed sobering, and alternative carbon-neutral production sources for energy and fuel are necessary.

Renewable Energy Systems

Hydroelectric schemes are among the most successful renewable energy technologies and their global energy output has increased at an average and relatively consistent rate of $\sim 3\%$ yr⁻¹ for the past 50 years [1]. Other renewable technologies such as solar photovoltaic/thermal and wind energy, have only recently been effectively deployed (almost 30-fold and 15-fold increase respectively from 2000 to 2010 [1]). Nonetheless, they are yet to reach globally significant levels (currently ~0.1% and 0.8% respectively, of current global energy consumption [1]). Though a welcome trend, most renewable energy systems target electricity, which only represents ~20% of our current energy consumption, and the need for energy dense, transportable fuels still remains. Even if increased electrification of our energy consumption can be achieved (increasingly likely with the emergence of new battery technologies such as the lithium-air batteries in development by IBM and collaborators [21]), transition from our current fuel consumption rates will take considerable time, effort, and cost.

Regardless of the future energy mix, there is an inextricable link between the transport of goods and people that requires high-energy density liquid fuels, at least into the foreseeable future. Second generation or advanced biofuel technologies (i.e. those that do not compete for arable land or with food crops) are being considered globally as the successor to fossil derived liquid fuels. However some biofuel technologies (heterotrophic oil production from carbohydrate feedstocks, and farnesene from sugar) are essentially carbon conversion methods and while they may boast impressive technology systems and can produce valuable demand-driven bioproducts, they draw from the existing energy and carbon pools of our primary production (i.e. first generation feedstocks). These heterotrophic systems do not directly capture solar energy at high efficiency and their scalability and ultimate global significance for energy solutions is therefore limited [3] just as first generation biofuel systems have been (e.g. corn ethanol). If such conversion technologies utilize second generation feedstocks or waste streams then they would be much more sustainable and scalable.

Next generation biofuel systems that have less need for a rable land and freshwater (and hence greater scalability) are in development (e.g. algae production and lignocellulosic processing of more abundant biomass sources) but while the technical challenge of 'spinning straw into gold' appears surmountable, the expense of these technologies has so far placed them outside of affordable reality (2 to 10 times the current cost of production for petroleum oil). Further, issues of sustainability may be mitigated - but not avoided entirely. It is clear that to ultimately be both environmentally sustainable and scalable to globally significant levels, algae biomass systems for large scale fuel production must be photoautotrophic (or employ waste streams that would otherwise generate CO_2), and must not compete with production of food crops.

Algae Production

The production of macroalgae and microalgae (Figure 3 and Table 1) utilise established technologies which have been practiced commercially for decades, primarily for waste water treatment and the production of food products for direct consumption, phycocolloids, nutraceuticals and other high value products (HVPs). The production of macroalgae in open ponds and coastal seawaters, and microalgae in high rate ponds (HRPs) and photobioreactors (PBRs) can achieve much higher yields than terrestrial crops [3,22,23], but the high capital cost of establishment has traditionally prevented the production of algal biomass at the low costs required for economically sustainable commodity fuel production.

Table 1 does not capture all relevant issues; for example algal systems are much more expensive to establish, operate and harvest than agricultural sugar cane, though more productive (see below) and more efficient in nutrient (due to prevention of leachate and nutrient

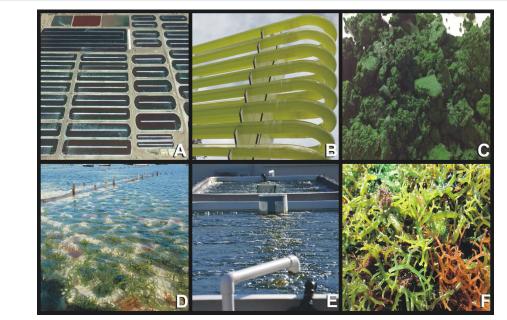


Figure 3: Microalgae and Macroalgae. (A) microalgae high rate pond cultivations of *Spirulina* (Earthrise farms in California USA) [65]; (B) microalgae cultivated in photobioreactors (example depicted is LGem tubular system at Solar Biofuels Research Centre, Australia) can have higher yields for specialty bioproducts[66]; (C) freshly harvested microalgal biomass[66]; (D) macroalgae coastal cultivations of *Kappaphycus* [67]; (E) macroalgae cultivation of Ulva in open ponds can be scaled to large ponds on land [68]; (F) freshly harvested macroalgal biomass [67].

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| | Macroalgae | Microalgae | Sugarcane |
|--|--|--|---|
| Production Yield | ~50-110 T ha-1 yr-1 dry weight [22, 23,69,70] | ~70-100 T ha-1 yr-1 dry weight [38] | ~71 T ha-1 yr-1 wet weight [8] |
| Oil content % w/w | up to 10% [61,71] | up to 30% (or more) [72] | N/A |
| Standard Calorific Value | ~5-20 MJ kg ⁻¹ [27,73] | ~20-25 MJ kg ⁻¹ [33,74] | ~3.9 MJ kg ⁻¹ |
| Calculated Captured Solar Energy (CCSE) | ~0.2-2.2 TJ ha-1 yr-1 | ~1.4-2.5 TJ ha-1 yr-1 | ~0.3 TJ ha ⁻¹ yr ⁻¹ |
| Photosynthetic Conversion Efficiency (PCE) | up to 3.0% | up to 3.4% | ~0.4% |
| Oil/Fuel Potential | HTL to biocrude 125-1100 GJ ha ⁻¹ yr ⁻¹ | HTL to biocrude 700-1250 GJ ha ⁻¹ yr ⁻¹ | Ferment/distill to ethanol ~100 GJ ha ⁻¹ yr ⁻¹ |

Table 1: Comparative Assessment of Macroalgae and Microalgae. HTL = Hydrothermal liquefaction; PCE calculated as CCSE/20 MJ m² d⁻¹ @ 365 d yr¹ solar energy (in regions where similar yields are obtained with lower average solar energy <20 MJ m² d⁻¹ then PCE rates might be reasonably up to 30% higher, but much below 15 MJ m² d⁻¹ and output would be expected to be adversely affected); HTL conversion efficiency for assumed at 50%; ethanol energy output calculated as 71 T ha⁻¹ yr⁻¹ harvest x ~80% for 'burn & crop' output x 1.7 GJ ethanol per tonne = ~100 GJ ha⁻¹ yr⁻¹.

recycling) and freshwater usage (for saline and wastewater systems freshwater consumption can be ~10-fold lower than conventional crops) [24]. Though macroalgae potential fuel/energy output is lower than that for microalgae, the capital and operating costs (especially harvesting [25,26]) associated with mass cultivation can be considerably less costly in some production models.

Obstacles to commercialization of algae fuels

The dream of algae fuels is a good one; massive algae farms absorbing CO_2 from the atmosphere and from our industrial emissions, to produce biomass at high efficiency. This biomass could be used for thermochemical conversion [27,28] or for biochemical derivation to produce liquid fuels [24]. The carbonaceous biomass residues can either be digested or gasified to CH_4 or H_2 [29,30] which can then be used to power the process or to generate nitrogenous fertilisers to make the process more sustainable. Furthermore, nutrient recycling is more efficient than in conventional agriculture allowing the potential for production of other bioproducts, and applications such as wastewater treatment and bioremediation.

The reality, as usual, is a lot tougher than the dream, despite the projections of over-sellers and the cheerleaders [31] who claim overestimated productivities and deliver premature promises of commercial success. While energy return on investment (EROI) can be sufficiently high in well designed production models (greater than that of tar sands oil extraction for example), economic sustainability remains the primary challenge [27,32].

The high capital cost of establishing algae farms, both for growth systems and for downstream processing equipment, is a primary economic factor in the cost of biocrude/oil production. The reduction of initial CAPEX and the improvement of biomass productivity are both primary effectors in sensitivity analysis of the economics [33]. The growth of algae in land-based aquatic systems necessitates high rates of water transfer and the high water content of algae biomass can also present challenges in achieving economical dewatering with low energy inputs. Water sustainability (due to evaporation losses) has been highlighted as an issue for mass cultivation of algae [34], although water sustainability is similarly a concern for other primary production systems [35-37] and with the use of saline and waste water resources algae biomass can be produced with around 10 times less freshwater for microalgae than many conventional crops [38] and even less freshwater required for macroalgae cultivation. Nevertheless, for the large scale of production required to contribute ~10% or more of global fuel use, good water management practices must be engaged and access to sufficient sources of suitable water must be ensured [39,40]. Importantly, the vast majority of the world's 15 million tonnes per annum production of macroalgae, valued at US\$8 billion (at costs of ~\$350-3,500 T⁻¹ [41]), is produced in-sea with natural flow delivering the requisite supply of nutrients and CO₂. The scalable production here is substantial and utilises well developed automated technologies in use across temperate and tropical climates [26,42]. At the large scales of production required to achieve significant global impact, the mass cultivation of microalgae can be limited by the availability of sources of enriched CO₂ and by the availability of major nutrients (nitrogen and especially phosphorous) [43]. One advantage of macroalgae is that it is less constrained by these limitations, as the vast majority (currently >95%) of macroalgae production is produced in-situ in the oceans with no use of added nutrients or freshwater.

It should be emphasised that the potential carbon neutrality of advanced biofuel production is not currently attributed a value, and thus price comparisons against fossil fuel resources are skewed. A balanced techno-economic and life-cycle comparison would need to impose carbon capture and storage (CCS) costs upon fossil fuels, such that the carbon balance is similar to carbon neutral fuel production systems, for a true 'apples to apples' assessment. Furthermore for a true comparison fossil fuel subsidisation should also be noted. The global cost of subsidising gasoline, diesel and kerosene exceeds US\$500 billion per year [44]. To put this into context, this is considerably more than Greece's national debt (\$331 billion) [45].

Current Advancement in Expanding Global Algae Cultivation

Algae production technologies continue to advance and old paradigms are being challenged, with new production strategies emerging for both microalgae [3] and macroalgae [46,47]. Both macroalgae and microalgae show considerable potential for integration with other systems [33,48-52] and this is arguably an attractive path towards early commercialisation, especially given the potential for mitigation of waste from other production outputs (e.g. CO, emissions from industry and waste water, and nutrient waste loads from agriculture, aquaculture, and other industries). However, while the ambition to develop dedicated fuel production systems from algae is more economically challenging, it is also being pursued and is a primary path towards globally significant scales of production (as energy production will most likely saturate markets of protein feedstocks, HVPs, and other applications). For microalgae, harvesting has received considerable attention [25,53], and the ongoing discovery of endogenous bioactives (e.g. dinoflagellate biotoxins) [54] as well as recent development of engineered HVPs including pharmaceuticals [55,56] demonstrates the potential of natural algae biodiversity and genetic engineering for valuable algae bioproducts.

Hydrothermal liquefaction (HTL) of whole algal biomass [27,28] to biocrude is being adopted as an option for improving the economics and energetics over conventional production models. HTL is a thermochemical processing of biomass at high pressure and temperature and importantly, can be operated with wet biomass slurries

of \geq 15%, minimising the need for intensive dewatering. But while this strategy is promising it is not without its technical challenges. Although traditional and expensive dewatering and extraction processes for oil rich algae are avoided in this HTL approach through the processing of whole biomass, the oil content and general composition of the biomass still impacts on biocrude quality (e.g. energy density). However, this process is the conversion method of choice for macroalgae which have a lower oil yield, (and therefore energy density) but higher productivity per unit area. Though the energy density of HTL algae biocrude of ~32-35 MJ kg⁻¹ [27,28] is not quite as high as specific extracted algal oils (which can even marginally exceed petroleum oil energy density of ~42 MJ kg⁻¹), conversion efficiencies of ~40 wt% currently to perhaps ~50 wt% as a future target show potential for this method. Nutrient recycling is also possible with this method, but not all nutrients can be retained and the minimisation of nitrogen in biocrude output is an important consideration to reduce NO₂ emissions from algae fuels [28], as is reduction of sulphur for SO.. The provision of biomass low in nitrogen and sulphur enhances biocrude quality while the use of catalysts can improve the quality of biocrude output [57] however, the economics and resource sustainability of this approach need to be properly examined. The removal of valuable nitrogenous components of the biomass in fact theoretically improves efficiencies in the biocrude process while adding to the total value of the biomass. Hydrothermal carbonisation and hydrothermal gasification technologies also exist but utilising these production strategies for algal biomass faces strong competition from the continued abundance of cheap coal and natural gas, though it is of note that it is estimated that of the 2850 billion tonnes of the world's total indicated fossil fuel reserves, only ~600 billion tonnes (~21%) can be extracted to stay within this 2°C safe limit [20].

Other methods of processing that can utilise wet biomass such as microwave pyrolysis are also worth investigation [58], while in microalgae, naturally occurring and genetically engineered oil secretion systems are also being studied for their potential [59,60]. The extraction of secreted oils from semi-continuous culture has many benefits but the 'milking' of extracellular lipids can require additional costs also (e.g. more complex bioreactors and/or agents to prevent degradation of secreted oils), and the economics of this strategy are yet to be properly examined.

Costs of algae fuel feedstocks are still higher than conventional petroleum but advancement in the last decade has been strong, and well configured production models for algal fuels can potentially achieve positive EROI (potentially up to 10x) and carbon neutrality. Although at full scale an algal fuels industry might not be capable of providing

more than 10-20% of global fuel due to resource constraints (CO_2 , water, and nutrients), this is nonetheless a highly desirable outcome.

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Future potential

For an expanding algae industry there is potential for further advancement in biology (strain development, engineering, crop protection and population management), engineering (improved growth systems, downstream processing, and technology integration for improved efficiency and lower costs), business and economics (markets for new products, contributing to stabilisation of energy security), and social aspects (anticipated higher valuation of renewable production systems).

Most algae production industries have traditionally produced only a small number of species commercially (dominant share from 6 microalgal species and 10 macroalgal species, Table 2) but capacity to reliably cultivate a wider range of species is increasing (e.g. large scale cultivation of *Scenedesmus* by Sapphire Energy (www.sapphireenergy. com) and *Tetraselmis* by Muradel (www.muradel.com)). Total algae biodiversity is very large (over 8,000 species of macroalgae and over 30,000 species of microalgae) relative to terrestrial crops utilised in conventional agriculture, and this remains an untapped and relatively unexplored bioresource [29,61,62].

Algae present a promising avenue for continued development of high efficiency systems to convert solar energy to hydrocarbon fuels, including the generation of more complex non-fuel bioproducts and other environmental applications. Solazyme has been a pioneer in the production of a range of specialty HVPs from algae, and while generally this and the production of mid value products (MVPs) like omega-3 oils for nutraceuticals markets (e.g. from *Schizochytrium* and *Cryphecodinium*) has utilised heterotrophic production, photoautotrophic production systems (e.g. omega-3 EPA from *Nannochloropsis* [38]) are approaching commercial reality. Algal potential for production of bulk protein and amino acids is being investigated for livestock feed markets, and also for renewable chemicals [46,63,64].

Conclusion

Macro- and microalgal fuel alternatives have advanced rapidly, but they still require further development before price parity with conventional oil can be achieved. The key challenge remains biomass productivity, as feedstock value is the key driver in all production models. Hydrothermal processing of whole biomass, advanced production strategies for specific oils, and integration of bioproduct

| Products | Macroalgae | Microalgae | |
|---------------------|--|---|--|
| Whole food products | <i>Porphyra</i> (nori) <i>Undaria</i> (wakame) <i>Saccharina</i> (kombu) | Spirulina, Chlorella | |
| Nutraceuticals | <i>Undaria</i> for fucoidans <i>Sargassum</i> for fucoidans <i>Ulva</i> for ulvans | Dunaliella for β-carotene Haematococcus for astaxanthin Schizochytrium for DHA Crypthecodinium for DHA | |
| Aquaculture feeds | Ascophyllum | Isochrysis, Chaetoceros, Tetraselmis, Thalassiosira, Pavlova | |
| Phycocolloids | Saccharina for alginates Kappaphycus for carrageenans Eucheuma for carrageenans Gracilaria for agar | - | |
| Agriculture | Ascophyllum for animal supplements Ascophyllum for fertilisers Ecklonia for fertilisers | - | |

Table 2: Conventional examples of commercial production systems for macro- and micro-algae.

outputs in biorefinery models can then each assist in development of sustainable systems. With a low level of investment into this early technology set (~US\$1-2 billion to date), relative to fossil fuels (US\$ trillions per year), the production of renewable fuel from algae is largely unexplored from an economic perspective. Given the challenge of minimising CO₂ emissions, increasing fuel security through distributed systems while providing a more sustainable fuel source to support economic development, serious questions should not only be asked at the scientific level, but also at the level of policy.

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