CURRENT ASPECTS OF CARBON DIOXIDE FIXATION BY MICROALGAE IN KOREA

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Key words: CO₂ fixation, flue gas from power plants, CO₂ tolerant microalgae.

ABSTRACT

The carbon dioxide fixation by microalgae has several merits such as the CO₂ recovery and the production of useful chemicals. Since the flue gas from a industry has some unfavorable conditions such as high CO₂ concentration and toxic chemicals like SO₂, NOₓ contained in flue gas for the cultivation of most microalgae, it is important to apply a suitable strain of microalgae for the fixation of carbon dioxide emitted from various industrial sources. The current status for carbon dioxide emission from thermal power plants, which are major in Korea, is going to be described. Some research work has been done in KIER to get a suitable microalgae. Among the various microalgae tested in our laboratory, Chlorella sp., HA-1 and Chlorellaceae littorale showed the satisfactory performance. The experimental results for culturing of the two microalgae will be presented.

INTRODUCTION

Global warming due to increased carbon dioxide concentration in the atmosphere is a threat causing widespread concern. CO₂ is a green house gas, as are methane, chlorofluorocarbons and water vapor. The CO₂ concentration in the atmosphere is reported to be risen by about 25% since industrial revolution(1,2). In the same time, the temperature of the northern hemisphere has also increased by 0.5°C. A prudent response is to reduce emissions of greenhouse gases while the science underlying global warming is resolved.

Various physicochemical methods such as wet and dry absorption, adsorption, and membrane separation technologies have been developed and the absorption method has been put into practice for the elimination of carbon dioxide(3) but further disposal of the trapped CO₂ is a costly process.

Biological methods, in particular using microalgal photosynthesis, have several merits such as no requirements for the pretreatment of flue gas and the further disposal of trapped CO₂ and mild conditions for CO₂ fixation. Carbon fixed by microalgae is incorporated into carbohydrates, lipids, so energy, chemicals, or foods can be produced from algal biomass.

The flue gas from power plants and steel mills contain about 10-20% of CO₂. If the CO₂ gas is once condensed by chemical or physical means to remove toxic chemicals, the gas fed for microalgal cultivation may contain higher concentration of CO₂. It has been reported, however, that high concentrations of CO₂ inhibits the rate of algal photosynthesis. Silva and Pirt reported that Chlorella vulgaris 211/8k strain, which is tolerant to high CO₂ concentration, showed a maximum growth rate at 7% CO₂ concentration(4). Practical growth studies with high concentrations of CO₂ have been initiated(5,6). Negoro et al. examined several strains of marine microalgae on their tolerance to 5 or 15% CO₂ and reported that some of them could grow without pH adjustment(7). Strains preferring low pH values can cut operation costs considerably by eliminating pH control. If the microalgae can be grown at high densities, the size of culturing facilities may be reduced. Desirable properties of microalgae, for the direct biological utilization of CO₂ from flue gas, are summarized in Table 1.

Many works have been carried out to find some microalgae to fit the requirements described above(8-10). Various microalgae, which may be used for CO₂ fixation work, have been obtained from several culture collections and tested in our laboratory for their feasibility for CO₂ fixation in Korea.

At first, in this paper, current aspects for the CO₂ emission in Korea is going to be described, and subsequently some preliminary works for the development of the biological fixation process of CO₂ from flue gas in KIER will be presented.

CURRENT ASPECTS OF CARBON DIOXIDE EMISSION IN KOREA

As Korea is getting developed, the amount of CO₂ emitted has been increased rapidly. Recently global warming by CO₂ have been emerged as a major environmental problem threatening global ecosystem and a concern over it is increasing gradually in Korea like in many other nations. On account of this, Korean government assisted national R&D program for CO₂ by energy conservation and renewable energy utilization, CO₂ fixation by various methods and conversion or utilization of CO₂ for various uses. Among these projects, the biological fixation of CO₂ is considered to be the most environmentally friendly technology, and hence it is started to be investigated in several universities, government institutes such as Korea Research Institute of Chemical Technology(KRICT) as well as Korea Institute of Energy Research(KIER).

Total CO₂ emission in the world was reported to be 5,896 million tons of carbon in 1986(11). Korea is responsible to a 0.88% of the total emission. It corresponds to 49.89 million tons of
carbon. The power generation shares 15.9% of total Korean CO₂ emission. Industry shares 34.1%, transportation 14.9%, others 35.1%. Among the major CO₂ emitters, only the industry and power generation sectors can take the measures to reduce or recover the CO₂ from exhausted gases.

The capacity of fossil-fuel burning power plants in Korea today is about 14,300 megawatts(MW), about 50% of it is driven by heavy oil burning plants. Coal burning power plants shares 31%, LNG burning power plants 18%. As shown in Figure 2, the contribution of several fuels for electricity generation and hence for CO₂ emission is predicted to be changed significantly in the future. According to the national plan, the number of coal-burning power plants will be remarkably increased; the capacity of coal-burning power plants is planned to be 67% of total thermal power capacity 2010 (Figure 2).

The flue gas composition is greatly dependent on the type of fuel used as shown in Table 2. The flue gas from coal-burning power plants generally has the highest concentrations of SO₂, NOₓ which are toxic compounds against the microalgal growth. Unless some pretreatments to reduce the SO₂, NOₓ concentrations is made, the gas can not be directly purged into microalgal culture. On the other hand, flue gas from LNG and diesel oil burning power plants is believed to have system-able concentrations of SO₂, NOₓ concerning literature. Carbon dioxide in the flue gas can be directly fixed by microalgae. The growth rate of microalgae is greatly dependent on the cultivation temperature and most microalgae exhibit the maximum growth rate between 25°C and 35°C. Since CO₂ fixation process by microalgae requires a large area for light absorption, it is believed to be installed outdoors for large scale application. Thus the control of cultivation temperature become normally very difficult.

In case of power plant application of the process, cooling water discharge temperature might determine the cultivation temperature of microalgae. Average temperature of cooling water from typical fossil-fuel burning power plant in Korea is shown in Table 3. The table shows that the minimum temperature recorded in February is 13.4°C. The lowest temperature is apparently too low for the proper cultivation of normal microalgae. However, the problem is believed to be overcome by thermal insulation or solar energy technologies such as a greenhouse in winter.

**BIological CARbon Dioxide FIXATION WORK IN KIER**

Recently several applied studies aimed at the direct biological fixation of CO₂ out of the flue gases from thermal power plants have been carried out(11-13). Although the direct use of discharged gases reduces the cost of pretreatment, it imposes extreme conditions on microalgae such as high concentrations of CO₂ and the presence of toxic chemicals like SO₂, NOₓ to microalgae. The best suited microalgal strain for this purpose should be selected in terms of tolerance to environmental stresses.

**Materials and methods**

**Strain**

A marine microalgae *Chlorococcum littorale* and a fresh-water microalga *Chlorella* sp. HA-1 were used in this work. Each strain was obtained from Marine Biotechnology Institute(Japan) and National Institute of Environmental Studies(Japan), respectively. These strains were selected on the basis of high growth rate at high CO₂ level. The medium used for culturing *C. littorale* has following composition: (in g/l) KNO₃ 1.25, KH₂PO₄ 1.25, MgSO₄·7H₂O 1.25, NaCl 15, 1 ml of Fe solution, and 1 ml of As solution. Fe solution consists of 1 l water, FeSO₄·7H₂O 2, and 1 ml of concentrated H₂SO₄. MBM media(7) used for culturing of *Chlorella* sp. HA-1 has the following composition: (in mg/l) KNO₃ 220, MgSO₄·7H₂O 75, KH₂PO₄ 75, K₂HPO₄·7H₂O 10, FeSO₄·7H₂O 2, H₂BO₃ 2.86, MnSO₄·7H₂O 2.5, ZnSO₄·7H₂O 0.22, CuSO₄·5H₂O 0.079, Na₂MoO₄·0.021. The initial pH was 6.6.

**Batch culture**

The microalgal culture experiments were conducted to investigate the growth characteristics of the microalgae under various culture conditions. The culture equipment is shown in Figure 3. The cultivation vessel of 1 l diameter flask as culture vessel, water bath, fluorescent lamp, CO₂ enriched air supplier. The maximum average light intensity at the surface of the culture vessel was 8 Klux. CO₂ enriched air was prepared by mixing pure CO₂ from a cylinder and air from an air pump, and filter sterilized. The temperature of the culture vessel was maintained in the water vessel equipped with a temperature controller(Jeo Tech Co., Korea). pH was not regulated. Light intensities, CO₂ concentrations, and temperature were varied in accordance with experimental conditions specified.

**Assay**

Light intensities were measured by a light sensor (Lichor Inc, USA). Cell growth was determined either by the optical density at 660 nm using UV-spectrophotometer (HP8452A, Hewlett-Packard Inc., USA) or by dry-cell weight after filtration on cellulose acetate filter(0.45µm, Millipore Co., USA), followed by drying at 105°C overnight.

**Results and discussion**

The effects of light intensities and CO₂ concentrations on the cultivation of microalgae were investigated for CO₂ fixation from concentrated sources such as a power plant. *C. littorale* and *Chlorella* sp. HA-1 were selected for further experiments after screening by their performance.

The effects of 3, 6, 8 Klux light intensities on the growth of *C. littorale* at 28°C and 10% CO₂ concentration were investigated. As shown in Figure 4, the growth rates of *C. littorale* were almost the same at 6 and 8 Klux with 0.18g cell/day-l growth. However, the growth rate at 3 Klux was 0.12g cell/day-1. This corresponds to only 60% of the growth rate at sufficient light. Figure 5 shows the growth of *Chlorella* sp. at various light intensities. Higher than 8 Klux light intensities is believed to inhibit the growth and the growth rate at 3 Klux was 0.15g cell/day-1, about 70% of its maximum at 6 Klux.
It is concluded that the light intensities around 6 Klux are sufficient for the proper growth of the tested microalgae and even harmful for the case of *Chlorella* sp. HA-1.

The industrial CO₂ sources are of relatively high concentration with concentration range from 10 to 20% CO₂ than natural sources. Therefore, the concentrated CO₂ resistance of the microalgae was experimented with 10, 20, 30% of CO₂ concentrations. The growth of *C. littorale* was not inhibited at 10 and 20% concentrations as shown in Figure 6, hence considering only CO₂ concentration, there might be no problem with the *C. littorale* for the CO₂ fixation application from power plant exhaust gas. However, the growth rate was declined to about half at 30% CO₂ concentration.

Figure 7 shows the CO₂ resistance of fresh water microalgae *Chlorella* HA-1. This species exhibits the growth inhibition at the CO₂ concentration higher than 10%. In consequence, the CO₂ resistance of the *Chlorella* HA-1 was believed to be lower than that of marine alga *C. littorale*.

Combined cycle power plants located in-land in Korea are burning LNG as fuel, and using fresh water as cooling water. Since these LNG power plants discharge the emissions containing only 9-10% CO₂, the *Chlorella* HA-1 could be applied for the CO₂ fixation in the case of in-land LNG power plants.

The effects of cultivation temperatures on the growth of microalgae were also considered. The two species showed maximum growth in the temperature range from 26°C to 30°C. The minimum average temperature of cooling water in a typical thermal power plant was 13.4°C in February, however, the problem is believed to be overcome by thermal insulation or solar energy technologies such as green house in winter.

ACKNOWLEDGEMENT
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REFERENCES
Table 1. Desirable properties of microalgae for CO₂ fixation

<table>
<thead>
<tr>
<th>High CO₂ tolerance</th>
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<tr>
<td>Low pH tolerance</td>
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<td>Stable and high growth rate in the linear phase</td>
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<td>Capability of growing at high cell densities</td>
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<td>SO₄, NO₃ tolerance</td>
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<td>Thermotolerance</td>
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Table 2. Flue gas composition of thermal power plants using various fuels

<table>
<thead>
<tr>
<th>Components</th>
<th>CO₂, %</th>
<th>SO₂, ppm</th>
<th>NOₓ, ppm</th>
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<tbody>
<tr>
<td>Coal</td>
<td></td>
<td></td>
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<tr>
<td>Anthracite*</td>
<td>15 - 16</td>
<td>860</td>
<td>200</td>
</tr>
<tr>
<td>Bituminous**</td>
<td>15 - 16</td>
<td>360</td>
<td>240</td>
</tr>
<tr>
<td>LNG</td>
<td>9 - 10</td>
<td>negligible</td>
<td>140</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>15 - 16</td>
<td>180</td>
<td>negligible</td>
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* : Produced in Korea
** : Imported low sulfur coal

Table 3. Temperature (°C) of the cooling water from fossil-fuel burning power plants in Korea.

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</thead>
<tbody>
<tr>
<td>Intake water</td>
<td>5.6</td>
<td>4.6</td>
<td>8.4</td>
<td>11.8</td>
<td>17.3</td>
<td>22.2</td>
<td>24.6</td>
<td>25.5</td>
<td>26.2</td>
<td>20.3</td>
<td>15.7</td>
</tr>
<tr>
<td>Cooling water</td>
<td>15.6</td>
<td>13.4</td>
<td>20.2</td>
<td>22.6</td>
<td>28.6</td>
<td>33.0</td>
<td>34.0</td>
<td>33.0</td>
<td>33.3</td>
<td>29.7</td>
<td>26.2</td>
</tr>
</tbody>
</table>
1. Domestic CO₂ emissions by sector of energy use in Korea.

2. CO₂ emission from fossil-fuel burning power plants in Korea.

3. Schematic diagram of microalgal CO₂ fixation equipment.

4. The effect of light intensities on the growth rate of *Clitoria*. The CO₂ concentration and the temperature were 10% and 25°C respectively.

5. The effect of light intensities on the growth rate of *Chlorella* sp., HA-1. The CO₂ concentration and the temperature were 10% and 25°C respectively.
Figure 6. The effect of CO₂ concentrations on the growth rate of *Clitorale*. The experiment was carried out at 30°C and at light intensity of 600 Lux.

Figure 7. The effect of CO₂ concentrations on the growth rate of *Chlorella* sp., HIA-. The experiment was carried out at 30°C and at a light intensity of 600 Lux.