INFLUENCE OF CO₂, SO₂ AND NO IN FLUE GAS ON MICROALGAE PRODUCTIVITY

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The influence of CO₂, SO_x, NO_x and soot dust on the productivity of microalgae was considered using *Nannochloropsis salina* and *Phaeodactylum tricornutum*. Microalgae are viewed as a possible means of combating global warming.

These microalgae can be easily cultivated in a high CO₂ gas concentration of 15 vol%.

SO₂ gas itself does not influence the growth of microalgae. However, when the SO₂ concentration is high, the pH of the medium decreases and the productivity of the microalgae is lowered.

The presence of NO does not influence the growth of microalgae. NO absorbed in the medium is changed to NO₂⁻ and utilized as a nitrogen source.

As for Ni and V contained in soot dust, when the dissolved concentrations of these metals in the medium exceed more than 1 and 0.1 ppm, respectively, the microalgae productivity decreases, however, under actual conditions, their concentrations are normally lower than these values.

The above results obtained in a small scale test using a simulated gas were confirmed in a field test using a raceway-type reactor with actual flue gas.

Introduction

Ever since the Industrial Revolution, CO₂ concentration in the atmosphere has been steadily increasing because of the increasing consumption of fossil fuels. Associated with this, the issue of global warming is now causing great anxiety. Under such circumstances, researchers have so far tried a variety of approaches for the recovery and fixation of CO₂.

Exhaust gas from power plants may be a useful source of CO₂ for the mass culture of microalgae. Since carbon fixed by microalgae is incorporated into carbohydrates, lipids and proteins, energy, chemicals or foods can be produced from the algal biomass. Processes leading to the conversion of algal biomass to such useful products could be an economical method for CO₂ fixation and disposal because they would indirectly decrease the dependence on non-renewable fossil fuels. Recovery and fixation of CO₂ has been studied using *Scenedesmus* sp., indicating that this microalgae can grow at a high CO₂ concentration (20 vol.%) (Karube, 1995). Detailed studies about the influences of CO₂, SO₂, NO and soot dust on the productivity of the microalgae, however, were not

carried out under actual conditions.

This article reports the influences of these elements on productivity of the microalgae.

1. Experimental

1.1 Microalgae

It is necessary to produce microalgae which have a high lipid and a high caloric value because they are used as a biomass fuel. It is also necessary to cultivate it with a sea water-based medium. From this point of view, *Phaeodactylum tricornutum* (PHAE02) and *Nannochloropsis salina* (NANNP2) from SERI (Solar Energy Research Institute, USA) were selected as the algal strains.

1.2 Apparatus

(1) Small scale test In Fig. 1, the apparatus used in the small scale test is shown. This apparatus consisted of a cultivator and a gas supplier system. A 1 l Roux bottle was used as the cultivator and placed in a thermostatted bath. Cylinder gases such as CO₂, O₂, N₂, SO₂ and NO were used as the gas supply system. The gas flow rate was measured using a mass flow controller. The gas concentration was measured by gas chromatography (SO₂) and an NO_x meter (NO). The algal concentration was measured by the filtration method using a membrane filter. The algal

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Fig. 1 Small scale test apparatus for algal cultivation

Fig. 2 Large scale test apparatus for algal cultivation

Table 1 Composition of sea water culture medium

NaNO ₃	300 mg
NaH ₂ PO ₄ ·H ₂ O	20 mg
Na ₂ SiO ₃ ·9H ₂ O	30 mg
Thiamine·HCl	100 µg
Biotin	0.5 µg
B ₁₂	0.5 µg
Trace elements stock solution	1 ml
Sea water (artificial sea water, Aquarium System Inc.)	1000 ml

Trace elements stock solution	
Na ₂ EDTA	4.36 g
FeCl ₃ ·6H ₂ O	3.15 g
MnCl ₂ ·4H ₂ O	180 mg
CuSO ₄ ·5H ₂ O	10 mg
ZnSO ₄ ·7H ₂ O	22 mg
CoCl ₂ ·6H ₂ O	10 mg
Na ₂ MoO ₄ ·2H ₂ O	6 mg
Distilled water	1000 ml

concentration was controlled by discharging a portion of the algal suspension and charging a new medium for make up. The culture medium used in this test is shown in Table 1.

(2) Large-scale test The test apparatus used in the large scale test is shown in Fig. 2. The apparatus consisted of a cultivator, a gas supplier system and a medium supplier system. A raceway-type reactor made of polyvinyl chloride (1.0 m width×2.0 m long×0.3 m depth) was used as a cultivator, and the liquid velocity was 0.2 – 0.3 m/s. An actual flue gas from a thermal power plant (CO₂=10 – 11%, O₂=1.3%, SO_x, NO_x=50 – 70 ppm) was used as the cultivation gas. The culture medium was composed of sterilized sea water as the solvent, which was filtered using 10 µm pore size media, and inorganic nutrients were used as the solute (Table 1).

Fig. 3 Influence of high CO₂ concentration on algal cultivation

2. Results and Discussion

2.1 Small scale test

(1) Productivity under high CO₂ concentration
The concentration of CO₂ discharged from a boiler is in the range of 8 to 15 vol%. We investigated the influence of CO₂ concentration on the productivity of microalgae. The test conditions were as follows:

microalgae	NANNP2
algal concentration	200(150)ppm
gas flow rate	100 ml/min
CO ₂ gas concentration	15 vol%
light intensity	10000 lx
light and dark cycle	16 h/8 h

The algal concentration was controlled at 200 ppm by discharging a portion of the algal suspension and charging new medium. As shown in Fig. 3, the productivity per day was constant and a stable continuous batch cultivation was conducted over one week at high CO₂ concentration. In this figure, the data for a 5% CO₂ gas concentration is also shown,

Fig. 4 Influence of SO₂ gas on algal cultivation

indicating almost the same productivity with that of the 15% CO₂ gas concentration. In the case of PHAEO2, the stability of the algal productivity is a little lower than that of NANNP2. As shown in Fig. 3, in a dark period, the algal concentration decreased due to algal respiration.

(2) Influence of SO₂ SO_x is contained in the gas discharged from the boiler. We investigated the influence of this gas on the productivity of the microalgae. The test conditions were as follows:

microalgae	NANNP2
CO ₂ gas concentration	13.5 vol%
light intensity	10000 lx

As shown in Fig. 4, at a 50 ppm SO₂ gas concentration, the productivity is not practically influenced, although the pH of the medium decreased from 7 to 6. However, when the SO₂ concentration is 400 ppm, the pH of the medium becomes lower than 4 after 20 h from the start of the experiment and the productivity of the microalgae gradually decreases. However, even in this case, when the pH is maintained at 8 using NaOH, the productivity does not decrease. Therefore, it is considered that the cause of the productivity decrease without pH adjustment is pH lowering of the medium.

(3) Influence of NO We investigated the influence of NO, which is contained in the flue gas, on the productivity of microalgae. The test conditions were as follows:

microalgae	NANNP2
CO ₂ gas concentration	15 vol%
light intensity	10000 lx

Fig. 5 Influence of NO gas on algal cultivation

As shown in Fig. 5, NO is absorbed in the medium and part of it is changed to NO₂⁻ and accumulated in the medium. When the O₂ concentration is 1.8 vol%, the productivity of the microalgae is not significantly influenced. When the O₂ concentration of the culture gas is increased from 1.8 to 16.2 vol%, accumulation of NO₂⁻ in the medium increases and the productivity decreases during the early stages of cultivation, but significantly increases later on. In order to investigate the influence of NO₂⁻, the nitrogen source of the medium was changed from NaNO₃ to NaNO₂. In this case, the productivity decreases during the early stages of the cultivation, and then it significantly increases. From these results, it is confirmed that NO is not an impediment but can be used as a nitrogen source for microalgae.

(4) Influence of soot dust The soot dust contained in discharged gas was mixed with the medium. We investigated the influence of dissolved components of the dust on the productivity of the microalgae. Leaching tests of the coal ash using sea water as a solvent indicated that the concentrations of Ni, V and Al ions were less than 0.1 ppm. In the case of heavy oil ash, Ni and V ions were dissolved into the sea water. Therefore, the actual heavy oil ash, which contained V₂O₅, NiO, Fe₂O₃, Al₂O₃, and CaO, was used as a sample of the soot dust. The test conditions were as follows:

microalgae	PHAEO2
CO ₂ gas condition	5 vol%
light intensity	10000 lx

Fig. 6 Influence of soot gas dust on algal cultivation

In Fig. 6, the relation between the algal productivity ratio, r , which is defined by the following equation, and the soot dust concentration is shown.

$$r = \frac{q_A \text{ with specified substance}}{q_A \text{ without specified substance}} \quad (1)$$

Here, q_A is algal productivity and the specified substance is soot dust. It is confirmed that when the soot dust concentration is higher than 0.2 g/l ($N_i=1$ ppm, $V=0.1$ ppm), algal productivity is influenced by the heavy metal ions. Since the soot dust concentration in a discharged gas is at most 50 mg/m³, it is probably only in very rare cases that the soot dust concentration in the culture becomes higher than 0.2 g/l.

(5) Influence of trace elements The influence of trace elements such as heavy metals (Mn, Fe, Co, Cu, Zn, Mo) and vitamins (biotin, B₁₂) on the productivity of the microalgae was confirmed. These test results are shown in Fig. 7. In this figure, the relationship between the algal productivity ratio, r , which is defined by Eq. (1), and the frequency the repeated batch cultivation, n , is shown. Here, the specified substances are the trace elements such as heavy metals and vitamins. In the case of NANNP2, the elimination of vitamins and Fe lowers the microalgae productivity. In the case where only Fe was not present, the productivity is not influenced in the first batch cultivation, but decreases after the second batch cultivation. Therefore, in the case of NANNP2, these trace elements are important for the cultivation. On the other hand, in the case of PHAE02, the elimination of Fe decreases the productivity but elimination of Si, vitamins and heavy metals other than Fe does not influence the productivity. Therefore, PHAE02 only needs Fe as a trace element.

Fig. 7 Influence of trace elements on algal growth

Fig. 8 Algal cultivation using actual flue gas (large scale test)

2.2 Large scale test

In order to substantiate the findings in the results of the small scale test, a field test was conducted with actual sea water, actual exhaust gas and sun light using a raceway-type reactor. The influence of the actual flue gas was investigated by conducting a reference test at the same time using a mixed cylinder gas containing CO₂ and N₂. The test conditions were as follows:

microalgae	NANNP2
CO ₂ gas concentration	10~11 vol%
pH	about 7
culture medium	Table 1

These test results are shown in Fig. 8. The time courses of the algal concentration and the productivity, which was calculated using the increase in the algal concentration for one day and the liquid volume, indicate the same tendency as that obtained with the cylinder gases. So, it is confirmed that cultivation of microalgae can be performed using actual flue gas. Also, the productivity of the large scale test is 8 – 10 g/(m² d) in the case of fine weather, and it is almost the same value (about 8 g/m² d) as that of the small scale test which was calculated from the data of Fig. 3.

Conclusion

The influence of the composition of the thermal power plant flue gas on the productivity of microalgae was investigated using *Nannochloropsis salina* and *Phaeodactylum tricornutum*.

(1) These microalgae can be cultivated effectively with a high CO₂ gas concentration (15 vol%).

(2) SO₂ gas itself does not influence the growth of microalgae. However, when the SO₂ concentra-

tion is high, the pH of the medium decreases and the productivity of the microalgae is lowered.

(3) NO gas does not influence the growth of microalgae. NO absorbed in the medium is changed to NO₂⁻ and utilized as a nitrogen source.

(4) As for Ni and V contained in the soot dust, when the dissolved concentrations of these metals in the medium exceeds 1 and 0.1 ppm, respectively, the productivity of the microalgae decreases, however, under actual conditions, their concentrations are normally lower than these values.

(5) The above results obtained in the small scale test using a simulated gas were confirmed in a field test using a raceway-type reactor with actual flue gas.

Nomenclature

C_A	= algal concentration	[ppm]
I_0	= light intensity	[lx]
I_s	= sunshine intensity	[Ly/d]
n	= repeated batch cultivation	[—]
q_A	= algal productivity	[g/(m ² d)]
r	= algal productivity ratio	[—]
T	= temperature	[°C]
t	= time	[h]

Literature Cited

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