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CO_2 Biomitigation and Biofuel Production Using Microalgae: Photobioreactors Developments and Future Directions

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1. Introduction

Increased concerns about global warming and greenhouse gas emissions as well as the exhaustion of easily accessible fossil fuel resources are calling for effective carbon dioxide (CO_2) mitigation technologies and clean and renewable energy sources. One of the major gases leading to global warming is carbon dioxide. CO_2 makes up 68% of the estimated total greenhouse gas emissions (Harrington & Foster, 1999).

There have been several approaches proposed for managing the levels of CO_2 emitted into the atmosphere, including ocean sequestration such as deep ocean injection or increasing the amount of CO_2 dissolved in the ocean. Another proposed form of sequestration is to sequester the CO_2 into terrestrial ecosystems (Halmann, 1993). The short term options of sequestration by direct injection into geologic or oceanic sinks are recognized as methods to reduce the CO_2 levels but do not address issues of sustainability (Stewart & Hessami, 2005). Carbon sequestration can also be accomplished through chemical approaches; some problems with these approaches are that they must be safe for the environment, stable for long- term storage, and cost - competitive to other sequestration options. Other technologies have been considered, such as chemical absorption, membrane separation, cryogenic fractionation and adsorption using molecular sieves, but they are even less energy efficient as to be considered economically viable (Stewart & Hessami, 2005).

One of the most understudied methods for CO_2 mitigation is the use of biological processes (via microalgae) in a direct CO_2 to biomass conversion from point source emissions of CO_2 in engineered systems such as photobioreactors. Microalgal biofixation of carbon dioxide (CO_2) in photobioreactors has recently gained renewed interest as a promising strategy for CO_2 mitigation. The use of photobioreactors for microalgal CO_2 sequestration offers the principal advantages of increased microalgae productivity, owing to controlled environmental conditions, and optimized space/volume utilization and, thus, more efficient use of costly land. In fact, the photosynthetic solution when scaled up would present a far superior and sustainable solution under both environmental and economic considerations.

Fig. 1 shows the importance of the microalgae photobioreactor and its general applications, microalgae used to capture waste CO_2 utilizing the nutrients in wastewater and natural

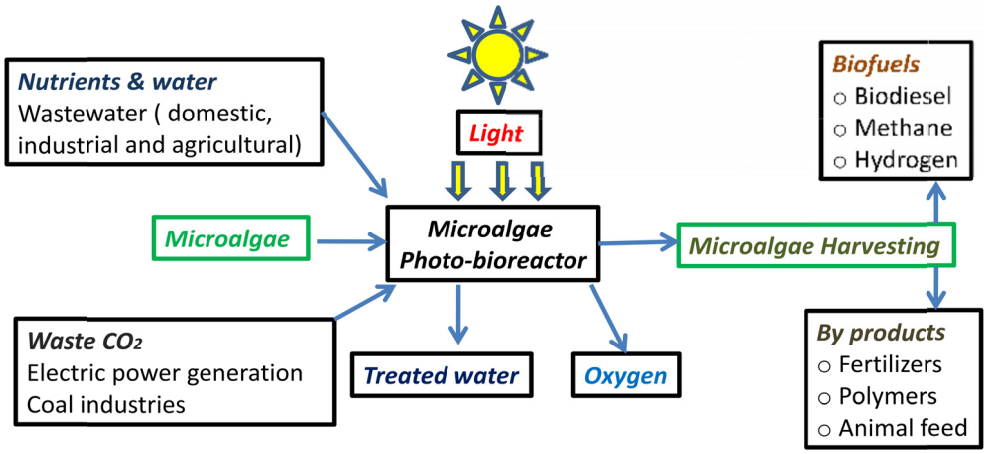

Fig. 1. Microalgae photobioreactors applications

solar light. The microalgae biomass produced can be used for biofuel production (such as biodiesel and methane) and other by products (such as animal feeds and polymers).

Broadly, photo-bioreactors can be classified as open (pond) systems or closed systems. Considering all the limitations and shortcomings of the pond systems, most researchers, had oriented their research works towards the development of an unconventional way for microalgae culture, which should be fully closed and compact with high surface-to-volume ratio and all the growth factors be optimized.

With these desired characteristics as the main goals, research on tubular and airlift photo-bioreactors were the right orientation and some forms of designs had in certain aspects succeeded when used in the lab scale. However, few of these forms could be really applicable in the pilot production scale, due to serious obstacles of operational problems and growth limitations. Amongst them, were primarily the oxygen build-up in the growth medium, photoinhibition, light saturation effect and the overheating inside the tube walls by the intensive solar radiation when operating in summer seasons especially in the midday light hours. Besides, the poor circulation of the growth medium causes the algal staining on the inner walls of the tubes, gave eventually an uneconomic results. Over the years, several solutions have been proposed to overcome these fundamental limitations to productivity. However, these systems are complicated to scale up and may be suitable for small-scale cultivation. Moreover, there is little knowledge about the feasibility of photobioreactors scale-up and developments.

The developmental state of the photobioreactor technology for CO_2 mitigation and biofuel production will be reviewed in this chapter, focusing on several essential issues, such as effective and efficient provision of light; supply of carbon dioxide while minimizing losses; removal of photo-synthetically generated oxygen that may inhibit metabolism or otherwise damage the culture if allowed to accumulate; sensible scalability of the photobioreactor technology; harvesting the microalgae biomass and biofuel production. The theoretical background of microalgae cultivation will be summarized in this chapter as well. The

chapter will present possibly new insights that could be gained in the future for the potential commercial exploitation of microalgae for CO_2 biomitigation and biofuel production.

2. Mechanism of the photosynthesis and biophotolysis

Photoautotrophic microorganisms like eukaryotic green microalgae, possess chlorophyll and other pigments to capture sunlight energy and use photosynthetic systems (PSII and PSI) to carry out plant-like oxygenic photosynthesis (Kruse et al. 2005). The pigments in PSII (P680) absorb the photons with a wavelength shorter than 680 nm, generating a strong oxidant capable of splitting water into protons (H^+), electrons (e^-) and O_2 as shown in Fig. 2.

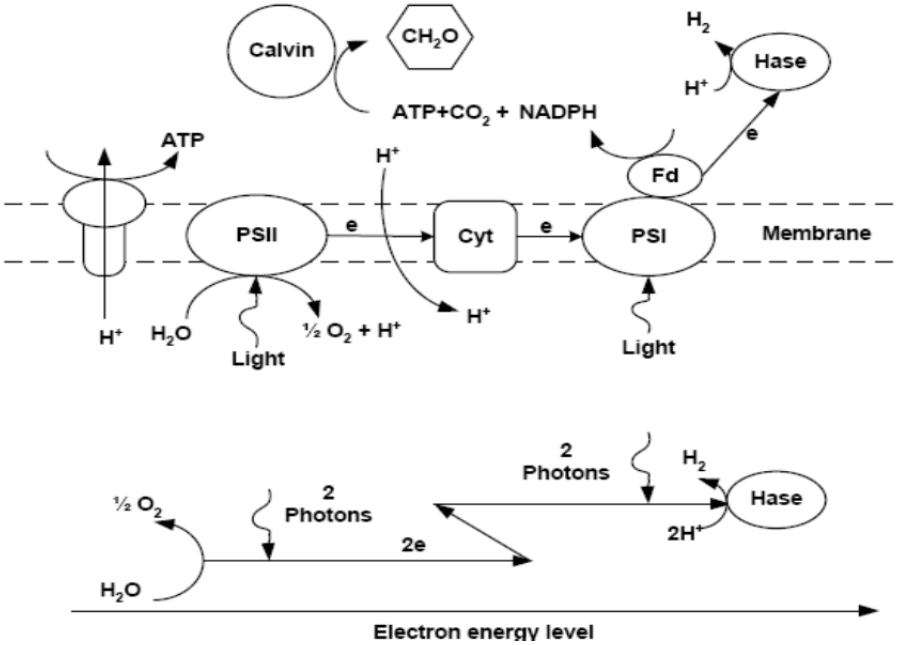

Fig. 2. Schematic mechanisms of photosynthesis and biophotolysis of photoautotrophic microbes (Amos, 2004).

The electrons or reducing equivalents are transferred through a series of electron carriers and cytochrome complex to PSI. The pigments in PSI (P700) absorb the photons with a wavelength under 700 nm, which further raises the energy level of the electrons to reduce the oxidized ferredoxin (Fd) and/or nicotinamide adenine dinucleotide phosphate (NADP+) into their reduced forms. The proton gradient formed across the cellular (or thylakoid) membrane drives adenosine triphosphate (ATP) production via ATP synthase. CO_2 is reduced with ATP and NADPH via a reductive pentose phosphate pathway or Calvin cycle for cell growth.

The excess reduced carbon is stored inside the cells as carbohydrates (CH_2O) and/or lipids. The type of carbohydrate product produced depends on the type of strain being

used. The reducing power (Fd) could also be directed to hydrogenase (Hase) for hydrogen evolution.

3. Microalgae and microalgae cultivation

Algae are a large and diverse group of simple, typically autotrophic organisms, ranging from unicellular to multicultural forms. The largest and most complex marine forms are called seaweeds. They are photosynthetic, like plants, and simple because they lack the many distinct organs found in land plants. Some unicellular species rely entirely on external energy sources and have limited or no photosynthetic apparatus. All algae have photosynthetic machinery ultimately derived from the cyanobacteria, and so produce oxygen as a byproduct of photosynthesis.

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

Table 1. Chemical composition of algae expressed on a dry matter basis (%) (Becker,1994)

Algae can be classified into two types based on their sizes, microalgae and macroalgae. Microalgae are microscopic photosynthetic organisms (less than 2 mm in diameter). However, macroalgae, these organisms that are found in both marine and freshwater environments. Biologists have categorized microalgae in a variety of classes, mainly distinguished by their pigmentation, life cycle and basic cellular structure (Amos, 2004). The most frequently cited microalgae as carrying one or more of the desirable features for efficient and economical combination of CO_2 biofixation, wastewater treatment and lipid synthesis toward biofuel production are:

1. The diatoms (Bacillariophyceae). These algae dominate the phytoplankton of the oceans, but are also found in fresh and brackish water. Approximately 100,000 species are known to exist. Diatoms contain polymerized silica (Si) in their cell walls. All cells store carbon in a variety of forms. Diatoms store carbon in the form of natural oils or as a polymer of carbohydrates known as chyrsolaminarin.
2. The green algae (Chlorophyceae). These are also quite abundant, especially in freshwater. They can occur as single cells or as colonies. Green algae are the evolutionary progenitors of modern plants. The main storage compound for green algae is starch, though oils can be produced under certain conditions.
3. The blue-green algae (Cyanophyceae). Much closer to bacteria in structure and organization, these algae play an important role in fixing nitrogen from the atmosphere. There are approximately 2,000 known species found in a variety of habitats.
4. The golden algae (Chrysophyceae). This group of algae is similar to the diatoms in pigmentation and biochemical composition. They have more complex pigment systems, and can appear yellow, brown or orange in color. Approximately 1,000 species are known to exist, primarily in freshwater systems. The golden algae produce natural oils and carbohydrates as storage compounds.

All algae primary comprise of the following, in varying proportions (Table 1): proteins, carbohydrates, fats and nucleic acids. While the percentages vary with the type of algae, there are algae types that are comprised of up to 40% of their overall mass by fatty acids that could be extracted and converted into biodiesel.

4. Photo-bioreactor for carbon dioxide sequestration

Photobioreactors for microalgae cultivation can be classified as open systems or closed systems. Open systems are ponds, constructed on the large open areas, in rows with growth medium exposed to environment and sunlight. Closed systems are those where growth medium enclosed from the environment. Open systems have many disadvantages over closed system, for instance they are hard to control and, contamination from external environment is high and could cause the microalgae mutate (Camacho Rubio et al., 1999). Closed systems are easy to monitor, less chances of contamination, better mass transfer (varies based on the type of bioreactor), occupy less space for the same algal growth. Closed systems can be classified as tubular photobioreactors; stirred photobioreactors; flat plate photobioreactors; hollow fiber membrane photobioreactors; airlift and sparged bubble column photobioreactors. Unfortunately, none of the these bioreactor configurations is able to control effectively all process parameters that are required for maximum CO_2 biofixation, microalgal growth and metabolic rates, particularly at large scale production. Below is a brief description for the most widely used photobioreactors for CO_2 biofixation and biofuel production:

4.1 Tubular photo-bioreactors

Tubular photo-bioreactors consist of long thin tubes arranged in different geometrical patterns (helical, straight tubes) to optimize irradiance from a point light source (sun). Generally liquid growth medium is circulated in these tubes by air bubbling and by injection of air into one end of the system and degassed at the other end. Construction, light regime, mass transfer and scale up issues of these photo-bioreactors have been discussed (Molina Grima, 2000). Experiments have showed that a large-scale tubular photo-bioreactor

has failed and the main reason attributed for its failure was the large dissolved oxygen in the system (Molina Grima, 2000). Hence a system should not at any stage be over saturated with oxygen as this would cause algae to shutdown photosynthesis and growth (Camacho Rubio et al., 1999). It was also reported that tubular photo-bioreactors are difficult to build and maintain, and have limited scalability.

4.2 Mechanically stirred photo-bioreactors

Mechanically stirred photo-bioreactors use baffles to stir the growth medium to attain a mass transfer of air/CO_2 into liquid. A drawback of the stirred medium is if stirred vigorously the algae cell wall would be damaged by the high fluid shear forces (Molina Grima et al., 1996). If it is stirred slowly, eddy currents will not be established that move the algae toward the light source thereby decreasing the efficiency of light available for the photosynthetic process and also reducing mass transfer of nutrients from the air/CO_2 to the liquid in the systems.

4.3 Airlift photo-bioreactors

Airlift photo-bioreactors are basically a column divided into two parts, air/CO_2 is bubble through only one side of the partition which causes a liquid current pattern to develop with the air bubble side called the riser and other part called the downcomer (Sánchez Mirón et al., 2000). These bioreactors are extensively investigated for fermentation process and wastewater treatment (Znad et al. 2004, Znad et al. 2006) but have not been looked at as a replacement for the popular tubular photo-bioreactors until recent times (Sánchez Mirón et al., 2000). The airlift photo-bioreactor characterized by; high mass transfer, good mixing with low shear stress, low energy consumption, high potentials for scalability, easy to sterilize, readily tempered, good for immobilization of algae, reduced photo-inhibition. However, the main limitations are; the small illumination surface area and decrease of illumination surface area upon scale-up. It has become clear that biological carbon sequestration and hydrogen production technologies have been poorly studied in the airlift photo-bioreactors and are in their infancy of development.

4.4. Bubble column photo-bioreactors

Bubble column bioreactors are vertical columns either cylindrical or rectangular filled with growth medium and air is bubble through a sparged system installed at the bottom. These systems have the highest gas hold ups rates which means they have the best mass transfer compared to other systems (Miron et al. 2000; Kommareddy & Anderson , 2003). A modified version of these bubble column bioreactors is porous membrane reactors, which have efficient aeration, give smaller bubbles, and pressure drop across the membrane is low compared with other rigid sparged bubble column reactors. These characteristics are achievable at high gas flow rates, with low energy costs (Poulsen & Iversen, 1997).

5. Factors affecting the photobioreactor performance

The key parameters that affect the photobioreactor performance, i.e., the growth of the microalgae in the photo-bioreactor, are the effective and efficient provision of light, carbon

dioxide level, photo-synthetically generated oxygen, Gas transfer, mixing rates, temperature, pH and nutrient requirements.

5.1 Light provision

Light is the basic energy source for phototrophic microorganisms. The intensity and utilization efficiency of the light supplied are thus of crucial importance in microalgal bioreactors. Light intensity decreases deeper within the culture medium, especially in high-density cultures; hence, the issue of optical depth, which measures the proportion of radiation absorbed or scattered along a path through a partially transparent medium, should be considered in microalgal bioreactor design (Kumar et al., 2010).

Both sunlight and artificial light have been used via outer surface exposure as well as inner volume exposure, through the placement of lighting devices (e.g. LEDs or optical fibers) inside the bioreactor itself (Suh & Lee, 2003). The photosynthetically active radiance is normally assumed to be 43–45% in the wavelength range of 400–700 nm (Laws et al. 1987). The light intensity available to microalgae in high-density cultures is significantly attenuated by mutual shading; to maximize light absorbance and minimize light attenuation, bioreactors should be designed with a high surface area-to-volume ratio, coupled with a short light path (Richmond et al. 2003).

Good microalgal growth rates have been reported (Hu et al. 1998) under a light intensity of 4000 μmol m^{-2} s^{-1}; this intensity is twice the solar flux in a medium latitude spot at midday during summer. However, a strong species-dependence exists that should be taken into account. By contrast, light above a saturation point causes light inhibition, which can be counterbalanced by exposing microalgal cells to very short cyclic periods of light and darkness (Pulz, 2001).

The ratio of light to dark (or low-intensity light) periods in a cycle is crucial for microalgal productivity (Munoz & Guieysse, 2006). Similar overall numbers of moles of photons do not necessarily produce equal growth rates of (or CO_2 assimilation by) microalgae. When the light/dark cycle period approaches the photosynthetic unit turnover time (equal to the dark reaction time, estimated to lie within 1–15 ms), maximum photosynthetic efficiencies can be achieved (Richmond et al. 2003). Moreover, compared with periodic darkness, periods of low light intensity significantly increase growth, CO_2 assimilation and lipid productivity in microalgae for a given whole light level (Cuello et al. 2008). This type of lighting design can be achieved via artificial light, such as hybrid lighting systems (Muhs, 2000). Different lamps generate distinct spectra, and different microalgal species possess dissimilar absorption optima; therefore, each individual case should be studied before deciding on the set point of this important operational parameter. Variation of the exponential growth rates of *Phorphyridium cruentum* have been recorded (Suh & Lee, 2003) with variable radiation energies and light spectra, concluding that blue light (400–500 nm) increases cell growth and polysaccharide production.

In terms of artificially illuminated bioreactors, the need for small reactor diameters to increase the illuminated surface area per unit volume of culture can be circumvented through provision of internal illumination. High biomass yields are more crucial in the case of artificially illuminated reactors, because the light provided adds to the overall operational cost of the underlying process. Such costs can be kept below acceptable

thresholds via in situ growth-monitoring and associated online control of the intensity of light supplied.

5.2 Carbon uptake

Biological CO_2 fixation can be carried out by higher plants and microalgae, yet the latter possess a greater ability to fix CO_2 (Li et al. 2008; Chisti, 2007; Tredici 2010). Usual sources of CO_2 for microalgae include atmospheric CO_2; CO_2 from industrial exhaust gases (e.g. flue gas and flaring gas); and CO_2 chemically fixed in the form of soluble carbonates (e.g. $NaHCO_3$ and Na_2CO_3) (Kumar et al., 2010). The tolerance of various microalgal species to the concentration of CO_2 is variable; however, the CO_2 concentration in the gaseous phase does not necessarily reflect the CO_2 concentration to which the microalga is exposed during dynamic liquid suspension, which depends on the pH and the CO_2 concentration gradient created by the resistance to mass transfer. Under heterotrophic or mixotrophic conditions, some microalgal species can metabolize a variety of organic compounds, including sugars, molasses and acetic acid, as well as compounds present in wastewater and petroleum (Becker, 1994). Atmospheric CO_2 levels (0.0387% (v/v)) are not sufficient to support the high microalgal growth rates and productivities needed for full-scale biofuel production.

Waste gases from combustion processes, however, typically contain >15% (v/v) CO_2; this percentage indicates, in principle, that combustion processes will provide sufficient amounts of CO_2 for large-scale production of microalgae (Doucha et al. 2005). Owing to the cost of upstream separation of CO_2 gas, direct utilization of power plant flue gas has been considered in microalgal biofuel production systems (Lackne, 2003). Flue gases that contain CO_2 at concentrations ranging from 5 to 15% (v/v) have indeed been introduced directly into ponds and bioreactors of various configurations that contain several microalgal species (Kumar et al., 2010).

5.3 Oxygen generated

Another specific issue of microalgal bioreactors is the accumulation of photosynthetically generated oxygen that may inhibit metabolism or otherwise damage the culture if allowed to accumulate, especially when the rate of photosynthesis, which often correlates with the rate of CO_2 transfer, is high (as typical in horizontal tubular reactors) (Kumar et al., 2010). Most solutions to this problem rely on the use of a degasser (or gas exchange unit), where dissolved oxygen can be released (Morita et al. 2000). However, to attain effective separation between the gas and liquid phases, the path through the degasser should be such that the smallest bubbles have sufficient time to disengage from the liquid.

In tubular bioreactors, connections between tubes can incorporate a tube specifically for oxygen degassing, or a layer of parallel tubes connected by two manifolds: the lower manifold is used to inject air into the culture, and the higher one acts as the degasser (Kumar et al., 2010). Nevertheless, microalgal productivities were lower than expected in these tubular systems, possibly because of build-up of dissolved oxygen during high light intensity periods and along the bioreactor path between manifolds. In systems with exhaust gas recirculation, dissolved oxygen accumulation can be avoided by bubbling exhaust gas through a sodium sulfite solution before its return to the bioreactor (Cien-Fernandez et al. 2005).

Unfortunately, the efficiencies of most techniques used to date for dissolved oxygen removal from microalgal cultures are still not satisfactory. As a result, the classical bubbling mode of operation has been employed to avoid the costlier need for degassing devices. The use of several small bioreactors instead of one large unit also alleviates this problem. Scale-up is indeed easier for facilities that use many small reactors in parallel, even though investment costs might be higher than with fewer large equipment units. Continued research is needed to accurately match the amount of CO_2 supplied to the actual uptake requirement of the metabolizing microalgae, as well as the amount of O_2 removed to the actual amount of O_2 produced.

5.4 Gas transfer

Gases introduced into bioreactors serve a number of purposes in microalgal cultivation, including: supply of CO_2 as sources of carbon for biomass primary and secondary metabolism; provision of internal mixing, which avoids nutrient concentration gradients; promotion of exposure of all cells to light (especially in high density cultures), while minimizing self-shading and phototoxicity; control of pH by assuring dissolution of CO_2 and avoiding gradients thereof; and stripping of accumulated dissolved oxygen, hence reducing its toxicity to microalgae ((Kumar et al., 2010, Pulz, 2001).

Among the various alternatives, bubbling CO_2-enriched air into the bottom of the bioreactor with bubble diffusers has been the most frequently used approach. Moderate overall transfer efficiencies (13–20%) can be achieved by this mode of gas delivery (Carvalho et al. 2006); however, associated drawbacks are loss of CO_2 to the atmosphere, biofouling of diffusers, and poor mass transfer rates owing to a relatively low interfacial specific surface area. Better overall efficiencies are expected for hollow-fiber membrane bioreactors in which the slightly lower mass transfer coefficients that arise from a less turbulent local hydrodynamic pattern are compensated by the much larger area per unit volume available for mass transfer. In addition, the area of mass transfer is well defined, and the pressure on the gas side can be controlled so as to supply only the required amount of CO_2, hence permitting more accurate control of the transfer rate and a dramatic reduction in the amount of CO_2 lost to the atmosphere (Carvalho & Malcata, 2001).

5.5 Mixing rates

Mixing is a key parameter for acceptable performance of microalgal bioreactors. Low mixing rates hamper gaseous mass transfer and might even permit biomass settling. In either case, poor mixing leads to emergence of stagnant zones, where light and nutrients are insufficiently available and anoxic/anaerobic conditions will thus prevail, which results in a decrease of productivity (Kumar et al., 2010). Culture viability might also be compromised by production and accumulation of toxic compounds in stagnant zones (Becker, 1994). Conversely, high mixing rates can cause shear damage to cells (Carlsson et al. (2007), besides requiring a large energy input.

The most common methods of mixing in microalgal bioreactors are pumping, mechanical stirring and gas injection. Pumping offers fair mixing efficiency, but low gas transfer rates; the associated hydrodynamic stress increases with the rotation speed of the pumps, or the number of passes of the microalgal suspension through the pump units (Jaouen et al. 1999).

Mechanical stirring has been reported to provide good mixing efficiency and gas transfer; however, it is likely to produce significant hydrodynamic stress (Tredici, 2003), which can be managed via adequate use of baffles to create a controlled turbulence pattern. Gas injection (bubbling) produces lower hydrodynamic stress, while providing good gas transfer and reasonable mixing efficiency (Richmond & Cheng-Wu, 2001); however, cell damage in sparged cultures increases as the biomass concentration increases, because exponentially higher degrees of stirring are needed to maintain a high-density culture at a predefined level of mixing (Pulz, 2001). One approach to minimize this problem is to maintain a low gas input per nozzle, so as to reduce shear stress and consequent cell damage (Barbosa et al. 2003).

5.6 Temperature effects

Temperature is one of the major factors that regulate cellular, morphological and physiological responses of microalgae: higher temperatures generally accelerate the metabolic rates of microalgae, whereas low temperatures lead to inhibition of microalgal growth (Munoz & Guieysse, 2006). The optimal temperature varies among microalgal species (Ono & Cuello, 2003); however, optimal temperatures are also influenced by other environmental parameters, such as light intensity. Optimal growth temperatures of 15–26 ^{o}C have been reported for some species, with maximum cell densities obtained at 23 ^{o}C. Only daytime higher temperatures were observed to have clearly favorable effects on microalgal growth rates due to photosynthesis, except when the night temperature was as low as 7 ^{o}C (Tamiya, 1957).

5.7 pH effects

Most microalgal species are favored by neutral pH, whereas some species are tolerant to higher pH (e.g. Spirulina platensis at pH 9) (Hu et al. 1998) or lower pH (e.g. Chlorococcum littorale at pH 4) (Kodama et al. 1993). There is a complex relationship between CO_2 concentration and pH in microalgal bioreactor systems, owing to the underlying chemical equilibria among such chemical species as CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. Increasing CO_2 concentrations can lead to higher biomass productivity, but will also decrease pH, which can have an adverse effect upon microalgal physiology. By contrast, microalgae have been shown to cause a rise in pH to 10–11 in open ponds because of CO_2 uptake (Oswald, 1988). This increase in pH can be beneficial for inactivation of pathogens in microalgal wastewater treatment, but can also inhibit microalgal growth. Similarly, the speciation of NH_3 and NH_4^+ in microalgal bioreactors is strongly dependent on pH – NH_3 uncouples electron transport in the microalgal photosystem and competes with water molecules in oxidation reactions, thus leading to release of O_2 (Hu et al. 1998).

5.8 Nutrient requirements

In addition to the carbon, nitrogen is the most important element that is required for microalgal nutrition (Becker, 1994) and, as a constituent of both nucleic acids and proteins, nitrogen is directly associated with the primary metabolism of microalgae. Fast-growing microalgal species prefer ammonium rather than nitrate as a primary nitrogen source (Green & Durnford, 1996); intermittent nitrate feeding, however, will enhance microalgal growth if a medium that lacks nitrate is used (Jin et al. 2006). Under partial nitrogen

deprivation, microalgae grow at lower rates, but produce significantly more lipids, which are reserve compounds synthesized under stress conditions, even at the expense of lower productivities (Lardon et al. 2009).

Phosphorus is the third most important nutrient for microalgal growth, and should be supplied to significant excess as phosphates because not all phosphorus compounds are bioavailable (e.g. those combined with metal ions) (Kumar et al. 2009). In the case of marine microalgae, seawater supplemented with commercial nitrate and phosphate fertilizers is commonly used for production of microalgae (Green & Durnford, 1996). Nevertheless, trace species, such as metals (Mg, Ca, Mn, Zn, Cu and Mb) and vitamins, are typically added for effective cultivation (Becker, 1994).

6. Microalgae harvesting and conversion to fuels

6.1 Microalgae biomass harvesting

Harvesting of the microalgae biomass, i.e., concentrating microscopic algal cells from the dilute solutions of the algal mass culture, is an essential step to secure high-quality effluents and to prevent cell washout (Richmond et al. 2003, Munoz & Guieysse, 2006). The main difficulties encountered in harvesting microalgae arise from the relatively low biomass concentration in conventional bioreactors, coupled with the small size of its constituent microalgal cells. Harvesting typically contributes to 20–30% of the total cost of microalgal biomass production (Carlsson et al. 2007). The major techniques presently applied in the harvesting of microalgae include coagulation, flocculation, sedimentation, centrifugation, foam fractionation, ultrasonic separation, flotation, membrane filtration, and electrophoresis techniques (Carlsson et al. 2007; Kumar et al., 2010; Uduman et al. 2010).

Selection of the harvesting method mainly depends on the properties of microalgae, such as density, size, the value of the desired products. Microalgae harvesting can generally be divided into a two-step process, bulk harvesting, to separate microalgal biomass from the bulk suspension, in this method, the total solid mater can reach 2–7% using flocculation, flotation, or gravity sedimentation; and the second step is thickening, to concentrate the slurry, using filtration and centrifugation. This step needs more energy than bulk harvesting (Brennan & Owende, 2010).

Microalgal cell immobilization has been proposed to circumvent the harvesting issue, but large-scale applications are limited. Further investigation is clearly needed to optimize operating conditions and design new processes (Mallick, 2002).

Following biomass harvest by centrifugation or filtration, microalgal paste traditionally consists of 90% (w/w) water, which meets the requirements for anaerobic digestion. However, it is necessary to reduce this value to a maximum of 50% (w/w) water for efficient oil extraction (Kumar et al., 2010). Despite its energy-intensive nature, drying has often been the dewatering process of choice.

Almost 90% of the energy required for biodiesel production is indeed accounted for by harvesting and dewatering of biomass, besides lipid extraction itself (Lardon et al. 2009). In addition to lipid extraction for biodiesel production, a novel process that gasifies biomass to methane and concentrated CO_2 has recently been proposed (Stucki et al. 2009) for improved overall energy efficiency.

Most microalgae exhibit the phenomenon of bioflocculation, which is the spontaneous aggregation of algal cells into large flocs. These flocs will then settle rather rapidly. The process yet not fully understood and need more investigation. It depends on the elaboration of polymers by the algal cells that makes the cells stick together (Benemann & Pedroni, 2008). Sufficient experience exists to suggest that bioflocculation, possibly in combination with centrifugation, could achieve the cost goals for efficient CO_2 biofixation and biofuel production. Further study and development of this process remains a central problem, next to productivity and controlled cultivation of specific algal species in the designed photobioreactor (Benemann & Pedroni, 2008).

6.2 Microalgae biomass conversion to fuels

For economic and environmental reasons the demand for liquid energy from renewable resources will have an ascending trend in the coming year. The advantages of biomass include that it is biodegradable, sustainable and also causes less pollution when compared with fuels being used. Microalgae with high lipid content produces higher biodiesel than commercially used oilseed crops (rapeseed, soybean oil) utilizing less amount of water (Sheehan et al. 1998).

Converting the harvested biomass to a biofuel considered the least difficulty step. The high water content of the harvested biomass makes drying or any thermochemical conversion process (e.g. combustion, gasification, pyrolysis) impractical, and an even more critical problem is the high nitrogen content of algal biomass. Any thermochemical processing would result in unacceptable NO_x generation and loss of this valuable nutrient and resource. Thus, microalgae biomass fuel conversion processes are dependent on fermentations to produce methane or ethanol, or the metabolism of the algae themselves, to produce oils and hydrocarbons, useable for conversion to biodiesel, or to evolve hydrogen. Methane production from microalgae biomass is technically and economically feasible, but still requires some research and development to improve yields and overall efficiency.

Compared to anaerobic digestion, very little work has been done on ethanol fermentations of algal biomass. The reason is that ethanol fermentations, typically carried out by yeast, are restricted to sugars, starches and similar easily degraded carbohydrates. Microalgae typically contain only about 20% or less of such carbohydrates, present as starch in green algae and glycogen in cyanobacteria. For practical ethanol production, an algal biomass with very high fermentable carbohydrate content, preferably over 60% on a dry weight basis, is required. Such high starch or glycogen accumulation is only observed under conditions of nitrogen limitation, where cell growth is reduced and much or most of the photosynthetically-fixed CO_2 is diverted to storage reserves. Thus the issue is whether it is possible to optimize for both high carbohydrate content and high productivity (e.g. CO_2 fixation) using nitrogen limitation (Benemann & Pedroni, 2008).

7. Conclusion

Microalgae have attracted a great deal of attention for CO_2 fixation and biofuel production because they can convert CO_2 into biomass via photosynthesis at much higher rates than conventional biofuel crops.

Several challenges, addressed in this chapter, for microalgal based CO_2 sequestration and biofuel production remain. Most studies reported to date have been performed on the bench-scale, and were conducted under strictly controlled conditions. As a result, little is known about the feasibility of the photobioreactor scale-up. Factors, such as supply of adequate amounts of CO_2, nutrients and light to microalgal cells, should be investigated and optimized at large scale.

Co-digestion of microalgae with wastewater sludge for biogas production should also be considered, because this strategy could be integrated into the existing wastewater infrastructure.

Microalga-based CO_2 fixation and biofuel production can be more sustainable by coupling microalgal biomass production with existing power generation and wastewater treatment infrastructures. Microalgae can utilize low-quality water, such as agricultural runoff or municipal, industrial or agricultural wastewaters, as a source of water for the growth medium as well as a source of nitrogen, phosphorus and minor nutrients (Becker, 1994). Hence, an additional economic and environmental incentive exists as a result of the decreased cost of water and chemicals required for the formulation of the growth medium, while providing a pathway for wastewater treatment (Kumar et al., 2010; Mallick, 2002; Demirbas, 2004). Such a coupling technology need to be further investigated. A number of crucial research gaps remain that must be overcome to achieve full-scale operation such as improved algal growth and nutrient uptake rates; integration of biosystems with waste gas, wastewater and water reclamation systems; improved gas transfer and mixing; and improved algal harvesting and dewatering.

Harvesting, dewatering and lipid extraction from microalgal biomass are still challenging issues because they consume large amounts of energy – mainly because of the small cell size and relatively low biomass levels of microalgal cultures. Therefore, more efficient and economic harvesting technology should be developed to enhance the commercial viability of microalgae biofuels industry (Kumar et al., 2010).

A key challenge for microalgal biodiesel production is the use of microalgal species that can maintain a high growth rate in addition to a high metabolic rate, thus leading to significant lipid yields. This major challenge can be duly addressed via extensive bio-prospecting or target oriented genetic engineering – currently such approaches starting to appear as promising approaches (Kumar et al., 2010).

Finally, it seems there is a lack of fundamental information needed to rationally optimize the performance of existing bioreactors. Novel bioreactor configurations and designs are also needed that promote microalgal growth and CO_2 biofixation, characterized by volumetric productivities at least one order of magnitude above those of conventional open pond systems.

8. References

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