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BIOFUEL PRODUCTION FROM ALGAE THROUGH INTEGRATED BIOREFINERY

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1. Introduction

Today, all over the world, energy crisis and environmental issues are the most important concern. It is projected that world energy demand will continue to expand by 45% from 2008 to 2030, an average rate of increase in 1.6%/year (World Energy Outlook, 2008). Nearly 81% of the energy supply is from fossil fuels, followed by 16% renewable energy and 2.8% nuclear energy (Fig. 1). Use of fossil fuels as energy is unsustainable due to depleting resources and the accumulation of greenhouse gases in the environment (Demirbas, 2010). Another problem is their uneven distribution in the world where 63% of the global petroleum fuel resources are located in the Middle East with equity, environmental, economic and geopolitical implications (Hacisalihoglu et al., 2009). Biomass-based energy can serve as an alternative energy source to meet the present and future demand, including transportation fuel, although presently only about 0.6% of transportation fuel are supplied as biofuels.

Biofuels include use of solid biomass, biohydrogen, biogas and liquid fuels such as bioethanol and biodiesel. Biological hydrogen production is still in an incipient phase; therefore, the most commonly used biofuels, aside from the burning of solid biomass, are biogas, biodiesel and bioethanol. According to Global Status Report Renewable-2011, about 86 billion litres of bioethanol and 19 billion litres of biodiesel were produced in 2010 compared to 17 billion litres of bioethanol and 0.8 billion litres of biodiesel produced in 2000 (Fig. 2). The USA is the biggest producer of biofuel, followed by Brazil and Germany (Fig. 3). Based on the source of feedstocks, liquid biofuels can be classified into four generations: First-generation biofuels are produced from food crops such as sugar cane, soybeans, cassava, potatoes, maize, etc., and animal fats; second-generation biofuels derived from non-food crops such as *Jatropha*, tobacco, *Miscanthus*, switch grass, wood, wheat straw, waste fruit pulp, etc.; third-generation biofuel from algae; and fourth-generation biofuel from genetically engineered organisms (Demirbas, 2011). In this chapter, we discuss various aspects of algal biofuel production through an integrated biorefinery approach.

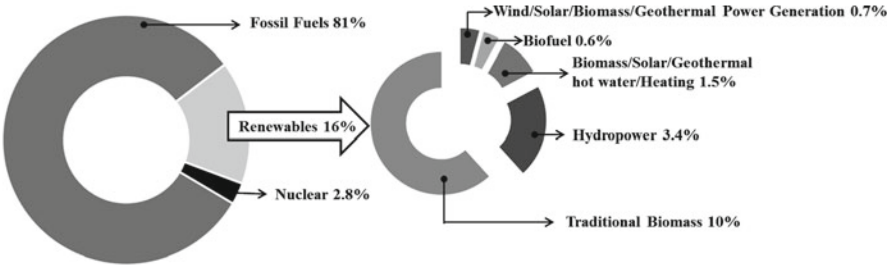

Figure 1. Global energy consumption (Renewables 2011-Global Status Report).

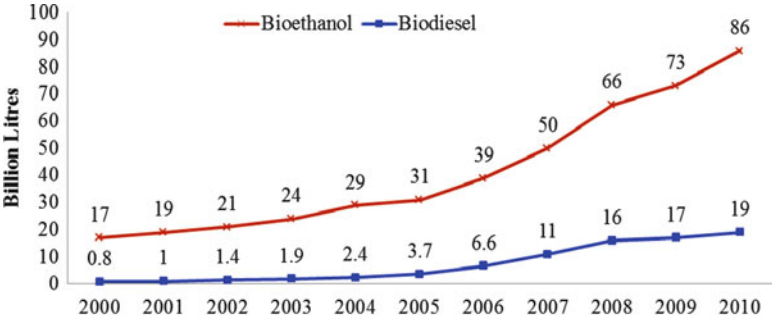

Figure 2. Bioethanol and biodiesel production, 2000–2010 (Courtesy F.O.Licht, Renewables 2011-Global Status Report).

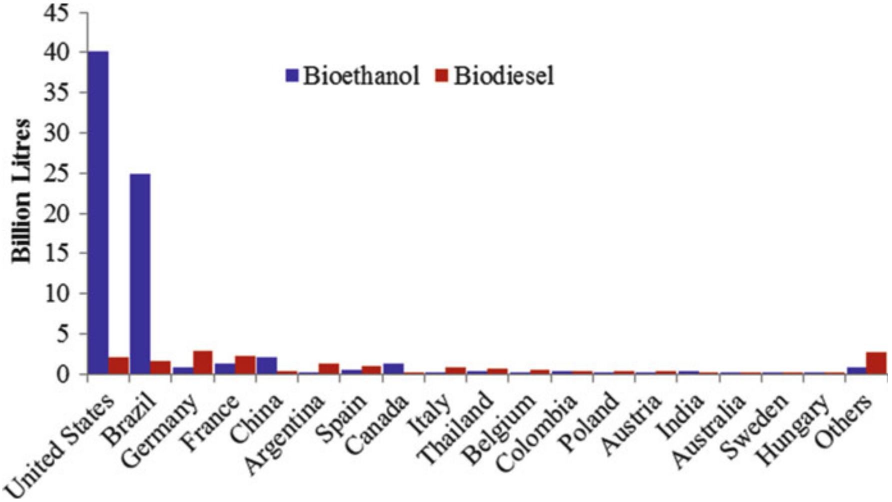

Figure 3. Top 20 bioethanol and biodiesel producer in the world (Reproduced from Biofuels Platform, 2010).

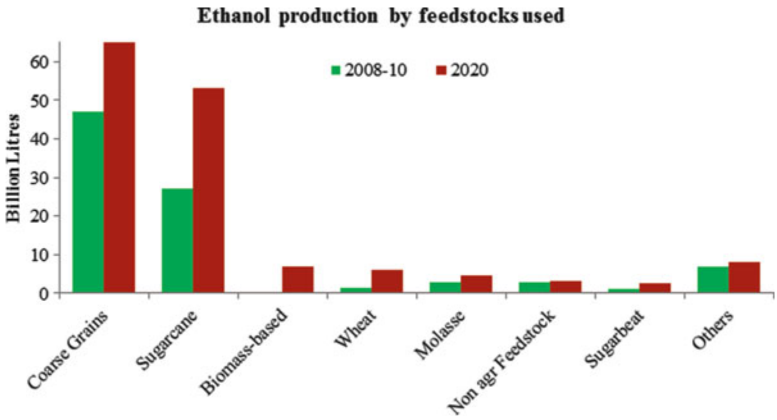

Figure 4. Bioethanol production from various feedstocks (Courtesy Biofuels-OECD-FAO Agricultural Outlook 2011–2020).

1.1. BIOETHANOL

Ethanol is a high-octane fuel which can be used in various combinations with petrol or gasoline such as E10 or E85 containing 10 and 85% ethanol, respectively. When blended with fossil fuel, bioethanol reduces cancer-causing compounds such as benzene, toluene, xylene and ethyl benzene. Bioethanol can be produced either from sugar, starch or lignocellulosic biomass. Sugar can be directly converted into bioethanol by yeast fermentation, whereas starch first needs to be converted to simple sugar like glucose, through a process called saccharification, before being fermented to ethanol. Production of ethanol from lignocellulosic materials is a more complex process, which is not yet at a commercial stage. Various feedstocks such as sugar cane, corn, cereal grains, potato, sweet potato, cassava and other plant materials are being used for the production of bioethanol all over the world (Fig. 4). World ethanol market is projected to reach around 105 billion litres in 2012 (Martin et al., 2010).

1.2. BIODIESEL

Biodiesel is defined as the monoalkyl esters of vegetable oil and animal fats (ASTM, 2008) and is produced by the transesterification of triglyceride with monohydric alcohols. Biodiesel is generally similar to petroleum-derived diesel in its main characteristics such as cetane number, energy content, viscosity and phase changes (Lin and Teong, 2010) and can be blended in any proportion with fossil-based diesel. Therefore, biodiesel has become the most common liquid biofuel in the world after ethanol. Biodiesel are mainly produced from vegetable oil such as,

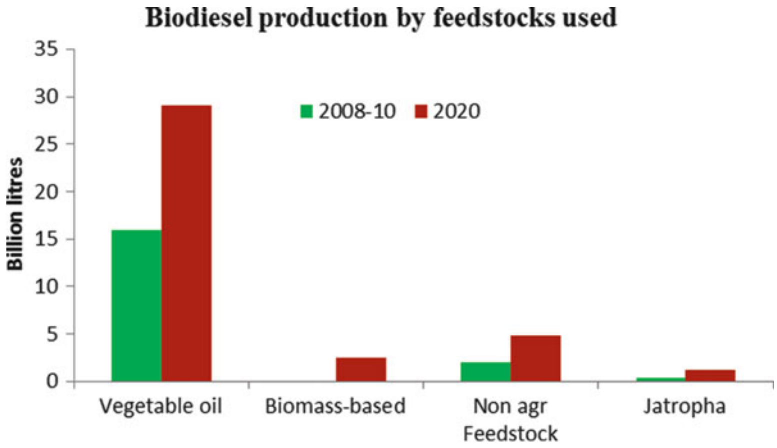

Figure 5. Biodiesel production from various feedstocks (Courtesy Biofuels-OECD-FAO Agricultural Outlook 2011–2020).

soybean, palm, sunflower oil, followed by biomass-based and non-agricultural feedstock (Demirbas, 2009), (Fig. 5). Huang et al. (2010) claim that biodiesel use can decrease by 90% air toxicity and by 95% cancers resulting from fossil diesel use.

2. Need for Alternative Feedstock for Biofuel

Biofuels offer a potential source of renewable energy and possibly large new markets for agricultural producers. But current biofuel programmes are unsustainable from environmental, economic and societal standpoints. The use of corn, sugar cane and vegetable oil has driven the food versus fuels debate because these feedstocks are components of the human food chain (Mata et al., 2010). Large-scale production of biofuels from crop plants usually damages the environment by the use of harmful pesticides and fertiliser, mostly nitrogen, which reduces the fertility of the soil (Fig. 6). Martin et al. (2010) discussed the repercussion of excessive use of agricultural land and water (Table 1). Water requirements also depend on the geographic, climatic variables and type of feedstock used.

3. Algae for Biofuel Production

Algae a novel biofuel feedstocks have several potential advantages including higher area productivity than traditional crops (Posten and Schaub, 2009; Sahoo, 2010), no competition with conventional agricultural land and utilisation of different water sources (e.g. seawater, brackish water and wastewater). Terrestrial plants in

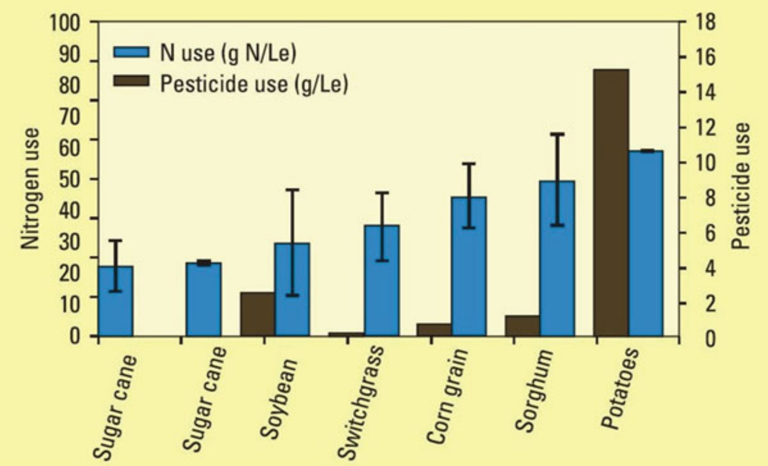

Figure 6. Use of nitrogen and pesticides for various biofuel feedstocks (Courtesy Faus et al., 2009).

Table 1. Water footprint, energy consumption and biofuel production (Courtesy Singh et al., 2011).

	Plant	**Water footprint (m^3 GJ^{-1})**	**Land use (m^3 GJ^{-1})**	**Energy (GJ $ha^{-1}a^{-1}$)**	**Biofuel yield (L $ha^{-1}a^{-1}$)**
Bioethanol	Cassava	148	79	126	6,000
	Wheat	93	305	33	1,560
	Paddy rice	85	212	47	2,250
	Corn grain	50	133	75	3,571
	Potatoes	105	114	88	4,167
	Sugar cane	50	81	124	5,882
	Sugar beet	46	95	105	5,000
	Sorghum	180	386	26	1,235
	Soybean	383	386	26	1,235
Biodiesel	Soybean	383	689	15	446
	Jatropha	396	162	62	1,896
	Rapeseed	383	258	39	1,190
	Cotton	135	945	11	325
	Sunflower	61	323	31	951
	Oil palm	75	52	192	5,906
	Coconut	49	128	78	2,399
	Groundnut	58	220	45	1,396
	Microalgae	<379	2–13	793–4,457	24,355–136,886

temperate climates can presently achieve a photo conversion efficiency of only about 1%, while microalgae might in the future convert up to 5% of the solar energy into chemical energy (Schenk et al., 2008). Several microalgae such as *Botryococcus, Scenedesmus, Chlorococcum* and *Chlorella* contain significant

Table 2. Biochemical composition of some biofuel feedstock.

	Plant	Carbohydrate	Protein	Lipid	References
	Soybean	25.4	46.7	21.2	Nikolić and Lazić (2011)
Crop plants	*Jatropha*	30.11	32.88	27.36	Azza and Abu-Salem (2010)
	Rapeseed	NA	NA	40–48	Carioca et al. (2009)
	Castor	NA	NA	43–45	Carioca et al. (2009)
	Palm Oil	0.4	0	99.6	Atchley (1984)
	Sugarcane, bagasse	75–80	1.5–2	<1	Han et al. (1983)
	Maize	66–76	5–13	NA	FAO (1993)
	Cassava	80–85	1–2	Trace	Charles et al. (2005)
	Sorghum	65–72	9–13	3–4	Neucere and Sumrell (1980)
Seaweeds	*Caulerpa lentillifera*	44–46	11–12	1–2	Matanjun et al. (2009)
	Ulva lactuca	70	7.06	1.64	Wong and Cheung, 2000
	Eucheuma cottonii	35–36	10–12	1–2	Matanjun et al. (2009)
	Gracilaria cervicornis	63	19.7	0.427	Marinho-soriano et al. (2006)
	Hypnea japonica	57.4	19	1.42	Wong and Cheung (2000)
	Sargassum vulgare	61	13.6	0.491	Marinho-soriano et al. (2006)
	Laminaria hyperborea	50–52	8.9	<1	Horn (2000)
	Ascophyllum nodosum	45–55	4.8–9.8	1–5	Horn (2000)
Microalgae	*Botryococcus braunii*	2	40	33	Eduardo et al. (2010)
	Prymnesium parvum	25–33	28–45	22–38	Singh et al., 2011
	Isochrysis sp.	15–5	29.5	23.4	Renaud et al. (1999)
	Scenedesmus dimorphus	21–52	8–18	16–40	Demirbas (2010)
	Chlorella vulgaris	12–17	51–58	14–22	Demirbas (2010)
	Porphyridium cruentum	40–57	28–39	9–14	Demirbas (2010)
	Spirogyra sp.	33–64	6–20	11–21	Demirbas (2010)

amount of lipids, whereas macroalgae such as *Sargassum, Laminaria, Ascophyllum, Gracilaria* and *Kappaphycus* are higher in their carbohydrate contents which make them possible feedstocks for biodiesel and bioethanol production, respectively (Table 2), (Fig. 7a–d). The use of algae for biofuel was investigated in the USA and Japan as an alternative energy source from the 1970s to 1990s after the oil crisis, but the studies were discontinued when oil prices stabilised (Yokoyama et al., 2007).

3.1. SEAWEEDS FOR BIOETHANOL

Marine macroalgae (seaweeds) lack lignin but contain high amount of carbohydrates which makes them potentially suitable feedstock for the production of bioethanol. The cell wall of algae consists of various forms of complex carbohydrates such as cellulose, hemicellulose, agar, alginate, carrageenan, fucoidan (Kloareg et al., 1986; Goh and Lee, 2010), the latter four being extracted and used in food, personal care products and some industrial applications (Sahoo, 2000). Seaweed industrial wastes, i.e. the remaining pulp after extraction of the high value

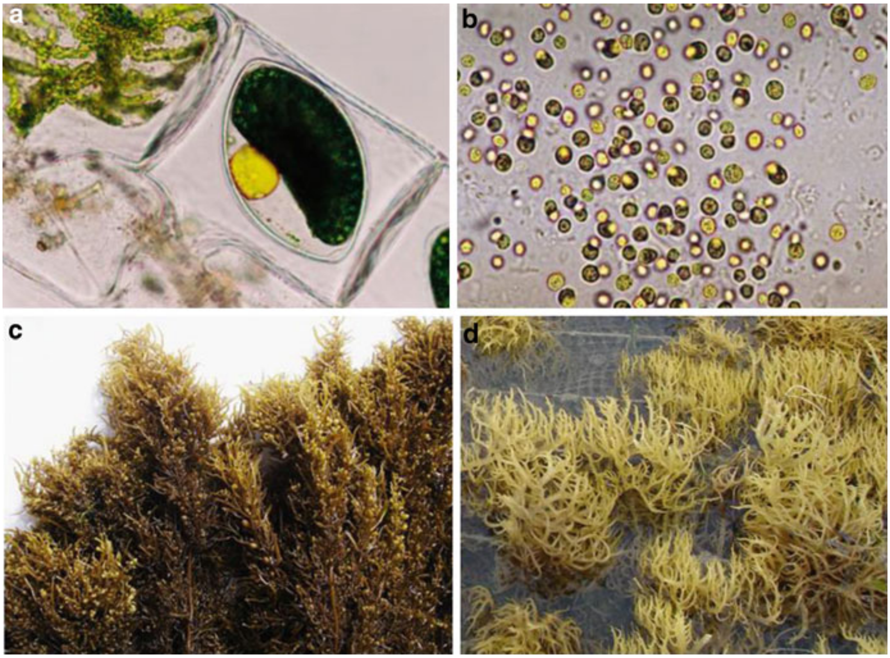

Figure 7. (**a**–**d**) Some of the potential algal species for biofuel production. (**a**) *Spirogyra* sp. showing oil droplets inside the cell, (**b**) *Chlorella* sp. showing accumulation of lipid in the cells, (**c**) *Sargassum* sp. and (**d**) *Kappaphycus* sp. under cultivation.

polysaccharides, still contain high amount of carbohydrate which may be used as a source of raw material for ethanol production (Kumar and Sahoo, 2012). It will also reduce organic load from sea which was washed and deposed into the sea during phycocolloids extraction process (Ge et al., 2011). Utilisations of seaweeds for bioethanol production are only of economic interest when integrated with a utilisation of the higher value components. Seaweeds and waste products can also be used for biogas production through anaerobic digestion (Gunaseelan, 1997).

3.2. PROCESSING OF SEAWEEDS BIOMASS FOR BIOETHANOL PRODUCTION

Seaweed phycocolloids can be converted into bioethanol, but direct use of these phycocolloids for bioethanol production will not be cost-effective. So, after the extraction of phycocolloids, the remaining pulp can be used for bioethanol production.

Since the pulp contains high amount of carbohydrate and other organic materials, these can be converted into bioethanol through saccharification and fermentation. *Saccharomyces cerevisiae*, a common yeast, and *Zymomonas mobilis,* a bacterium, are the two most important microorganisms used for bioethanol production (Dumsday et al., 1997), but they have a very narrow substrate range. However, *Pichia angophorae* is a more suitable organism for ethanol production from seaweed extract. It can utilise both substrates, mannitol as well as laminaran, simultaneously (Horn et al., 2000).

Apart from alginate, agar and carrageenan, the cell wall of algae also contains cellulose, fucoidan and protein. Anaerobic degradation of fucoidan has not been reported (Forro, 1987), and algal proteins have been reported to have a low digestibility (Michel et al., 1996). This may be due to their cellular localisation or their putative associations with cell wall polysaccharides (Kloareg and Quatrano, 1988). Presence of polyphenols and salt (Ghosh et al., 1981) reduces the biodegradability of algae. For most algae, aspartic and glutamic acids constitute together a large part of the amino acid fraction (Fleurence, 1999). Degradation of cellulose is catalysed by cellulases and occurs both under aerobic and anaerobic conditions. A combined enzymatic attack of agarases, alginate lyases, proteases and cellulases may be necessary to degrade the algal cell wall, as seen in the case of protoplast isolation (Butler et al., 1989).

3.3. MICROALGAE FOR BIODIESEL

Microalgae appear to be one of the important sources to capture solar energy as they are sunlight-driven cell factories that convert carbon dioxide to potential biofuel, food, feeds and high bioactive compounds (Metting and Pyne, 1986; Spolaore et al., 2006). Some species of microalgae contain much higher percentage of oil than conventional oil crops (Table 3). Microalgae can duplicate their biomass in less than 7 days, whereas higher plants take many months or years (Vonshak et al., 1982). Another advantage of microalgae is that their chemical composition can be manipulated by altering the growth environment of the algal species. Carbon dioxide emitted from combustion processes such as power plant, cement plant, steel plant, etc., can be used as a source of carbon for algal growth (Sahoo et al., 2012). Microalgae can be cultivated in seawater or brackish water, raceway ponds on non-arable land and do not compete for resources with conventional agriculture. Microalgal biomass can be harvested during all seasons. Studies on screening of potential microalgae for biodiesel have been reported (Devi, 2008; Devi et al., 2009), but the actual production of biodiesel from microalgae is only in incipient phase.

3.4. PROCESSING OF MICROALGAL BIOMASS FOR BIODIESEL PRODUCTION

The recovery of microalgal biomass requires processes such as dewatering, disruption of the microalgae cells and extraction of the oil fraction. Dewatering mechanisms can be grouped as physical (e.g. centrifugation, spray drying and

Table 3. Comparison of microalgae with other biodiesel feedstocks (Courtesy Mata et al., 2010).

Plant source	Seed oil content (% oil by in biomass)	Oil yield (L oil/ha year)	Land use (m^2 year/kg biodiesel)	Biodiesel productivity (kg biodiesel/ha year)
Corn/maize (*Zea mays* L.)	44	172	66	152
Hemp (*Cannabis sativa* L.)	33	363	31	321
Soybean (*Glycine max* L.)	18	636	18	562
Jatropha (*Jatropha curcas* L.)	28	741	15	656
Camelina (*Camelina sativa* L.)	42	915	12	809
Canola/rapeseed (*Brassica napus* L.)	41	974	12	862
Sunflower (*Helianthus annuus* L.)	40	1,070	11	946
Castor (*Ricinus communis*)	48	1,307	9	1,156
Palm oil (*Elaeis guineensis*)	36	5,366	2	4,747
Microalgae (low oil content)	30	58,700	0.2	51,927
Microalgae (medium oil content)	50	97,800	0.1	86,515
Microalgae (high oil content)	70	136,900	0.1	121,104

filtration), biological (e.g. auto flocculation) or chemical (e.g. alum flocculants). Mechanisms of cell disruption and extraction include grinding, direct solvent extraction, explosive decompression, freeze-drying and supercritical fluids amongst others.

3.4.1. Flocculation

Microalgae are very small so they are very difficult to harvest. Flocculation is the process where the microalgal cells are aggregated in order to increase the particle size. Some flocculating agents such as alum, ferric chloride, ammonium sulphate, ferric sulphate, (Brennan and Owende, 2010) polyacrylamide polymers, (Lee et al., 2009) surfactants, chitosan and other man-made fibres are normally used as flocculating agents (Divakaran and Pillai, 2002).

3.4.2. Filtration

Filtration is another very simple method for harvesting of microalgae. But this method depends largely on the microalgal sizes. During filtration, the pore size of the filter depends on the size of the microalgae and the aggregation rate of microalgae. Culture purity is also important while choosing the filter pore size.

3.4.3. Centrifugation

Centrifugation is also widely used for the harvesting of microalgal biomass. The process is rapid and energy intensive, and biomass recovery depends on the settling characteristics of the cells which are again depending on the density and the radius of the microalgal cells and sedimentation velocity (Brennan and Owende, 2010).

3.4.4. Drying

The harvested microalgal biomass must be processed rapidly for drying. There are various methods for drying which include sun-drying, low-pressure shelf drying, drum drying (Prakash et al., 1997), spray drying (Desmorieux and Decaen, 2006), fluidised bed drying (Leach et al., 1998), freeze-drying (Grima et al., 1994) and Refractance Window™ technology drying (Nindo and Tang, 2007). Sun-drying is the cheapest drying method, but it takes long time to dry, and a large drying surface is required. Spray drying is commonly used for extraction of high value products, but it is relatively expensive and can cause significant deterioration of some algal pigments. Freeze-drying is also an expensive method.

3.4.5. Disruption of Microalgal Biomass

Alternatively to drying, oil can be extracted from wet algal biomass. For this, the algal cells must be broken, or lysed, to extract the oil. Some of the disruption methods for cell rupture include osmotic shock, explosive decompression, mechanical press and mechanical and biological shear. Interestingly, some microalgae degrade through the shearing action of the pumps used in bioreactors, so mechanical shear may also be an option (Shields et al., 2008).

3.4.6. Oil Extraction

Once the cell is ruptured, the lipid fraction, consisting of fatty acids and glycerol, needs to be separated from the remaining cell contents. This can be done by solvent or some other extraction process. Biodiesel is then produce by transesterification in which triglycerides are reacted with methanol to yield glycerol and methyl esters of fatty acids (Mata et al., 2010).

4. Algal Biorefinery for Biofuel Production

According to International Energy Agency (2008), “biorefining is a sustainable processing of biomass into a spectrum of marketable products and energy such as biofuel”. A biorefinery is a network of facilities that integrates biomass conversion processes and equipment to produce transportation biofuels, power and chemicals from biomass. This concept is analogous to today’s petroleum refinery, which produces multiple fuels and products from petroleum (Cherubini, 2010).

Production of food and fuel is complexly adjoined. Sustainable production of food and fuel is crucial in a carbon-smart society. Integration of the emerging biorefinery concept with other industries in many environmental deliverables while mitigating several sustainability-related issues with respect to greenhouse gas emissions, fossil fuel usage and land use changes for fuel production and future food insufficiency (Subhadra and Grinson-George, 2011).

Production of biofuel from both micro and macro algae is capital intensive energy consuming which involves various chemical and physical processes. Therefore, production of only biofuels from algal biomass will not be cost-effective and environment friendly. Therefore, it is important to produce biofuel

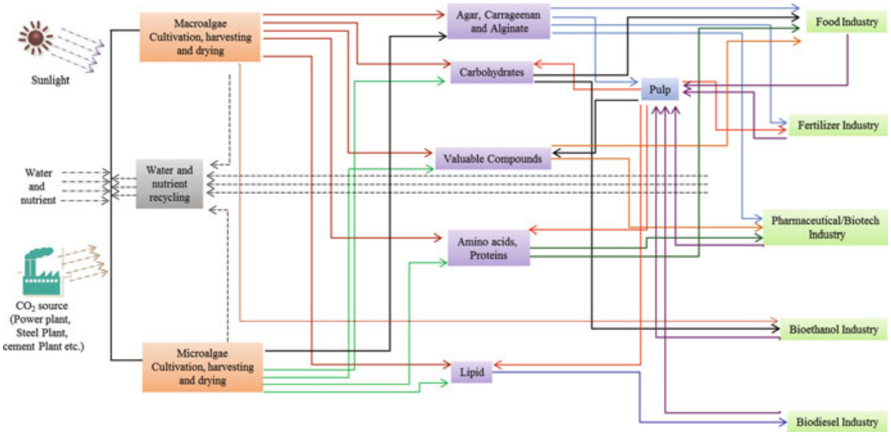

Figure 8. Schematic representation of integrated biorefinery concept.

as co-products along with other by-products through an integrated system of biorefinery approach.

The present biorefinery concept (Fig. 8) emphasises large-scale cultivation of algal biomass (both micro- and macroalgae) and their on-site processing for production of biofuel and other co-products. The most important energy products which can be produced in algal biorefineries are liquid biofuels which include bioethanol, biodiesel, etc. The most important biomass products in algal biorefineries are:

- Biomass – health food, functional food, feed additive, aquaculture, biofertiliser
- Phycocolloids – agar, carrageenan, alginates
- Pigments/carotenoids – astaxanthin, phycocyanin, phycoerythrin, fucoxanthin,
- Vitamin – A, B1, B6, B12, C, E, biotin, riboflavin, nicotinic acid, pantothenate and folic acid
- Other/pharmaceuticals – antifungal, antimicrobial, antiviral, toxins, amino acids, proteins and sterols
- Antioxidants – β-carotene, tocopherol
- Antioxidant extracts – arachidonic acid (ARA polyunsaturated omega-6 fatty acid, docosahexaenoic acid) (DHA omega-3 fatty acid), PUFA extracts (polyunsaturated fatty acids)

Various products and by-products derived from integrated algal biorefinery can feed various industries such as pharmaceutical and food production sector (Subhadra and Grinson-George, 2011). In addition to the above-mentioned products and by-products, the following benefits are also associated with integrated algal biorefinery:

- Net energy gain
- Fulfilling a large portion of world food demand without affecting current food supply

- Can provide livelihood and employment to millions of people worldwide
- Environmental benefits in the form of carbon sequestration and nutrient recycling
- Minimum use of water, energy and land than other plant
- Prospect of setting up in wide range of water

5. Conclusion

Biofuels derived from oil crops, waste cooking oil and animal fats are carbon neutral alternatives to petroleum fuels. However, they cannot realistically satisfy even a small fraction of the existing demand for transport fuels. Therefore, the future of biofuels will depend on the accelerated diffusion of new technologies, with an appropriate and market-friendly regulatory environment. Biofuels from algae can become one of the alternative options for supplementing the petroleum-based fuel without affecting the human food chain and environment.

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