Life Cycle Assessment of Algal Biofuels

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1 Introduction

First-generation biofuels are produced directly from food crops (e.g., biodiesel from soybean or rapeseed and ethanol from corn or sugarcane) and have a number of associated problems. However, the most problematic issue with first-generation biofuels is the "fuel vs. food" controversy. Production of biofuels from crop plants has resulted in an increase in diversion of crops from the global food market towards biofuel generation and resultant escalation of food prices.

Second-generation biofuels have been developed to overcome the limitations of first-generation biofuels. They are produced from non-food crops, therefore eliminating the main problem with first-generation biofuels, but they can potentially cause large-scale land use and land cover changes as vast land area would be required for meeting the growing demand of biofuels. Land use changes have the potential to offset the greenhouse gas balance of second-generation biofuels. High water, fertilizer, and pesticide use are major concerns.

Biofuels from algae are among the third generation of biofuels and have several advantages over first- and second-generation biofuels including higher productivity over terrestrial counterparts. Research has shown that microalgae are comparatively more suited as feedstock for large-scale biofuel production than their terrestrial counterparts. Suitability of algae as biofuel feedstock is attributed to its (1) higher CO_2 assimilation rate and photosynthetic efficiency, (2) high lipid accumulation, (3) minimal competition with food crops, (4) minimal land use changes, (5) ease to cultivate and metabolically manipulate, and (6) ability to utilize wastewater and saline water for growth. Although algae offer immense potential for exploitation as a biofuel feedstock, cultivation of algae, concentration and harvesting of biomass, extraction of lipids, and processing of biomass to biofuel remain highly energy-intensive processes. It is necessary to estimate material and energy inputs and associated environmental impacts of algal biofuels based on the concept of LCA in order to determine its suitability over fossil fuels and biofuels from non-algal biomass.

2 Life Cycle Assessment (LCA)

As with most of the industrial products (including biofuels), the impact associated with only the end use of product does not give a true picture of its environmental performance as impacts associated with its production, transportation of extracted raw materials and end product to the point of use or distribution, and its final disposal into the environment may have negative impacts. Therefore, it is vital to also consider processes upstream of product use for their environmental performance in order to get a holistic view of the impacts. LCA has emerged as a tool of choice for assessing the environmental performance of a production chain, process, or policy throughout its life cycle—from extraction of raw materials, production of energy used to create the product, production of goods and services, transportation to the point of use or distribution system, product use, to its final disposal into the environment. LCA is a systematic set of procedures for compilation and examination of the inputs and releases of energy and materials and the associated cumulative environmental impacts directly attributable to the functioning of a product or process throughout its life cycle (i.e., consecutive and interlinked stages of a product or process system from the extraction of resources to its final use disposal). Thus, LCA provides a holistic and comprehensive evaluation of environmental burdens associated with a production system or service and can help avoid a narrow outlook on environmental concerns (Fig. 14.1).

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B. Singh et al. (eds.), *Algae and Environmental Sustainability*, Developments in Applied Phycology 7,
DOI 10.1007/978-81-322-2641-3_14

LCA is based on comparison of alternative products, products from alternative sources, or different production techniques in terms of their environmental benefits. LCA is mostly used to compare different processes, products, or services that deliver similar functions. However, LCA can also be used as an independent tool that can help identify hotspots in a production system (Gasafi et al. 2003). When comparing and selecting between different alternative options, LCA allows the decision-makers to select alternative options that are most environment friendly. LCA studies can scrutinize all of the steps based on inputs and outputs and thus allow us to identify major environmental burdens associated with individual steps and also highlight improvement opportunities to increase the environmental sustainability of the process system. Some stages of a product's life cycle may be more troublesome for the environment than the other and thus suggest stepwise improvement opportunities. A full LCA involves a "cradle-to-grave" approach which includes all of the stages of a product, process, or activity encompassing extraction of raw materials from the environment and its processing; manufacturing, transportation, and distribution; use, reuse, and maintenance; recycling; and final disposal into the environment. The basic principle behind LCA is based on the perspective that all stages of a product life cycle are interdependent and one operation or activity leads to the next.

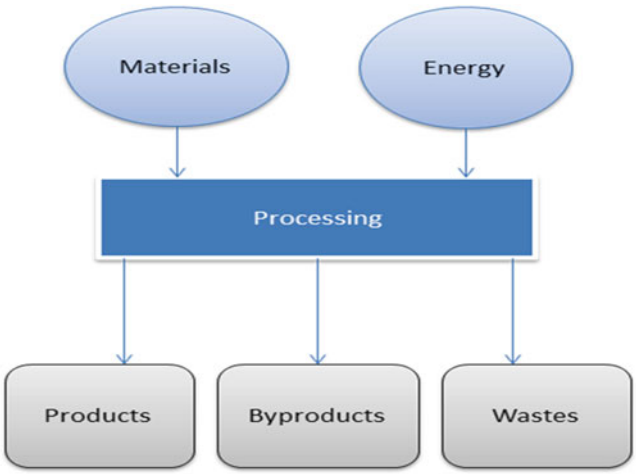

Fig. 14.1 General life cycle inputs and outputs

LCA enables managers to estimate the cumulative impacts resulting from all individual stages in a product life cycle, as it includes impacts usually not considered in traditional approaches of impact assessment such as raw material extraction, material transportation, product manufacturing, ultimate product disposal, etc. LCA therefore provides a comprehensive and analytical view of environmental aspects of the system and an accurate picture of the true environmental trade-offs in product and process systems.

LCA involves the following four types of activities in sequential order: (1) goal and scope definition of the LCA, (2) collection of life cycle inventory data on material and energy flow and environmental releases, (3) life cycle impact assessment based on inventory data, and (4) analysis of the major findings to support decision-making.

LCA can provide a comprehensive analysis of environmental impacts associated with a process or a production chain throughout its life cycle, but *data* and *knowledge* limitations imply that LCA entails selection of a "system boundary" that delineates processes included in the analysis versus those excluded which is usually based on a cut-off value. Cut-off criteria are often included in LCA studies for boundary delineation. For example, Sills et al. (2012) included life cycle inventory of all relevant energy and material inputs, with a 5 % cut- off for each unit process. Since LCA is a relative approach, it involves a reference system against which all of the products or processes delivering similar functions are compared to ascertain their environmental friendliness over alternatives. Biofuels are compared against their fossil fuel-based counterparts (e.g., petrol vs. ethanol, diesel vs. biodiesel, etc.).

There are four major algal biofuel LCA approaches, including (1) well-to-wheel approach in which cultivation of algae, harvesting of algal biomass, extraction of lipids, processing into biofuels to its end use, and disposal all are included in LCA inventory; (2) well-to-gate approach in which life cycle stages are limited up to biomass production only; (3) pump-to-wheel approach in which only the end use of the biofuel is included; and (4) well-to-pump approach in which LCA is limited to biofuel production and does not consider its end use and disposal (Fig. 14.2). LCA is structured around a functional unit which provides a reference to which all of the inputs and outputs are related. However, a

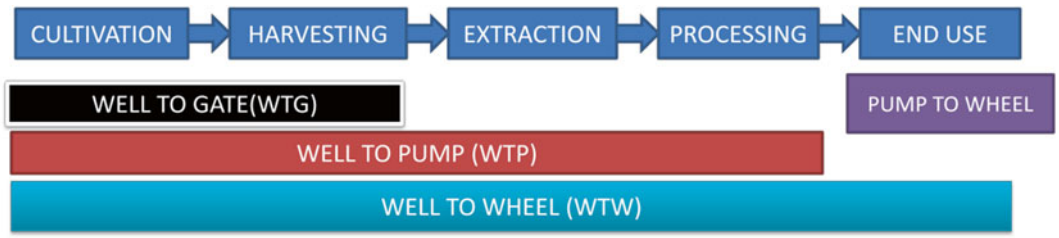

Fig. 14.2 Different LCA approaches for algal biofuels

variety of functional units exist which complicate the comparability among different studies. A diversity of functional units exist for a biofuel production system and may include volume of algal oil or biofuel produced (e.g., 1 L of biofuel), mass (e.g., 1 kg of biofuel or biomass produced), energy content of product (e.g., 1 MJ of biodiesel), energy released upon combustion (e.g., combustion of 1 MJ of methane), distance traveled (e.g., 10 km of traveling), etc. All of the inputs and outputs are compared against the functional unit such as energy required for producing 1 L of biodiesel or amount of greenhouse gasses (GHGs) released per liter of biodiesel produced.

Due to the absence of any large-scale industrial system dedicated to biofuel production, real-life data are unavailable and most of the studies are based on certain assumptions and on extrapolation of lab scale experimental data and software-based modeling.

Accounting for various by-products is an important issue which can sometimes provide misleading results depending on the by-product allocation method employed as it can affect the values of sustainability indicators on which assessment is based. Different allocation approaches include allocation by energy; allocation by economic value; use of residual algal biomass as animal feed, organic manure, and raw material for fermentation or anaerobic digestion; use of glycerol (by-product of transesterification) as an industrial or commercial chemical; recycling of waste heat; etc. Several studies have shown that coproduct allocation by several means is required for net gains in energy.

Although ISO standards (ISO 14044 and ISO 14040) exist which specify the structure for implementing LCA studies and a general approach and methodology to be followed, many important elements are up to the particular researcher, such as coproduct allocation, boundary delineation, impact categories to be included, and selection of a functional unit. This has created a problem in terms of comparability of different LCA studies. Different researchers have used different impact indicators, functional units, boundary delineation criteria, coproduct allocation strategies, different assumptions, and different modeling system and procedures which have resulted in a range of values for impact indicators, even for a particular production chain. Sills et al. (2012) in their work on LCA of algal biofuel production emphasized the need to conduct quantitative uncertainty analysis to better understand variability in LCA results.

Often with algae biofuel LCA the only aspect considered is the climate change impact, usually based on the global warming potential of environmental releases. This impact is clearly important; however, it means that other impacts are often overlooked and is not compliant with ISO 14040/44 (UNEP 2009). To assess the overall environmental sustainability of transportation fuels, LCA practitioners must address other impact categories like energy return on investment (EROI), climate forcing (global warming potential), other pollutant emissions and impacts, impact on water resources, land use changes, nutrient needs, ozone depletion potential (ODP), acidification, eutrophication potential, human and ecological health impacts, and other external costs. Social impacts and economic factors are usually not considered in LCA as accounting for these is difficult; however, several software-based modeling procedures are available which can account for these factors as well (UNEP 2009).

2.1 Algae Cultivation

2.1.1 Appropriate Species

The success of biofuel production from algae is dependent on many factors. Selection of an appropriate algal strain is especially important. An appropriate species and strain should have a clear-cut advantage over others and should (1) have high lipid productivity, (2) be robust and able to survive the stresses common in open ponds and photobioreactors, (3) be able to outcompete wild strains in open pond production systems, (4) have high CO_2 absorption capacity, (5) have limited nutrient requirements, (6) be tolerant to a wide range in temperatures resulting from the diurnal cycle and seasonal variations, (7) provide valuable coproducts, (8) have a fast productivity cycle, (9) have a high photosynthetic efficiency, and (10) have self-flocculation characteristics. These are very demanding conditions.

No known algal strain is capable of meeting all of these requirements. But certain species have a clear advantage over others, which cannot be ignored. Certain cyanobacteria have an inherent capability for atmospheric nitrogen fixation. Therefore, their ability to thrive even under environments lacking readily available nitrogen sources such as ammonia, nitrate, or urea is a potential growth advantage, besides offering economic savings in terms of nitrogenous fertilizer use. However, since nitrogen fixation is an energy-demanding process, biomass and oil production might be reduced.

There are algal species which are known to accumulate high levels of lipids under nitrogen-starved media conditions. Lipid accumulation in microalgae occurs when a nutrient (which is typically nitrogen) is exhausted from the medium or becomes the growth-limiting factor. Under limited nitrogen availability proliferation of algae is hampered but carbon assimilation by the cell is not affected, and it is converted to triacylglycerol (TAG) lipids that are stored within cells, thereby increasing their concentration. Lipids can be processed into biodiesel and "green" diesel via

transesterification and hydrotreating, respectively. TAGs are the best suited lipids for transesterification into biodiesel (Gong and Jiang 2011).

Different species may have different growth rates under identical conditions, and hence selection of an appropriate species is vital. Species having higher productivity or lipid accumulation are more feasible for biofuel production as costs related to infrastructure, nutrients, and water requirements remain virtually the same but decrease inputs in terms of energy requirement per unit of biofuel produced over species having low productivity. Selection of an appropriate species should be based on the composition of biomass under a given growth mode (auto-/hetero-/mixotrophic), culture system (open/closed ponds), nutrient availability (with/without N stress), and the intended product.

2.1.2 Autotrophic Growth Mode

Algae are chlorophyll-bearing cells that are capable of photosynthesizing carbohydrates using CO_2 and water in the presence of photosynthetically active radiation from sunlight or an artificial source. Algae have a comparatively higher photosynthetic efficiency (fraction of light energy that is fixed as chemical energy during photoautotrophic growth) than terrestrial plants owing to their simpler structure. This allows microalgae to achieve a higher productivity rate. During exponential growth phase microalgae can double their biomass in periods as short as 3.5 h (Chisti et al. 2007; Spolaore et al. 2006). Use of solar radiation is economically superior to artificial illumination, but spatial and temporal variability in amount of sunlight is problematic. Besides economic constraints associated with artificial illumination, its environmental performance depends on the local energy mix. Bioelectricity generated from direct combustion of unutilized algal biomass can be used to power fluorescent lamps for providing artificial photosynthetically active radiation in a biorefinery-based approach. Biological H_2 production can be achieved via algal biophotolysis using solar radiation. This can be achieved by inducing sulfur stress which inhibits O_2 mobility, which otherwise disrupts the conversion of H^+ to H_2 (Melis and Happe 2001). This leads to biological H_2 production that is one of the cleanest fuels. Combining hydrogen production through algal biophotolysis with other algal biomass-based production systems can significantly help improve energy return on investment (EROI) and other sustainability parameters of biomass-based production chains.

2.1.3 Heterotrophic Growth Mode

A number of microalgae are capable of growing heterotrophically on organic substrates and thus do not depend on sunlight for energy. Carbon in some form is necessary to provide the energy and carbon skeletons for cell growth. Heterotrophic algae derive their energy from organic substrates (often provided in the form of acetate or glucose) (Vazhappilly and Chen 1998). Other carbon sources include carbohydrates such as fructose, sucrose, lactose, and starch. C/N ratio is an influencing factor which affects cellular lipid content as it controls the switch between lipid and protein syntheses (Gordillo et al. 1998). Nitrogen deficit (high C/N ratio) in the culture media triggers lipid accumulation (Pal et al. 2011). Several researchers have suggested higher technical viability of heterotrophic production mode compared to photoautotrophic methods (Graverholt and Eriksen 2007; Xiong et al. 2008; Chojnacka and Noworyta 2004). Miao and Wu (2006) reported lipid content of 55 % when *C. protothecoides* was grown heterotrophically and only 15 % when grown photoautotrophically under similar conditions. Hence, heterotrophic cultivation of some algae could result in higher biomass production and high lipid accumulation in cells. Generally, an organism used for heterotrophic production should possess the following characteristics: (1) the ability to divide and metabolize in the dark, (2) the ability to grow on inexpensive media, (3) short or no lag phase when inoculated to fresh media, and (4) the ability to tolerate hydrodynamic stresses in fermenters and related peripheral equipment.

In microalgal culture, heterotrophic growth can be a cost-effective alternative to photoautotrophic growth. This mode of culture eliminates the requirement for light and, hence, offers the possibility of greatly increasing cell density and productivity (Chen et al. 1996). Heterotrophic algal cultivation can be carried out at large scale in stirred tank bioreactors or fermenters. Although technically viable, the energy required for producing an organic carbon source for algal growth and the related environmental impact can potentially offset the benefits obtained. Hence, exploration and development of an organic carbon source from waste materials is important.

2.1.4 Mixotrophic Growth Mode

Some algae are mixotrophic (i.e., they have the ability to photosynthesize and acquire exogenous organic nutrients heterotrophically) (Lee 2001). Certain algal species like the cyanobacteria *Spirulina platensis* and the green alga *Chlamydomonas reinhardtii* are well-known examples possessing this ability (Chen et al. 1996). This means that light is not an absolute limiting factor for algal growth. This allows for the integration of both photosynthetic and heterotrophic components during the diurnal cycle and during limited light availability conditions. This reduces the impact of biomass loss during dark respiration and decreases the amount of organic substances utilized during growth (Brennan and Owenda 2010). Chojnacka and Noworyta (2004) studied *Spirulina* sp. and reported improved growth rates over both autotrophic and heterotrophic cultures when compared to mixotrophic culture.

2.1.5 Open Pond Production Systems

Open ponds are shallow (usually 25–35 cm deep) circuits, raceways, or tanks wherein the contents of the pond are cycled continuously around the circuit by the action of a paddlewheel. Even mixing of inputs is achieved by a paddlewheel. Inocula produced in smaller ponds or photobioreactors are fed into open ponds to cultivate algae. Open ponds are the cheapest production system employed for large-scale algal cultivation. They do not necessarily compete with arable land since they can be installed in areas with little crop production potential (Chisti et al. 2008). They also have lower energy input requirement (Rodolfi et al. 2008), and regular maintenance and cleaning are easier and therefore may have the potential to return large net energy production (Ugwu et al. 2008). In all open pond systems the amount of sunlight, temperature, nutrient level, and water chemistry will change with the seasons and fluctuations in weather, thus impacting growth. Frequent cleaning and maintenance to deal with challenges from climate, competitors, grazers, and pathogens are inherent challenges associated with open pond production system. Some areas of the world will provide more uniform environments that reduce the complexity of pond management. However, even in the most favorable climates, continuous operation of raceway ponds for 365 days of the year without significant intervention (i.e., draining, cleaning, refilling, and inoculating) is unlikely to be achievable. Continuous operation of a paddlewheel to keep the contents in suspension is an energy-intensive process. Capturing H_2 produced by algae-mediated biophotolysis can be a difficult and energy-intensive affair. CO_2 utilization rates for open systems are comparatively lower than other systems because of its diffusion into the atmosphere and poor mass CO_2 transfer rates. This can result in lower biomass production (Ugwu et al. 2008).

2.1.6 Photobioreactors

Photobioreactors consist of an array of glass or plastic tubes (with a diameter of 0.1 m or less) in which the tubular array captures sunlight and can be aligned horizontally, vertically, inclined, or as a helix. Photobioreactors are designed to overcome some of the major problems associated with the open pond production systems as photobioreactors permit culture of single species of microalgae for prolonged durations with lower risk of contamination. These systems are more appropriate for sensitive strains as the closed configuration better assures control of potential contamination. Photobioreactors are more efficient than open pond system in terms of biomass productivity. Owing to the higher cell mass productivities attained, harvesting costs can also be significantly reduced. Algal cultures are recirculated either with a mechanical pump or airlift system. The airlift system allows CO_2 and O_2 to be exchanged between the liquid medium and aeration gas as well as provides a mechanism for mixing. Mixing and agitation are important to encourage gaseous exchange in the tubes. However, the costs of closed systems are substantially higher than open pond systems (Carvalho et al. 2006). This system, although more efficient than open systems, has considerably higher energy demand.

In a comparative life cycle energy analysis of the *Nannochloropsis* biomass production in photobioreactors and open ponds, Orlando et al. (2010) reported EROI >1 of biomass and lipid produced for photobioreactors and open ponds but that the open pond performed better than photobioreactors with EROI values of biomass and lipid produced 2.56 and 7.01, respectively. The total energy input for producing biomass in open ponds and photobioreactors was 450 and 729 GJ/year, respectively.

2.1.7 Hybrid Production Systems

Hybrid production systems combine distinct growth stages in photobioreactors and in open ponds. The first stage of growth is usually in a photobioreactor where carefully controlled condition allows for optimal growth, and this is followed by cultivation in open systems in which the algae can be subjected to nitrogen stress for enhanced lipid accumulation or sulfur stress to produce H_2 gas. Rodolfi et al. (2008) described a hybrid production system in which cultivation was carried out in photobioreactors followed by open ponds. 22 % of the plant was dedicated to a photobioreactor under N-sufficient conditions and 78 % dedicated to open pond under N-deficient conditions. He estimated lipid production equivalent to be 90 kg ha^{-1} day^{-1} (10 and 80 kg ha^{-1} day^{-1} in the first and second stage, respectively).

2.1.8 Stirred Tank Bioreactors or Fermenters

Stirred tank bioreactors or fermenters are suitable for heterotrophic algae cultivation. The scale-up possibilities are much simpler for these systems than photobioreactors, as growth is independent of light, which enables smaller reactor surface-to-volume ratio. High cellular densities are achievable as these systems allow for a high degree of growth control and consequently lower harvesting cost. The setup cost is comparatively lower, but the initial production of organic carbon sources is energy intensive (Christi et al. 2007).

2.1.9 Water

Like all life, water is a major and important constituent of algal cells. Fresh water, saline water, and even wastewater (usually after secondary treatment) can be used to meet cultivation water demand. This is in contrast to cultivation of terrestrial plants, which usually have high fresh water demand, and only a limited number of plants can be grown using saline water. Although large quantities of water are usually required for algal cultivation in open ponds, this water is essentially recyclable and can be used repeatedly. However, evaporation loss in open ponds has a cooling effect

and adds to an increase in the water footprint. Further, inputs from precipitation and runoff must be regulated to prevent drastic changes in culture media composition. Several algal species flourish in salt water that is readily available in coastal localities. Wastewater has been successfully employed to cultivate algae for biofuel production. Wastewater after secondary treatment is usually fit for culturing algae, and this can be used as a bio-treatment method for wastewater treatment. Biofuel production in conjunction with wastewater treatment can minimize the impacts associated with chemical remediation and provide economic returns (Christenson and Sims 2011).

Yang et al. (2010) reported that using fresh water requires 3726 kg of water to produce 1 kg of algal biodiesel if harvested water is not recycled. He reported a decrease in water demand by 84 % if recycling of water is practiced, while wastewater and saline water usages can decrease the water demand by 90 %. The O_2 released by microalgae assists aerobic bacteria in biodegrading pollutants, thus lowering the BOD and COD of wastewater. After harvesting and dewatering of algal biomass, the remaining water can be used several times. But this would necessitate the use of pumps which can significantly affect the energy balance of the system.

2.1.10 Nutrients

Nitrogen, sulfur, and phosphorus are among the major nutrients ("macronutrients") required for algal growth in relatively large amount. Nitrogen-based synthetic fertilizers are derived almost exclusively from ammonia. Ammonia is synthesized via the Haber process where nitrogen and hydrogen react in the gas phase to form ammonia. Steam reforming of methane produces H_2, which reacts with nitrogen present in air to form ammonia. Natural gas serves both as feedstock and process heat source and can be sourced from a variety of sources. Gasification (partial oxidation) remains the second preferred option after steam reforming to obtain hydrogen. Energy associated with ammonia production dominates the life cycle energy usage for the nitrogen fertilizers most relevant to algae. Jensen and Nielsen (2003) reported industry energy input averages as 36 MJ kg-ammonia^{-1} for European plants and 38 MJ kg-ammonia for the US operational plant energy use. Production plant age is a defining factor in estimating energy efficiency (Johnson et al. 2013). Urea, ammonium monophosphate, ammonium diphosphate, ammonium polyphosphate, ammonium nitrate, and ammonium sulfate are all derived from ammonia. Urea is manufactured by reacting ammonia with carbon dioxide. Kongshaug (1998) reported average Western Europe urea process energy at 4.13 MJ kg-urea^{-1}, and Davis and Haglund (1999) reported the total energy for older, less efficient plants to be 4.58 MJ/kg-urea. Process energy breakup is 3.70 MJ kg-urea^{-1} for process heat from steam and 0.53 MJ kg-urea^{-1} for electricity. The nitrogenous solution consisting of urea and ammonium nitrate (UAN) is produced by blending urea(s) and ammonium nitrate(s) or by adding urea into hot ammonium nitrate. Typically, UAN is prepared from 39 to 45 % ammonium nitrate and 31 to 36 % urea and contains approximately 28 to 32 % N by weight. Nitrate is usually manufactured from nitric acid (ammonium nitrate, calcium nitrate, nitro phosphate, and potassium nitrate).

The oxidation steps in nitric acid production release heat that can be used to produce steam to be used for other purposes including electricity generation (Johnson et al. 2013). Davis and Haglund (1999) reported direct energy inputs for nitric acid production to be 0.032 and 1.47 MJ kg-HNO_3^{-1} for electricity and steam heat export, respectively. Sulfuric acid manufacturing is a highly exothermic process. Phosphoric acid production requires heat for evaporation, so heat integration between the two processes is desirable (Table 14.1).

Higher nonrenewable energy demand leads to higher emission of greenhouse gases (GHGs). Handler et al. (2012) reported greenhouse gas (GHG) emissions associated with nitrogen fertilizers range from 2.6 kg CO_2e kg-N^{-1} to 16 kg CO_2e kg-N^{-1} depending on fertilizer and its nitrogen content, where mass of CO_2 equivalent (CO_2e) is the global warming potential of all emissions (Table 14.2).

Water remaining after harvest of algal biomass can be reused several times, and after lipid extraction and anaerobic digestion of the algal biomass the residual biomass can be effectively recycled back to cultivation medium to meet some of the nutrient demand, and this can reduce the energy demand and related emissions associated with synthetic fertilizers. Wastewater resources are often loaded with excess

Table 14.1 Values of direct material and energy inputs in fertilizer production (Johnson et al. 2013)

Product	Material input	Total direct energy input
Ammonia	–	37.0 MJ/kg-ammonia
Urea	Ammonia 0.567 kg/kg-urea	5.16 MJ/kg-urea
Nitric acid	Ammonia 0.288 kg/kg-HNO_3	0.032 MJ/kg-HNO_3
Ammonium nitrate(s)	Ammonia 0.213 kg/kg-AN, Nitric acid 0.787 kg/kg-AN	0.99 MJ/kg-AN
UAN	Ammonia 0.567 kg/kg-product, Ammonium nitrate 0.788 kg/kg-product	0.018 MJ/kg-AN
Monoammonium phosphate	Phosphoric acid 0.53 kg/kg-MAP, Ammonia 0.133 kg/kg-MAP	0.43 MJ/kg-MAP
Diammonium phosphate	Phosphoric acid 0.477 kg/kg-DAP, Ammonia 0.220 kg/kg-DAP	0.37 MJ/kg-DAP
Sulfuric acid	–	0.109 MJ/kg H_2SO_4

Table 14.2 Noncombustion process emissions associated with fertilizer production (Johnson et al. 2013)

Fertilizer	Air pollutant	g-emission/kg-product
Ammonia	CO	4
	VOC	4.7
Nitric acid	N_2O	7.8
Phosphoric acid	CO	3.9e−2
	VOC	3.0e−2

nutrients, which can potentially reduce the dependence on synthetic fertilizers if used for culturing algae. This brings about wastewater treatment and reduces impact on freshwater resources simultaneously (a "win-win" or mutually beneficial process). In their LCA uncertainty analysis, Sills et al. (2012) reported nonrenewable energy demands for cultivation of algae ranging from 1.7 to 4.9 (low productivity 2.4–16 g m^{-2} day^{-1}), 0.94 to 1.8 (base productivity of 17–33 g m^{-2} day^{-1}), and 0.7 to 1.3 MJ (high productivity of 34–50 g m^{-2} day^{-1}) per MJ biofuel produced.

Yang et al. (2010), in their LCA study, reported a nutrient demand of 0.33 kg nitrogen, 0.71 kg phosphate, 0.58 kg potassium, 0.27 kg of magnesium, and 0.15 kg sulfur for producing one liter of algal biodiesel using freshwater without recycling. They reported a decrease in nutrient demand by 55 % in harvested water that is recycled, and if wastewater or saline water is used, nutrient requirement is minimal except for phosphates.

2.1.11 Carbon Dioxide (CO_2)

During normal photoautotrophic growth, CO_2 dissolved in the water is captured along with sunlight by microalgae to produce carbohydrate via photosynthesis. CO_2 from three sources can be provided during cultivation—atmospheric CO_2, CO_2 from industrial emission or coal-fired thermal power plants, and CO_2 from carbonates (Na_2CO_3 and $NaHCO_3$). Limited biomass productivity can be achieved via utilization of atmospheric CO_2 because of lower concentration (390 ppm). Higher CO_2 usually translates into higher productivity under optimal growth conditions. CO_2 concentration up to 150,000 ppm can be easily utilized by most microalgal species. Therefore, waste CO_2 from combustion processes can be effectively sequestered by microalgae; however, only a small number of algal species are tolerant to the high levels of SOx and NOx that are usually present in flue gases. Cooling of flue gas stream is also often a prerequisite.

Algal species are also known to assimilate CO_2 from soluble carbonates such as bicarbonate and carbonate of sodium ($NaHCO_3$ and Na_2CO_3). These compounds raise the alkalinity of water and can bring about cost-effective concentrating with chemical flocculants. Higher pH can also reduce contamination possibilities due to other unwanted species (Wang et al. 2008). Several authors have reported improved environmental performance of coal-fired thermal power plants if algal cultivation is utilized for biomitigation of CO_2 and biomass cultivation.

2.1.12 Light

Light is not an absolute limiting factor for algal cultivation as heterotrophic and mixotrophic growth modes are well established. Sunlight has spatiotemporal variability in its availability. Hence, artificial illumination of the culture medium can be performed depending on absorption characteristics of algal pigments. Light penetration in open ponds is limited, which can affect biomass production. Thus, photobioreactors are more suited for photoautotrophic growth. However, photobioreactors are expensive and more energy intensive than open ponds. Heterotrophic growth in fermenters is independent of light, and high lipid accumulation can be achieved, but production of carbon source is energy intensive (Fig. 14.3).

Large-scale biofuel production would require sustainable industrial algal cultivation pathways which at the same time should be economically viable. Researchers have come up with different cultivation practices to enable industries to choose the pathway most suited to them involving a combination of approaches having different ratings for environmental sustainability and economic feasibility. There are a variety of cultivation pathways, involving different light requirements (solar, artificial, or dark), different growth modes (auto-, hetero-, or mixotrophic), different culture system (open pond, photobioreactor, fermenter, or a combination of these at different stages of growth), nitrogen/sulfur stress at times, etc. Thus, different combinations of approaches yield different values for sustainability indicators (e.g., EROI, GHG balance, or water footprint). Therefore, a holistic evaluation approach is vital. Selection of a particular approach would depend largely on the type of industry and the intended end product. The concept of biorefinery would be of great help to achieve economical production of a number of products and can potentially help offset environmental trade-offs associated with a particular production chain.

2.2 Harvesting Algal Biomass

There are a variety of harvesting methods for microalgae, and the choice is dependent on characteristics of the microalgae (e.g., density, size, and the value of the target products). Harvesting of algal biomass involves solid–liquid separation steps and is a challenging part of the production chain that can have a high impact on the resultant LCA. Harvesting may account for as much as 20–30 % of the total cost of production (Gudin and Therpenier 1986) and a proportionate energy input requirement. The selection of

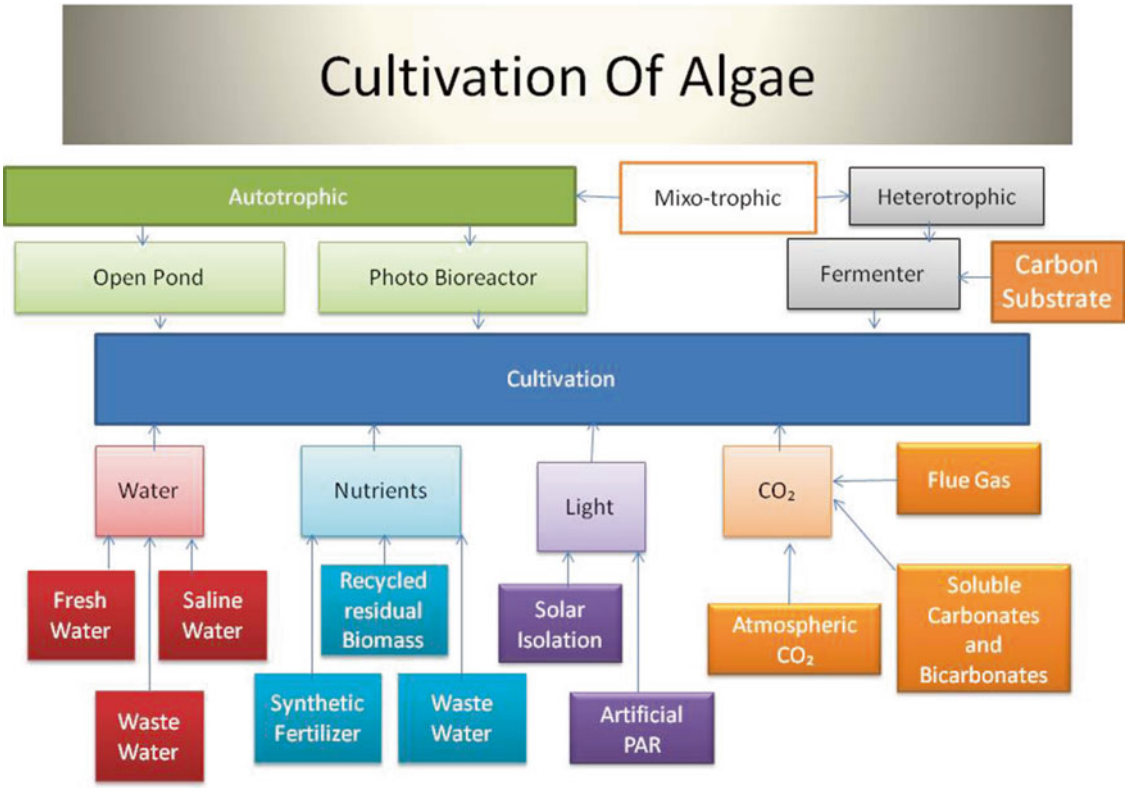

Fig. 14.3 Algal cultivation options

an appropriate harvesting technology is crucial to economic production of algal biomass. Algal species having spontaneous settling or bio-flocculation characteristics are inherently suited for easy, effective, and environmentally friendly harvesting. Certain species such as the cyanobacterium *Spirulina*, which have a long spiral shape (20–100 mm long), can be concentrated with the relatively cost-efficient and energy-efficient microscreen harvesting method (Benemann and Oswald 1996). Harvesting methods usually employed include flocculation, filtration, flotation, and centrifugal sedimentation, some of which are highly energy intensive. Microalgae cells carry a negative charge that prevents natural aggregation of cells in suspension. Addition of multivalent metal salts like ferric chloride ($FeCl_3$), aluminum sulfate ($Al_2(SO_4)_3$), and ferric sulfate ($Fe_2(SO_4)_3$) neutralizes or reduces the negative charge and thus promotes flocculation and subsequent sedimentation under gravity. Most of the chemical flocculants are most efficient under alkaline conditions, and thus careful monitoring and control of media pH is vital. Acoustically induced aggregation involves use of ultrasound to optimize the aggregation efficiency and subsequent sedimentation. Harvesting by flotation is based on the trapping of algal cells using dispersed micro-air bubbles and, therefore, unlike flocculation, does not require any addition of chemicals. Some strains naturally float at the surface of the water as the algal lipid content increases (Bruton et al. 2009). Centrifugation is one of the most efficient harvesting methods in which harvesting efficiencies of >95 % and increased slurry concentration by up to 150 times is achievable. Centrifugation recovery is preferred for harvesting of high-value metabolites and extended shelf-life concentrates for hatcheries and nurseries in aquaculture. The process is rapid but highly energy intensive (Grima et al. 2003). In addition to these high energy costs, other disadvantages include potentially higher maintenance requirements due to freely moving parts.

Biomass filtration under pressure or suction is most appropriate for harvesting of relatively large (>70 mm) microalgae such as *Coelastrum* and *Spirulina*. Mohn (1988) reported a concentration factor of 245 times the original concentration for *Coelastrum proboscideum* to produce sludge with 27 % solids using biomass filtration as the harvesting technique.

2.3 Dehydration of Harvested Biomass

The harvested biomass slurry (typically 5–15 % dry solid content) is perishable and must be processed rapidly after harvest. Dehydration or drying is commonly used to extend the viability depending on the final product required. After the separation of algal cells from the liquid phase, the algal biomass has to be dried using methods like thermo-drying or lyophilization ("freeze drying"); both are rather energy-demanding procedures. Dehydration or drying is usually required to extend the

viability of harvested biomass depending on the final product required. Several methods are available for drying the harvested biomass including sun, low-pressure shelf, spray, drum, fluidized bed, and freeze drying. Sun drying does not require fossil fuel energy but is both weather and volume dependent. It is the cheapest dehydration method, but the main disadvantages include long drying times, need for large drying surfaces, and risk of material loss. Spray drying is commonly used for extraction of high-value products, but it is relatively expensive and can cause significant deterioration of some algal pigment. Freeze drying is equally expensive, especially for large-scale operations, but it eases extraction of oils. Intracellular elements such as oils are difficult to extract from wet biomass with solvents without cell disruption but are extracted more easily from freeze-dried biomass. Drying of harvested biomass can be very energy demanding depending on several factors. Energy extraction methods for wet algae include hydrothermal liquefaction, fermentation, and anaerobic digestion. These energy extraction methods do not require biomass drying and thus have higher upstream EROI values for processing into biofuels. Biomass processing pathways that require dry algal biomass include direct combustion, pyrolysis, gasification, and transesterification to biodiesel. Sills et al. (2012), in their "well-to-wheel" LCA study, reported that the thermal drying of harvested biomass for base productivity (25 g m^{-2} day^{-1}) required 1.8 MJ of nonrenewable energy per MJ of biofuel (biodiesel in this case) produced. Thus, competitive wet lipid extraction techniques must be explored to minimize impacts associated with algal dewatering and drying processes.

2.4 Extraction of Oil from Algal Biomass

Extraction methods are aimed at removing lipids from algal biomass, later to be processed into lipid-based biodiesel, renewable diesel, jet fuel, and similar products. The remaining biomass that is rich in other bio-molecules can further be processed into other biofuel via different conversion processes. Alternatively, biofuels can also be produced via treatment of intact algal cell. Various methods are available for extraction of oil from algae, each with its advantages and disadvantages.

2.4.1 Heated Oil Extraction

Benemann and Oswald (1996) proposed mixing algae wet paste from a gravitational thickener with heated oil and then combining centrifugal dewatering with oil extraction in a three-phase centrifuge which could separate oil, water, and solids (i.e., residual biomass). In this extraction, a fraction of the oil is returned to the heater and then to extraction, and the remainder is used for biofuel production.

2.4.2 Mechanical Extraction

Mechanical treatments, such as ultra-sonication (disruption with high-frequency sound waves) and homogenization (carried out by rapid pressure drops), may be used to disrupt cell walls and lead to enhanced oil recovery. In mechanical press, algal biomass is subjected to high pressure, resulting in ruptured cell wells and release of oil. This method is easy to use, no solvent is required, and a large percentage (70–75 %) of the oils are extracted from the algal biomass.

2.4.3 Ultrasonic-Assisted Extraction

Ultrasonic-assisted extraction can be used which is based on cavitation, which occurs when vapor bubbles of a liquid form in an area where pressure of the liquid is lower than its vapor pressure. These bubbles grow when pressure is negative and compress under positive pressure, which causes a violent collapse of the bubbles. If bubbles collapse near cell walls, damage can occur and the cell contents are released. Advantages of this method over other extraction methods include lower extraction time, reduced solvent consumption, greater penetration of solvent into cellular materials, and improved release of cell contents into bulk medium. This can extract almost 76–77 % of the oils.

2.4.4 Solvent Extraction

Algal oil can be extracted using chemicals. Organic solvents such as benzene, cyclohexane, hexane, acetone, and chloroform, when mixed with microalgae biomass, degrade algal cell walls and extract the oil which has a high solubility in organic solvents. Solvents used in this method are relatively inexpensive, results are reproducible, and the solvent is recycled. 60–70 % of the oil is extracted by this method.

2.4.5 Supercritical Fluid Extraction

This method is more efficient than traditional solvent separation methods. Supercritical fluids have increased solvating power when they are raised above their critical temperature and pressure points. It produces highly purified extracts that are free of potentially harmful solvent residues, and extraction and separation are quick as well as safe for thermally sensitive products. This can extract almost 100 % of the oils. In the supercritical fluid CO_2 extraction, CO_2 is liquefied under pressure and heated to the point that it has properties of both a liquid and a gas. This liquefied fluid then acts as the solvent in extracting the oil.

2.4.6 Enzymatic Extraction

In this process water is used as solvent with the cell wall degrading enzymes to facilitate an easy and mild fractionation of oil, proteins, and hulls. The oil is found inside plant cells, linked with proteins and a wide range of carbohydrates like starch, cellulose, hemicellulose, and pectin. The cell content is surrounded by a rather thick wall that has to be opened so the protein and oil can be released. Thus, when opened by enzymatic degradation, downstream processing makes fractionation of the components possible to a degree which cannot be reached when using a conventional technique like mechanical pressing. This is the biggest advantage

of enzymatic extraction process over other extraction methods. But the cost of this extraction process is estimated to be much higher than most popularly used solvent-based extraction methods. The high cost of extraction serves as a limitation factor for large-scale utilization of this process.

2.5 Algal Biomass to Biofuel Conversion Technologies

2.5.1 Gasification

In gasification, partial oxidation of algal biomass into a combustible gas mixture is carried out at high temperatures (800–1000 °C) (Clark and Deswarte 2008). This process involves partial oxidation of biomass with oxygen and water (steam) to generate syngas (a mixture of CO, H_2, CO_2, N, and CH_4) (Demirbas 2001). Syngas is a low calorific value gas (typically 4–6 MJ m^{-3}) that can be burned directly or used as a fuel for gas engines or gas turbines. Hirano et al. (1998) estimated a marginal positive energy balance of 1.1; this low value is attributed to the energy-intensive centrifuge process during biomass harvesting. EROI value for gasification technology is dependent on factors such as biomass harvesting and drying.

2.5.2 Thermochemical Liquefaction

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 obtain bio-oil from algal biomass.

Reactors for thermochemical liquefaction and fuel-feed systems are complex and therefore expensive but have advantages in their ability to convert wet biomass into energy. The process utilizes the high water activity in subcritical conditions to decompose biomass materials down to shorter and smaller molecular materials with a higher energy density. Thermochemical liquefaction is a process that can be employed to convert wet algal biomass material into liquid fuel, and thus energy investment for drying is not required. In a similar study, Minowa et al. (1995) obtained an oil yield of 42 % dry wt. from *Dunaliella tertiolecta*, giving a HHV of 34.9 MJ kg^{-1} and positive energy balance of 2.94:1. These results indicate that thermochemical liquefaction is a viable option for the conversion of algal biomass to liquid fuel.

2.5.3 Pyrolysis

For biomass to liquid fuel conversion, pyrolysis is deemed to have the potential for large-scale production of biofuels that could replace petroleum-based liquid fuel (Demirbas 2006).

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. Flash pyrolysis conditions utilizing moderate temperature (500 °C) and short hot vapor residence time (about 1–2 s) have a biomass-to-liquid conversion ratio of 95.5 % (Demirbas 2006). However, there are technical challenges as pyrolysis oils are acidic, unstable, viscous, and contain solids and chemically dissolved water (Chiaramonti et al. 2007). Therefore, the process oil requires upgrading hydrogenation and catalytic cracking to lower oxygen content and remove alkalis. Compared to other conversion technologies, research on pyrolysis of algal biomass is quite extensive and has achieved reliable and promising outcomes that could lead to commercial exploitation. Miao and Wu (2004) used flash pyrolysis to enhance oil yield from *Chlorella protothecoides* after manipulating its metabolic pathway towards heterotrophic growth. The recorded oil yield of 57.9 % dry wt. basis from heterotrophic cultivation (HHV of 41 MJ kg^{-1}) was 3.4 times higher than achieved by phototrophic cultivation, and the results suggest that pyrolysis has potential in algal biomass to liquid conversion. Miao and Wu (2004) achieved bio-oil yields of 18 % (HHV of 30 MJ kg^{-1}) and 24 % (HHV of 29 MJ kg^{-1}) with fast pyrolysis of *C. protothecoides* and *Microcystis aeruginosa* grown phototrophically, respectively. Demirbas (2001), experimenting with *C. protothecoides*, showed that bio-oil yield increased with temperature increases up to a point and then decreased at higher temperatures. For example, the yield rose from 5.7 to 55.3 % with an increase from 254 to 502 °C and subsequently decreased to 51.8 % at 602 °C. They recorded a HHV from microalgae of 39.7 MJ kg^{-1} with temperatures ranging from 502 to 552 °C. Results indicate that bio-oils from microalgae are of a higher quality than those extracted from lignocellulosic feedstock.

2.5.4 Direct Combustion

In direct combustion process, biomass is burned in the presence of air just like any other fuel to convert the stored chemical energy in the biomass to hot gases, usually in a boiler, furnace, or steam turbine at temperatures >800 °C. Direct combustion is only feasible for biomass with moisture content <50 % dry weight. The heat produced must be used immediately as storage is not a viable option (Clark and Deswarte 2008). Direct combustion of biomass can be carried out for heat, power, and steam generation. Energy conversion by direct biomass combustion has the disadvantage of biomass generally requiring pretreatment processes such as drying, chopping, and grinding which incur additional energy demand and therefore cost (Goyal et al. 2008). Conversion efficiency in large biomass to energy plants compares favorably to that of coal-fired power plants but may incur higher cost due to high moisture content of biomass. Generation of combined heat and power (CHP) is desirable to improve overall plant efficiency. Net energy conversion efficiencies for biomass combustion power plants range from 20 to 40 %, with higher efficiencies obtained in larger systems (>100 MW) or when biomass is co-combusted in coal-

fired power plants (Demirbas 2001). There is little evidence of technically viable utilization of algal biomass in direct combustion, but a LCA suggested that coal-algae co-firing could lead to lower GHG emissions and air pollution (Kadam 2002). Further, flue gas CO_2 from coal-fired thermal power can be used to cultivate algae, which improves environmental performance of the combined system. Due to limited data, this area will require further research to determine viability.

2.5.5 Biophotolysis

As part of natural photosynthesis, photolysis of water produces hydrogen ions (H^+), oxygen, and electrons. While electrons are used in the electron transport chain, the remaining two are by-products of photolysis. H^+ can subsequently be converted to hydrogen (H_2) by a reversible reaction catalyzed by hydrogenase enzymes, but hydrogenase remains ineffective under aerobic conditions. Photosynthetic oxygen production causes rapid inhibition to the hydrogenase enzyme, and the photosynthetic H_2 production process is impeded. Consequently, microalgae cultures for H_2 production must be subjected to anaerobic conditions. Microalgae are capable of metabolic biohydrogen production via by direct or indirect photolysis. In direct photolysis of water, sunlight breaks water into H_+, e^-, and O_2. This is followed by hydrogenase-catalyzed reaction which recombines H^+ and e^- to produce H_2. In indirect photolysis, microalgae first produce hydrates that later produce hydrogen by dark anaerobic processes. Hydrogen is a clean fuel and has the highest energy content (142 KJ g^{-1}) per unit weight compared to other fuels (Das and Veziroglu 2008). This production process becomes limited with time, as H_2 yield will begin to level off after 60 h of production. The use of this production system does not generate toxic or environmentally harmful products but could yield value-added products as a result of biomass cultivation (Melis and Happe 2001) (Fig. 14.4).

Studies have shown that when algal cultures are deprived of sulfur, it induces anaerobic conditions and stimulates consistent H_2 production (Melis 2002). Several algal species have been used for experimental biohydrogen production including *Chlamydomonas reinhardtii*, *Scenedesmus obliquus*, *Chlorococcum littorale*, and *Monas subcordiformis* (Ghasemi et al. 2012). Melis and Happe (2001) found that by using the two-stage photosynthesis process (where photosynthetic O_2 production and H_2 gas generation are spatially separated), a theoretical maximum yield of H_2 by green algae could be about 198 kg H_2 ha^{-1} day^{-1}.

2.5.6 Transesterification

Biodiesel is produced via a reaction called transesterification that involves transformation of glycerol-based ester derived from biomass-based lipids into monohydric alcohol-based ester usually known as fatty acid methyl ester (FAME). After extraction of lipids from algal biomass, it is transesterified using an alcohol (usually methanol) and a catalyst. Oleaginous microalgae are an attractive non-edible biodiesel feedstock having oil productivity significantly higher (5000–100,000 L ha^{-1} a^{-1}) than terrestrial feedstock. Some microalgae respond to nitrogen stress and certain other chemical and physical stimuli through the accumulation of intracellular triglycerides, thus accumulating higher amounts of lipid than in the absence of such stimuli. Heterotrophic algal culture has been reported to accumulate higher amounts of lipids than photoautotrophic culture. Unlike terrestrial oilseeds, microalgae are cultivated in dilute aqueous suspensions that make lipid recovery complicated. Biomass harvesting, dewatering, and drying and lipid extraction are challenging prospects. Microalgae, when grown outdoors in open ponds, have typical cell density and productivity ranging from 0.5 to 2 g dry biomass L^{-1} and 10 to 40 g m^{-2} d^{-1}, respectively (Doucha et al. 2005). Although higher biomass densities (5–200 g L^{-1}) can be achieved in photobioreactors (Doucha et al. 2005) and fermenters (Xiong et al. 2008), dewatering and drying remain energy- and cost-intensive processes (Molina et al. 2003). Biomass drying and organic solvent use for oil extraction could lead to significant energy and cost debt. Biodiesel has remained the biofuel of choice for conducting LCA studies, but comparison between studies is limited due to different boundary delineation criteria, different function unit, different assumptions, and other variables. Yang et al. (2010) reported that about 400 kg kg^{-1} biodiesel of freshwater must be used for culture even if sea-/wastewater serves as the culture medium, irrespective of the amount of harvested water recycling. Frank et al. (2012) reported that in baseline studies with assumed 25 g m^{-2} d^{-1} productivity and 25 dry wt.% lipids, per million BTU of biodiesel produced 55,400 g CO_2 equivalent compared to 101,000 g for fossil diesel having low sulfur content. Woertz et al. (2014) estimated total well-to-wheel GHG emissions for algal biodiesel to be 28.5 g CO_2e/MJ of biodiesel. Total energy requirement for well-to-tank was reported to be 1.2 MJ per MJ biodiesel produced. Cumulative well-to-wheel energy requirement (including energetic costs of production for methanol and hexane for biodiesel production and oil extraction) was estimated to be 2.2 million J/MJ biodiesel (Fig. 14.5).

2.5.7 Fermentation

Alcoholic fermentation of algal biomass yields ethanol, which is compatible with gasoline engine vehicles. Raw material required for alcohol fermentation is carbohydrate. Some microalgae (*Chlorella*, *Dunaliella*, *Chlamydomonas*, *Scenedesmus*, and *Spirulina*) are known to contain >50 % of the dry weight as starch, cellulose, and glycogen, which are raw materials for ethanol production (Singh et al. 2011). Microalgae such as *C. vulgaris* are a good source of ethanol due to their high starch content (ca. 37 % dry wt.), and up to 65 % ethanol conversion efficiency has been recorded

Fig. 14.4 Biophotolysis types

Direct Photolysis:

$2H_2O \rightarrow 2H_2+O_{2\rightarrow}$

Indirect Photolysis:

$12H_2O+6CO_2 \rightarrow C_6H_{12}O_6+6O_2$

$C_6H_{12}O_6+12H_2O \rightarrow 12H_2+6CO_2$

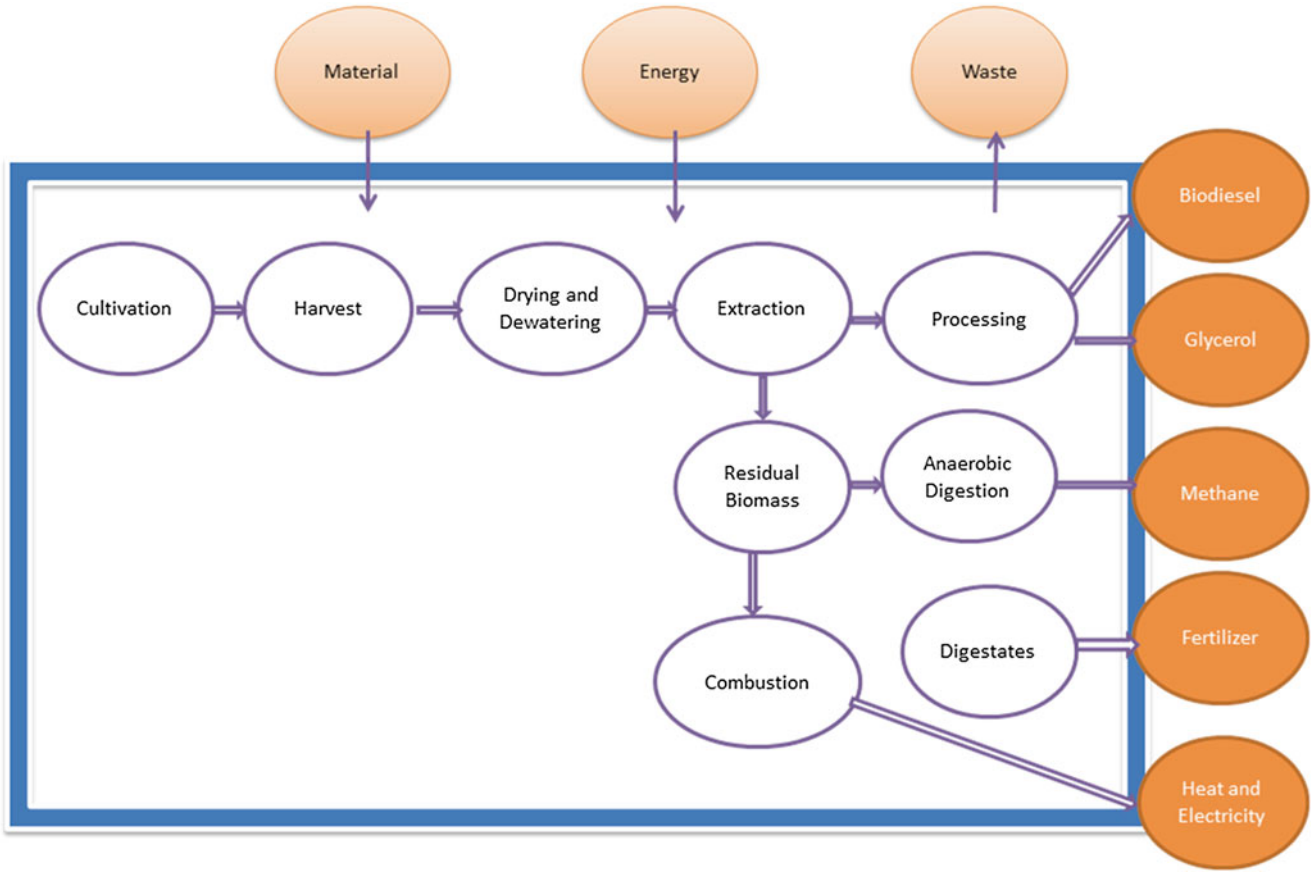

Fig. 14.5 Biodiesel production pathway and residual processing options

(Hirano et al. 1998). Chemical reaction is composed of enzymatic hydrolysis of complex carbohydrates followed by fermentation of simple sugars. 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 (Demirbas 2001). Yeast breaks down the carbohydrate and converts it to ethanol. Distillation is required to remove the water and other impurities in the diluted alcohol product (10–15 % ethanol). The concentrated ethanol (95 % volume for single distillation) is drawn off and condensed into liquid form, which can be used as a supplement or substitute for petrol in cars (Demirbas 2001). The solid residue from the process can be used for cattle feed or for gasification.

2.5.8 Anaerobic Digestion

Anaerobic digestion is the conversion of biomass into a biogas—a combustible mixture consisting primarily of methane and carbon dioxide, with traces of other gases such as hydrogen sulfide (H_2S). Anaerobic digestion of biomass proceeds via breakdown of organic matter to produce biogas, having an energy content of about 20–40 %, which is the lower heat-

ing value of the feedstock. One major advantage with anaerobic digestion is its ability to process high moisture content (80–90 %) biomass. This excludes the energy-intensive process of dewatering and drying of biomass. Anaerobic digestion of biomass proceeds in three sequential stages—hydrolysis, fermentation, and methanogenesis. In hydrolysis, the complex compounds are broken down into soluble sugars. Then, fermentative bacteria convert these into alcohols, acetic acid, volatile fatty acids, and a gas containing H_2 and CO_2, which is metabolized into primarily CH_4 (60–70 %) and CO_2 (30–40 %) by methanogens in methanogenesis. Microalgae having high proportion of proteins can result in low C/N ratios that can affect the performance of the anaerobic digester. This problem may be resolved by co-digestion with a high C/N ratio product (e.g., waste paper). Yen and Brune (2007) achieved a significant increase in methane production with the addition of waste paper to algal biomass. High protein content in the algae can also result in increased ammonium production, which can inhibit anaerobic microorganisms. Besides carbon, nitrogen, and phosphorus, which are major components in microalgae composition, other nutrients such as iron, cobalt, and zinc are also found (Grobbelaar 2004) and are known to stimulate methanogenesis.

2.5.9 Jet Fuel

Aviation fuels account for approximately 8 % of global petroleum usage and account for approximately 2 % of total anthropogenic CO_2 emission (end use). Jet fuels can be derived from biomass-based sources. Algal lipid serves as feedstock for jet fuel in addition to biodiesel and green diesel. Jet fuels can be produced from algal oil by removing the oxygen molecules (to raise the heat of combustion) and converting olefins to paraffins by reacting it with hydrogen and removing metals and heteroatoms like oxygen, nitrogen, and sulfur (increases the thermal stability of the fuel). This is followed by selective cracking/isomerization which produces jet-range paraffins (improves the freeze point) (Rahmes et al. 2009). O'Neil et al. (2015) used olefin metathesis of alkenones (a type of lipid composed of long chains with 37–39 carbon atoms) derived from *Isochrysis* which cleaved carbon-carbon double bonds present in alkenones to produce compounds containing 8–13 carbons, which can be used as jet fuel.

2.5.10 Green Diesel

Green diesel can be produced from triglycerides present in algal biomass via its hydroprocessing, which involves (1) hydrocracking and (2) hydrogenation to produce hydrocarbons having C_{15}–C_{18} chain (a liquid mixture within the boiling point range of fossil diesel). This is different from biodiesel, which is composition-wise an ester, while green diesel consists of hydrocarbons, mainly heptadecane and octadecane. Hydroprocessing of triglycerides to green diesel requires temperatures around 300 °C, pressure of 5 MPa of hydrogen, and a bifunctional solid catalyst in a continuous-flow process. Hydroprocessing is superior to transesterification in terms of energy requirement for drying the harvested algal biomass as it can process wet biomass (Fig. 14.6).

2.5.11 Greenhouse Gas Balance of Algal Biomass-Based Energy and Energy Carriers

Depletion of fossil fuels and its impact on climate are the driving forces for exploration and development of biofuels. Algae have higher photosynthetic efficiency than their terrestrial counterparts and are capable of biomitigation of CO_2. Since captured CO_2 is converted into biomass and biomass-based energy and energy carriers, algal biofuels do not cause any net emission of CO_2. Algal biofuels can even sequester more CO_2 than its emission depending on the production technique employed. The GHG balance of algal biofuels is usually reported in terms of CO_2 equivalent emissions (Table 14.3).

2.6 Algal Biorefinery

The concept of an algal biorefinery is analogous to the petroleum refinery. It is a facility that integrates different biomass conversion systems to produce biofuels, heat, power, and other valuable chemicals of ecological, economic, and health benefit. It is a system that involves sustainable processing of algal biomass into a spectrum of biologically derived products including chemicals, food, feed, chemicals, and bioenergy including biofuel power and heat. Thus, the biorefinery process has immense potential for sustainable bio-based production systems in which principles of industrial ecology are applied. Material and energy that come out of one production system is used as input for other systems and thus involves interdependence between individual systems. Depending on the scale of operation and individual processes, biorefinery can be an independent system in which minimal external support/input is required. The interdependence can avoid waste output to the environment and can potentially minimize several impacts associated with individual production chains (Fig. 14.7).

The impacts associated with any particular production system are strongly correlated to the electricity input required for producing a particular biofuel. These impacts are further dependent on the nature of the electricity source and nonrenewable energy sources and may lead to significantly greater environmental impacts. These impacts can be minimized to some extent by producing some of the electricity at the biofuel production facility through employing some conversion technique and by using less energy-intensive processes. Numerous alternatives exist which need to be integrated

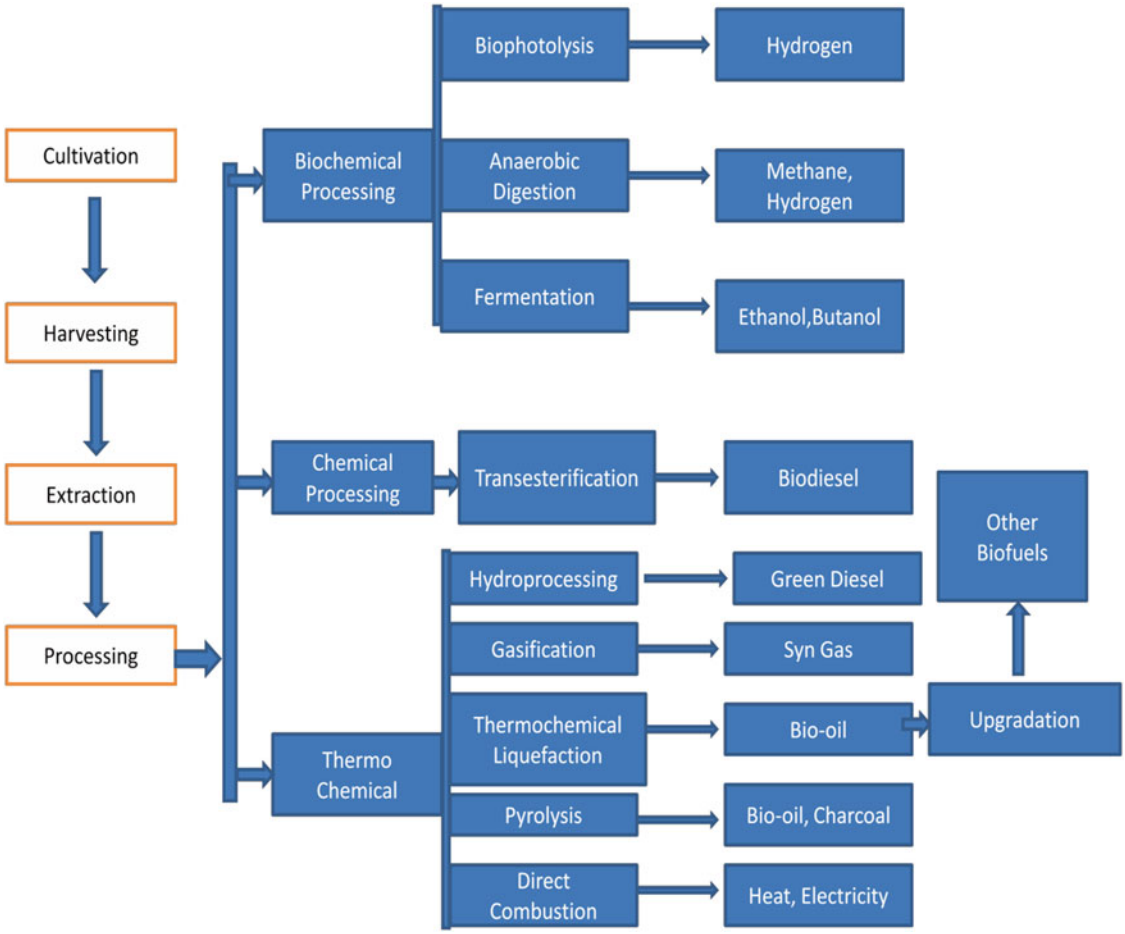

Fig. 14.6 Biomass conversion techniques

Table 14.3 Greenhouse gas balance of production and use of bioenergy from algae

Energy carrier	(g CO_2 eq/MJ)	Approach	Reference
Electricity	0.061	Flue gas CO_2 from coal-fired thermal power plant captured by algae (50 %) and used to produce electricity (WTW)	Kadam (2002)
Biodiesel	59.9	Open pond cultivation with N stress and dry extraction (WTW)	Lardon et al. (2009)
Biodiesel	18.5	PBR under greenhouse, waste heat from power plant as heat source (WTP)	Baliga and Powers (2010)
Biodiesel	−75.3 (without combustion)	PBR based on the GREET modeling (WTP)	Batan et al. (2010)
	−1.31 (with combustion)		
Biomass	56.8	Open raceway and chemical fertilizer (WTG)	Clarens et al. (2010)
Biodiesel	−18.0	Culture in two stages, GREET modeling (WTP)	Sander and Murthy (2010)
Biodiesel	13.6	Anaerobic digestion of extraction residue, digestates as fertilizer (WTW)	Stephenson et al. (2010)
Biodiesel	−0.729	Open ponds, CO_2 produced during the synthesis of nitrogen fertilizer used as carbon source (WTW)	Campbell et al. (2011)
Electricity	48.7	Direct combustion of algal biomass for bioelectricity production (WTW)	Clarens et al. (2010)
Biomethane	61.02	Open raceways, anaerobic digestion of biomass, digestates as fertilizer (WTW)	Collet et al. (2011)
Biodiesel	15.0	Open raceways, sea water (WTW)	Hou et al. (2011)
Biodiesel	310	Two-phase cultivation, first in photobioreactors then in open raceway (WTP)	Khoo et al. (2011)
Biodiesel	534 (base configuration)	Base configuration—open raceways, hexane extraction of dry algae, methanol transesterification, oilcakes as waste	Brentner et al. (2011)
	80.5 (best configuration)	Best configuration—PBR, extraction with in situ esterification by supercritical methanol, anaerobic digestion of oilcakes, digestates as fertilizers (WTP)	

Modified from Collet et al. (2013)

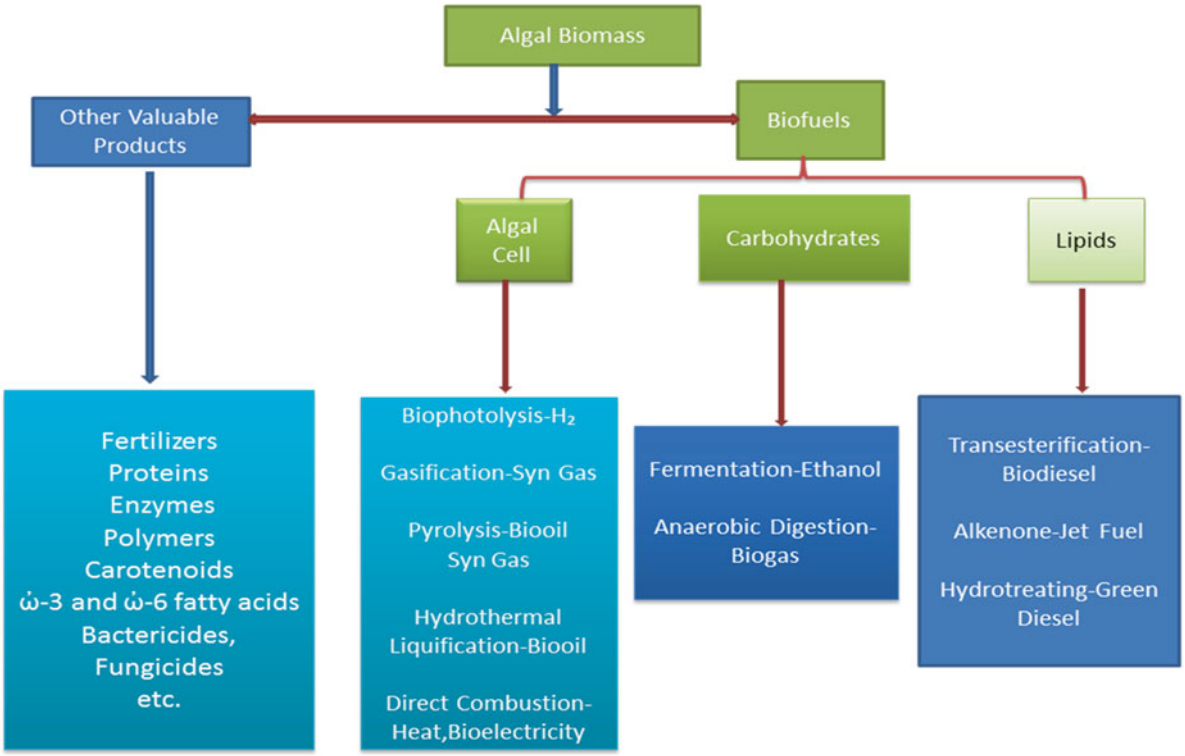

Fig. 14.7 Concept of algal biorefinery

judiciously for achieving a self-dependent biofuel production system which is sustainable in the long term (Subhadra 2010).

3 Conclusions

LCA is an analytical tool which can be employed to assess suitability of algal biofuels over their fossil fuel-based counterparts. Several types of biofuels can be produced from algae: bioethanol, biogas, biohydrogen, biodiesel, green diesel, jet fuel, etc. The performance of any biofuel is greatly dependent on the route taken for its synthesis. The various stages of any algal biofuel production system include cultivation of algae, harvesting of algal biomass, drying and dewatering of algal biomass extraction of lipids, and processing into biofuels. Each of these stages has multiple routes to choose from, and a careful selection of a particular combination of routes is critical which determines its performance on environmental front. GHG balance and EROI are widely used indicators in LCA studies to assess the overall suitability of a particular biofuel over its counterparts. In order to achieve environmental and economic goals of sustainable development, any production chain should use minimum amount of energy and should generate minimum amount of waste possible per unit of output. Algal biorefinery is an emerging system which is analogous to petroleum refinery and involves material, waste, and energy synergy at several stages in order to achieve environmental sustainability and economic feasibility.

Acknowledgement One of the authors (Dipesh Kumar) is thankful to UGC for providing Junior Research Fellowship (JRF).

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