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Full Length Research Paper

Making biofuels from microalgae - A review of technologies

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As the world hunts eagerly for alternative fuel sources, microalgae are attracting wide interest. Lipids derived from algae hold great promise as a biofuel feedstock. The high-lipid content found in some species is a fundamental edge. So are algae's high per-acre productivity and its ability in thriving in areas not already used for food production. Therefore, there are vigorous research initiatives aimed to develop alternative renewable and potentially carbon neutral solid, liquid and gaseous biofuels as alternative energy resources. However, alternate energy resources akin to first generation biofuels derived from terrestrial crops such as sugar beet, sugarcane, rapeseed and maize place an enormous strain on world food markets, contribute to water shortages and precipitate the destruction of the world's forests. Second generation biofuels derived from lignocellulosic agriculture and forest residues; however there is a serious concern over competing land use or required land use changes. Therefore, on the base of current knowledge and technology projections, third generation biofuels specifically derived from microalgae are considered to be a technically viable alternative energy resource that is devoid of the major drawbacks associated with first and second generation biofuels. Microalgae are photosynthetic microorganisms with very simple growing requirements (sugars, light, N, P, CO2, and K) that can produce lipids, proteins and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and valuable co-products. This study reviewed the technologies underpinning microalgae-to-biofuels systems, focusing on the biomass production, harvesting, conversion technologies, and the extraction of useful co-products. It also reviewed the synergistic pairing of microalgae propagation with carbon sequestration and wastewater treatment potency for mitigation of environmental impacts associated with energy conversion and utilisation. It was found that, whereas there are outstanding issues related to photosynthetic efficiencies and biomass output, microalgae-derived biofuels could progressively substitute a significant proportion of the fossil fuels required to meet the growing energy demand.

Key words: Bioenergy conversion, biomass recovery, photobioreactor, microalgae

INTRODUCTION

Fossil fuel and environmental issues

In 2008 the annual world primary energy consumption was estimated at 11,295 million tonnes of oil equivalent (mtoe) (BP, 2009). Fossil fuels accounted for 88% of the primary energy consumption, with oil (35% share), coal (29%) and natural gas (24%) as the major fuels, while nuclear energy and hydroelectricity account for 5% and 6% of the total primary energy consumption, respectively. Given the current technological progress, potential reserves, and increased exploitation of newer unconventional reserves (e.g. for natural gas), it is highly probable that fossil fuels will continue to be available at low cost for a considerable period of time. Unfortunately,

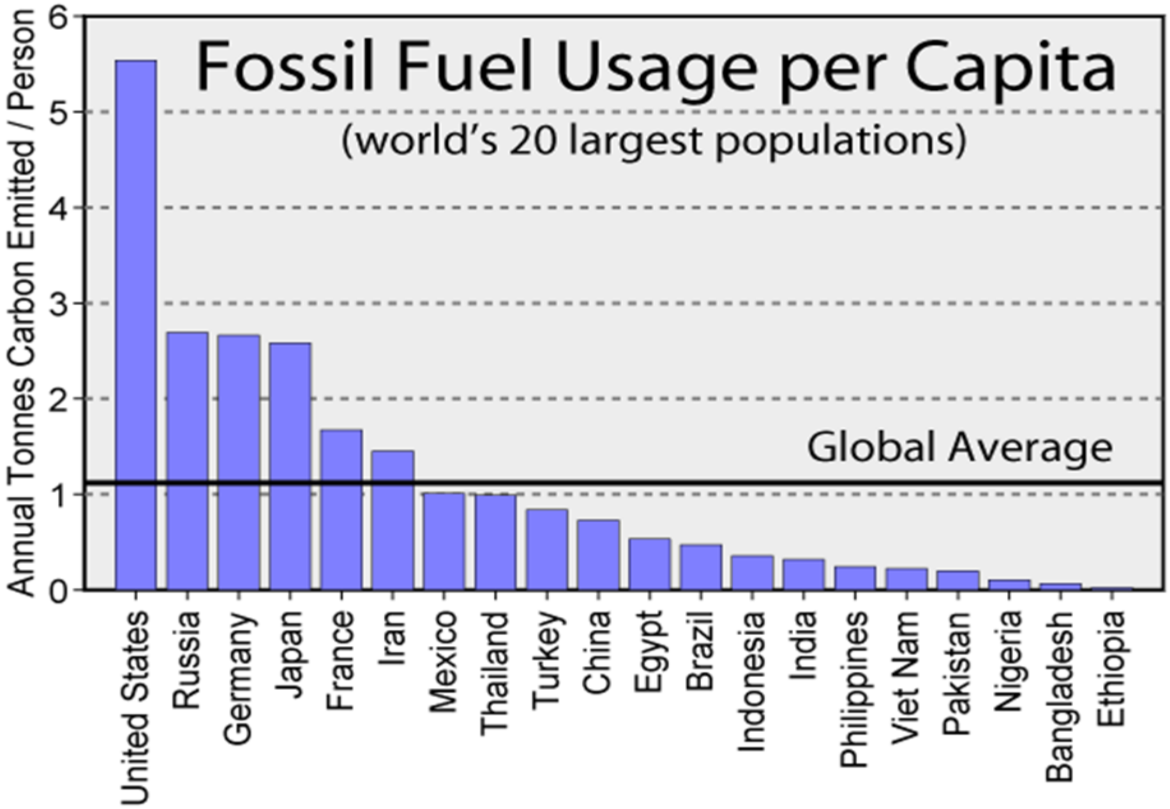

Figure 1: Annual tones carbon emittions per person in world's 20 largest population countries.

the potential threat of global climate change has increased, and for a major part, this has been attributed to greenhouse gas emissions from fossil fuel usage. The burning of fossil fuels produces around 21.3 billion tonnes (21.3 gigatonnes) of carbon dioxide (CO_2) per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tonnes of atmospheric carbon dioxide per year (one tonne of atmospheric carbon is equivalent to 44/12 or 3.7 tonnes of carbon dioxide) (European Commission, 2007). Annually 5.5 tonnes of carbon emitted per person in United States of America. In 2010 Russia, Germany and Japan, the emission of carbon quantity is 2.8, 2.7 and 2.5 tonnes respectively (Figure 1). China is 10^{th} largest population country having 0.8 tonnes of carbon emission per person annually. Carbon dioxide is one of the greenhouse gases that enhances radiative forcing and contributes to global warming and climate change.

Combustion of fossil fuels generates sulfuric, carbonic, and nitric acids, which fall to Earth as acid rain, impacting both natural areas and the built environment. Monuments and sculptures made from marble and limestone are particularly vulnerable, as the acids dissolve calcium carbonate. Fossil fuels also contain radioactive materials, mainly uranium and thorium, which are released into the atmosphere. In 2000, about 12,000 tonnes of thorium and 5,000 tonnes of uranium were released worldwide from burning coal (Alex, 2008). It is estimated that during 1982, US coal burning released 155 times as much radioactivity into the atmosphere as the Three Mile Island incident (Gordon and Aubrecht, 2003). Burning coal also generates large amounts of bottom ash and fly ash. Coal mining methods, particularly mountaintop removal and strip mining, have negative environmental impacts, and offshore oil drilling poses a hazard to aquatic organisms. Oil refineries also have negative environmental impacts, including air and water pollution. Transportation of coal requires the use of diesel-powered locomotives, while crude oil is typically transported by tanker ships, each of which requires the combustion of additional fossil fuels. It is estimated that natural processes remove only about 12 G tonnes, therefore, compatible mitigation strategies are required to neutralize the excess CO2 (Bilanovic et al., 2009).

Development of biofuel resources

In recent years, the use of liquid biofuels in the transport sector has shown rapid growth, driven mostly by finance policies focused on achievement of energy security (IEA, 2007). First generation biofuels have been mainly extracted from food and oil crops including rapeseed oil, sugarcane, sugar beet, and maize (FAO, 2008) as well as vegetable oils and animal fats using conventional technology (FAO, 2007). It is projected that the consumption of liquid biofuels will continue, but their impacts demands in the transport sector will remain limited due to: competition with food and fibre production for the use of arable land (IEA, 2007). the use of first generation biofuels has generated a lot of controversy, due to their impact on global food markets and on food security because there are 1% (14 million hectares) of the world's available arable land is used for the production of biofuels, providing 1% of global transport fuels, which cause severe impact on the world's food supply. The most serious problem regarding liquid biofuels is the demand for food crops such as corn, rapeseed oil, sugarcane, sugar beet and maize grows for biofuel production; it could also raise prices for necessary staple food crops. Massive quantities of water are required for proper irrigation of biofuel crops as well as to manufacture the fuel, which could strain local and regional water resources are also the serious impact. Conditions for economically viable biofuel resource are competitively low cost less than petroleum fuels; low to no additional land use; enable air quality improvement (e.g. CO2 sequesteration), and minimal water use. Judicious exploitation of microalgae could meet these conditions and therefore make a significant contribution to meeting the primary energy demand, while simultaneously providing environmental benefits (Wang et al., 2008).

Biofuels from microalgae

In this review, all unicellular and simple multi-cellular microorganisms, including both prokaryotic microalgae, that is,cyanobacteria (Chloroxybacteria), and eukaryotic microalgae, e.g. green algae (Chlorophyta), red algae (Rhodophyta) and diatoms (Bacillariophyta) comes in microalgae. The yield of oil productivity of microalgae cultures exceeds than the best oilseed crops, e.g. biodiesel yield of 12,000 liter per hactor for microalgae (open pond production) compared with 1190 liter per hectors for rapeseed (Schenk et al., 2008), and also they grow in aqueous media, but need less water than terrestrial crops therefore reducing the load on freshwater sources (Dismukes et al., 2008). Microalgae have a rapid growth potential and many species have oil content in the range of 20–50% dry weight of biomass, the exponential growth rates can double their biomass in periods as short as 3.5 h (Spolaore et al., 2006). Microalgae biomass production can effect biofixation of waste CO2 (1 kg of dry algal biomass utilize about 1.83 kg of CO2) (Chisti, 2007). The energy crisis and the world food crisis have ignited interest in alga culture (farming algae) for making biodiesel and other biofuels using land unsuitable for agriculture. Among algal fuels' attractive characteristics are that they can be grown with minimal impact on fresh water resources, can be produced using saline and waste water, have a high flash point, and are biodegradable and relatively harmless to the environment if spilled. Algae cost more per unit mass than other second-generation biofuel crops due to high capital and operating costs, but are claimed to yield between 10 and 100 times more fuel per unit area. The United States Department of Energy estimates that if algae fuel replaced all the petroleum fuel in the United States, it would require 15,000 square miles (39,000 km^2), which is only 0.42% of the U.S. map, or about half of the land area of Maine. This is less than $^1/_7$ the area of corn harvested in the United States in 2000 (Cantrell et al., 2008).

Nutrients for microalgae cultivation (especially nitrogen and phosphorus) can be obtained from wastewater, therefore, apart from providing growth medium, there is dual potential for treatment of organic effluent from the agricultural food industry. Algae cultivation does not require herbicides or pesticides application (Rodolfi et al., 2008); they can also produce valuable co-products such as proteins and residual biomass after oil extraction, which may be used as feed or fertilizer, or fermented to produce ethanol or methane (Hirano et al., 1997); the biochemical composition of the algal biomass can be modulated by varying growth conditions, therefore, the oil yield may be significantly enhanced (Qin, 2005). Microalgae are also capable of photobiological production of 'biohydrogen' (Ghirardi et al., 2000). The outlined combination of potential biofuel production, CO2 fixation, biohydrogen production, and bio-treatment of wastewater underscore the potential applications of microalgae.

Biology of microalgae

Algae are recognised as one of the oldest life-forms (Falkowski and Raven, 1997). Unlike higher plants, microalgae do not have roots, stems and leaves. Microalgae, capable of performing photosynthesis, are important for life on earth; they produce approximately half of the atmospheric oxygen and use simultaneously the greenhouse gas carbon dioxide to grow photoautotrophically. Prokaryotic cells (cyanobacteria) lack membrane-bound organelles (nuclei, Golgi bodies, plastids, mitochondria, and flagella). Eukaryotic cells, which comprise of several different types of common algae, do have these organelles that control the functions of the cell, allowing them to survive and reproduce. Eukaryotes are classified into a variety of classes mainly based on their pigmentation, life cycle and basic cellular structure (Khan et al., 2009). The most important classes are: green algae (Chlorophyta), red algae (Rhodophyta) and diatoms (Bacillariophyta). Algae can either be autotrophic or heterotrophic; the former

Table 1: Advantages and limitations of open ponds and photobioreactors (adapted from Brennan and Owende, 2009).

Production system	Advantages	Limitations
Raceway pond	Relatively cheap Easy to clean Utilises non-agricultural land Low energy inputs Easy maintenance	Poor biomass productivity Large area of land required Limited to a few strains of- algae Poor mixing, light and CO2- utilisation Cultures are easily contaminated
Tubular photobioreactor	Large illumination surface area Suitable for outdoor cultures Relatively cheap Good biomass productivities	Some degree of wall growth Fouling Requires large land space Gradients of pH, dissolved- oxygen and CO2 along- the tubes
Flat plate photobioreactor	High biomass productivities Easy to sterilize Low oxygen build-up Readily tempered Good light path Large illumination surface area Suitable for outdoor cultures	Difficult scale-up Difficult temperature control Small degree of hydrodynamic- stress Some degree of wall growth
Column photobioreactor	Compact High mass transfer Low energy consumption Good mixing with low shear stress Easy to sterilize Reduced photoinhibition and photo-oxidation	Small illumination area Expensive compared to open- ponds Shear stress Sophisticated construction

require only inorganic compounds such as CO_2, salts and a light energy source for growth; while the latter are nonphotosynthetic therefore require an external source of organic compounds as well as nutrients as an energy source. Some photosynthetic algae are mixotrophic, that is, they have the ability to both perform photosynthesis and acquire exogenous organic nutrients (Lee, 1980). For autotrophic algae, photosynthesis is a key component of their survival, whereby they convert solar radiation and CO_2 absorbed by chloroplasts into adenosine triphosphate (ATP) and O_2 the usable energy currency at cellular level, which is then used in respiration to produce energy to support growth (Zilinskas et al., 1974).

Technologies for microalgal biomass production

The use of natural conditions for commercial algae production has the advantage of using sunlight as a free natural resource (Janssen et al., 2003). However, this may be limited by available sunlight due to diurnal cycles and the seasonal variations; thereby limiting the viability of commercial production to areas with high solar radiation. For outdoor algae production systems, light is generally the limiting factor (Pulz and Scheinbenbogan, 1997). Artificial lighting allows for continuous production, but at significantly higher energy input. Frequently the electricity supply for artificial lighting is derived from fossil fuels thus negating the primary aim of developing a price-competitive fuel and increasing the systems carbon footprint. This review considers three distinct algae production mechanisms, including photoautotrophic, heterotrophic and mixotrophic production, all of which follow the natural growth processes.

Photoautotrophic production

Photoautotrophic production is autotrophic photosynthesis; heterotrophic production requires organic substances (e.g. glucose) to stimulate growth, while some algae strains can combine autotrophic photosynthesis and heterotrophic assimilation of organic compounds in a mixotrophic process. Currently, photoautotrophic production is the only method which is technically and economically feasible for large-scale production of algae biomass for non-energy production (Borowitzka, 1999). Two systems that have been deployed are based on open pond and closed photobioreactor technologies (Borowitzka, 2007). The technical viability of each system is influenced by intrinsic properties of the selected algae strain used, as well as climatic conditions and the costs of land and water (Borowitzka, 1992). Algae cultivation in open pond production systems have been used since the 1950s. Open pond is the cheaper method of large-scale algal biomass production. Open pond production does not necessarily compete for land with existing agricultural crops, since they can be implemented in areas with marginal crop production potential (Chisti, 2008). They also have lower energy input requirement. In respect to biomass productivity, open pond systems are less efficient when compared with closed photobioreactors. This can be attributed to several determining factors, including, evaporation losses, and temperature fluctuation in the growth media, CO_2 deficiencies, inefficient mixing, and light limitation (Brennan and Owende, 2009, Table 1). Microalgae production based on closed photobioreactor technology is designed to overcome some of the major problems associated with

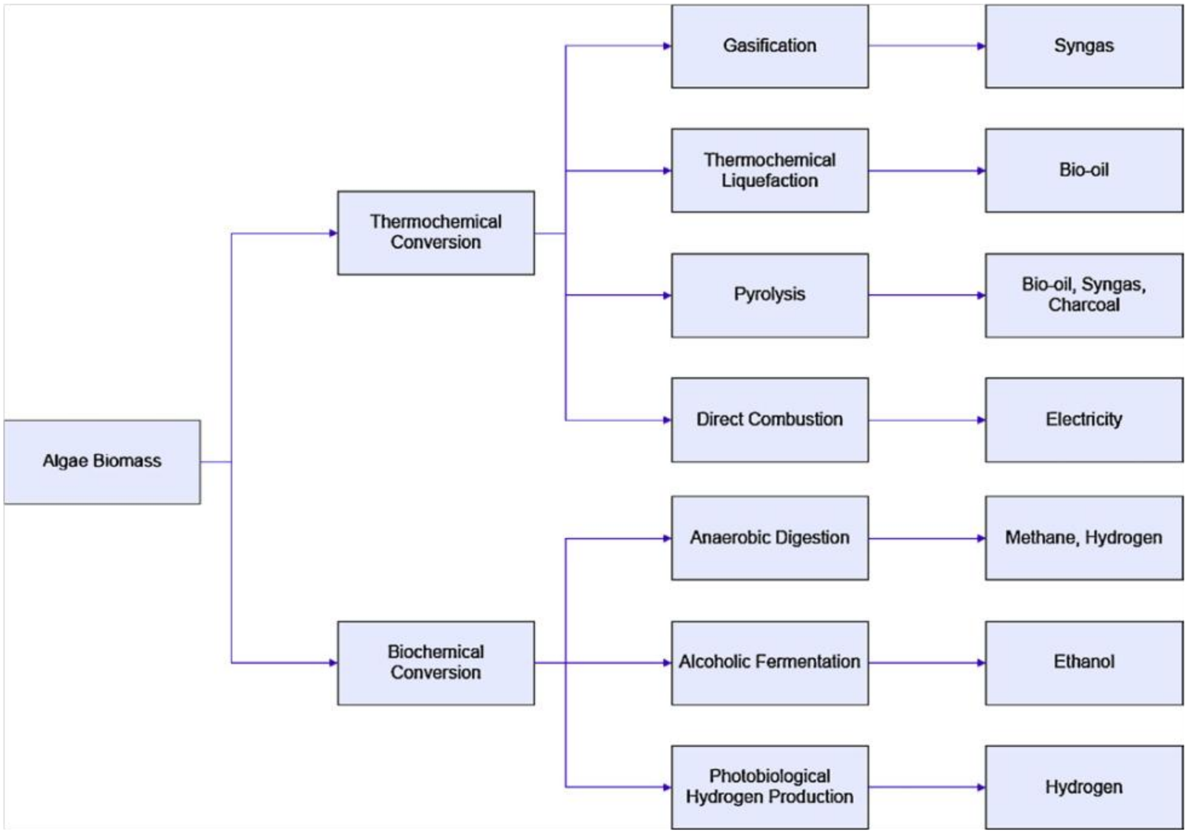

Figure 2: Potential algal biomass conversion processes (adapted from Tsukahara and Sawayama (Weissman and Tillett, 1992)

the described open pond production systems. For example, pollution and contamination risks with open pond systems, for the most part, preclude their use for the preparation of high-value products for use in the pharmaceutical and cosmetics industry (Ugwu et al., 2008).

Heterotrophic and Mixotrophic production

Heterotrophic production has also been successfully used for algal biomass and metabolites (Miao and Wu, 2006; Chen et al., 1996). In this process microalgae are grown on organic carbon substrates such as glucose in stirred tank bioreactors or fermenters. Algae growth is independent of light energy, which allows for much simpler scale-up possibilities since smaller reactor surface to volume ratio's may be used (Eriksen, 1998). These systems provide a high degree of growth control and also lower harvesting costs due to the higher cell densities achieved (Chen and Chen, 2006). The set-up costs are minimal, although the system uses more energy than the production of photosynthetic microalgae because the process cycle includes the initial production of organic carbon sources via the photosynthesis process. Many algal organisms are capable of using either metabolism process (autotrophic or heterotrophic) for growth, meaning that they are able to photosynthesise as well as ingest prey or organic materials (Graham et al., 2009; Zhang et al., 1999). The ability of mixotrophs to process organic substrates means that cell growth is not strictly dependent on photosynthesis, therefore light energy is not an absolutely limiting factor for growth (Andrade and Costa, 2007) as either light or organic carbon substrates can support the growth.

Algal biofuels conversion technologies

In this section, the technically viable conversion options for algal biomass and end-use of derived energy or energy carriers (liquid or gaseous fuels) are considered. The conversion of algal biomass-to-energy encompasses the different processes ordinarily used for terrestrial biomass and which depend, to a large extent, on the types and sources of biomass, conservation options and endues (Lee, 2001). The conversion technologies for utilising microalgae biomass can be separated into two basic categories of thermochemical and biochemical conversion (Figure 2). Factors that influence choice of conversion process include: the type

Table 2: Potential of microalgae as primary PUFA resources.

PUFA	Potential application	Microalgal producer
Docosahexaenoic acid (DHA)	Infant formulas; Nutritional supplements; Aquaculture	Crypthecodinium, Schizochytrium
Eicosapentaenoic acid (EPA)	Nutritional supplements; Aquaculture	Nannochloropsis, Phaeodactylum, Nitzschia, Pavlova
g-Linolenic acid (GLA)	Infant formulas; Nutritional supplements	Spirulina
Arachidonic acid (AA)	Infant formulas; Nutritional supplements	Porphyridium

and quantity of biomass feedstock; the desired form of the energy; economic consideration; project specific; and the desired end form of the product (Setlik et al., 1970).

Thermochemical conversion

Thermochemical conversion covers the thermal decomposition of organic components in biomass to yield fuel products, and is achievable by different processes such as direct combustion, gasification, thermochemical liquefaction, and pyrolysis (Tsukahara and Sawayama, 2005). Gasification involves the partial oxidation of biomass into a combustible gas mixture at high temperatures (800–1000 ˚C) (Samson and Leduy, 1985). In the normal gasification process, the biomass reacts with oxygen and water (steam) to generate syngas. Thermochemical liquefaction is a process that can be employed to convert wet algal biomass material into liquid fuel [43]. Thermochemical liquefaction is a low-temperature (300–350 ˚C), high pressure (5–20 MPa) process aided by a catalyst in the presence of hydrogen to yield bio-oil. Pyrolysis is the conversion of biomass to bio-oil, syngas and charcoal at medium to high temperatures (350–700 ˚C) in the absence of air [44]. For biomass-to-liquid fuel conversion, it is deemed to have the potential for large scale production of biofuels that could replace petroleum based liquid fuel [45]. In a direct combustion process, biomass is burnt in the presence of air to convert the stored chemical energy in biomass into hot gases, usually in a furnace, boiler, or steam turbine at temperatures above 800 ˚C.

Biochemical conversion

The biological process of energy conversion of biomass into other fuels includes anaerobic digestion, alcoholic fermentation and photobiological hydrogen production (Sanchez Miro´n et al., 2002). Anaerobic digestion (AD) is the conversion of organic wastes into a biogas, which consists of primarily methane (CH4) and carbon dioxide, with traces of other gases such as hydrogen sulphide (Huntley and Redalje, 2007). It involves the breakdown of organic matter to produce a gas with an energy content of about 20–40% of the lower heating value of the feedstock. Anaerobic digestion process is appropriate for high moisture content (80–90% moisture) organic wastes, which can be useful for wet algal biomass. Alcoholic fermentation is the conversion of biomass materials which contain sugars, starch or cellulose into ethanol. The biomass is ground down and the starch is converted to sugars which is then mixed with water and yeast and kept warm in large tanks called fermenters. The yeast breaks down the sugar and converts it to ethanol. Photobiological hydrogen production is also one of the technologies for the algal biomass conversion.

Other applications of microalgae

The commercial potential for microalgae represents a largely untapped resource. Microalgae use as human nutrition, also used for medicinal value such as protection against renal failure and growth promotion of intestinal lactobacillus (Yamaguchi, 1992). Specific algal species are suitable for preparation of animal feed supplements. Algae species such as Chlorella, Scenedesmus and Spirulina have beneficial aspects including improved immune response, improved fertility, better weight control, healthier skin and a lustrous coat (Pulz and Gross, 2004). Microalgae as source of polyunsaturated fatty acids (PUFAs) are essential for human development and physiology (Hu et al., 2008). Among other things, PUFAs have been proven to reduce the risk of cardiovascular disease (Anonymous, 2004; Ruxton et al., 2007). Microalgal recombinant proteins extracts include b-carotene, astaxanthin, and C-phycocyanin (C-PC). The carotenoid b-carotene has a wide range of applications Table 2. It can be used as a food colouring agent, a source of pro-vitamin A and as a additive to cosmetics (Garcia-Gonzalez et al., 2005). The carotenoid astaxanthin has potential applications in the nutraceuticals, cosmetics, food and feed industries (Guerin et al., 2003). It is a potent antioxidant (Waldenstedt et al., 2003) and has possible roles in human health such as UV-light protection, immune enhancement, hormone precursor, pro-vitamin A source and for anti-inflammation (Lorenz and Cysewski, 2000).

CONCLUSIONS

This review demonstrates the existing technical viability for the development of biofuels from microalgae as a renewable energy resource and for mitigation of GHG related impacts of petroleum derived fuels. The achievable high yields for both lipids and biomass, combined with some useful co-products if purposefully exploited, could enhance algae's economic viability as a source for biofuels. Phototrophic production is the most effective in terms of net energy balance. However, productivity values vary immensely and are significantly lower when compared with heterotrophic production. Overall, the technical viability of a production system hinges on the intrinsic properties of the selected algae strain, indicating a need for greater species screening, as well as research on culture conditions and production systems. Bio-mitigation of CO2 emissions with microalgae provides a complementary function that may be exploited to moderate the cost of biofuels production. The use of waste CO2 from power plants to enhance production has been shown to be technically feasible, and hence, may be deployed to reduce production costs and for GHG emission control. Harvesting of algal biomass accounts for the highest proportion of energy input during production, but currently, there are no standard harvesting techniques. Adaptation of technologies already in use in the food, biopharmaceutical and wastewater treatment sector may provide possible solutions. Lipids are the most readily extractible biofuel feedstock from algae, but potential storage is hindered by the presence of polyunsaturated fatty acids (PUFAs) causing oxidation reactions and high moisture content of algal feedstock. This review also suggests that both thermochemical liquefaction and pyrolysis appear to be the most technically feasible methods for conversion of algal biomass-to-biofuels, after the extraction of oils from algae.

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