Biodata of **Professor Chris Rhodes**, author of "***Making Fuel from Algae: Identifying Fact Amid Fiction***."

Professor Chris Rhodes has a visiting position at the University of Reading and is director of Fresh-lands Environmental Actions. He was awarded a D.Phil from the University of Sussex in 1985 and a D.Sc in 2003. He has catholic scientific interests (www.fresh-lands.com) which cover radiation chemistry, catalysis, zeolites, radioisotopes, free radicals and electron spin resonance spectroscopy and more recently have developed into aspects of environmental decontamination and the production of sustainable fuels. He has published more than 200 peer reviewed articles and 3 books, and he is also a published novelist, journalist and poet.

E-mail: **cjrhodes@fresh-lands.com**

R. Gordon and J. Seckbach (eds.), *The Science of Algal Fuels*,
Cellular Origin, Life in Extreme Habitats and Astrobiology, 177–192
DOI 10.1007/978-94-007-5110-1_10, © Springer Science+Business Media Dordrecht 2012

MAKING FUEL FROM ALGAE: IDENTIFYING FACT AMID FICTION

CHRISTOPHER J. RHODES
Fresh-Lands Environmental Actions, 88 Star Road,
Caversham, Berkshire RG4 5BE, UK

1. Introduction

Without crude oil, modern civilisation would not exist. In total, some 84 million barrels of oil per day, or in excess of 30 billion barrels a year, are used throughout the world, and 1 quarter of that quantity is consumed alone by the United States of America. The majority of crude oil is refined into fuel for transportation, but it also provides a raw feedstock for a plethora of industries, which produce an almost bewildering number of products ranging from plastics to pharmaceuticals. We are also entirely dependent on oil (and indeed natural gas for fertilisers) to produce the majority of the food consumed in the world. The USA was formerly the world's main oil-producing nation, a mantle that has now been taken by Saudi Arabia which supplies almost 10 million barrels a day to the world oil markets, closely followed by Russia. The price of oil has fluctuated wildly according to world economic and geopolitical influences, and over a 10-year period has varied in the range $16–$147 a barrel (Rhodes, 2008a). The issue of peak oil (Hubbert, 1956; Deffeyes, 2005) describes an ultimate situation when world oil production meets a geological maximum, beyond which it must fall inexorably, leading to a gap between rising demand and ultimately falling supply. The term "gap oil" has been coined to describe this situation (Rhodes, 2009). Within a decade or less, the world economies and mechanisms of civilisation will no longer be able to depend on a relentless increase in the output of cheap crude oil nor even on current levels of supply. Recent geopolitical tensions across the Middle East threaten further the secure supply of oil, particularly light crude oil which is most readily refined into petrol (gasoline) to fuel spark-ignition engines, while doubt becomes more urgently insistent over the Saudi Arabian oil reserves, which may prove far less plentiful than has been claimed (Rhodes, 2011). The aspect of carbon emissions, and the consensus that these will lead to unfavourable climate change, further compels the search for low-carbon alternatives to oil since 38% of all the energy used by humans on Earth is derived from oil and fuels refined from it (Rhodes, 2010b), to be compared with 23% from natural gas and 26% from coal. Thus, the origin of the majority of carbon emissions for which humans are responsible is crude oil.

In an effort to address the oil problem, the substitution of oil-based fuels by biofuels has been explored, mainly derived from land-based crops. However, the area of arable land available to a single country and indeed the world overall is limited, and hence growing fuel crops must inevitably compete with growing food crops. For example, if the United Kingdom were to cease growing food entirely and turn over all of its cropland to rapeseed (canola), it could only match, in the form of biodiesel, around 17% of the fuel used nationally as derived from crude oil. In addition to considerations over their energy content, there are vital differences in the properties of biofuels, for example, biodiesel and bioethanol, from conventional hydrocarbon fuels such as petrol and diesel, which will necessitate the adaptation of engine designs to use them, for example, with regard to high viscosity at low temperatures, in planes flying in the frigidity of the troposphere. Raw ethanol needs to be burned in a specially adapted (high compression ratio) engine to recover more of its energy in terms of tank-to-wheel miles; otherwise, it can deliver only about 70% of the energy content of petrol, kilogram for kilogram in accord with its lower enthalpy of combustion (29 MJ/kg) than is typical for an oil-based fuel like petrol (gasoline) or diesel. The energy content of crude oil is usually reckoned at 42 MJ/kg (Rhodes, 2009). It is important to note that the amount of energy recovered in actual vehicles depends on their engine design. This is normally expressed in terms of well-to-wheel miles efficiency. If the energy originally present in the fuel is accounted against the energy that is actually recovered in terms of how far the fuel will push the vehicle along in terms of miles, this efficiency is about 14% for petrol engines and 20% for diesel engines. The difference is a combination of energy losses when the fuel is actually burned in the vehicle and the energy costs of extracting the crude oil and refining the fuel in the first place.

2. Biofuels

Most biofuels produced in Europe are made from plant oils, such as rapeseed oil, in the form of biodiesel, with a smaller amount of bioethanol that is produced from sugar beet (Duffield et al., 2006). In the USA, the situation is reversed, and huge amounts of corn are turned over to the production of "corn ethanol". The ethanol industry in Brazil is mature, as made from sugar cane which grows well there, with the USA as its major customer for exports. While it is not thought that the Brazilian ethanol industry compromises land on which food crops could be otherwise grown, this is a strong objection made to the diversion of corn grown in the USA from the world food markets to making ethanol. Indeed, part of the huge increases in the price of basic staple foods has been blamed on the use of arable land to produce biofuels rather than to grow food (Reuters, 2008). There are consequently shortages of rice and wheat and a significant reduction in the market stockpile of corn, all of which contributes to a potential food crisis, particularly in developing nations, including China and India. The yields of biodiesel that can be produced from a hectare of land suitable for different "fuel crops" are shown in Table 1.

Table 1. Yield of various plant oils.

Crop	Oil in L/ha
Castor	1,413
Sunflower	952
Safflower	779
Palm	5,950
Soy	446
Canola/rapeseed	1,000
Coconut	2,689
Algae	*80,000*

Data from Becker (1994).

3. Oil from Algae

Of the various means that are being considered to provide alternatives to oil-based fuels, one is making biofuel from algae. There are many advantages claimed as are indicated in the bullet points below, but most noteworthy are the quoted very high yields of oil that might be derived from algae per hectare, compared with that even from high-oil-yielding plants such as palm, which translates to around 6 tonnes of diesel per hectare. In contrast, it is reckoned that some species of high-oil-yielding algae might furnish annually more than 100 tonnes of biodiesel per hectare – an attractive prospect indeed since on this basis an area, say, the size of the United Kingdom, could fuel the entire world (Rhodes, 2009). In principle, the production of algae, to make fuels from, has the following benefits:

- Algae can be grown in tanks to yield over 100 tonne of algal oil per hectare. Hence, the entire fuel demand for the United Kingdom (40 million tonnes of biofuel) could be met on an area of 4,000 km^2.
- No need to use cropland; hence, food production is unaffected.
- Grows well on saline water or wastewater so no demand on freshwater, unlike biofuel crops.
- Can be “fed” nutrients from agricultural run-off water and sewage water, avoiding the need for mineral inputs of N/P fertilisers and cleaning the water/effluent to prevent “algal blooms”.
- Can be “fed” CO_2 from power plants, improving algal growth and reducing carbon emissions.
- Easier to process than other biomass, for example, into CH_4, biodiesel, ethanol or hydrocarbons.
- Biodiesel is more biodegradable than petroleum and fuel derived from it.
- Fifty percent of algae can be oil (lipid) c.f. 5–10% for land-based crops (e.g. soya, rapeseed).
- Reduces CO_2 release by replacing oil-based fuels and absorbs CO_2 when it grows through photosynthesis.
- Can be used as a chemical feedstock, plastics.

- Algae (and other biomass) can be processed into organic chemicals, in a "biorefinery", as a basis for a new "bio-organic" chemicals/industry.
- ExxonMobil, Shell, Unilever and many private companies are working on algae to make fuels and other products, therefore, there are serious commercial prospects.
- One recent study shows that growing algae is most efficient as integrated with cleaning CO_2 from power station smokestacks (or a cement plant) and N/P from sewage wastewaters.

3.1. YIELDS OF OIL FROM ALGAE

Claims for the amount of oil that can be "grown" from algae over that from land-based crops like soya tend to vary but range from around 30–182 tonne of oil/ha (Rhodes, 2009). The corresponding figure for rapeseed (canola) is around 1 tonne/ha. Walker has concluded that there is no firm evidence to support the notion that photosynthetic algae are intrinsically more productive than terrestrial plants grown for food (Walker, 2009). He argues that algae may in fact be less productive. Under optimal conditions, all green organisms undergo photosynthesis at the same rate in light of low intensity, and while "sun" species may show differences in full light, these do not necessarily translate into particularly different rates of accumulation of biomass. Thus, whatever the crop, land-based plants or algae, a single acre of land can produce roughly sufficient biomass to either provide fuel for one car or feed several people. Walker concludes that only a very small contribution can be made to road transport by biofuels, but such use of land crops contributes to shortages of food and an escalation of food prices. This indeed we have seen in developing nations such as India and China (Reuters, 2008). Rhodes has challenged some of the claims made for the yields of oil from algae which, in one case once additional biomass is accounted for, appears to exceed the maximum photosynthetic limit (12.7%), and either are exaggerations or imply that some forcing technology has been implemented over the use of simple pond systems (Rhodes, 2009). The issue of which strains of algae should be selected has been discussed by Chisti (2007) who concludes that it is the oil "productivity" that should be maximised not the oil yield nor the growth rate. In an algal culture device, the oil productivity is the mass of oil produced per unit volume of the algal broth in a unit time, that is, the oil yield (gram of oil per gram of biomass) multiplied by the biomass concentration in the algal broth, all divided by the time required to produce the biomass. Productivity is sometimes reported on an area basis, that is, yield (by volume or by mass) per square meter or per hectare. Many algae have been reported to have high oil productivity, for example, by Griffiths and Harrison (2009). Controversy does reign, however, over the matter of whether it is better to grow algae or terrestrial plants to make biofuels, and Chisti has defended his original thesis that making biodiesel from algae is a more energy-effective means to displace petroleum-derived fuels than biodiesel or bioethanol made from agricultural crops by existing means (Chisti, 2008a) with further hard numbers (Chisti, 2008b), against the conclusions of Reijnders (2008) that algae are net energy-negative sources of fuel (i.e. provide less energy than the fossil fuel energy used to produce them) compared with the overall energy yield of fuels derived from land-based plants such as sugar cane (ethanol) and oil palm (palm oil). Hirano et al. have concluded that methanol can be produced from Spirulina with an energy content that is similar to the fuels derived from the land-based plants (Hirano et al., 1998), but Reijnders stresses that it remains to be seen whether or not the annual yields assumed by Hirano et al. can be obtained in open pond systems in reality. Chisti responds (2008b) that Reijnders' conclusions (2008) are based on two simplistic analyses by Hirano et al. (1998) and Sawayama et al. (1999), which have miscomprehended aspects of large-scale algae production and grossly overestimated the input of fossil energy required to produce algal biofuels. He offers energy costs for all aspects of the process including fertilisers, cultivation, harvesting, oil recovery, energy content of the algal oil and of the biogas produced from the residual biomass. Indeed, as we see later, the production of algae and algal fuel becomes increasingly attractive when it is integrated with the use of other outputs, that is, biogas, and inputs, for example, carbon, nitrogen and phosphorus, that originate from smokestacks (CO_2), and N and P from sewage effluent, such that the production of algae is part of an environmental clean-up strategy (Clarens et al., 2010). A theoretical maximum for algal oil production has been estimated at 354,000 L/ha/year (38,000 gal/ac/year), to be compared with 40,700–53,200 L/ha/year (4,350–5,700 gal/ac/year) determined from a number of actual cases (Weyer et al., 2010).

If algal fuel production is to be carried out on a worldwide scale, rather than merely in tropical and equatorial locations, it is important to consider those aspects pertinent to regions of higher latitude where the ambient solar energy is considerably reduced. In principle, the majority of solar harvesting into algae could be done in sunny desert areas, for example, the Sahara, in analogy with the Desertec project which intends to collect solar energy in the Sahara desert using concentrating solar thermal (CCS) power plants which then convert it to electricity to be exported to southern Europe. It is thought that some 20% of Europe's electrical power demand could be met by this technology (Rhodes, 2010b). Baliga and Powers (2010) have presented a paper which reports a model life-cycle analysis aimed to determine the most effective operating conditions for algae biodiesel production in cold climates intended to minimise impacts on the environment and energy consumption using photobioreactors. It is assumed that the photobioreactor is adjacent to a fossil fuel or biomass power plant that provides excess heat and CO_2 to feed the algae. The model yields a high productivity for biodiesel of 19–25 L/m^2/year (160–210 tonne/ha/year) and a total life-cycle energy consumption of 15–23 MJ/L for algal biodiesel to be compared with 20 MJ/L for soy biodiesel. The energy consumption and air emissions are much lower for algal biodiesel than soy biodiesel when waste heat is utilised.

Chisti has presented a strong case for photobioreactors (Chisti, 2007). Clearly, if these are run with artificial light from lamps, the overall strategy might prove highly energy inefficient (Rhodes, 2009), but if natural light is employed, the yield of "oil" per unit area is greater than can be derived from open pond systems. For example, there are demonstrated biomass productivities leading to 136,900 L/ha of oil from algal strains with a 70% wt% lipid content and 58,700 L/ha from strains containing 30 wt% of oil. Around 80% of the oil that is produced translates into biodiesel, and so these numbers amount to 91 and 39 tonne of algal biodiesel/ha, respectively. Chisti (2007) has pointed out that while feasible technology exists to replace petroleum by algal biodiesel, at present the strategy is not economically viable, mainly due to the costs of harvesting and processing the algae crop. On October 15, 1973, the world faced its first oil crisis when the members of Organization of Arab Petroleum Exporting Countries or the OAPEC (consisting of the Arab members of OPEC plus Egypt and Syria) decided to launch an oil embargo against the West in retaliation for its support of Israel during the Yom Kippur War, also known as the Ramadan War (Bergman and Meltzer, 2004). In an awareness that the United States was particularly vulnerable to vagaries in the supply of imported oil, the Aquatic Species Program (http://www.nrel.gov/docs/legosti/fy98/24190.pdf) was founded. This was a research project implemented in the USA in 1978 under the auspices of the then President Jimmy Carter and was funded by the United States Department of Energy (DoE). The programme ran for the best part of two decades and investigated all aspects of energy production from algae and finally concentrated on the production of biodiesel from them. In excess of 3,000 algal species were evaluated, and from those species that appeared most promising, developmental work was undertaken in the effort to increase their lipid content by reducing the supply of key nutrients, such as nitrogen and silicon. It is an interesting fact that algae, when placed under such conditions of stress, tend to increase their lipid content almost as a self-defence mechanism, probably in an effort to store energy as fat. The open pond system was explored for the mass production of algae, involving the construction of 1,000 m^2 ponds in Roswell, New Mexico, with some success. However, the algal yields were inconsistent, and although 50 g of algae/m^2/day could be achieved, the yields were restricted on those occasions when the ambient temperature fell. To place this in context, this amounts to 50×10^{-6} tonne/(m^2/day) $\times 10^4$ m^2/ha $\times$ 365 day/year = 182.5 tonne/ha/year. If 50% of this mass of oil can be recovered, this amounts to 91 tonne/ha/year which is about two-thirds of the figure claimed in a study by the University of New Hampshire (Rhodes, 2009) but is in the same ballpark and could probably be optimised further. The DoE research staff compiled their work and conclusions into a report that was published in July 1998. In 1995, as part of the overall efforts to lower budget demands, the DoE decided to end the programme. The coincidence between this figure and that deduced from Chisti's result (2007) for the areal yield in a photobioreactor with a 70% oil-yielding algae should be noted, both at 91 tonne of algal biodiesel/ha.

4. Production of Algae

4.1. OPEN PONDS

Raceway-type ponds and lakes are open to the elements and are thus often referred to as "open pond" systems. They are, however, vulnerable to contamination by other microorganisms, such as invasive algal species or bacteria, and so the number of species successfully cultivated in such systems for a specific purpose (such as food, oil or pigment production) is relatively limited. Further disadvantages are that the water temperature and light intensity are not controllable. Since the growing season is largely dependent on location, and mostly limited to the warmer months, open ponds can only be used for less than half the year, unless they are placed in tropical regions. Open ponds are, however, fairly cheap to build since in its simplest form, it is only necessary to dig a trench or a pond. The production output may be very high too, in relation to other systems of comparable size and cost. The approach may be of particular advantage if the desired algae benefits from (or can survive) extreme conditions, say, of cold or salinity, that would kill off other types of algae. As an example, *Spirulina* sp. can grow in water with a high concentration of sodium bicarbonate, and *Dunaliella salina* will grow in extremely salty water. Open culture is also effective if there is a simple and inexpensive system available to select out the desired algae with which to inoculate new ponds with a high starting concentration of it: this has the effect of outcompeting other invasive strains. Some chain diatoms fall into this category because they can be filtered from the outflowing water stream, using a "pillow case" of fine muslin cloth which is tied over the end of the outflow pipe. Most kinds of algae are small enough to pass through the bag, while the chain diatoms are retained and can be used to feed shrimp larvae and to inoculate further tanks or ponds.

4.2. PHOTOBIOREACTORS

Alternatively, a photobioreactor (PBR) can be used to grow algae in, which is generally a closed system fitted with a light source of some kind. The latter may include an artificial lamp, but really any container able to transmit PAR light can act as a PBR. It is possible to vary the basic "open pond" design by covering it with a transparent or translucent barrier or to enclose the pond within a greenhouse. A pond covered with a greenhouse could be considered a PBR. While the system will most likely be smaller if made in this way, it does allow more different species to be grown and those that are being grown to remain dominant. Furthermore, the growing season may be extended, and if the system is heated, it can produce algae all year round. Due to its enclosed nature, it is necessary to introduce all the nutrients essential for the algal growth to the system directly.

A "batch mode" operation is possible for a PBR, in which a continuous stream of sterilised water can be introduced, containing nutrients, air and carbon dioxide. As the alga grows, it overflows the reactor and is harvested. If sufficient care is not taken, continuous bioreactors often stop working very quickly, but if this induction period is successful, they should continue to operate over a long period. An advantage of this type of algae culture is that algae in the "log phase" are produced which are generally of higher nutrient content than old "senescent" algae. It can be shown that the maximum productivity for a bioreactor occurs when the "exchange rate" (time to exchange one volume of liquid) is equal to the "doubling time" (in mass or volume) of the algae.

Different types of PBRs include:

- Tanks provided with a light source
- Polyethylene sleeves or bags
- Glass or plastic tubes

It is worth noting that if artificial lamps are employed to produce the light with which to irradiate the algae in a PBR, there is the issue of overall energy efficiency to be considered. For example, while an efficiency of perhaps 6% is obtained in algal photosynthesis in terms of usefully absorbed light from the solar spectrum, natural sunlight costs nothing to produce, and whatever is gained may be considered gratis. In contrast, an artificial "sunlamp" is run on electricity that is recovered at only around the Carnot cycle determined efficiency of 36% from a conventional coal-, gas- or nuclear-fired power station, that is, two-thirds of the original fuel energy has already been lost as heat. If therefore we are only to recover 6% of that, then the overall efficiency of the process, intended to make artificial "oil" is around a mere 2%. Put another way, some 98% of the original fossil fuel energy is wasted. Using the electricity directly would be a much better deal. However, such artificially lit PBRs can become economically viable to make "value products", for example, pharmaceuticals, or to provide pure algal strains with which to initiate production in cheaper open pond systems, thus overwhelming invading competitors to grow specific kinds of algae on the large scale fuelled by free sunlight (Rhodes, 2009).

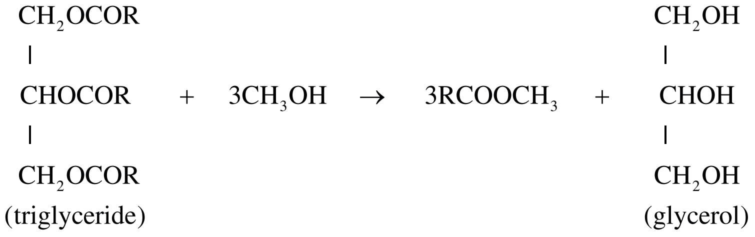
5. Screening Algae for Oil Content Using Near-Infrared (NIR) Spectroscopy

A new method (Lewcock, 2010) has been introduced for investigating the lipid content of algal strains with the view of producing biodiesel from them, based on near-infrared (NIR) spectroscopy. The near-infrared spectrum runs the range of wavelengths 800–2,500 nm and is therefore just below the visible region of the electromagnetic spectrum but above the more usually encountered mid-infrared, at 2,500–30,000 nm. The discovery of infrared radiation is attributed to the British/German Astronomer William Herschel, a polymath who in addition to his astronomical work wrote 24 symphonies. NIR only came to practical use in the 1950s as an analytical device, and while it is less sensitive than normal (mid) IR, NIR radiation can penetrate samples more easily, meaning they need less analytical preparation and in the case of algae can be examined in their raw state. For the production of biodiesel, the "algal oil" should contain a high level of fatty acids to be converted into biodiesel: triglycerides rather than phospholipids, which are readily distinguished. IR spectroscopy measures the fundamental vibrations (stretching frequencies) of covalent chemical bonds in molecules if they have a dipole moment. NIR measures the "overtones" of fundamental stretching modes, and of coupled vibrations, and thus the spectra are more complex to assign but provide useful fingerprints of particular functional groups. The NIR method is highly specific for the detection of different kinds of fatty acids, and it is intended to develop a database of fingerprints for different fatty acid components in algal biomass, with which to analyse actual algae. The method offers the promise of a rapid and precise screening of algae directly rather than the existing time-consuming, cumbersome and error-prone wet chemical means for analysing algae and may prove pivotal in the development of a putative fuel industry based on algae (Rhodes, 2010a).

6. Processing Algae: Transesterification or Hydrothermal Liquefaction?

6.1. TRANSESTERIFICATION

Most discussions of growing algae for fuel production focus on high-lipid (high-oil-yielding) strains of algae, from which the algal oil is extracted, and this is converted to biodiesel in much the same way as oil from land-based crops like soya by transesterification (Maio and Wu, 2006): refluxing the oil in methanol with a KOH catalyst to convert triglycerides to fatty acid methyl esters plus glycerol (Eq. 1):



$$\begin{array}{ccccccc} CH_2OCOR & & & & & & CH_2OH \\ | & & & & & & | \\ CHOCOR & + & 3CH_3OH & \rightarrow & 3RCOOCH_3 & + & CHOH \\ | & & & & & & | \\ CH_2OCOR & & & & & & CH_2OH \\ \text{(triglyceride)} & & & & & & \text{(glycerol)} \end{array} \qquad (1)$$

There are some truly astounding figures about the amount of biodiesel that might be obtained from farming algae rather than from growing crops. This strategy, however, is beset by the opposing factor that most algae with a high oil content grow more slowly and in lower yield than their less-fatty analogues. The variation in lipid content of algae is illustrated in Table 2. All algae primary comprise proteins, carbohydrates, fats and nucleic acids but in varying proportions.

Table 2. Chemical composition of algae expressed on a dry matter basis (%).

Strain	Protein	Carbohydrates	Lipids	Nucleic acid
Scenedesmus obliquus	50–56	10–17	12–14	3–6
Scenedesmus quadricauda	47	–	1.9	–
Scenedesmus dimorphus	8–18	21–52	16–40	–
Chlamydomonas rheinhardtii	48	17	21	–
Chlorella vulgaris	51–58	12–17	14–22	4–5
Chlorella pyrenoidosa	57	26	2	–
Spirogyra sp.	6–20	33–64	11–21	–
Dunaliella bioculata	49	4	8	–
Dunaliella salina	57	32	6	–
Euglena gracilis	39–61	14–18	14–20	–
Prymnesium parvum	28–45	25–33	22–38	1–2
Tetraselmis maculata	52	15	3	–
Porphyridium cruentum	28–39	40–57	9–14	–
Spirulina platensis	46–63	8–14	4–9	2–5
Spirulina maxima	60–71	13–16	6–7	3–4.5
Synechococcus sp.	63	15	11	5
Anabaena cylindrica	43–56	25–30	4–7	–

Source: Becker (1994).
Algal oil is very high in unsaturated fatty acids. Some UFAs found in different algal species include arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid, gamma-linolenic acid and linoleic acid.

While the percentages differ with the type of algae, some algae contain up to 40% of their overall weight in the form of fatty acids. It is this fatty acid component (oil) that can be extracted and converted into biodiesel.

It is also necessary to dry the algae prior to extraction of the oil, which is a highly energy-intensive process. As an alternative, the method of hydrothermal liquefaction may be employed, which converts all kinds of biomass into potential gaseous and liquid fuels as is discussed in the next section.

6.2. HYDROTHERMAL LIQUEFACTION

As an alternative route to the generation of fuel from microalgae, the method of hydrothermal liquefaction may be employed (Brown et al., 2010; Patil et al., 2008; Stucki et al., 2009; Peterson et al., 2008; Tsukahara and Sawayama, 2005). In effect, the raw algae are heated in the presence of water under pressure, with or without a catalyst being present. The conditions of temperature and pressure may be adjusted so that the water enters the supercritical state (Stucki et al., 2009; Peterson et al., 2008), when it transforms from a polar liquid with a dielectric constant of around 80 under normal conditions to around 3, when it displays properties akin to an organic solvent, for example, n-hexane. The hydrothermal processing may also be carried out in the presence of acids or alkali (Ross et al., 2010). In one report (Dote et al., 1994) of a study in which *Botryococcus braunii*, an algae with a high water content, was heated under pressure at 300°C, an oil said to be equivalent in quality to petroleum oil was obtained, in a yield of 57–64%, and >95% of which was recovered. A range of liquid and gaseous fuels (e.g. methane) can be obtained from algae using this technology.

7. An Integrated Algae/Environmental Management System

A recent study (Clarens et al., 2010) suggests that overall the CO_2 emissions attendant to producing biofuel from algae may be worse than those from corn, canola (rapeseed) or switch grass. The main problem is the use of carbon dioxide brought from elsewhere in gas bottles and inputs of fertiliser, particularly nitrogen and phosphorus. According to a life-cycle analysis, the land-based crops all were found to sequester more carbon than that emitted in growing them, while the contrary was true for growing algae, meaning that replacing fossil fuels by algal fuels could cause an overall increase in carbon emissions. On closer inspection, the report is in fact very positive about growing algae, particularly in the latter two respects. Read in more detail, the data are only in opposition to making fuel from algae if nitrogen and phosphorus nutrients are added in their mineral forms and if the CO_2 has to be injected into the system (transported as a compressed gas) as made mainly by the process of steam reforming methane (Eq. 2), along with most of the world's available hydrogen:

$$\text{(Overall) } CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (2)$$

H_2 is used to furnish nitrogen (ammonium sulphate and nitrate) fertiliser by reacting it with N_2 via the Haber-Bosch process to make ammonia (NH_3), and so there is in a way a symbiosis between the production of CO_2 and NH_3. The phosphorus would likely be provided by mining "rock phosphate", a process which also requires energy. However, the figures in this "cradle to farm gate" analysis (i.e. they do not include the energy costs of processing the algae or other biomass into fuel *per se*) show that if the production of algae is combined with a wastewater treatment strategy, so that N and P are removed from it by the algae (an otherwise energy-intensive procedure), and fed with CO_2 from smokestacks, most of the environmental burdens attendant to growing algae are offset (i.e. an algae production plant, a power station and a sewage works should all be placed in mutual proximity). Of three possible municipal wastewater effluents evaluated as a source of N and P, the most effective was source-separated urine with a very high content of these elements, in which case growing algae became more environmentally beneficial than the land-based crops. Another life-cycle analysis (Lardon et al., 2009) essentially confirms the conclusions of Clarens et al. (2010). Two different culture conditions, nominal fertilising or nitrogen starvation, in addition to two different extraction options, dry or wet extraction, were examined. The results confirm that microalgae offer considerable potential as an energy source but highlight the imperative necessity of decreasing the energy and fertiliser consumption during the process. Even if there remains some dispute over the exact figures used, the results emphasise the importance of developing an integrated paradigm of production and recycling for algal fuel production stressed by Rhodes (2008a, b) in the context of rare metals, which are required to maintain the electronics and solar power industries.

8. First "Artificial Cell" May Provide Source of Algal Fuel

A report (Birch, 2010) has been published describing "the first synthetic cell". What has in fact been done is to insert a chemically synthesised genome into a bacterial cell. The *M. mycoides* genome contains over a million letters of genetic code, and current DNA technology delivers perhaps a few thousand units in one go. The team led by Dan Gibson and Craig Venter has exploited the ability of yeast to join together small pieces of DNA using enzymes. Grown in a Petri dish, the synthetic bacterium looks almost identical to the natural version and can similarly self-replicate. For the development of tailor-made life, it is necessary to understand what each gene codes for. The longer run might be that genomes could be designed, but achieving that is some way off. It is more probable that a simple artificial genome could be created that has the essential properties of a living organism. This could permit other gene circuits being introduced, for example, to produce biofuels or fine chemicals. Dr Venter's company, Synthetic Genomics, intends to use the cell synthesis technology to produce modified algae cells from which to make biofuel. The aim is to make a complete algal genome from which "superproductive organisms" could be derived. It is possible that the designer method can overcome some of the drawbacks involved with making fuel from algae, namely, robustness and competitiveness of particular strains over other organisms, enhanced growth rate and yields of algal oil. The method might be the key to the widescale production of fuel from algae, which is thought to be the better option over making fuel from land-based crops such as soya (biodiesel) and corn (ethanol), since the yields are much greater and there is no competition with food-crop production and provide a real alternative to a globalised world that is utterly dependent on supplies of imported crude oil.

9. Conclusions

So, according to the title of this review, have we managed to identify fact amid fiction over algal biofuels? The present summary is highly selective, but it seems to indicate that a yield of around 40–90 tonne/ha of biodiesel can be produced using either a photobioreactor or an open (raceway) pond system, the latter under favourable conditions. If the strategy is to be implemented on the grand scale, it will entail considerable engineering and energy costs. In either case, there will be a demand on N and P fertilisers, which depend respectively on natural gas and rock phosphate, both of which are in finite supply, and so it will be necessary in the longer term to utilise human and animal wastes to provide these elements as algal nutrients. At present, it is uneconomic to produce algae in quantities to match those of the world's petroleum consumption, which it is intended strategically to replace. If photobioreactors are to be used in earnest, they will require the production of vast amounts of plastic to fabricate them, most probably derived from crude oil. That said, algae are probably the only way forward to a future civilisation which is independent of oil.

10. References

Baliga R, Powers SE (2010) Sustainable algae biodiesel production in cold climates. Int J Chem Eng 2010. Article ID 102179. doi: 10.1155/2010/102179. http://www.hindawi.com/journals/ijce/2010/102179.html

Becker EW (1994) In: Baddiley J et al (eds) Microalgae: biotechnology and microbiology. Cambridge University Press, Cambridge/New York, p 178

Bergman R, Meltzer G (2004) Yom Kippur war, real time: the updated edition. Yediot Ahronoth/Hemed Books, Tel Aviv. ISBN 965-511-597-6

Birch H (2010) The first synthetic cell. http://www.rsc.org/chemistryworld/News/2010/May/20051002.asp

Brown TM et al (2010) Hydrothermal liquefaction and gasification of *Nannochloropsis* sp. Energy Fuel 24:3639–3646

Chisti Y (2007) Biodiesel from microalgae. Biotech Adv 25:294–306

Chisti Y (2008a) Biodiesel from microalgae beats bioethanol. Trends Biotechnol 26:126–131

Chisti Y (2008b) Response to Reijnders: do biofuels from microalgae beat biofuels from terrestrial plants? Trends Biotechnol 26:351–353

Clarens F et al (2010) Environmental life-cycle comparison of algae to other bioenergy feedstocks. Environ Sci Technol 44:1813–1819

Deffeyes KS (2005) Beyond oil. Hill and Wang, New York

Dote Y et al (1994) Recovery of liquid fuel from hydrocarbon-rich microalgae by hydrothermal liquefaction. Fuel 73:1855–1857

Duffield JA et al (2006) Assessment of biofuels. In: Dewulf J, Van Langenhove H (eds) Renewables-based technology. Wiley, Chichester, pp 231–245

Griffiths MJ, Harrison STL (2009) Lipid productivity as a key characteristic for choosing algal species for biodiesel production. J Appl Phycol 21:493–507

Hirano A et al (1998) Temperature effect on continuous gasification of microalgal biomass: theoretical yield of methanol production and its energy balance. Catal Today 45:399–404

Hubbert MK (1956) Nuclear energy and the fossil fuels. In: American Petroleum Institute Drilling and production practice proceedings, Spring, pp 5–75

Lardon L et al (2009) Life-cycle assessment of biodiesel production from microalgae. Environ Sci Technol 43:6475–6481

Lewcock A (2010) Striking algal oil. http://www.rsc.org/chemistryworld/News/2010/March/12031001.asp

Maio X, Wu Q (2006) Biodiesel production from heterotropic microalgal oil. Bioresour Technol 97:841–847

Patil V et al (2008) Towards sustainable production of biofuels from microalgae. Int J Sci 9:1188–1195

Peterson AA et al (2008) Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy Environ Sci 1:32–65

Reijnders L (2008) Do biofuels from microalgae beat biofuels from terrestrial plants? Trends Biotechnol 26:349–350

Reuters (2008) Biofuels blamed for food price crisis. http://uk.reuters.com/article/businessNews/idUKL0340750020080704

Rhodes CJ (2008a) The oil question: nature and prognosis. Sci Prog 91:317–375

Rhodes CJ (2008b) Short on reserves. Chem Ind 16:21–23

Rhodes CJ (2009) Oil from algae; salvation from peak oil. Sci Prog 92:39–90

Rhodes CJ (2010a) Looking for algal oil… with near infrared light. http://ergobalance.blogspot.com/2010/08/looking-for-algal-oil-with-near.html

Rhodes CJ (2010b) Solar energy: principles and possibilities. Sci Prog 93:37–112

Rhodes CJ (2011) The price of oil. Sci Prog 94:1–9

Ross AB et al (2010) Hydrothermal processing of microalgae using alkali and organic acids. Fuel 89:2234–2243

Sawayama S et al (1999) Possibility of renewable energy production and CO2 mitigation by thermochemical liquefaction of microalgae. Biomass Bioenergy 17:33–99

Stucki S et al (2009) Catalytic gasification of algae in supercritical water for biofuel production. Energy Environ Sci 2:535–541

Tsukahara K, Sawayama S (2005) Liquid fuel production using microalgae. J Jpn Petrol Inst 48:251–259

Walker DA (2009) Biofuels, facts, fantasy and feasibility. J Appl Phytocol 21:509–517

Weyer KM, Bush DR, Darzins A, Willson BD (2010) Theoretical maximum algal oil production. Bioenergy Res 3:204–213