

Article

Design of Ecological CO₂ Enrichment System for Greenhouse Production using TBAB + CO₂ Semi-Clathrate Hydrate

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Abstract: This paper proposes an innovative CO₂ enrichment system for crop production under a controlled greenhouse environment by means of tetra-*n*-butylammonium bromide (TBAB) + CO₂ semi-clathrate hydrate (SC). In this system, CO₂ is captured directly from exhaust gas from a combustion heater at night, which can be used for stimulating photosynthesis of crops in greenhouses during daytime. Although the gas capacity of TBAB + CO₂ SC is less than that of CO₂ gas hydrate, it is shown that TBAB + CO₂ SC can store CO₂ for CO₂ enrichment in crop production even under moderate pressure conditions (<1.0 MPa) at 283 K.

Keywords: CO₂ separation; CO₂ storage; flue gas; gas hydrate; horticulture

1. Introduction

Sustainability of agriculture is a challenging subject because of future rapid global population increase [1]. Controlled environmental horticulture in a greenhouse is one of the most modern and sophisticated forms of horticulture systems for obtaining a high yield beyond the cultivation season in the field, by maintaining an optimum temperature in every stage of the crop [2]. However, temperature in the greenhouse without a heating system can fall below the optimum range for crops, especially during winter or nighttime, so an appropriate heating system is required to maintain the optimum temperature by means such as fossil-fuel combustion heating systems or heat pumps [3,4]. Thus, greenhouse horticulture leads to a rise in energy demand in the agricultural industry, which faces many difficulties, such as increased fuel cost [5,6] and the emission of greenhouse gases [7]. Therefore, the development of innovative technologies for production under a controlled greenhouse environment to establish a cost-effective, energy-effective, and environmentally-friendly greenhouse horticultural production system is of critical importance [8].

In greenhouse horticulture, carbon dioxide (CO₂) enrichment is effective to promote photosynthesis and thereby increase crop yield and grower income [9,10]. A variety of CO₂ enrichment systems have been studied using CO₂ gas from a storage tank or exhaust gas of combustion heaters [11,12]. A biomass-based boiler system has also been developed recently, for which energetic efficiency is improved by reusing biomass from agricultural/industrial waste [13]. However, because of greenhouse air ventilation to prevent its overheating, CO₂ is released from the greenhouse. CO₂ concentration in the greenhouse decreases and cancels out the CO₂ enrichment. Therefore, a cooling system to limit ventilation time [14,15] or a combustion-type CO₂ enrichment system connected to heat pump has been studied [16]. Here again, the economic benefit depends on the balance between increase in crop value and the cost of introducing the CO₂ enrichment system. For the above reasons, an innovative such system coupled with a greenhouse air-conditioning system based on a high-efficiency and low-cost cooling technique is desirable.

Owing to high CO₂ gas capacity of CO₂ gas hydrates, an application of CO₂ gas hydrates to agriculture is proposed; i.e., usage of CO₂ hydrate to increase CO₂ concentration in culturing algae [17]. We also evaluated CO₂ gas hydrates as cold energy and the source of CO₂ for the greenhouse [18]. It is shown that CO₂ gas supply capacity of the CO₂ gas hydrate is sufficient to stably maintain high concentrations of CO₂ for the stimulation of photosynthesis of tomato crops in greenhouses. CO₂ gas hydrate can be used as a source of stored cold thermal energy to reduce the amount of electricity consumed, which contributes to partial removal of heat from greenhouses in combination with other innovative methods such as root zone cooling [19,20] or nocturnal cooling in summer. The drawback to this approach is that CO₂ gas hydrate is formed under high-pressure and low-temperature conditions (e.g., >1.2 MPa at 273 K). It would be feasible to apply CO₂ gas hydrate as unconventional media for CO₂ transportation from industrial to agricultural areas [21], but it would not be feasible to form CO₂ gas hydrate at sites of greenhouse horticulture.

In this paper, we propose a novel concept of a CO₂ enrichment system for greenhouse production using semi-clathrate hydrate (hereafter SC). SC is formed under milder conditions (lower pressure and higher temperature) than CO₂ gas hydrate, and greater economic benefit can be expected. In this system, at night, tetra-*n*-butylammonium bromide (TBAB) + CO₂ SC is formed using CO₂ gas supplied from the exhaust gas of a combustion (or biomass-based) heater. During daytime, CO₂ gas and cold thermal energy from the dissociating SC is supplied in the greenhouse to stimulate crop photosynthesis.

2. Theoretical Background

TBAB is nontoxic and widely used as an ionic guest substance. Melting points of TBAB SC of ~285 K under atmospheric pressure are higher than those of gas hydrates and ice. Because TBAB SC forms a slurry that can be transported through a pipeline, SCs have been expected to be a new phase-change material [22,23]. In addition, SCs have been anticipated as a medium for gas storage and separation [24,25].

2.1. CO₂ Gas Storage Using SC

Different SC structures form depending on the concentration of aqueous TBAB solution. The crystal structure of TBAB SC with hydration number 38 (TBAB·38H₂O) was revealed [26] according to X-ray crystal structure analysis. The crystal structure of TBAB SC in Figure 1 shows that tetrakaidecahedral cages (5¹²6²) and pentakaidecahedral (5¹²6³) cages are occupied by tetra-*n*-butylammonium (TBA) cations, and anions (bromide; Br) form cage structures bonding to water molecules. There are also empty pentagonal dodecahedral (5¹²) cages in the structure of TBAB SC. TBAB·36H₂O hydrate is isostructural to the orthorhombic hydrate of TBAB·38H₂O, but tetragonal hydrates of TBAB·32H₂O and TBAB·26H₂O have not been refined yet [27,28]. Crystal structures of gas hydrates are comparable with that of SC. Three main structural families of gas hydrate are known, and they form depending mainly on the size of the guest molecules. These three are cubic structure I (sI)

and structure II (sII) hydrates and hexagonal structure H (sH) hydrate. Crystallographic data of each hydrate are summarized in Table 1.

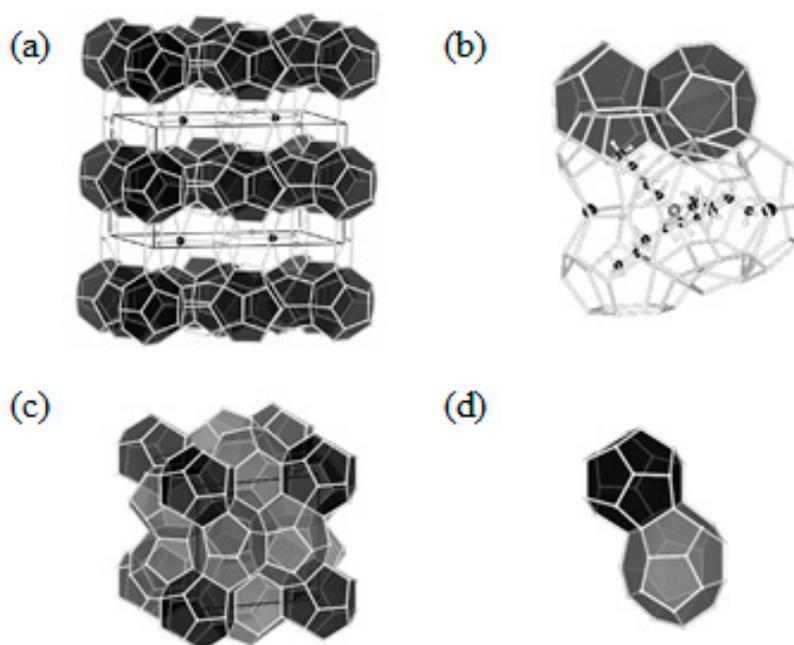


Figure 1. Host structure of a semi-clathrate hydrate (SC) and gas hydrate. (a) Schematic representation of orthorhombic SC; and (b) polyhedral host cages in SC: 5^{12} cage (dark gray), $5^{12}6^2$ and $5^{12}6^3$ cages occupied by a tetra-*n*-butylammonium (TBA) cation; (c) Schematic representation of sI hydrate; and (d) polyhedral host cages in sI hydrate: 5^{12} cage (dark gray) and $5^{12}6^2$ cage (light gray).

Table 1. Crystallographic data of four types of clathrate hydrates.

Structure	Space Group	Hydration Number	Lattice Constant/Å	Cage Type Number of Cages	Promoter	$\Delta H/\text{kJ mol}^{-1}$
sI	Cubic <i>Pm3n</i>	46	$a \approx 12$	$5^{12}/5^{12}6^2$ 2/6	Non	65 [29]
sII	Cubic <i>Fd-3m</i>	136	$a \approx 17$	$5^{12}/5^{12}6^4$ 16/8	THF	142 [30]
sH *	Hexagonal <i>P6/mmm</i>	34	$a \approx 12$ $c \approx 10$	$5^{12}/4^35^66^3/5^{12}6^8$ 3/2/1	NH	61 [31]
SC	Orthorhombic <i>Pmma</i>	76	$a \approx 21$ $b \approx 13$ $c \approx 12$	$5^{12}/5^{12}6^2/5^{12}6^3$ 6/4/4	TBAB	140 [32]

* sH hydrates necessarily form with two different guest substances; one is a large-molecule guest substance such as neohexane (NH), and the other is a small-molecule guest substance such as CH_4 .

Pure CO_2 gas forms sI hydrate, in which CO_2 is engaged in both 5^{12} and $5^{12}6^2$ cages. The CO_2 hydrate contains about 150 volumes of CO_2 gas per volume of hydrate crystal at standard temperature and pressure (150 V/V(STP)) [33]. Other structural gas hydrates of sII and sH also include CO_2 in the presence of other guest molecules, such as tetrahydrofuran (THF) [34] or 3,3-dimethyl-2-butanone (pinacolone) [35]. Likewise, it is known that small molecules are selectively incorporated in TBAB SC, but large molecules such as ethane and propane are not [36]. It is shown that small molecules such as methane (CH_4), nitrogen (N_2), and CO_2 are engaged into 5^{12} cages during the formation of TBAB SC by ^{13}C NMR [37], and their cage occupancies were determined by X-ray structure analysis [38–40].

2.2. Gas Separation Using SC

CO₂ gas separation from combustion flue gas is feasible through the crystallization of SC and gas hydrates. When hydrate crystals form from a mixture of CO₂ and other gases such as nitrogen (N₂) or hydrogen (H₂), the crystalline phase of SC or gas hydrate is enriched with CO₂, while the concentration of the other gas is increased in the gas phase.

Generally, there are two types of hydrate formation promoters: chemical additives for gas hydrate that have no effect on structures of the water cages (e.g., tetrahydrofuran, cyclopentane, and anionic/non-ionic surfactants), and SC types such as TBA salts that form SC [24,25,41]. These additives reduce hydrate formation pressures. Equilibrium pressures of mixed-gas hydrate such as CO₂ + N₂ are between the respective dissociation pressures of CO₂ and N₂ hydrates. Equilibrium pressures of mixed-gas hydrates are also moderated by these hydrate formation promoters (Figure 2).

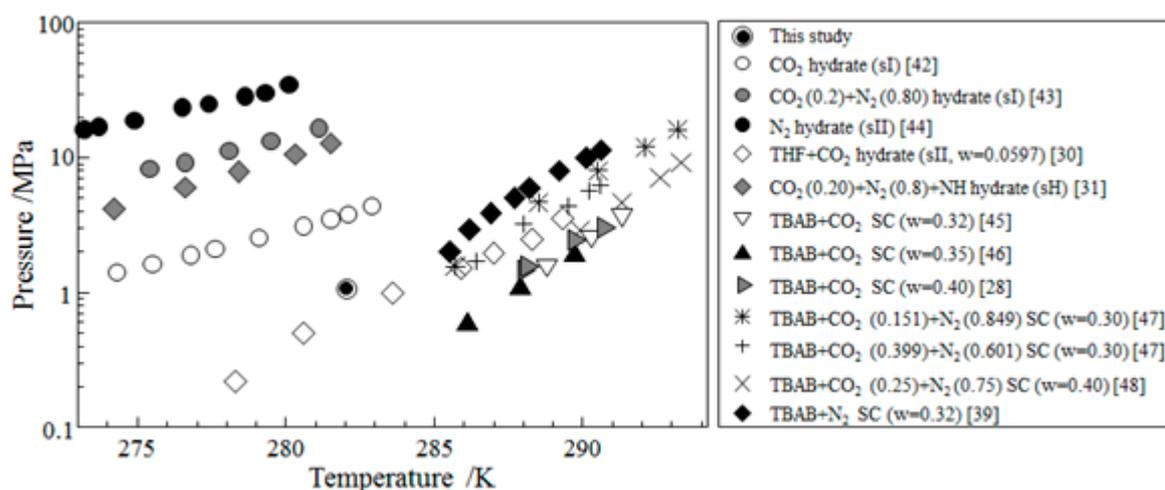


Figure 2. Formation conditions of gas-containing semi-clathrate hydrates and gas hydrates [28,30,31,39,42–48]. Double circle represents formation condition in the present study. Here, w denotes mass fraction of promoters in aqueous phase. NH: neohexane; TBAB: tetra-*n*-butylammonium bromide; THF: tetrahydrofuran.

3. TBAB (+CO₂ + N₂) SC with Mixed Gas of CO₂ + N₂

In this study, we synthesized TBAB + CO₂ + N₂ SC samples using the same method as our previous paper [49]. To synthesize the SC samples, a high-pressure cell of 223 cm³ volume was charged with 30 g of an aqueous TBAB solution with 0.320 mass fraction for TBAB (>0.99 mass fraction, Sigma-Aldrich). The hydrate formation pressure and temperature was 1.0 MPa and 282.2 K, respectively. After the supply of aqueous solution, the reactor was sealed and vacuumed by a vacuum pump. Subsequently, it was charged and discharged with CO₂ + N₂ mixed gas with the aid of the vacuum pump. When residual air was removed, we supplied CO₂ + N₂ mixed gas (CO₂/N₂ = 0.151/0.849, Japan Fine Products) to the cell and started stirring for dissolution of the gas into liquid phase. For comparison, TBAB SC without CO₂ + N₂ gas was formed from an aqueous TBAB solution with $w = 0.320$ for TBAB at 283.1 K under atmospheric pressure, and grown for 17 h. Both samples were taken out from the cell after quenching at a temperature <220 K. Detailed procedures on SC formation and gas analysis are treated in our previous study [50].

During the formation of the TBAB + CO₂ + N₂ hydrate, an initial rapid pressure drop ended in two hours and no further pressure drop was observed over 40 h. The gas amount contained in the SC sample was calculated from the pressure drop during the formation process. There was 4.3 mmol of CO₂ + N₂ gas absorbed in the SC formed from 30 g of the aqueous TBAB solution. In the previous study [49], it was shown that CO₂ is selectively captured in the SC, and the CO₂ mole fraction in the

SC phase was ~ 0.7 under the same experimental conditions as the present study. Thus, it is assumed that about 3 mmol of CO_2 was contained in the TBAB + CO_2 SC sample formed in this study.

To confirm the crystal structure of the sample formed under conditions of the proposed system, we carried out powder X-ray diffraction (PXRD) measurements at 93 K to avoid leakage of $\text{CO}_2 + \text{N}_2$ molecules in the SC sample under atmospheric pressure. Figure 3 shows PXRD patterns of TBAB + $\text{CO}_2 + \text{N}_2$ SC and that of TBAB SC formed without $\text{CO}_2 + \text{N}_2$ gas compression at the same temperature, for comparison. These two PXRD patterns do not show noteworthy diffraction peaks from hexagonal ice, which suggests that nearly all the TBAB solution transformed into the TBAB SC during its formation and after quenching for sampling. The obtained PXRD pattern of the TBAB + $\text{CO}_2 + \text{N}_2$ SC is consistent with that of the TBAB SC with orthorhombic *Pmma* phase [26]. This result agrees with our previous study of TBAB + CO_2 (or CH_4) SC [51]. Under substantial pressure of the gases, the TBAB solutions with $w = 0.320$ are likely to form the orthorhombic phase but not the tetragonal phase. However, the TBAB SC sample formed without $\text{CO}_2 + \text{N}_2$ gas was a mixture of the orthorhombic and other phases. It is unclear whether these structural differences are due to the occurrence of $\text{CO}_2 + \text{N}_2$ gas. It could be caused by a pressure–temperature effect or capture efficiency of gases, or it could be an extrinsic effect such as sample treatment after its synthesis. For further understanding of detailed crystallographic properties of TBAB SC, other studies from a physicochemical point of view are necessary. However, the fact that TBAB + $\text{CO}_2 + \text{N}_2$ SC were likely to form a pure orthorhombic structure is useful to estimate and assess its gas capacity within a crystalline structure from an application standpoint of the TBAB SC.

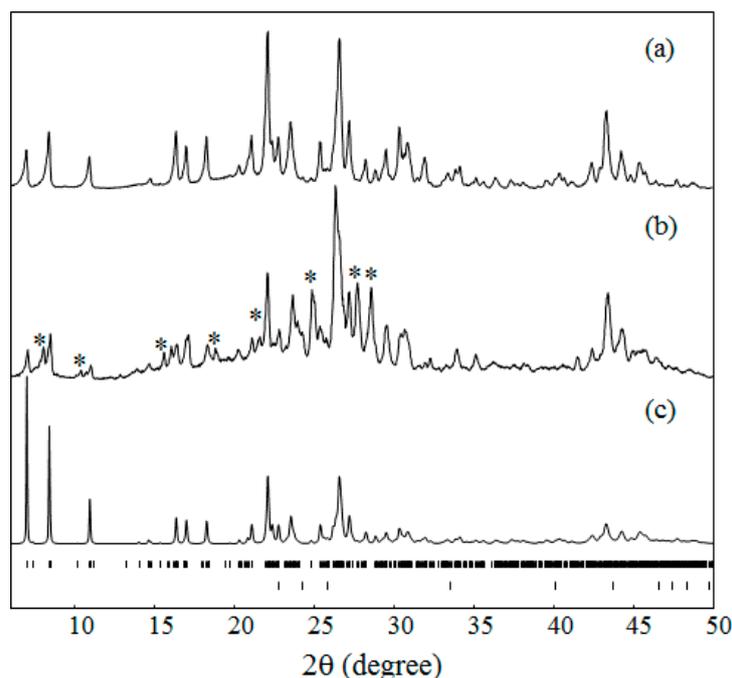


Figure 3. X-ray diffraction patterns of TBAB semi-clathrate hydrate (SC). Upper tick marks under powder X-ray diffraction (PXRD) profile represent calculated peak locations for the SC and lower tick marks represent those for hexagonal ice. (a) TBAB + $\text{CO}_2 + \text{N}_2$ SC at 93 K; (b) TBAB SC without $\text{CO}_2 + \text{N}_2$ gas at 93 K; and (c) orthorhombic TBAB SC without $\text{CO}_2 + \text{N}_2$ gas simulation [26]. Asterisks (*) represent diffraction peaks other than orthorhombic phase.

The CO_2 gas amount contained in the SC sample was assessed by comparing crystallographic structure data. The total amount of CO_2 gas contained in four different hydrate crystals (sI, sII, sHI and SC) as a function of gas amount encaged into 5^{12} cage (so-called cage occupancy) were simulated based on their crystal structures (Figure 4). The total amount of gas in the TBAB + $\text{CO}_2 + \text{N}_2$ SC

sample in this study is also plotted in this figure. Then, the overall apparent cage occupancy of 5^{12} cage (~ 0.15) was estimated. Other results based on cage occupancies determined by X-ray structure analysis [33,34,38] are plotted for comparison. Figure 4 suggests the possibility of forming greater gas occupation in the TBAB + CO_2 + N_2 SC sample, which could be achieved by improving the formation process of the SC sample.

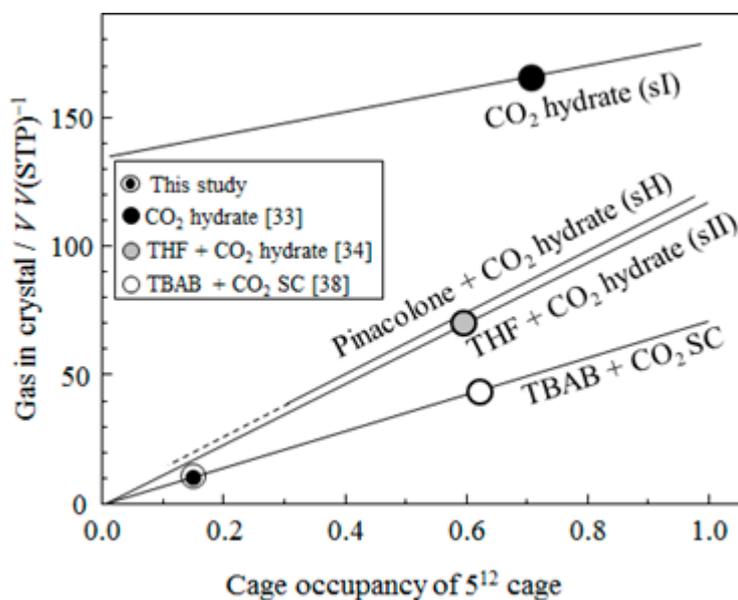


Figure 4. Gas amount contained in semi-clathrate hydrate and gas hydrates as function of cage occupancy of 5^{12} cage. Here, cage occupancy of $4^35^66^3$ cage in sH is assumed identical to that of 5^{12} cage. Each circle represents experimentally obtained CO_2 gas amount in hydrate crystals, and the result of this study represents the amount of CO_2 + N_2 ($\text{CO}_2/\text{N}_2 \sim 0.7/0.3$) gas.

The CO_2 gas capacity of sI hydrate was the greatest of the four hydrates (sI, sII, sH, and SC). However, the equilibrium pressure of CO_2 (+ N_2) hydrate formed from mixed gas of CO_2 + N_2 ($\text{CO}_2/\text{N}_2 \sim 0.15/0.85$) was >10 MPa as shown in Figure 2. Additionally, since the hydrate promoters such as THF are basically volatile and harmful, they are unsuitable for use in agricultural fields, and especially in closed greenhouses. Accordingly, we conclude that TBAB + CO_2 + N_2 SC is suitable for use in CO_2 enrichment within a closed greenhouse.

Other materials such as activated carbon, zeolite, or porous materials have been investigated, toward the development of a CO_2 capture technology based on adsorption [52]. Specifically, activated carbons or zeolites are also cost-effective candidate materials for CO_2 storage. These have higher CO_2 adsorption capacity than TBAB + CO_2 SC, but also high humidity because of mist spraying for crop growth and yield, and wet exhaust gas generally reduces their capacity. Thus, overall assessment of the total system is required to evaluate and compare potentials of these media.

4. Design of CO_2 Enrichment System Using SC

4.1. Operation Cycle of System

Performance of the TBAB + CO_2 SC formation/dissociation cycle for CO_2 enrichment depends on gas capacity in TBAB SC and thermal efficiency of the temperature cycle with alternate actions of hydrate formation and dissociation. Figure 5 conceptually illustrates the SC formation/dissociation cycle on a pressure-temperature plane together with the TBAB + CO_2 + N_2 SC phase equilibrium curve. Each process in the SC formation/dissociation cycle is described below.

During the night, exhaust gas of the combustion heater is trapped and cooled to near ambient temperature. Here, we can use cool energy of the environment as a supplement during the night. Pollutants such as NO_x and SO_x in the gas are washed out by a water scrubber. It is noteworthy that because the gas capture medium used in this system is a water-based material, a water-type scrubber can be used to clean the flue gas. The gas is compressed to 1.0 MPa or less to flow into TBAB solution within a formation reactor. Although equilibrium conditions of TBAB + CO_2 + N_2 SC are mild (<1.0 MPa at 283 K), supercooling of TBAB solution is generally necessary for nucleation. Thus, the TBAB solutions must be cooled to 280 K or lower for SC nucleation. Once SC nucleation occurs, temperature is set to near the equilibrium temperature for slow SC growth.

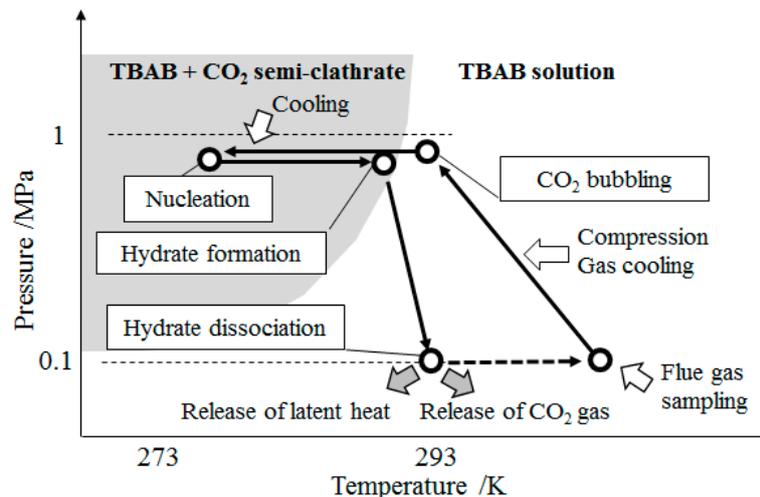


Figure 5. Conceptual diagram of semi-clathrate hydrate cycle.

During the day, the temperature controller ceases operation and the temperature of the reactor warms to the ambient temperature above the equilibrium point of SC hydrate, and CO_2 + N_2 gas automatically emerges for CO_2 enrichment. At the same time, because the SC dissociation is an endothermic reaction, cold heat may be obtained and used to cool parts of the greenhouse. After completion of TBAB SC dissociation, reactor conditions are reset to the initial state.

4.2. Configuration of CO_2 Enrichment System Using TBAB + CO_2 SC

Figure 6a is a conceptual process diagram of the proposed system, which is composed of three sections. The first is a conventional combustion heater to heat the greenhouse. The heater is connected to the second section of the water scrubber system and compressor for outflow of exhaust gas. The third section is a TBAB SC reactor with a temperature control unit.

As shown in Figure 6b, CO_2 gas supply from the storage tank has been widely used for CO_2 enrichment. In this case, some CO_2 gas is released to the atmosphere during daytime. Additionally, exhaust gas from the heater for greenhouse heating is released during nighttime. However, the advantage of the present system is that it is not necessary to provide CO_2 gas from a storage tank, and exhaust gas can be used for the stimulation of photosynthesis of crops in greenhouses. From carbon balance estimates, the environmental benefit of the proposed system is to remove the CO_2 emissions of a combustion heater. This then becomes a low-cost and environmentally friendly CO_2 enrichment and heating/cooling system. Moreover, the proposed temporally varying process can achieve additional economic benefits when balanced against the conventional heat pump system for daytime cooling.

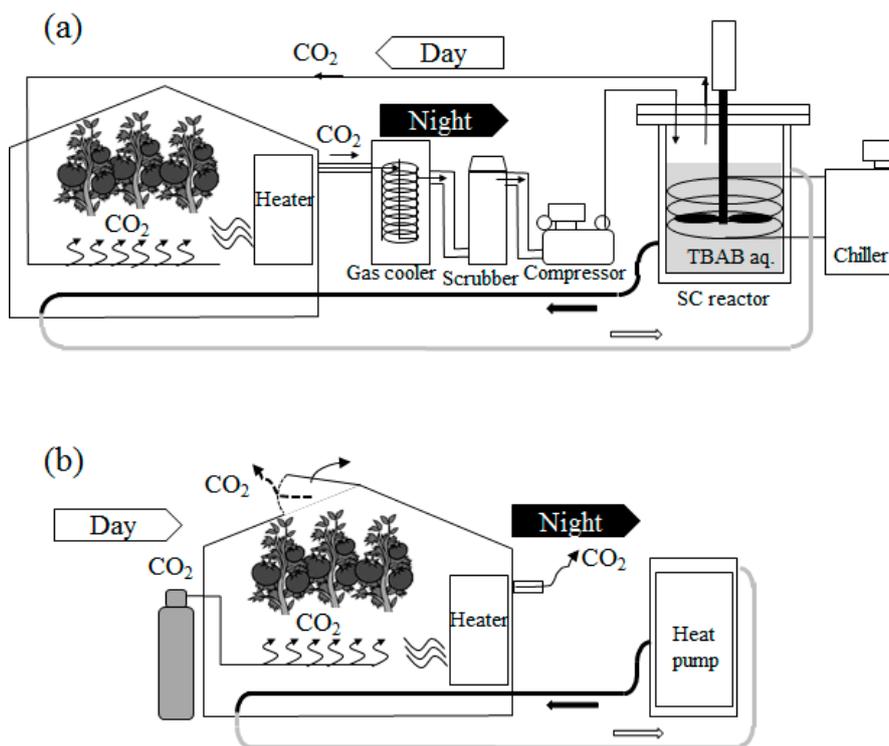


Figure 6. Configuration of CO₂ enrichment system, using (a) TBAB + CO₂ SC and (b) CO₂ gas from a tank.

4.3. Quantitative Evaluation of CO₂ Enrichment System Using TBAB + CO₂ SC

We evaluated cultivation conditions of non-everbearing strawberry (*Fragaria x ananassa* Duch.) cultivars of Japanese “Tochiotome”. For a preliminary field study of the system in a greenhouse of 150 m² in size, ~4.5 kg/day of CO₂ is required. According to our results, 3 mmol of CO₂ gas was absorbed in the SC formed from 30 g of aqueous TBAB solution due to SC formation. Thus, it is estimated that 0.004 kg/L of CO₂ is captured by the TBAB solution with $w = 0.32$ mass fraction. That is 1125 L of TBAB solution and ~1500 L of a SC reactor needed for storing 4.5 kg of CO₂. Our bench-scale test of TBAB + CO₂ SC using a larger reactor (1000 cm³) with continuous gas flow showed similar or less CO₂ capacity in the system [49].

It is necessary to control the CO₂ enrichment system as follows. During nighttime (e.g., from 9 pm. to 6 am.), the greenhouse is heated to avoid temperature drop below 281 K. For example, the heating can be via a combustion heater (NEPON Inc., Model KA-125, Tokyo, Japan) that exhausts ~22.6 m³/h (STP) of flue gas containing 2.84 kg/h of CO₂ caused by the combustion of kerosene. CO₂ enrichment using the TBAB + CO₂ SC system needs 4.5 kg of CO₂ from this flue gas to provide sufficient CO₂ to a 150-m² field during the day, as noted above. The minimum performance for the CO₂ capture rate in our system is 4.5 kg/9 h = ~0.5 kg/h on average, and that required for CO₂ capture efficiency is ~0.18 (=0.5 kg/h/2.84 kg/h). Regardless of formation rate, this value was confirmed by our previous study [49], in which it was calculated at 0.16–0.29 from data with 1 MPa operation pressure. These values would be further improved by a practical process. Upon morning, temperature maintenance of the SC reactor is terminated and the temperature of the reactor is warmed to ambient temperature above the equilibrium point of SC hydrate to dissociate the SC and release the captured CO₂. Using CO₂ concentration monitors in the greenhouse, CO₂ concentration is controlled in the range 700–1000 ppm, which is effective for the crops [10]. The suggested temporally varying CO₂ enrichment is promising for enhancing energy efficiency; i.e., at night, there is heating and CO₂ storage from a flue gas, and in daytime there is CO₂ release and enrichment.

The system proposed herein is still being upgraded. However, it can be expected that the CO₂ condensation process from the flue gas before gas injection to the hydrate reactor may improve system CO₂ gas capacity. Additionally, optimization of the formation temperature of TBAB + CO₂ SC, a method for flue bubbling into the aqueous TBAB solution, or other parameters may promote kinetic hydrate formation (e.g., [53–55]). These procedures to improve the SC system will enable downsizing of the SC formation reactor. Further study based on bench-scale experiments in an agricultural field will be necessary to improve the concept for estimation of energy balance. This would also contribute to the reuse of CO₂ gas from the heater exhaust gas for carbon capture and utilization technology.

5. Summary

In this paper, a new concept of CO₂ enrichment system for crop production under a controlled greenhouse environment for horticulture was proposed, based on new and environmentally friendly tetra-*n*-butylammonium bromide (TBAB) + CO₂ semi-clathrate hydrate (SC). The feasibility of this system was assessed based on experimentally obtained CO₂ capacity in TBAB + CO₂ + N₂ SC formed at 1.0 MPa and 282.2 K. As a result, 0.004 kg/L of CO₂ was obtained by SC formation from TBAB solution with $w = 0.320$ mass fraction of TBAB. There was 1125 L of TBAB solution and SC reactor of ~1500 L needed for CO₂ enrichment for a typical greenhouse of 150-m² size. It is anticipated that the CO₂ condensation process from the flue gas before gas injection to the hydrate reactor will improve CO₂ gas capacity of this system. Another additive or other parameters may promote kinetic hydrate formation. These processes to improve the SC system will enable downsizing of the SC formation reactor.

We specified requirements of the SC reactor with regard for the CO₂ capture rate based on the CO₂ enrichment process in the cultivation of a Japanese strawberry cultivar as a standard case. In this system, a CO₂ storage tank is not necessary to provide CO₂ gas, and exhaust gas is effectively and efficiently used for the stimulation of crop photosynthesis in greenhouses.

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References

1. Tilman, D.; Cassman, K.G.; Matson, P.A.; Naylor, R.; Polasky, S. Agricultural sustainability and intensive production practices. *Nature* **2002**, *418*, 671–677. [[CrossRef](#)] [[PubMed](#)]
2. Sethi, V.P.; Sharma, S.K. Survey and evaluation of heating technologies for worldwide agricultural greenhouse applications. *Sol. Energy* **2008**, *82*, 832–859. [[CrossRef](#)]
3. Bartzanas, T.; Tchamitchian, M.; Kittas, C. Influence of the heating method on greenhouse microclimate and energy consumption. *Biosyst. Eng.* **2005**, *91*, 487–499. [[CrossRef](#)]
4. Tarnawski, V.R.; Leong, W.H.; Momose, T.; Hamada, Y. Analysis of ground source heat pumps with horizontal ground heat exchangers for northern Japan. *Renew. Energy* **2009**, *34*, 127–134. [[CrossRef](#)]
5. Woods, J.; Williams, A.; Hughes, J.K.; Black, M.; Murphy, R. Energy and the food system. *Phil. Trans. R. Soc. B* **2010**, *365*, 2991–3006. [[CrossRef](#)] [[PubMed](#)]
6. Vadiee, A.; Martin, V. Energy management in horticultural applications through the closed greenhouse concept, state of the art. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5087–5100. [[CrossRef](#)]
7. Vermeulen, S.J.; Campbell, B.M.; Ingram, J.S.I. Climate change and food systems. *Annu. Rev. Environ. Resour.* **2012**, *37*, 195–222. [[CrossRef](#)]
8. Cuce, E.; Harjunowibowo, D.; Cuce, P.M. Renewable and sustainable energy saving strategies for greenhouse systems: A comprehensive review. *Renew. Sustain. Energy Rev.* **2016**, *64*, 34–59. [[CrossRef](#)]

9. Peet, M.M.; Willits, D.H. CO₂ enrichment of greenhouse tomatoes using a closed-loop heat storage: Effects of cultivar and nitrogen. *Sci. Hortic.* **1984**, *24*, 21–32. [[CrossRef](#)]
10. Mortensen, L.M. Review: CO₂ enrichment in greenhouses. Crop responses. *Sci. Hortic.* **1987**, *33*, 1–25. [[CrossRef](#)]
11. Chalabi, Z.S.; Biro, A.; Bailey, B.J.; Aikman, D.P.; Cockshull, K.E. Optimal control strategies for carbon dioxide enrichment in greenhouse tomato crops—Part 1: Using pure carbon dioxide. *Biosyst. Eng.* **2002**, *81*, 421–431. [[CrossRef](#)]
12. Chalabi, Z.S.; Biro, A.; Bailey, B.J.; Aikman, D.P.; Cockshull, K.E. Optimal control strategies for carbon dioxide enrichment in greenhouse tomato crops—Part II: Using the exhaust gases of natural gas fired boilers. *Biosyst. Eng.* **2002**, *81*, 323–332. [[CrossRef](#)]
13. Sanchez-Molina, J.A.; Reinoso, J.V.; Acien, F.G.; Rodriguez, F.; Lopez, J.C. Development of a biomass-based system for nocturnal temperature and diurnal CO₂ concentration control in greenhouses. *Biomass Bioenergy* **2014**, *67*, 60–71. [[CrossRef](#)]
14. Heuvelink, E.; Bakker, M.; Marcelis, L.F.M.; Raaphorst, M. Climate and yield in a closed greenhouse. *Acta Hort.* **2008**, *801*, 1083–1092. [[CrossRef](#)]
15. Qian, T.; Dieleman, J.A.; Elings, A.; De Gelder, A.; Marcelis, L.F.M.; Van Kooten, O. Comparison of climate and production in closed, semi-closed and open greenhouses. *Acta Hort.* **2011**, *893*, 807–814. [[CrossRef](#)]
16. Yang, S.H.; Lee, C.G.; Ashtiani-Araghi, A.; Kim, J.Y.; Rhee, J.Y. Development and evaluation of combustion-type CO₂ enrichment system connected to heat pump for greenhouses. *Eng. Agric. Environ. Food* **2014**, *7*, 28–33. [[CrossRef](#)]
17. Nakano, S.; Chang, K.H.; Shijima, A.; Miyamoto, H.; Sato, Y.; Noto, Y.; Ha, J.Y.; Sakamoto, M. A usage of CO₂ hydrate: Convenient method to increase CO₂ concentration in culturing algae. *Bioresour. Technol.* **2014**, *172*, 444–448. [[CrossRef](#)] [[PubMed](#)]
18. Umeda, H.; Ahn, D.H.; Iwasaki, Y.; Matsuo, S.; Takeya, S. A cooling and CO₂ enrichment system for greenhouse production using CO₂ clathrate hydrate. *Eng. Agric. Environ. Food* **2015**, *8*, 307–312. [[CrossRef](#)]
19. Sakamoto, M.; Uenishi, M.; Miyamoto, K.; Suzuki, T. Effect of root-zone temperature on the growth and fruit quality of hydroponically grown strawberry plants. *J. Agric. Sci.* **2016**, *8*, 1916–19760.
20. Llorach-Massana, P.; Pena, J.; Rieradevall, J.; Montero, J.I. Analysis of the technical, environmental and economic potential of phase change materials (PCM) for root zone heating in Mediterranean greenhouses. *Renew. Energy* **2017**, *103*, 570–581. [[CrossRef](#)]
21. Matsuo, S.; Umeda, H.; Takeya, S.; Fujita, T. A feasibility study on hydrate-based technology for transporting CO₂ from industrial to agricultural areas. *Energies* **2017**, *10*, 728. [[CrossRef](#)]
22. Zhang, P.; Ma, Z.W.; Wang, R.Z. An overview of phase change material slurries: MPCS and CHS. *Renew. Sustain. Energy Rev.* **2010**, *14*, 598–614. [[CrossRef](#)]
23. Castellani, B.; Morini, E.; Filippini, M.; Nicolini, A.; Palombo, M.; Cotana, F.; Rossi, F. Clathrate hydrates for thermal energy storage in buildings: Overview of proper hydrate-forming compounds. *Sustainability* **2014**, *6*, 6815–6829. [[CrossRef](#)]
24. Babu, P.; Linga, P.; Kumar, R.; Englezos, P. A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. *Energy* **2015**, *85*, 261–279. [[CrossRef](#)]
25. Ma, Z.W.; Zhang, P.; Bao, H.S.; Deng, S. Review of fundamental properties of CO₂ hydrates and CO₂ capture and separation using hydration method. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1273–1302. [[CrossRef](#)]
26. Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-*n*-butylammonium bromide–water (1/38). *Acta Cryst.* **2005**, *61*, o65–o66. [[CrossRef](#)] [[PubMed](#)]
27. Rodionova, T.V.; Komarov, V.Y.; Villevald, G.V.; Karpova, T.D.; Kuratieva, N.V.; Manakov, A.Y. Calorimetric and structural studies of tetrabutylammonium bromide ionic clathrate hydrates. *J. Phys. Chem. B* **2013**, *117*, 10677–10685. [[CrossRef](#)] [[PubMed](#)]
28. Chazallon, B.; Ziskind, M.; Carpentier, Y.; Focsa, C. CO₂ capture using semi-clathrates of quaternary ammonium salt: Structure change induced by CO₂ and N₂ enclathration. *J. Phys. Chem. B* **2014**, *118*, 13440–13452. [[CrossRef](#)] [[PubMed](#)]
29. Kang, S.P.; Lee, H.; Ryu, B.J. Enthalpies of dissociation of clathrate hydrates of carbon dioxide, nitrogen, (carbon dioxide + nitrogen), and (carbon dioxide + nitrogen + tetrahydrofuran). *J. Chem. Thermodyn.* **2001**, *33*, 513–521. [[CrossRef](#)]

30. Delahaye, A.; Fournaison, L.; Marinhas, S.; Chatti, I.; Petitet, J.P.; Dalmazzone, D.; Furst, W. Effect of THF on equilibrium pressure and dissociation enthalpy of CO₂ hydrates applied to secondary refrigeration. *Ind. Eng. Chem. Res.* **2006**, *45*, 391–397. [[CrossRef](#)]
31. Lee, Y.; Lee, D.; Lee, J.W.; Seo, Y. Enclathration of CO₂ as a co-guest of structure H hydrates and its implications for CO₂ capture and sequestration. *Appl. Eng.* **2016**, *163*, 51–59. [[CrossRef](#)]
32. Lin, W.; Delahaye, A.; Fournaison, L. Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of CO₂ +TBAB. *Fluid Phase Equilib.* **2008**, *264*, 220–227. [[CrossRef](#)]
33. Udachin, K.A.; Ratcliffe, C.I.; Ripmeester, J.A. Structure, composition, and thermal expansion of CO₂ hydrate from single crystal X-ray diffraction measurements. *J. Phys. Chem. B* **2001**, *105*, 4200–4204. [[CrossRef](#)]
34. Moudrakovski, I.L.; Udachin, K.A.; Alavi, S.; Ratcliffe, C.I.; Ripmeester, J.A. Facilitating guest transport in clathrate hydrates by tuning guest-host interactions. *J. Chem. Phys.* **2015**, *142*, 074705. [[CrossRef](#)] [[PubMed](#)]
35. Tezuka, K.; Shen, R.; Watanabe, T.; Takeya, S.; Alavi, S.; Ripmeester, J.A.; Ohmura, R. Synthesis and characterization of a structure H hydrate formed with carbon dioxide and 3,3-dimethyl-2-butanone. *Chem. Commun.* **2013**, *49*, 505–507. [[CrossRef](#)] [[PubMed](#)]
36. Kamata, Y.; Oyama, H.; Shimada, W.; Ebinuma, T.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Gas separation method using tetra-*n*-butyl ammonium bromide semi-clathrate hydrate. *Jpn. J. Appl. Phys.* **2004**, *43*, 362–365. [[CrossRef](#)]
37. Lee, S.; Park, S.; Lee, Y.; Lee, J.; Lee, H.; Seo, Y. Guest gas enclathration in semiclathrates of tetra-*n*-butylammonium bromide: Stability condition and spectroscopic analysis. *Langmuir* **2011**, *27*, 10597–10603. [[CrossRef](#)] [[PubMed](#)]
38. Muromachi, S.; Udachin, K.A.; Shin, K.; Alavi, S.; Moudrakovski, I.L.; Ohmura, R.; Ripmeester, J.A. Guest-induced symmetry lowering of an ionic clathrate material for carbon capture. *Chem. Commun.* **2014**, *50*, 11476–11479. [[CrossRef](#)] [[PubMed](#)]
39. Muromachi, S.; Hashimoto, H.; Maekawa, T.; Takeya, S.; Yamamoto, Y. Phase equilibrium and characterization of ionic clathrate hydrates formed with tetra-*n*-butylammonium bromide and nitrogen gas. *Fluid Phase Equilib.* **2016**, *413*, 249–253. [[CrossRef](#)]
40. Muromachi, S.; Udachin, K.A.; Alavi, S.; Ohmura, R.; Ripmeester, J.A. Selective occupancy of methane by cage symmetry in TBAB ionic clathrate hydrate. *Chem. Commun.* **2016**, *52*, 5621–5624. [[CrossRef](#)] [[PubMed](#)]
41. Duc, N.H.; Chauvy, F.; Herri, J.M. CO₂ capture by hydrate crystallization—A potential solution for gas emission of steelmaking industry. *Energy Convers. Manag.* **2007**, *48*, 1313–1322. [[CrossRef](#)]
42. Adisasmitho, S.; Frank, R.J., III; Sloan, E.D. Hydrates of carbon dioxide and methane mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68–71. [[CrossRef](#)]
43. Lee, Y.; Lee, S.; Lee, J.; Seo, Y. Structure identification and dissociation enthalpy measurements of the CO₂ + N₂ hydrates for their application to CO₂ capture and storage. *Chem. Eng. J.* **2014**, *246*, 20–26. [[CrossRef](#)]
44. Jhaveri, J.; Robinson, D.B. Hydrates in the methane-nitrogen system. *Can. J. Chem. Eng.* **1965**, *43*, 75–78. [[CrossRef](#)]
45. Ye, N.; Zhang, P. Equilibrium data and morphology of tetra-*n*-butyl ammonium bromide semiclathrate hydrate with carbon dioxide. *J. Chem. Eng. Data* **2012**, *57*, 1557–1562. [[CrossRef](#)]
46. Mohammadi, A.H.; Eslamimanesh, A.; Belandria, V.; Richon, D. Phase equilibria of semiclathrate hydrates of CO₂, N₂, CH₄, or H₂ + tetra-*n*-butylammonium bromide aqueous solution. *J. Chem. Eng. Data* **2011**, *56*, 3855–3865. [[CrossRef](#)]
47. Mohammadi, A.H.; Eslamimanesh, A.; Belandria, V.; Richon, D.; Naidoo, P.; Ramjugernath, D. Phase equilibrium measurements for semi-clathrate hydrates of the (CO₂ + N₂ + tetra-*n*-butylammonium bromide) aqueous solution system. *J. Chem. Thermodyn.* **2012**, *46*, 57–61. [[CrossRef](#)]
48. Deschamps, J.; Dalmazzone, D. Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N₂, CO₂, N₂ + CO₂ and CH₄ + CO₂. *J. Therm. Anal. Calorim.* **2009**, *98*, 113–118. [[CrossRef](#)]
49. Hashimoto, H.; Yamaguchi, T.; Kinoshita, T.; Muromachi, S. Gas separation of flue gas by tetra-*n*-butylammonium bromide hydrates under moderate pressure conditions. *Energy* **2017**, *129*, 292–298. [[CrossRef](#)]
50. Muromachi, S.; Takeya, S.; Yamamoto, Y.; Ohmura, R. Characterization of tetra-*n*-butylphosphonium bromide semiclathrate hydrate by crystal structure analysis. *CrystEngComm* **2014**, *16*, 2056–2060. [[CrossRef](#)]
51. Muromachi, S.; Yamamoto, Y.; Takeya, S. Bulk phase behavior of tetra-*n*-butylammonium bromide hydrates formed with carbon dioxide or methane gas. *Korean J. Chem. Eng.* **2016**, *33*, 1917–1921. [[CrossRef](#)]

52. Sayaria, A.; Belmabkhouta, A.; Serna-Guerrero, R. Flue gas treatment via CO₂ adsorption. *Chem. Eng. J.* **2011**, *171*, 760–774. [[CrossRef](#)]
53. Kumano, H.; Hirata, T.; Mitsuishi, K.; Ueno, K. Experimental study on effect of electric field on hydrate nucleation in supercooled tetra-n-butyl ammonium bromide aqueous solution. *Int. J. Refrig.* **2012**, *35*, 1266–1274. [[CrossRef](#)]
54. Brinchi, L.; Castellani, B.; Rossi, F.; Cotana, F.; Morini, E.; Nicolini, A.; Filipponi, M. Experimental investigations on scaled-up methane hydrate production with surfactant promotion: Energy considerations. *J. Petrol. Sci. Eng.* **2014**, *120*, 187–193.
55. Mori, Y.H. Thermal resistances in stirred-tank and tubular reactors for clathrate-hydrate formation: Estimating their reactor-scale dependences. *Chem. Eng. Res. Des.* **2017**, *117*, 715–724. [[CrossRef](#)]



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