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# EVALUATION STRATEGIES FOR CHEMICAL AND BIOLOGICAL FIXATION/UTILIZATION PROCESSES OF CARBON DIOXIDE

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Abstract - Various chemical and biological processes have so far been proposed for carbon dioxide recovery, conversion into organic matter and reutilization, which is called the carbon recycling system. In this paper, their evaluation strategies are discussed. They are classified into two categories; with and without energy which is utilized artificially. It is clarified that most of the chemical and biological carbon dioxide fixation systems or carbon recycling systems with artificial energy should be evaluated from the energy point of view as primary and secondary energy systems, and comparing them with other alternative soft energy paths so far proposed. Chemical and biological processes which should be evaluated separately from new soft energy paths are only those which essentially require no artificial energy, such as afforestation of deserts, fertilization to ocean and utilization of rock weathering reaction.

#### 1. INTRODUCTION

Developments of alternative energy sources and highly efficient energy utilization systems, and reconstruction of energy consumption systems are the most essential measures for the  ${\rm CO_2}$  problem. However, various chemical and biological processes have been proposed for carbon dioxide recovery, conversion into organic matter and reutilization, which is called the carbon recycling system. In this paper, their evaluation strategies are discussed.

### 2. CHEMICAL PROCESSES FOR CARBON FIXATION/UTILIZATION

# <u>Global resources of energy and use of low carbon fuel</u>

In various chemical processes so far proposed,  $CO_2$  is reduced to produce organic matter using a non-carbonaceous energy source such as hydrogen or a low carbon source such as methane. However, the hydrogen does not exist as a natural resource and the natural gas would be consumed after around 30 years if all energy sources were altered to it [1]. If we consider the problem as that on the order of 100 years or more, we could not rely on such resources. The HYDROCARB Process [2], which uses only non-carbonaceous materials in fossil fuels, is attractive, however, the consumption of coal resources needs to be remarkably enhanced.

## Enhancement of rock weathering

The long term carbon cycle is governed by the following rock cycle. Eqn. (1) is the weathering of limestone and eqn. (2) is the deposition of limestone occurring in the ocean surface layer. Therefore, the net absorp-

tion of  ${\rm CO}_2$  is expected when we enhanced eqn. (1) and the products are stored in the deep sea. It is expected that the products are easily transported into the deep sea with pulverized and suspended limestone because of their high apparent density. The longer term rock cycle is expressed by eqn. (3), i.e., the historical reduction of global  $CO_2$  in the atmosphere. Furthermore, the estimated amount of silicates is large. Even when eqn. (3) is coupled with eqn. (2), the net absorption of  ${\rm CO_2}$  is expected as shown in eqn.(4), though the rate of eqn. (3) is much slower than that of eqn.(1) [3]. The energy balance should be evaluated by taking the pulverization energy of rocks and their absorption rates into account.

$$2HCO_3^- + Ca^{2+} \rightarrow CO_2 + CaCO_3 + H_2^0$$
 (2)

$$2CO_2 + CaSiO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$
 (3)

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$$
 (4)

Production of alternative energy by chemical fixation of  ${\rm CO}_2$  Chemical  ${\rm CO}_2$  fixation processes other than above need more energy than that produced when a fossil fuel is converted into  ${\rm CO}_2$ . The necessary energy is to be supplied from atomic or natural energy such as solar energy as shown in Fig. 1a. Most products are thought to be used as an alternative energy source because the amount of fixed carbon is very large (Fig. 1b).

The secondary or transportation system for the utilization of solar energy is shown in Fig. 1c. It is easily understood that the present carbon recycle system is a soft energy path for solar energy utilization. No positive meaning can be found in the carbon dioxide recovery or recycling system itself as a countermeasure against the  ${\rm CO_2}$  problem.

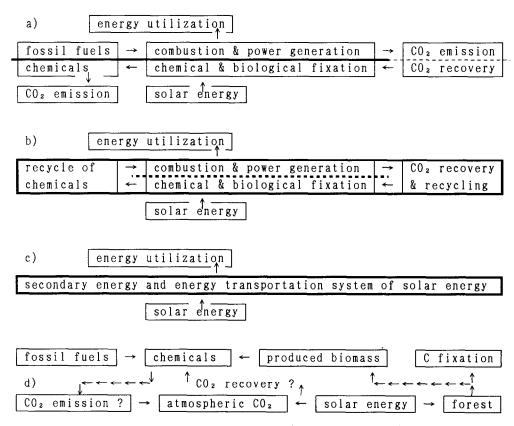


Fig. 1. Chemical and biological fixation (a), recycling (b), secondary energy system (c) and production system of chemicals (d)

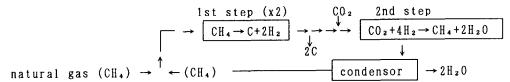


Fig. 2. Catalytic fixation process of  $CO_2$  to C [4].

Production of carbonaceous materials by chemical fixation of CO2

For the case that the produced organic materials are used as chemicals such as plastics, the same discussion as above is possible. Furthermore, the produced chemicals should finally produce  $\mathrm{CO}_2$  when they decompose or are used as transportation fuel, irrespective of their source,  $\mathrm{CO}_2$  or fossil fuel. The evaluation strategy should be, which is better to produce chemicals, directly from fossil fuel and the equivalent amount of energy from solar, or the system shown in Fig. 1a, from the view point of effective energy utilization. The only positive case will be that the product can be synthesized only from  $\mathrm{CO}_2$  or more effectively from it, while the latter case is mostly negative, since much energy is produced when  $\mathrm{CO}_2$  is produced. A small amount of chemicals may be allowed to be produced from fossil fuels. Otherwise, it is possibly produced from biomass even if we should completely stop  $\mathrm{CO}_2$  emission, as shown in Fig. 1d.

Carbon dioxide as an energy transportation medium

The CO<sub>2</sub>/methanol transportation system is one of the most feasible systems when solar energy is converted into electricity in desert areas and the produced energy is transported to Japan. However, a fair evaluation is essential in order to compare it with other transportation systems.

Examples of energy balance evaluation

A critical evaluation for a chemical fixation process [4], shown in Fig. 2, is conducted here. In Fig. 2, the reaction is expressed by eqns. (5-7).

In the process [4], eqns. (5-7) accompany eqn. (8). The sum of eqns. (6-8) is equivalent to eqn. (9). The simpler eqn. (9) is actually expected to produce more energy than the sum of eqns. (6-8). Eqn. (5) is essentially the same as the HYDROCARB process [2]. Therefore, the present system is thought to be a meaningless modification of the HYDROCARB Process [2].

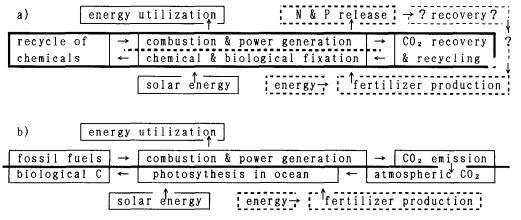


Fig. 3. Biological fixation process (a) compared with coupled process of fossil fuel use and  $CO_2$  absorption by ocean fertilization (b).

### 3. BIOLOGICAL PROCESSES FOR CARBON FIXATION/UTILIZATION

# Fixation of carbon by coral reef

The carbon fixation reaction by coral reef is essentially the CO<sub>2</sub> release reaction of eqn. (2). The weathering reaction of eqn. (1) can possibly cancel eqn. (2), however, it will be better to accelerate eqn. (1) without the coupling of eqn. (2). The high primary production is focused in the coral ecosystem, however, the organic carbon stock in it is small. Therefore, only a positive possibility of the present measure may be insisted under the case that a fairly large fraction of the organic matter produced with less phosphate and nitrate than the Redfield ratio is transported to the deep ocean without its decomposition at the sea surface.

#### Other biological processes

The structure of the biomass production system is the same as the case of the chemical processes in Fig. 1a. The evaluation should be conducted, as to which system is more efficient and cheaper between Fig. 1a and the solar cell system. The biomass production system by cultivation of ocean biota has another problem to be evaluated, i.e., supply of nutrients. The present system with fertilization is shown in Fig. 2a, compared with the combined system of energy production from fossil fuel and ocean fertilization for CO<sub>2</sub> absorption, shown in Fig. 2b [5]. Fig. 2b possibly produces more energy than Fig. 2a with the same amount of fertilizer consumption and without any increase in atmospheric  ${\rm CO}_2$ , if the recovery of nutrients from the waste of biomass-fired power plants is difficult in Fig. 2a. Furthermore, no artificial devices are needed in Fig. 2b because the photosynthesis is automatically conducted and the produced organic matter is stocked in the deep ocean forever [5], without energy which can be artificially utilized.

The other possible measure is the afforestation. The organic matter is also produced automatically by photosynthesis and stocked in its large capacity ecosystem. Thus, the energy efficiency is not the primary factor in this case because the plant fixes  ${\rm CO}_2$  with solar energy which is not effectively utilized artificially. The detail evaluation strategy for this measure is discussed in another paper [6].

# 4. CONCLUSION

Most of chemical and biological processes so far proposed for carbon dioxide recovery, conversion into organic materials and their reutilization, called the carbon recycling system, should be evaluated from the energy point of view as primary and secondary energy systems, and compared with the other alternative soft energy paths so far proposed.

The chemical and biological processes which should be separately evaluated from new soft energy paths are only those which essentially require no artificial energy, such as prevention of deforestation, afforestation of unused land or desert, fertilization of the ocean with nutrients, and utilization of the rock weathering reaction.

### REFERENCES

- 1. T.Kojima, "Nisankatanso Mondai-Uso to Honto" (Question and Answer in
- Carbon Dioxide Problem, in Japanese), Agune Shofusha, Tokyo (1994). 2. M.Steinberg, Proc. Intern. Conf. Coal Science, IEA, pp.1059-1062 (1989).
- 3. J.Nagamine, K.Horiuch, S.Uemiya and T.Kojima, Tsukuba Meeting of Society of Chemical Engineers Japan, SD111, Tsukuba, July 27 (1994).
- 4. T.Ishihara, T.Fujita, Y.Miyashita and Y.Takita, Shokubai (Catalyst), 35 324-327 (1993).
- 5. K.Horiuchi, T.Kojima and A.Inaba, submitted to Energy Conversion and Management.
- 6. T.Kojima, Y.Kakubari and H.Komiyama, submitted to Energy Conversion and Management.