

Review of Advances in Biological CO₂ Mitigation Technology

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Abstract CO₂ fixation by microalgae has emerged as a promising option for CO₂ mitigation. Intensive research work has been carried out to develop a feasible system for removing CO₂ from industrial exhaust gases. However, there are still several challenging points to overcome in order to make the process more practical. In this paper, recent research activities on three key technologies of biological CO₂ fixation, an identification of a suitable algal strain, development of high efficient photobioreactor and utilization of algal cells produced, are described. Finally the barriers, progress, and prospects of commercially developing a biological CO₂ fixation process are summarized.

Keywords: CO₂ mitigation, microalgae, photobioreactor, utilization of microalgae

INTRODUCTION

As the concerns over global warming are increasing, many research works on carbon sequestration have been carried out. However, the high cost of CO₂ disposal is a major barrier for dissemination. The cost of removing CO₂ from a conventional thermal power plant is estimated to be in the range of \$128-967/ton of carbon (tC) [1]. The sequestration cost should be around \$10/ tC for disposal to be economically feasible. It is very difficult to achieve the goal only by developing new large-scale sequestration technologies such as CO₂ separation and storage. If the utilization of CO₂ into high value added products is possible, the sequestration cost may be reduced. That is why intensive research work, including chemical and biological, has been carried out to convert CO₂ into useful chemical products.

Among various CO₂ utilization technologies, the biological methods, particularly the ones using microalgal photosynthesis, have several merits such as mild conditions for CO₂ fixation, no requirements for the further disposal of recovered CO₂, and direct CO₂ fixation from flue gases if a suitable microalga is available. The last advantage is quite important because the separation of CO₂ from flue gases takes a major portion (over 70%) of the total sequestration costs (Fig. 1). In addition to these advantages, carbon fixed by microalgae is incorporated into carbohydrates and lipids, so that energy, chemicals, or foods can be produced from algal biomass [2-6]. Because of the advantages mentioned before, many works have been carried out to incorporate the CO₂ fixation process by microalgae into practical uses [7-11].

The major research projects, which have been per-

formed, are 1) the isolation of a suitable algal strain 2) the development of the photobioreactor having higher CO₂ fixation rates and its scale-up 3) the utilization of algal cells produced from the fixation process. 1) As mentioned above, direct CO₂ fixation from flue gases may reduce the sequestration cost significantly. However, the flue gases having high CO₂ concentrations (10~30%) and the toxic compounds like SO_x and NO_x, are extremely inhibitory to growth of most algal strains. 2) Like other biological processes, the CO₂ fixation rates by microalgae are very low. Therefore, the reactor sizes will become very large if the process applies to fix CO₂ emitted from the industrial sources. Light limitation will be a major problem for such large reactors, which are usually employed for the biological CO₂ fixation process. Therefore, the design of the large-scale photobioreactor minimizing its light limitation will be a critical issue. Finally 3) Utilization technology of algal cells into value added products may make the process commercially viable. This review will describe recent works done for the development of biological CO₂ fixation processes.

IDENTIFICATION OF SUITABLE MICROALGAE FOR CO₂ FIXATION

As it is known that the concentrations of CO₂ above 5% adversely influence growth of most microalgae [12, 13], the strains that may grow fast under high CO₂ concentrations (up to 20%) would be required. Extensive work has been carried out to find a suitable algal strain for the direct recovery of CO₂ from industrial sources [14-20]. The criteria used for the screening work were not only tolerances to high CO₂, temperature, and toxic compounds (NO_x and SO_x) but high growth rate and maximum cell densities.

Watanabe *et al.* [14] isolated a fresh-water green alga,

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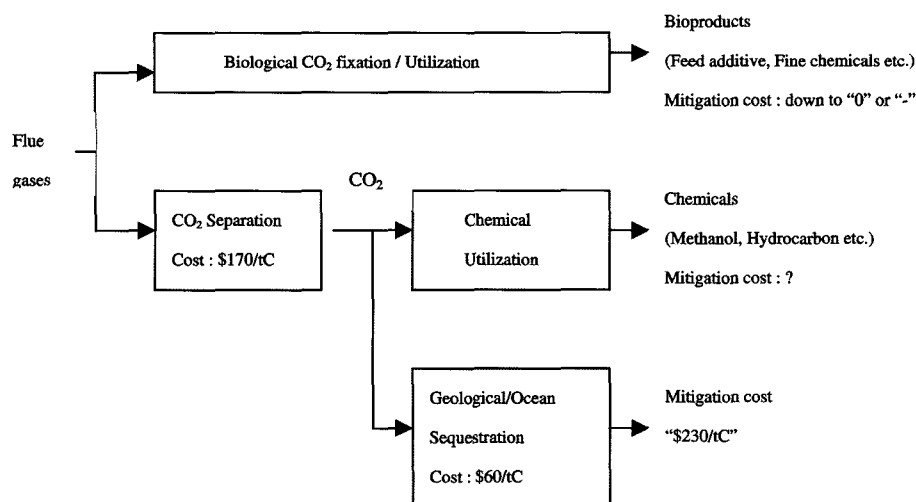


Fig. 1. General scheme of CO₂ mitigation by various technologies.

named *Chlorella* HA-1, from a paddy field. *Chlorella* HA-1 showed maximum growth at 5 and 10% CO₂ but the growth rate decreased remarkably with increasing concentration of CO₂ higher than 10%. They proposed that *Chlorella* HA-1 may be used to fixing CO₂ directly out of stack gas from LNG thermal power plants which contains about 10% CO₂ and a small amount of NO_x. The strain showed a broad range of responses with changes in pH and temperature. But the growth rate of the strain drastically decreased when CO₂ concentration was higher than 20% (v/v). Kodama *et al.* [15] reported that a new highly CO₂ tolerant marine microalga, *Chlorococcum littorale* suitable for high density cultures, has been isolated. Though the alga had an optimum growth rate in cultures with 5 and 10% CO₂, the algal growth rate with 20% CO₂ was comparable to the optimum. No growth was observed, however, at 70% CO₂. The strain may be applied to the power plants located at sea-shore.

If the hot flue gases from industrial sources are directly introduced into the algal cell cultures, the thermal stability of the cells will also be an important criterion in screening a suitable strain. Several studies have been reported the isolation of a strain having a high thermal stability [16-18]. Hanagata *et al.* [16] screened five freshwater green microalgae for tolerance to high CO₂ concentrations and reported that *Scenedesmus* and *Chlorella* species had high growth rates in up to 50% CO₂. The strains showed stable growth rates against high temperatures but no information about pH stability was given. Maeda *et al.* [17] isolated an algal strain, to be named *Chlorella* sp. T-1, which has the optimum temperature of 35°C for growth and maintains good growth up to 40°C. Sakai *et al.* [18] isolated very thermo-tolerant strains from various hot springs. The strains were identified to belong to the genus *Chlorella* and were named H-84 and A-2. Both strains exhibit the highest growth rate at 40°C and grow well up to 42°C. With regard to CO₂ tolerance, the strains could grow well up to 40%. Other works, such as mutation or adaptation studies, have been reported to

enhance the tolerances of microalgae in high concentrations of CO₂ [21,22].

Other important inhibitory compounds for CO₂ fixation in algal cells are NO_x and SO_x. Flue gases emitted from industrial sources usually contain up to 200 ppm of NO_x and SO_x. Most highly CO₂ tolerant algal cells, however, may survive only under 50 ppm of NO_x and SO_x [14,25,24]. Therefore, the inhibition by the toxic compounds in the gases would be inevitable if the flue gas is directly introduced into the microalgal culture. To overcome the inhibition effects, several studies have been carried out [25-27]. Recently Sung *et al.* [19] isolated a highly CO₂ tolerant microalga and named it *Chlorella* KR-1. Growth of the strain was not inhibited in conditions up to 20% of CO₂, 100 ppm of NO_x and 50 ppm of SO_x [25]. Tolerances of *Chlorella* KR-1 to the toxic compounds could be increased by controlling pH of culturing medium and the cells could grow well up to 250 ppm of SO_x and 300ppm of NO_x [26]. However, controlling the pH was effective only for some specific microalgae. Several strains of microalgae, which are suitable for CO₂ fixation, have been listed (Table 1).

Cases of direct CO₂ fixation from actual flue gases have been also reported [17,25,32-35]. *Chlorella* KR-1 can fix CO₂ directly from the actual flue gas emitted from LNG boilers [25]. The growth rate of KR-1 cultured with the LNG flue gas was approximately equivalent to that obtained from 10% CO₂ gas mixtures. Hamasaki *et al.* [33] reported that the algal strains, *N. salina* and *P. tricornutum*, can fix CO₂ from flue gases emitted from a power plant. The flue gas contains about 10-15% CO₂ and 70-150 ppm of NO_x and SO_x, each. The biomass productivity was about 11 g m⁻² day⁻¹ in raceway reactors. At Cyanotech Corp., the algal production facility in Kona Hawaii, a small power plant was built to produce both power and allow the capture of the CO₂ required for algal production ponds. Two 180 kW generators produce the electricity required to operate the algal production ponds and other power production needs. The stack gas comes

Table 1. Growth characteristics of microalgal candidates for biofixation of carbon dioxide

Microalgae	CO ₂ , %	NO _x , ppm	SO _x , ppm	Growth rate in linear phase, g L ⁻¹ day ⁻¹	Ref
<i>C. littorale</i>	70	50	30	0.47	[27]
<i>Chlorella</i> HA-1	20	100	50	0.51	[28]
<i>Synechocystis</i> sp.	100	600*	100*	-	[29]
<i>C. caldarium</i>	15	50	-	-	[23]
<i>Chlorella</i> KR-1	30	100	100	0.78	[30, 31]

*: NO₃⁻ and SO₃⁻ concentrations in aqueous phase.

Table 2. Aerial productivity of biomass grown outdoors in the different photobioreactors

Photobioreactor	Microalgal strains	Culture volume, L (light path, cm)	Highest productivity, g m ⁻² day ⁻¹	Ref.
Raceway pond	<i>Chlorella</i> sp.	200 (20.0)	13.2	40
"	<i>Chlorophyta</i> sp.	" (")	8.2	"
Helical tubular	<i>Chlorella</i> sp.	30 (2.5)	28.1	41
Vertical flat-plate	<i>Synechocystis aquatilis</i>	24 (1.5)	31.0	42
" (Continuous)	<i>Nannochloropsis</i> sp.	1000 (10.0)	12.0	43
Tubular (in vertical arrangements)	<i>Chlorella</i> sp.	700,000 (5.0)	35.7	44
Tubular (Horizontal)	<i>Haematococcus pluvialis</i>	25,000 (41.0)	13.0	6
Tubular (Inclined)	<i>Chlorella pyrenoidosa</i>	50 (1.2)	130.0	45
Annular	<i>Nannochloropsis</i> sp.	140 (3.5)	52.5	46

out at 20 m³/min and contains 8% CO₂ and is transferred to the microalgae culture systems for CO₂ fixation [34].

DEVELOPMENT OF PHOTOBIOREACTOR SYSTEMS

Although significant progress has been made in finding a suitable microalga, there are still several major problems to overcome in order to make the biological CO₂ fixation applicable. Since the CO₂ fixation rate is too low, a large capacity is required for the system to do a meaningful CO₂ sequestration. For example, a raceway pond, the most widely used photobioreactor for commercial production of microalgae, requires 1.5 km² to fix the CO₂ emitted from a 150 MW thermal power plant [7]. Thus, it is important to maximize both volumetric productivity and photosynthetic efficiency to reduce the capacity of the system. However, it is not an easy task because the two objectives are, in part, contradictory. In most cases, the high cell concentration may decrease the photosynthetic efficiency because of the shadowing effects by the cells themselves. Many photobioreactors with various configurations, which may introduce light energy efficiently into the dispersion of microalgae, have been developed.

As enclosed photobioreactors have many advantages

over raceway ponds, such as higher productivity and possible application for various microalgae species, the application of the closed photobioreactor has been a focus of the R&D activities to develop microalgae greenhouse gas mitigation technologies. Thus, extensive work for the development of a highly efficient enclosed photobioreactor having a high aerial productivity and a low cost for construction has been done over the last few decades [35-39]. The aerial productivities of various photobioreactors have been compared in Table 2 [6,40-46].

Recently several technical approaches to improve the light utilization efficiency of the reactor with higher cell densities have been tried by using Fresnel lenses and optical fibers [47-49]. Takano *et al.* reported that they could obtain 4.44 g CO₂ L⁻¹ day⁻¹ with a cell concentration of 6.8 g/L [47]. The CO₂ removal rate is two or three times higher than that obtained at a small tubular reactor. However, the optical fiber reactor has not been in application because of the high capital cost. However, this principle seems to be applicable only for the aquaculture of certain species in the future. Among various photobioreactors, the enclosed photobioreactor has the highest productivity based on capital cost (Fig. 2). While many experimental photobioreactors have been designed, constructed and deemed successful, very few have been actually successful on the commercial scale [6,38,40,41].

Scaling up of the research photobioreactor to a com-

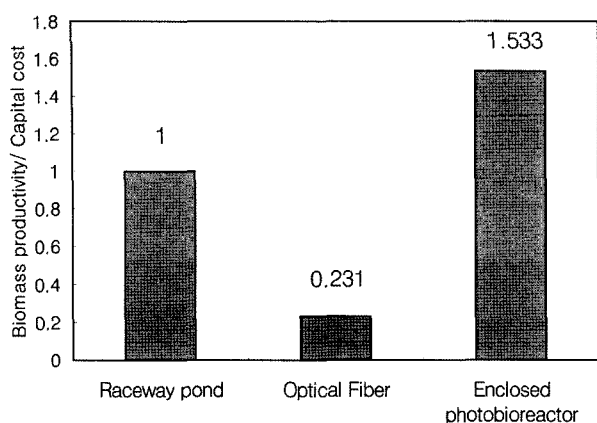


Fig. 2. Comparison of the photobioreactors [50].

mercial scale is not trivial. Problems related to the scale-up of the photobioreactor were reviewed by Tredici [36]. Currently only three commercial enclosed photobioreactors have been constructed and are under operation. IGV-GmbH developed a commercial scale photobioreactor system, which consists of compact and vertically-arranged, horizontally running glass tubes of a total length of 500,000 m and a total reactor volume of 700 m³. The system takes 10,000 m² for installation and 260~300 tons of CO₂ which results in the annual production of 130~150 tons dry biomass. Because the length of photobioreactor is too long, shear stress should be high. Therefore, the reactor may not be used for the cultivation of shear sensitive algal cells. The system is used for culturing *Chlorella*. Mera Pharmaceuticals, Inc. (formerly Aquasearch Inc.) developed another horizontal enclosed photobioreactor suitable for the culturing of shear sensitive cells. The volume of the unit system is 25,000 L. The reactor is now used for the culturing of *Haematococcus pluvialis*. Dome-shaped photobioreactor has been developed and used for culturing *H. pluvialis* [51]. However, none of them are currently used for CO₂ mitigation.

Another important factor responsible for low productivity is the light saturation effect. Microalgae cultures can utilize only a fraction of the sun light to which they are exposed, typically one third or less. The reason for this is that the algal photosynthetic pigments capture more photons under full sunlight conditions than can be processed by photosynthesis. Recent research demonstrated that algal cultures and mutants with reduced antenna sizes can exhibit increased photosynthetic rates under high light intensities [52,53].

UTILIZATION OF MICROALGAE

As microalgae grown from CO₂ fixation contain various useful compounds, the strategy for utilizing algal cells obtained from CO₂ fixation is very important for the CO₂ fixation process to be economically viable. Since most actual flue gases may contain some toxic compounds, several studies were done for the utilization of

microalgae into non-edible products. Frenz *et al.* [53] recovered hydrocarbon from *B. braunii* by solvent extraction and proposed the use of hydrocarbon as a fuel to replace diesel. Sawayama *et al.* [2] investigated the feasibility of producing liquid fuels from *B. braunii* by thermochemical liquefaction. However, those processes to utilize algal cells as fuels were reported to be not economically viable because the value of fuel was not high enough. If the algal cells are utilized as fuel, the CO₂ mitigation costs are predicted to be between \$150/tC and \$280/tC [54]. Zhong *et al.* [55] studied the use of microalgae as fillers in plastics. By mixing *Chlorella vulgaris* with polyvinylchloride (PVC) and forming them into molds, building materials have been produced. Because microalgae are in a chemically stable form, long-term storage of CO₂ may be possible. For long-term storage of CO₂, gene manipulation technology has been applied to convert CO₂ into the high quality of cellulose by microalgae [56]. Hirano *et al.* [57] studied the process of methanol production by the gasification of algal cells and obtained 1.1 of energy balance which showed that the process was plausible as a process for energy production. They also reported that the energy balance could be even higher if the more efficient production of microalgal biomass was developed. When the processes mentioned above utilize algal cells in non-edible products, there will be no toxicity problems but the economic feasibility of the processes is very doubtful.

Therefore, several studies have been done to fix CO₂ from cleaner flue gases and utilize the biomass products in higher value products like feed additive or pigments. Lee *et al.* [3] reported that algal cells produced from CO₂ fixation using LNG flue gas were successfully used as a feed additive for chicks. They also reported that toxicity was not detected throughout the experiments. The demonstration work for the production of algal cells using CO₂ produced from a lime production plant and the utilization of the biomass in feed for chicks also has been reported [38]. Nakamura *et al.* [35] reports that they are working on a project involved in extracting high value products of \$100,000 per kg of C from microalgae produced from CO₂ fixation. When the project is completed, it is expected that the net CO₂ sequestration cost may be decreased to zero from \$100/tC.

One successful example for the practical biological CO₂ fixation system has been reported. Cyanotech Corp., located at Kona, Hawaii, constructed a small power plant to produce both power and fed flue gases that were emitted from the power plant to algal production ponds in order to recover CO₂ in flue gases. The company could expect an annual net income (credit) of almost \$300,000 from power and CO₂ savings from the operation of the system [34].

CONCLUSION

In this review, we have discussed the potential and applications of the biological CO₂ fixation technology for CO₂ mitigation. Although some progress has been made

in finding a suitable algal strain for CO₂ fixation and developing a photobioreactor, there are still too many problems to apply a biological CO₂ fixation process for CO₂ sequestration purposes. For example, the productivity of microalgae required for a meaningful CO₂ sequestration should be three orders higher in magnitude levels than the current system—a daunting goal. Thus, some short-term approaches to microalgae CO₂ fixation/ utilization are possible by combining CO₂ from the fossil fuel combustion system and nutrients in a photobioreactor where microalgae photosynthetically convert the CO₂ into high commercial value products, such as feed additive and pharmaceuticals. The approaches may contribute to reduce the CO₂ sequestration cost.

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