Biosequestration of carbon dioxide – potential and challenges

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Abstract

Anthropogenic activities leading to release of carbon dioxide and other greenhouse gases have been directly linked to the increase in global temperature and consequent climate change. Methods to manage the release of CO2 through sequestration by physical and chemical methods have been worked out. These techniques of CO2 containment are prohibitively expensive. Of late, the prospect of biological carbon fixation for remediation of CO2 is being explored. Plants are CO2 sinks – they fix CO2 during daytime. Tiny (microscopic) aquatic plants – the microalgae have even more efficient CO2 fixing ability than large plants and trees. They have a very quick growth rate. Some of these species are rich in oil suitable for converting to diesel (fuel) and with nutrient properties (with omega fatty acids). Some species have carotenes and other pigments; some are rich in proteins. They can be mass cultured in lands not suitable for agriculture and their biomass can be beneficially used in production of biodiesel, nutraceuticals for humans and as animal feed. Flue gas (a mixture of CO2 and the other greenhouse gas NOx) released from Industries can be used to fertigate the mass culture units of microalgae thus effectively sequester them. The proofs of concept experiments of this biosequestration option have been demonstrated in 2005. Large scale industries based on this principle are yet to take off – despite the lure of biodiesel. The challenges in this technology are many — both technical and fiscal. Technical issues relate to mode of transfer of flue gases to the algal culture medium and means of harvest of microalgae. Fiscal concerns are with regard to the cost of set up of the facility and the running costs.

Key words: Biosequestration, Flue gas, Microalgal mass culture, Biotechnological use, photo bioreactors, open ponds, microalgal harvest

1. Introduction

The disastrous consequences arising from increasing levels of anthropogenic carbon dioxide (CO2) emissions and the predicted catastrophe if unabated, is now widely recognized. The 2007 Nobel peace prize was awarded to Rajendra Pachauri (Chairperson of the Intergovernmental Committee on Climate Change- IPCC) and Albert Arnold (Al) Gore for their “efforts to build up and disseminate greater knowledge about man-made climate change, and to lay the foundations for the measures that are needed to counteract such change”. The documentary film “An inconvenient truth” presenting the slide show of Al Gore on climate change has equally been rewarded with a couple of Academy awards in 2007. After the ratification of Kyoto protocol by ~191 states in 2005, research has geared up to explore and develop appropriate methods for CO2 capture and storage (long term/permanent) – dubbed as CCS (carbon capture

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and storage/sequestration). CCS has evolved to CCUS with the insertion of Utilization in this programme aiming to utilize the captured carbon for commercial purposes.

Fossil fuel fired power plants are responsible for 40% of total CO$_2$ emissions [1]. The flue gases contain besides CO$_2$ another greenhouse gas (GHG) – the oxides of nitrogen (NOx) besides oxides of sulphur (SOx) – the cause of acid rain. Developing an optimal system to capture and subsequently store or utilize CO$_2$ in the flue gases from the power plants is crucial in managing the CO$_2$ levels in the atmosphere. Carbon sequestration is being attempted through physical and chemical means. Of late, biological sequestration is also being considered. Each of these approaches has a potential but several challenges as well.

Biological sequestration involves use of living organisms – plants, because they use carbon dioxide for synthesis of carbohydrates in the process called photosynthesis. Some of the methods used are:

1.1 Terrestrial sequestration
Afforestation of barren lands will serve as CO$_2$ sinks. Therefore, growing more trees and replacement of cut trees with a new sapling (reforestation) are an age old tradition. In realization of the impending high global temperatures in the near future, research efforts are on to recognize the plant species which would survive and flourish under high temperature. At higher temperatures, the microscopic pores (stomata) on leaves through which CO$_2$ diffuses into the plant get bunged to avoid evaporation of water (through a process called transpiration). Plant species tolerant to high CO$_2$ and temperatures are therefore being identified through simulated experimental studies of CO$_2$ X environment interaction on plant growth [2].

1.2 Ocean fertilization
Ocean is considered to be the largest sink for CO$_2$. The microscopic algae (phytoplankton) which constitute the primary producers in the marine ecosystem, utilize CO$_2$ for photosynthesis. About 6-8% of the atmospheric carbon is believed to be fixed by them [3]. Iron is a mineral present in limiting amounts to support phytoplankton growth. Fertilization of ocean with iron, termed–ferrigation (hypothesis proposed by Martin [4]) is believed to promote luxurious growth of phytoplankton and thereby increase the sequestration of CO$_2$. Reeburgh [5] reported that ferrigation induced diatom-dominated phytoplankton blooms accompanied by considerable CO$_2$ fixation in the ocean surface layer. But the fate of bloom biomass could not be resolved in these experiments because of the mass mortality of the diatom species in the bloom and assumed that at least half the bloom biomass sank to a depth of 1000 meters. It was proposed that iron-fertilized diatom blooms might fix carbon for centuries in the bottom of ocean. However this idea casted several apprehensions on its efficacy, the ratio of iron added to carbon sequestered and various side effects of ocean ferrigation. Moreover, the idea is unpopular with the public because it is perceived as meddling with nature [6].

2. Mass culture of microalgae
Cultivation of microalgae on a mass scale is also perceived as a measure of large scale biosequestration of CO$_2$. This would be a good option for the CCSU programme as the algal biomass can be used for various purposes. The opportunities and challenges of this method are herewith discussed.

Microalgae are small (microscopic) photosynthetic microorganisms. They constitute a large group in the living world, represented by thousands of species. They can be unicellular, filamentous or colonial. (Figure1). They are aquatic and live in all kinds of water – fresh, sea, estuarine and sewage water; species that thrive in different waters being different. They have the following features that make them good candidates for carbon sequestration.
They multiply very fast with a generation time of less than a day under suitable environmental conditions.

The rate of photosynthesis in these organisms is much higher than the land plants. They can thus fix CO\textsubscript{2} more efficiently compared to land plants.

The CO\textsubscript{2} enters the cells passively through diffusion and there is no regulated entry through stomata as in land plants. Hence, CO\textsubscript{2} uptake remains uninterrupted even at high temperatures compared to land plants in which stomata close at high temperatures.

Algal biomass can be used for various economically important products (Table 1). One of the perceived potential that has been realized is in nutraceuticals – nutrient with positive therapeutic and health benefits. There are species rich in proteins, pigments like β carotene, lutein, astaxanthin, and lipids with omega fatty acids (poly unsaturated fatty acids (PUFAs) [7, 8]. Of late, there is a renewed interest in exploring microalgae as source of biofuel [9-11]. The concept of biofuel from microalgae has drawn the attention of many due to its many advantages [12].
Table 1. Biotechnological use of microalgal biomass

<table>
<thead>
<tr>
<th>Microalgal species</th>
<th>Biotechnological use</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Spirulina platensis</em></td>
<td>Protein and pigments[13, 14]</td>
</tr>
<tr>
<td><em>Chlorella protothecoides</em></td>
<td>Nutraceutical (Lutein) &amp; biofuel [15]</td>
</tr>
<tr>
<td><em>Dunaliella salina</em></td>
<td>Nutraceutical (β-carotene) &amp; Mariculture[16,17]</td>
</tr>
<tr>
<td><em>Haematococcus pluvialis</em></td>
<td>Nutraceutical (Astaxanthin) [18]</td>
</tr>
<tr>
<td><em>Skeletonema costatum</em></td>
<td>Mariculture [19]</td>
</tr>
<tr>
<td><em>Pavlova lutheri</em></td>
<td>Mariculture [19]</td>
</tr>
<tr>
<td><em>Isochrysis galbana</em></td>
<td>PUFAs &amp; mariculture [19]</td>
</tr>
<tr>
<td><em>Porphyridium sp.</em></td>
<td>PUFAs &amp; polysaccharide [20]</td>
</tr>
<tr>
<td><em>Nannochloropsis</em> sp.*</td>
<td>PUFAs &amp; mariculture [21]</td>
</tr>
<tr>
<td><em>Tetraselmis suecica</em></td>
<td>Mariculture, biofuel [19]</td>
</tr>
<tr>
<td><em>Chaetoceros calcitrans</em></td>
<td>Mariculture [19]</td>
</tr>
<tr>
<td><em>Phaeodactylum tricornutum</em></td>
<td>Mariculture [19] &amp; Biofuel [22]</td>
</tr>
<tr>
<td><em>Cryptothecidium colnii</em></td>
<td>PUFAs [23]</td>
</tr>
<tr>
<td><em>Schizochytrium sp.</em></td>
<td>Mariculture [19]</td>
</tr>
<tr>
<td><em>Synechococcus sp.</em></td>
<td>Bioactive compounds [24]</td>
</tr>
<tr>
<td><em>Botryococcus braunii</em></td>
<td>Biofuel [25]</td>
</tr>
<tr>
<td><em>Chlamydomonas rheinhardii</em></td>
<td>Bio hydrogen and biofuel [26]</td>
</tr>
<tr>
<td><em>Neochloris oleoabundans</em></td>
<td>Biofuel [27]</td>
</tr>
<tr>
<td><em>Nannochloropsis</em> sp.*</td>
<td>Biofuel [28]</td>
</tr>
<tr>
<td><em>Euglena gracilis</em></td>
<td>Biotin [29]</td>
</tr>
<tr>
<td><em>Pleurochrysis carterae</em></td>
<td>Biofuel [19]</td>
</tr>
</tbody>
</table>

3. Flue gas mitigation by microalgae

Flue gas is a mixture of carbon dioxide, oxides of nitrogen (NOx, 70 – 420 ppm) and sulphur (SOx, 50 – 400 ppm). Microalgae can assimilate all the constituents of the flue gas mixture because they can utilize NOx as their nitrogen supplement for growth, CO2 for photosynthesis and they can tolerate and absorb up to 300 ppm SOx [30]. The NOx dissolves in water and becomes available in an assimilatory form to the microalgae. Many industrial set ups and thermal power plants are installed with sulphur scrubbers as a mandatory pollution check practice. Land plants can utilize only CO2 but not the NOx component of flue gases.

A proof of concept experiment on biosequestration of CO2 in flue gases was conducted by Isaac Berzin at MIT Boston, USA funded by the Green fuel technologies [31]. The flue gas from the chimneys of the thermal power plant near the MIT campus was fed to a microalgal culture system set up on the terrace of an MIT building (Figure 2).

An international network on biofixation of CO2 for greenhouse gas abatement using microalgae was proposed in 2002 for the development of this technology [32]. The feasibility of using microalgae bioreactors at an industrial scale to sequester CO2 from power plant exhaust gases (flue gas) has been considered [33].
Following the proof of concept demonstration of Berzin several set ups have been established. Electric company (Israel Electric Corporation–IEC) in Ashkelon, Israel utilizes SO\textsubscript{2} free flue gas for the cultivation of algae. It has a continuous supply of free, filtered and chlorinated sea water that can be obtained at the rate of 450,000 m\textsuperscript{3} per hour. Seambiotic Ltd. has designed systems for the removal of high SOx content in the flue gas mixture from coal-fired power plant in IEC, by using flue gas desulphurization (FGD) techniques. FGD treated flue gas is supplied to salt water algae race way ponds for the growth of \textit{Nannochloropsis} sp. The alga showed increased growth rate with FGD treated flue gas than pure CO\textsubscript{2} (US patent number US2008/0220486 A1).

US patent 5,659,977 by Cyanotech Corporation, Hawaii describes methods to use CO\textsubscript{2} from exhaust gas of a fossil fuel fired power plant for algae production. 188 Kg/h CO\textsubscript{2} from the flue gas chimney is transferred to the bottom of a CO\textsubscript{2} absorption tower (6.4 m high packing material) which can provide 67 tons of CO\textsubscript{2} per month that aids in the production of 36 tons per month Spirulina. The patent also describes the utilization of heat from fossil fuel engine to dry the algal biomass and the electrical energy is used to drive motors, pumps and also to provide illumination for algal growth. Nature beta technologies Ltd. Eilat city, Israel reported \textit{Dunaliella salina} biomass production of 20 g/m\textsuperscript{2}/d by. Cost of dry biomass when cultured with flue gas mixture was estimated at USD 0.34/Kg as compared to USD 17/Kg cultivation in normal environment[34]. RWE’s algae project, Germany, erected at the Niederaussem power plant location, utilized desulphurized flue gases for algal growth which was operated for three years until 2011 (http://www.rwe.com/).

4. Microalgal cultivation with flue gases: Opportunities

Microalgal cultivation poses no competition to agriculture both in terms of usage of water and land. Fresh water is not required for many species – sea water can be used to culture marine and estuarine species. Even sewage water can be used when the algae are cultivated for biofuel [35]. Cultivation facility – a shallow circular or a race way pond can be set up on barren lands – even deserts; fertile land is not required [36, 37].

Sequestration of carbon from flue gas emissions through physical and chemical methods requires separation of CO\textsubscript{2} from the other gases. A major component of flue gases is NO\textsubscript{x} which is also a greenhouse gas. This is not taken care of in physical and chemical methods of carbon sequestration. In biosequestration with microalgae, both the CO\textsubscript{2} and NO\textsubscript{x} in the flue gas is utilized – the former for photosynthesis and the latter as a source of nitrogen – a nutrient required for growth. The NO\textsubscript{x} dissolves in water and is converted into an assimilatory form to the microalgae. Jiang et al. [38] reported that
*Scenedesmus dimorphus* has a tolerance to high concentration of CO$_2$ (20%), NOx (150 – 500 ppm) and SOx (100 ppm). *Nannochloris* sp. is reported to grow under 100 ppm of nitric oxide (NO) [39]. *Tetraselmis* sp. was found to flourish when supplied with flue gas with 185 ppm of SOx and 125 ppm of NOx in addition to 14.1% CO$_2$ [40]. *Dunaliella tertiolecta* was found to grow well in flue gas with 1000 ppm of NO and 15% CO$_2$ concentration assimilating ~51 to 96% of nitric oxide depending on the growth condition [41]. Maeda et al [42] examined the tolerance of a strain of *Chlorella* and found that the strain could grow in the presence of different combinations of trace elements.

The algal biomass can be used for various purposes as listed in table 1.

Flue gas cooling, compression, transport and supply to the algal mass cultivation units like open race way ponds or photobioreactors constitutes a major share of total production cost. It is not always possible to set up algal cultivation system adjacent to flue gas chimneys in the thermal power plant units or in the industries because of space constraint. A high level of dust and other air other pollutants in the industrial units also have an impact on the algae cultivated in the open ponds. Also, photobioreactors do not have an effective control on emission of CO$_2$ from exhaust gases because CO$_2$ is usually bubbled through the reactor with the excess CO$_2$ being emitted to the atmosphere and this technology is very expensive to operate [43]. An alternate strategy is to enrich the water with flue gases until saturation and transport the water to algal cultivation units located away from industrial units. This method avoids cooling and compression costs of flue gases and algal production units need not be constructed near power plants. If fresh water is used the pH of the water falls to as low as 2 (our unpublished results) because of dissolution of CO$_2$ (carbonic acid) and NOx and SOx. For sea water (pH 8.0) even after continuous supply of flue gas for two continuous days, the pH did not change much (7 to 7.5) perhaps due to the buffering capacity of sea water [44]. The pH of flue gas enriched water can be adjusted to optimum based on the type of alga that is cultivated. The general optimum pH for fresh water algae is 6 and for marine algae it is ~8.

There are reports of experiments of testing growth of microalgae in flue gas enriched water [45-48]. In our own laboratory we studied the growth rate of some fresh water and marine microalgae in water enriched with flue gas emissions from a gas fired furnace in the Steel industry situated in our city (Visakhapatnam Steel Plant). The results are encouraging (Table 2).

**Table 2.** Growth of different microalgal species with in nutrient medium made from flue gas enriched water (fresh/sea) in comparison to normal water (fresh/sea) and CO$_2$ enriched water (fresh/sea)

<table>
<thead>
<tr>
<th>Microalgal species</th>
<th>% Increase (+)/decrease(−) in growth in flue gas enriched water compared to Normal water</th>
<th>CO$_2$ enriched water</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Chlorella protothecoides</em></td>
<td>+50</td>
<td>+19</td>
<td>Flue gas enriched water is more effective than pure CO$_2$</td>
</tr>
<tr>
<td><em>Scenedesmus dimorphus</em></td>
<td>+193</td>
<td>+21</td>
<td>Flue gas enriched water is more effective than pure CO$_2$ alone</td>
</tr>
<tr>
<td><em>Desmodesmus sp.</em></td>
<td>+36</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><em>Haematococcus pluvialis</em></td>
<td>+25</td>
<td>−16</td>
<td>Pure CO$_2$ supply is more effective than flue gases</td>
</tr>
<tr>
<td><em>Neochloris oleoabundans</em></td>
<td>+38</td>
<td>+35</td>
<td>Flue gas enriched water has profound influence on growth than pure CO$_2$ supply</td>
</tr>
<tr>
<td><em>Dunaliella salina</em></td>
<td>0</td>
<td>+20</td>
<td>No advantage in flue gas enriched water*</td>
</tr>
<tr>
<td><em>Tetraselmis sp.</em></td>
<td>0</td>
<td>+18</td>
<td>No advantage in flue gas enriched water*</td>
</tr>
</tbody>
</table>

*flue gas might not have dissolved in sea water as the pH did not fall from ~8 to not below 7.5
4.1 Microalgal cultivation with flue gases: challenges

In most cases the flue gases have to be transported to the microalgal cultivation site away from the industrial set up. This is true for physical and chemical methods of carbon sequestration from flue gases. The major cost in carbon sequestration involves these transportation costs.

Microalgae can be cultivated in closed or open systems. The closed systems are called photobioreactors and they are designed in various configurations like flat-plate and tubular reactors (Figure 3). They are highly automated with controlled temperature, pH and other physical and chemical conditions. Therefore, there is optimal growth of algae and high biomass productivity. Also, since it is a contained system there is no problem of contamination of the algal biomass by other algal species or bacteria. Photobioreactors are being used for the cultivation of *Haematococcus pluvialis* [49], *Tetraselmis suecica* [50], *Nannochloropsis sp.* [9] and *Chlorella vulgaris* [51].

![Figure 3. Photobioreactors: Designed in various configurations like flat-plate and tubular reactors](http://www.et.byu.edu/~wanderto/homealgae/project/Photobioreactor http://www.uanews.org/story/biofuels-algae-hold-potential-not-ready-prime-time http://www.algaeindustry.com/aim-interview-asus-dr-milton-sommerfeld/)

The drawback with photobioreactors is scalability, with maximum unit size ~100 m² and the cost of construction. The costs become forbidding—far exceeding the value of the algal biomass. Cleaning and maintenance of photobioreactors is also very difficult with the algae often clinging to the walls of the reactor. Running a photobioreactor is an energy intensive process and nullifies the aim of carbon sequestration. Construction of photobioreactors to cater to sequestration of large volumes of flue gas is highly unrealistic both in terms of maintenance and economy.
Open pond systems are therefore the only option for mass cultivation of microalgae. These are shallow ponds which are either lined with concrete or other materials or just left with the retaining mud walls (Figure 4). They are 10 – 50 cm deep to allow good penetration of light. Natural sun shine is utilized. These ponds are fitted with paddle wheels for gas/liquid mixing and circulation. Such open pond systems are especially suitable in areas with abundant sunshine for most part of the year. Much less energy is utilized in operation (for paddle wheels) of raceway ponds. However contamination by other microalgal species and microbes or grazers is an inevitable contingency. Consistent production levels are not possible because of the variation in the climate like temperature, rainfall etc. Therefore hardy microalgal species can only be mass cultivated in open pond systems.

Though many microalgal species have potential for various biotechnologically useful products commercial success has only been possible with three species *Chlorella* (Centre pivot ponds– Taiwan and Japan), *Dunaliella salina* (Cognis–Hutt Lagoon, Western Australia, Nature Beta– Eilat, Israel) and *Haematococcus pluvialis* (Cyanotech– Kona, Hawaii, Algatech Ltd., Israel). These systems are typically used in commercial large scale cultivation of algae— *Dunaliella salina* [52], *Arthrospira platensis* [53], *Pleurochysis carterae* [54] and *Nannochloropsis* sp. [55].

![Figure 4. Open ponds for mass culture of microalgae: Race way and circular with paddle wheels.](http://www.nature.com/nature/journal/v474/n7352_supp/full/474S015a.html; http://www.et.byu.edu/~wanderto/homealgaeproject/Photobioreactor.html)
To commence mass culture in open ponds, seed culture is required. The seed culture is developed in the laboratory under controlled conditions. The culture is initiated in a small volume which is gradually up scaled to larger volumes and the process takes several days (15 – 25) depending up on the scale of mass culture. Microalgae being phototrophic, growth to a level where dense cultures like bacteria and yeast are attained is not possible—light becomes a limiting factor. Indoor culture of seed culture to feed outdoor ponds is an energy intensive process as it requires artificial light, temperature control etc. Moreover flue gas mitigation using microalgae requires set up of large scale culture units.

To reduce the time and thus energy costs in generating seed culture indoors mixotrophy culture can be resorted to. Mixotrophy involves culture under light in an inorganic nutrient medium supplemented with an organic carbon source $^{56}$. The algae in such cultures photosynthesize and simultaneously use the ready carbon source in the medium. Because they are not exclusively dependant on light, dense growth occurs in mixotrophy cultures. The duration of the seed culture development time is substantially reduced compared to photoautotrophically cultures. Glycerol and acetate are the most commonly used carbon sources because they can be obtained as by-products from various industries $^{57, 58}$. Several microalgal species—Chlorella vulgaris $^{59}$, Botryococcus braunii $^{60}$ Phaeodactylum tricornutum $^{22}$ have been reported to be adaptable to mixotrophic culture. Scenedesmus dimorphus, Neochloris oleobundans, Dunaliella salina, Chlorella protothecoides and Desmodesmus sp. were found to respond favourably to mixotrophic cultures in our studies (unpublished results). Thus the unique feature of microalgae—mixotrophy can be used to develop seed culture in the laboratory to inoculate outdoor ponds, where CO2/flue gases can be used for algal growth.

Harvesting algal biomass is yet another challenging task. It contributes to 20-30% of total production costs $^{61}$. The microalgal cultures are dilute (usually < 0.5 kg m$^{-3}$ dry mass) and large volumes of water have to be processed for harvesting the cells. Flocculation is followed by centrifugation; filtration or sedimentation techniques are in practice. Filtration is not a practical approach for larger volumes of water have to be processed for harvesting the cells. Flocculation technique is widely used in several mass culture systems. Multivalent metal salts such as alum have been widely used to flocculate algal biomass in wastewater treatment processes $^{63-66}$. Alum is an effective flocculent for Scenedesmus and Chlorella $^{67}$; however, flocculation by metal salts may be unacceptable if biomass is to be used in certain aquaculture and other applications. Edible, non-toxic polymeric flocculants like chitosan are reported to be effective with Tetraselmis chui, Isochrysis sp. and Thalassiosira pseudonana $^{68}$. An optimum method of harvesting is yet to be designed for each algal species. More research is required in the area of flocculants.

The production costs of algal biomass are high even when cultivated in open pond systems. That’s why economic viability is possible only for high value products like those used as nutraceuticals (beta carotene with a global market of $US 247 million, astaxanthin $US 200 million, lutein $US 233 million and PUFAs $US 700 million). As of now the economic feasibility of microalgae as source of biofuel looks bleak $^{69-71}$. The scientist maverick Craig Venter is engaged in research on microalgal biofuel (http://www.forbes.com/sites/christopherhelman/2012/06/24/milking-oil-from-algae-craig-venter-makes-progress-in-exxon-backed-venture/). There is thus a beacon of hope that a technology breakthrough may result in the realization of flue gas sequestration to produce carbon neutral renewable source of fuel. A considerable amount of production costs can also be compensated via carbon credits, which was formalized in the Kyoto protocol. Carbon credits and carbon markets are a component of national and international attempts to mitigate the growth in concentrations of greenhouse gases, where allowances are given to companies/organizations for each ton of CO2 removed from environment. Three mechanisms—Joint implementation (JI), Clean Development Mechanism (CDM) and International Emission Trading (IET) are in operation by Kyoto protocol to provide carbon credits.
5. Conclusions

Biosequestration of greenhouse gases in flue gases through microalgal mass culture conceptualized and being experimented because of the several advantages has challenges to surmount. Containment of greenhouse gases in the modern industrial world is imperative to abate further dire consequences of climate change. Plurality of approaches is required for this task and biosequestration through microalgae thus remains a potential option.

References


