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CONTINUOUS PRODUCTION OF CO2 HYDRATE SLURRY ADDED ANTIFREEZE PROTEINS

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ABSTRACT

The purpose of this study is to develop the production method of CO2 hydrate-slurry. In this paper, the production process of CO2 hydrates with pure water dissolved antifreeze proteins (AFPs) is discussed. CO2 hydrate-slurry can be transported from a production place to storage one with a small pressure loss. The AFPs have made the hydrate particles be small and well disperse. It is revealed that the Type III AFPs are effective for the inhibition of structure I hydrate production. By the present experiments, the induction time for the hydrate production increases, and moreover the formation rate of the hydrate and the increasing rate of an agitator torque decrease.

Keywords: antifreeze proteins, CO2 hydrate, slurry

INTRODUCTION

As one of the anti-global warming measure, it has been examined that to discharge and dissolve CO2 in seawater makes CO2 isolate in global carbon cycle for several decades or hundreds years. Ocean storage of CO2 hydrate is possible in deep sea under the low temperature and the high pressure conditions.

When the hydrate is produced in large quantities continuously, it plugs pipelines and can't be formed any more. Adding antifreeze proteins (AFPs) prevent the hydrate crystals from growing and make the hydrate particles small and well disperse. Then, there is a prospect that the hydrate behaves like slurry. CO2 hydrate-slurry can be transported from a production place to storage one with a small pressure loss.

The purpose of this study is to develop the production method of CO2 hydrate-slurry. Being affected by presence of the AFPs, the induction time for the hydrate production, the formation rate and the increasing rate of an agitator torque are observed.

ANTIFREEZE PROTEINS

AFPs are proteins that are present in the body fluids of some polar fishes, plants or insects. The proteins adsorb to surfaces of an ice crystal and

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inhibit the ice crystal growth any more. There are four types of the AFPs that differ according to molecular structures.

In recent research of the AFPs, Zeng have showed a prospect that type I spiral AFPs inhibit the formation of the structure II hydrate[1]. Uchida have showed a prospect that type III spheral AFPs inhibit formation of the structure I hydrate[2].

However, in above research, the hydrate was produced only a small quantity because they put a droplet of the AFPs solution in a high-pressure vessel. Therefore we examined the behavior of CO2 hydrate formation under the conditions of using a larger scale vessel and an agitator. Also type III AFPs originated from fish (Zoarces Elongatus Kner) was used, and their average molecular weight is about 6.5kda. The proteins were provided by AIST Functional Protein Research group, Research Institute of Genome-based Biofactory.

EXPERIMENTAL FACILITIES

In the present research, an autoclave experimental apparatus is used for the production of the hydrate. Figure 1 shows the schematic diagram of the experimental apparatus. A high-pressure vessel bath (500cm^3), two pistons (300cm^3 each), used for supplying the gas to the high-pressure vessel, filled with the gas, an agitator in the vessel and a vacuum pump are configured. A torque meter is equipped with the agitator.

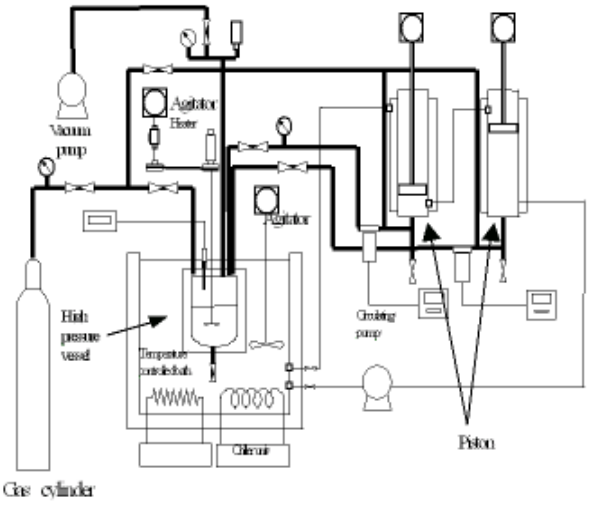

Figure 1. Experimental apparatus

EXPERIMENTAL METHOD

At the first, 200ml of the sample solution was supplied into the high-pressure vessel and all of the experimental equipments were degassed. Then the pistons were filled with CO2, at the pressure of CO2 partial pressure 3MPa. The water temperature in the bath was kept at 283K. Those conditions were decided referring to the phase equilibrium of CO2 hydrate[3].

When the valves between the high-pressure vessel and the piston were opened, CO2 in the piston was injected to the high-pressure vessel, and the agitator in the vessel was rotated at 400rpm. CO2 started to dissolve into water at this time. After 12 hours and dissolution has finished, the bath temperature was decreased to 274K and hydrate was produced in the cooling period. A beforehand dissolution of CO2 fastens the hydrate formation[4].

The following conditions were used in the present research.

1. AFPs:0mg/ml (pure water)
2. AFPs:0.01mg/ml
3. AFPs:0.1mg/ml

The concentration of AFPs was decided referring to Uchida's research[2].

RESULTS AND DISCUSSIONS

Induction time

The processes of the hydrate formation for each case are shown in Figure 2-3. In the case of AFPs 0.1mg/ml, it couldn't be observed the hydrate formation within 48 hours.

In the Figure 2, at the point of 8.8 hours, the increase of the water temperature was observed. This phenomenon is thought to be the release of the latent heat of the hydrate formation. Also at the same time, the CO2 supply increased rapidly. Therefore the hydrate formation was recognized. After 0.4 hours from the hydrate formation, the agitator torque increased.

In the Figure 3, the hydrate was formed at 30.3 hours later, and the agitator torque increased the same time. Compared to pure water experiment, the induction time increased 244% in AFPs 0.01mg/ml experiment.

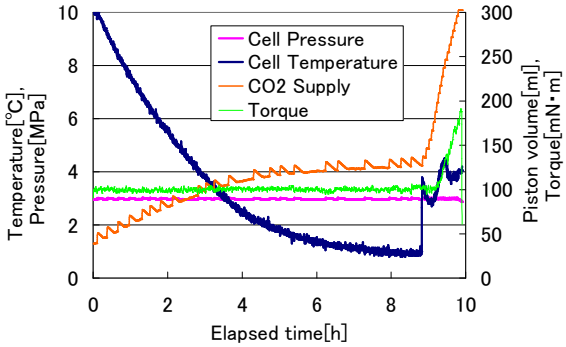

Figure 2. Hydrate formation from pure water

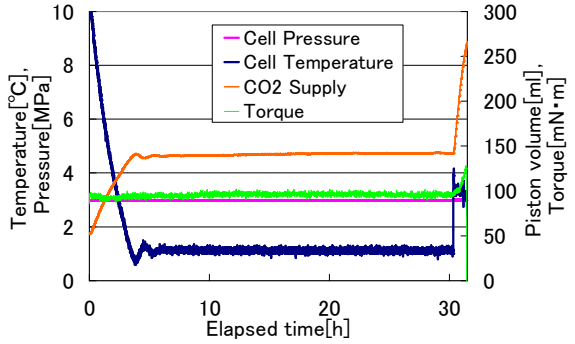

Figure 3. Hydrate formation from AFPs 0.01mg/ml

Formation rate and agitator torque

To compare the formation behavior, the increase of the CO2 supply and the agitator torque and is shown in Figure 4. Here, it is defined a point in time when the torque increases as 0min. After the hydrate formation begins, the CO2 supply is assumed as an amount of the hydrate formation.

From the Figure 4, compared to the experiment of pure water, the increasing rate of the torque decreased 76%, and the increasing rate of CO2 supply (=the formation rate) decreased about 48% in the experiment of AFPs 0.01mg/ml. Then it is revealed the effect of an inhibition on the hydrate formation by adding AFPs in pure water.

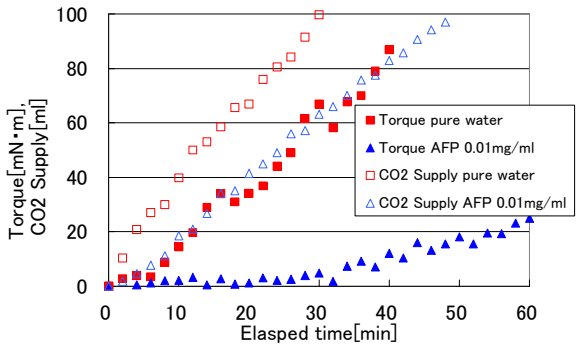

Figure 4. Torque and CO2 supply

Appearance of produced Hydrate

To confirm the production of hydrate, the high-pressure vessel was opened after experiment. The pictures shown in Figure 5-6 are the produced hydrate. From the Figures, the hydrate from AFPs was less than another one. Also it was solid and we couldn't confirm CO2 hydrate-slurry.

Figure 5. CO2 hydrate from pure water

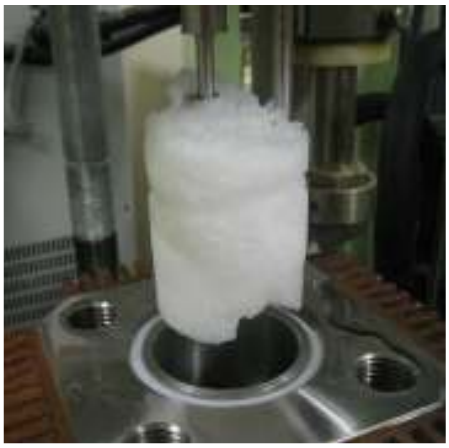

Figure 6. CO2 hydrate from AFPs 0.01mg/ml

CONCLUSIONS

In this study, the prospect of inhibition effect for CO2 hydrate formation by adding AFPs was presented. Under the conditions of AFPs 0.01mg/ml, a shift of the induction times, the formation rate and the torque of the agitator were revealed. The following conclusions can be drowned.

(1) It is able to product CO2 hydrate from AFPs 0.01mg/ml solution.

(2) Compared to pure water, the induction times increased 244%, the formation rate decreased 76% and the increasing ratio of

the torque decreased 48% by adding AFPs 0.01mg/ml.

(3) CO2 hydrate slurry didn't be observed in this study.

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