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A Review on Formation Enhancement of CO₂ Hydrate Slurry in Cool Storage Application

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Abstract CO₂ hydrate slurry, a kind of two-phase fluid, is made of CO₂ hydrate particles suspended in liquid water. It is considered as a good candidate in cool storage or secondary refrigerant due to its high latent heat for phase change. In this paper, the state of art of CO₂ hydrate slurry research is reviewed, the main focuses include its characteristics of the formation dynamics, and its characteristics of flow and heat transfer. Meanwhile, a novel apparatus is introduced to continuously produce CO₂ hydrate slurry for cool storage application. Challenges in the technology are discussed and measures of promoting the application of CO₂ hydrate slurry in cool storage are suggested.

Keywords formation enhancement, cool storage, secondary refrigerant, CO₂ hydrate slurry, flow and heat transfer properties

1 INTRODUCTION

Recently, it has become more and more necessary to reduce power consumption and propagation of the refrigerants in the atmosphere along with the growth of world population and development. The chlorinated hydrocarbon refrigerants, including CFCs and HCFCs, were prohibited by the Montreal Protocol in 1987 due to their ozone depletion potentials (abbr. ODPs). HFCs were proposed to substitute CFCs and HCFCs in order to avoid the ozone depletion issue, however the Kyoto Protocol in 1997 also prohibited the utilization of HFCs due to their global warming potentials^[1]. Research and development of alternative refrigerants with environment-friendly and excellent thermophysical properties have never become so urgently since the ratification of the treaties^[2]. In this

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context, the use of phase change materials in cool storage or secondary refrigeration applications is a promising approach for energy conservation and environmental sustainability. Secondary refrigerant is a kind of fluid to transport cold from a primary refrigerating machine to the room for cooling. Water, ice slurry, and eutectic salt are commonly used as secondary refrigerants. However, water is sensible heat storage medium, resulting in a huge volume of water storage tank and high pump power consumption. Ice slurry is a two-phase thermal fluid with smaller size of equipment than that of water, but the ice-making process needs low evaporation temperature, leading to lower energy efficiency. Eutectic salt is easily aged and corrode metal device. However, CO₂ hydrate slurry, with a large cool storage capacity, can be a better option for cool storage. CO₂ hydrate slurry, similar to the ice slurry, is a kind of two-phase suspension consist of solid hydrate particles and liquid water. It can be generated at mild temperature and pressure. In many literatures, cool storage mediums such as ice slurries, tetra-n-butyl ammonium bromide (abbr. TBAB) hydrate slurry, etc., have been discussed in detail, but a review on CO₂ hydrate slurry is inadequate. Except for the refrigeration, CO₂ hydrate can be used in many other applications including ocean carbon sequestration, seawater desalination, food preservation and gas mixture separation^[3,4].

CO₂ hydrate, as a promising cool storage material, was firstly presented in the 1980s^[5]. It had been investigated that the usable enthalpy can reached 11.5 kJ/kg (water) when the hydrate fraction in the slurry is 2.8 vol%, and the temperature is 276.24 K^[6]. Interestingly, the first case of hydrate in refrigeration process was related to CFC hydrate crystallization, which was found in expansion valves^[7]. Since then, a lot of works have been done on CO₂ hydrates for cool storage application. Osmann *et al*^[8] investigated CO₂ hydrate slurry and the results showed that dissociation enthalpy of CO₂ hydrate slurry was about 54 kJ/kg at pressure of 30 bars and temperature of 0~7°C, corresponding to 10.8% of solid fraction. CO₂ hydrate slurry has the following advantages: (1) both CO₂ and water are environmentally friendly substances; (2) dissociation enthalpy of pure CO₂ hydrate is approximately 500 kJ/kg, which is one and a half higher of ice (333 kJ/kg)^[9]. For instance, when the temperature difference is 5~12°C, the cooling capacity of chilled water of 5.6°C is about 29.26Mcal/m³, only 1/3 that of hydrate^[10]; (3)it can be formed and decomposed above freezing point^[11]; (4)compared with the ice slurry, which uses mechanical processes to scrap or brush from surface of heat exchangers, it can save approximately 40% energy in the production process without any mechanical process^[10,11]; (5)it has excellent flow and heat transfer characteristics and is easy to transport^[12].

As it well known^[4,5], only a small amount of CO₂ hydrate can be generated at the interface of water and CO₂

under natural conditions. Therefore, enhancement methods should be adopted during the hydrate production. Different enhancement methods were tested previously include stirring, spraying and bubbling, combined with different additives such as tetrahydrofuran (THF), TBAB, etc. This paper will provide a review on the enhancement of CO₂ hydrate slurry formation as well as its characteristics of flow and heat transfer. Meanwhile, a novel device which can produce CO₂ hydrate slurry continuously is introduced.

2. ENHANCEMENT METHODS of CO₂ HYDRATE SLURRY FORMATION

2.1. Mechanical mixing

2.1.1. Stirring

Stirring is the most common and mature method for hydrate formation, especially for fundamental studies on the formation and dissociation of gas hydrates in laboratories [13]. Generally, the action of stirring makes the liquid surface into a conical shape for enhancing the contact interface between water and CO₂ molecules. CO₂ hydrates formation is a crystallization process, which requires a supersaturated and subcooled environment. When the solution approaches that condition, a large number of gas molecules instantaneously turn into a state of nucleation. Then during the next process of growth phase, these nuclei continuously form the hydrate crystals. Furthermore, stirring can accelerate the heat dissipation to maintain the solution in subcooled state, which shortens the induction time and promotes hydrate generation. The majority of the experimental formation data from the literatures are obtained in a semi-batch stirred tank. The experimental schematic is shown in Fig. 1.

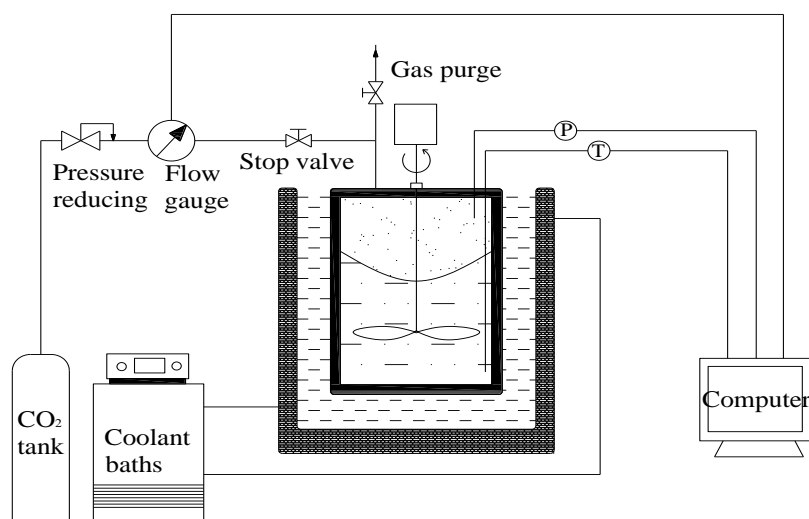


Fig.1. schematic diagram of stirred vessel.

Liu *et al.* [14] investigated the effect of stirring on the CO₂ hydrate formation. Their experimental data showed

that stirring could improve the CO₂ gas dissolution effectively during the hydrate formation process. The solution reached saturation within only three minutes with a stirring rate of 250 r·min⁻¹. Moreover, hydrates could form completely about 100 minutes earlier than that in a quiescent system. Liu *et al.* [15] also found that the effect of stirring was stronger than that of the additive SDS on CO₂ dissolution. Clarke and Bishnoi [16] investigated the effect of stirring velocity on the gas consumption and hydrate formation in a semi-batch stirred reactor. Their results showed the gas consumption increased with the increasing of stirring velocity. Duc *et al.* [17] found that CO₂ hydrate grew fast within a classical batch reactor, and the amount of CO₂ stored in hydrate was about 30~35m³·m⁻³.

It was suggested that the suitable stirring velocity should be at 300 ~ 500 r·min⁻¹[18]. In fact, the speed of gas molecules dissolved in aqueous solution is determined by the mixing time. Additional heat due to a high stirring velocity in the reactor would cause the temperature raising that is not desirable for hydrate formation. Liu *et al.* [15] carried out experiments with 40-minute stirring in the temperature cooling down process, the hydrate formation showed almost the same effect as that introduced by the continuous stirring, and the energy consumption was reduced effectively. In addition, with hydrate accumulation in the reactor, the increasing viscosity could hinder the stirring action and finally will affect the rate of hydrate formation. At the moment, the stirring action can avoid hydrate accumulation on the liquid surface as well as improve gas diffusion, and thus reduce the barrier of hydrate formation. Therefore, it's important to select an appropriate stirring velocity.

However, the stirring method also has some disadvantages, the reaction system with stirring increases the equipment investment and equipment maintenance charge, and the stirring will increase the additional energy consumption, which is not conducive to industrial application. Stirred reactor is not convenient to separate the generated hydrate from the pore water and compact it into the storage tank, which is not conducive to continuous production [19,20,21].

2.1.2. Spraying

Spraying is the process that small droplets of aqueous solution are thrown into the reactor full of gas. It allows to maximize the interfacial area of the reactants and minimize the heat and mass transfer barriers, which negatively affect the conversion of reactants into hydrates [22]. The schematic diagram of the spraying reactor is shown in Fig.2.

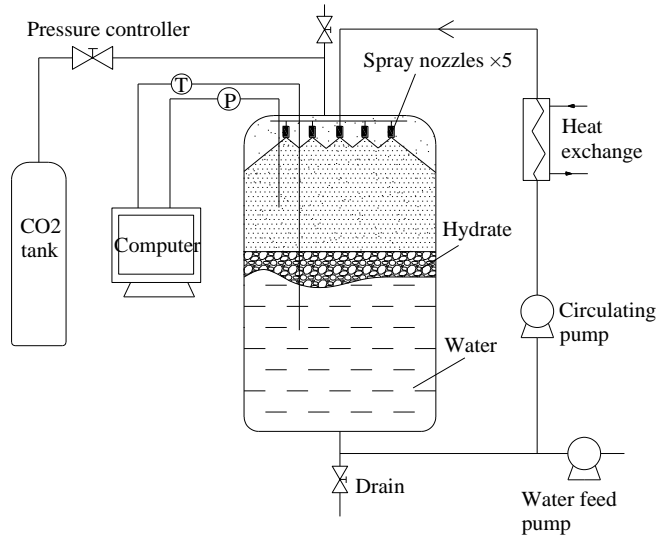


Fig.2. schematic diagram of spray reactor.

Li *et al.* [23,24,25] investigated on effect factors for CO₂ hydrate formation in a water-spraying apparatus. They found that the hydrate formation rate, gas storage capacity, and formation heat of oscillating gas supply in the reactor were larger than that of continuous gas supply due to the larger mass-transfer driving force caused by pressure disturbance. This phenomenon also was observed with a higher initial pressure and a larger volume of water or nozzle atomizing angle. The larger volume of water with larger gas dissolution quality as well as larger nozzle atomizing angles created higher gas-liquid contact probability, which help hydrate formation. Zhong *et al.* [26] carried out the experiments of CO₂ hydrate formation in a water spraying reactor. The results indicated that the rate of hydrate formation and the gas storage were 0.531~9.53 mmol·s⁻¹, 14~24 m³·m⁻³ respectively.

More recently, Rossi *et al.* [27] developed a novel scale-up spraying reactor for fast and continuous production of gas hydrates. One of their results confirmed that the reaction time including induction time and growth time was quite short, compared to that of the laboratory scale experiments which usually reacted in hundreds of minutes. Koji *et al.* [28] researched the hydrate formation in the entire jet-impingement/ atomization system. Their experimental data showed that both the absolute rate of hydrate formation and water-to-hydrate conversion ratio tended to increase with increasing in the jet-flow rate. They also noted that the efficiency of hydrate conversion of the jet-impingement operations was higher than that of the conventional water-spraying operations using high-pressure spray nozzles. A continuous spray reactor for gas hydrate formation was developed at Oak Ridge National Laboratory, which was original for the purpose of carbon sequestration. Nevertheless, it had been proven to be effective and feasible in the reference [29,30,31]. Szymcek *et al.* [3] developed a continuous small-scale CO₂ hydrate formation spray injector. Experimental results indicated that the device improved the diffusion degree of reactants, reduced

the barriers of heat and mass transfer, and successfully enhanced the efficiency of CO₂ hydrate formation. An *et al.* [32] improved experimental device and enhanced CO₂ hydrate formation by setting a buffer tank in the gas supply pipe. The experimental results showed that under the same conditions, when the buffer tank was added, the duration of CO₂ hydrate generation was about 20 minutes, while that without the buffer tank was about 40 minutes. The impact of the buffer tank allowed the CO₂ gas to enter the atomization system evenly and stably, and thereby enhanced the atomization effect and doubled the hydrate formation rate.

The shortcomings of the spraying method are also obvious. The hydrate layer will cover the surface of water, so that the heat generated by the reaction will gather in the interior of the liquid phase which will be difficult to remove and affect the further growth of the hydrate crystal nuclei. Therefore, the spray device (nozzle) at the top of the reactor needs to be specially designed [33]. Rossi *et al.* [34] developed a new type of spraying reactor. There is a concentric annular high-pressure nozzle at the top of reactor as shown in Fig.3, in which the gas and the liquid are pressurized in the same direction and sprayed. Due to the full atomization and high-speed perturbation of the nozzle, the gas-liquid contact area was increased as much as possible and enhanced mass transfer and heat transfer.

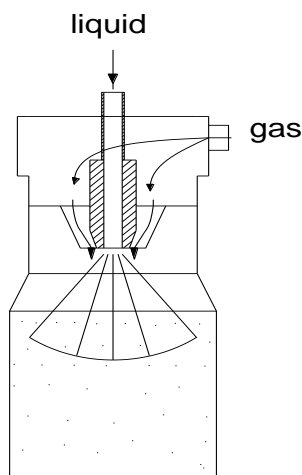


Fig.3. Concentric annular high pressure nozzle.

Compared with the traditional stirring system, spraying accelerates the process of dissolution, nucleation and crystal growth to a greater extent, resulting in the formation velocity doubling or more as well as the increasement of gas storage capacity. Therefore, spraying is theoretically better than stirring.

2.1.3. Bubbling

Bubbling is a traditional method for the gas-liquid reactants to form hydrates in experiments. The diagram of

the working principle is shown in Fig.4. The gas is charged into the reactor column filled with water or solution. Hydrates form at the interface of gas-liquid with the rising bubbles that can collapse by slight disturbance. The crushing of bubbles increases the contact surface between gas and solution, and enhances the dissolution capacity of gas, and promotes the heat dispersing and the hydrate formation rate.

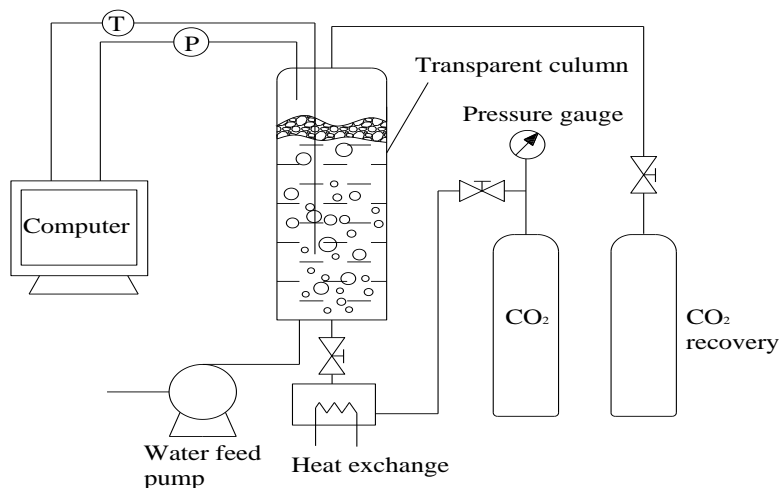


Fig.4 schematic diagram of bubble column

Hashemi *et al.*^[35] found that the mass transfer resistance of the gas-liquid interface was significant, especially at lower superficial gas velocity, higher pressures and lower temperatures. Maini *et al.*^[36] observed that the hydrate only generated at the bubble surface and then the hydrate shed from the bubble surface with the rise of bubbles. Qiunan *et al.*^[37] investigated that the hydrate formation rate increased with the increase of gas flow rate. This is mainly due to the large gas flow rate, which enhances fluid turbulence and interphase mixing, enhances mass transfer between the gas phase, liquid phase, and solid phase. As the gas flow rate increases, it can provide rich gas-liquid contact area for the formation of hydrate. Myre *et al.*^[38] have some similar conclusions, they found that at low CO₂ flow velocity, mass transfer was the main factor limiting the growth of the CO₂ hydrate because the low fluid turbulence led to the formation of a shell at the surface of the bubbles, and thus reduce the rate of hydrate formation. At a higher pressure, denser slurry was seen even though the gas velocity was small. While at high gas velocity and low temperature, the rate of hydrate formation was limited by the rate of the heat removal rather than mass transfer since the rapid hydrate formation resulted in a sudden increase of temperature. Xu *et al.*^[39] employed bubbling method to find that the shape of CO₂ hydrate was affected by the gas flow rate. The hydrate was acicular crystal at the low gas flow rate, while the hydrate was fine sand-like crystal at the high gas flow rate. The conclusions of Myre^[38] and Xu^[39], in some way, support the conclusion drawn by Hashemi^[35] who have

simulated the CO₂ hydrate physical properties. The bubble size and the gas flow rate also had an obvious impact on the hydrate formation. Cai *et al.* [40] investigated that the gas bubble size of 50µm was optimal for the hydration process. Either too big or too small bubble has no obvious effect on the formation of natural gas hydrate. In addition, they also found that the gas consumption was enhanced by increasing the gas flow rate.

Recently, Zhang *et al.* [41] invented a multi-stage bubble reactor as shown in Fig.5. The reactor consists of three parts. The lower part is reaction part composed of an outer shell and a column tube. The gas and water flow and react in the inside tube, while the shell side provides refrigerating capacity. The middle section is the mixture residence zone. The upper section is the gas cap used to regulate the pressure inside the reactor. A crystal modulator is arranged on the side of the reactor to adjust the hydrate residence time and quality. Zhang introduced the gas storage rate of this bubbling reaction vessel is high up to 174.2V / V.

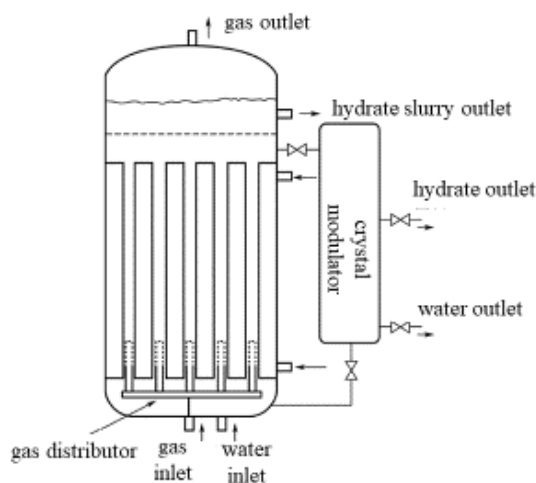


Fig.5 schematic diagram of a multi-stage bubble reactor.

From the views of thermodynamics and dynamics, hydrate layer on the surface of the rising bubble is the result of the interface reaction between gas and liquid. Although bubbling reaction has a great advantage in heat transfer, it was limited by some factors. For instance, hydrate is apt to form and aggregate on the orifice plate, which greatly affects gas intake. It needs gas pump or compressor to produce gas bubble, which cost additional energy.

2.1.4. Novel mechanical mixing methods

In response to the deficiencies of traditional mechanical mixing, researchers continuously explore new technologies such as fluidized bed [42], supergravity, sound wave [43], impinging streams and magnetic field.

- 1) Fluidized bed technology

Fluidized bed technology means a large amount of solid particles are suspended in a moving fluid so that the particles have certain characteristics of the fluid [42]. Fluidization can significantly increase the heat and mass transfer rate and uniform the temperature distribution.

A single tube-in-shell fluidized bed heat exchanger is shown in Fig.6 [44]. The reactor consists of a tube side for internal heat exchange and a shell side. Refrigerant absorbs hydration heat through evaporation in the shell. The feed gas and water mixing with the inert particles are fluidized, then passed through the tubes from bottom to top. When the temperature in the reactor drops to the hydration temperature, part of the gas react with water to form hydrate which is separated by a separator.

Zhou *et al.* [45] studied the formation of CO₂ hydrate in a fluidized bed through numerical simulation and experiment. As shown in Fig.7, the CO₂-water solution entered the column from the bottom, and the R134a entered the column from the top. With the R134a's evaporating, heat in the column's surface was extracted which resulting in the formation of CO₂ hydrate slurry. Then the CO₂ hydrate slurry on the fluidized bed column/inner tube are removed by the fluidized inert particles and stored in the cold storage vessel.

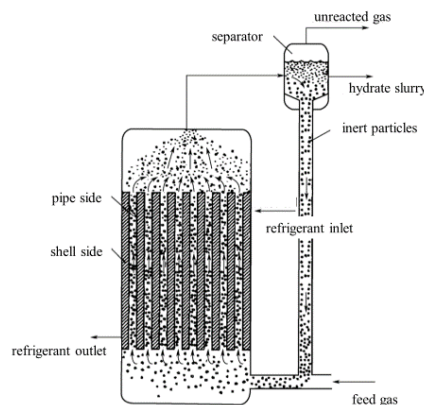


Fig.6 fluidized bed reactor

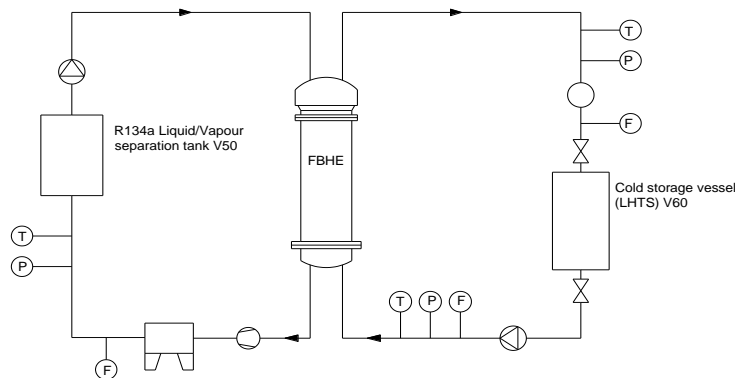


Fig. 7. Process of the fluidized bed CO₂-hydrate generator and a CO₂-hydrate slurry cold storage

Fluidized bed reactors are expected to be applied to large-scale industrial production of hydrates, but some problems need to be solved, such as high energy consumption, large equipment wear, and it is difficult to store amounts of CO₂ hydrate slurry resulting from the effect of airflow crushing.

2) Sound wave technology

Sound wave technology has been studied to promote the CO₂ hydrate formation [46-48]. Dontsov *et al.* [49-50] noticed that with the increasing of relative amplitude of shockwave, the velocity of CO₂ dissolution and the CO₂ hydrate formation increased. Ultrasonic refers to sound waves with a frequency range of 20 kHz to 10 Mhz. Because of short wavelength, it has some advantages, such as excellent directivity, large energy and strong penetration ability, so its sound energy can be concentrated easily [44]. When ultrasonic waves act on hydrates, cavitation causes the liquid to vibrate and produce tiny bubbles, increase the contact area between liquid and gas, and furthermore promote the hydrate formation [44,51]. Liu *et al.* [51] did some experimental research as shown in Fig.8. and suggested that the action of the exponential cone probe is more beneficial to the formation of CO₂ hydrate than the action of the exponential cone probe. The ultrasonic power range that promotes the growth of hydrates was $50W < P < 1000W$.

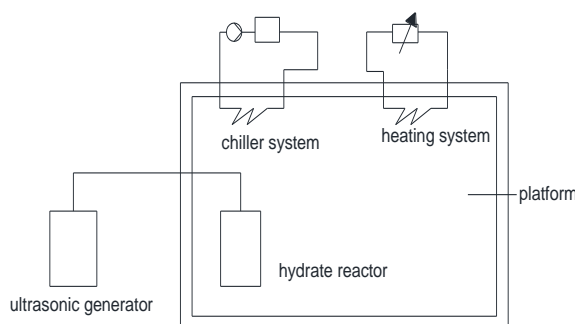


Fig. 8. Hydrate reactor under the ultrasonic

The disadvantage of ultrasonic is that it is restricted by the attenuation factor. In the above experiment of Liu [46], when the diameter of the reactor exceeds a certain range, the formation of hydrate will be hindered under the action of ultrasonic waves. Also, large-volume reactors which need high ultrasound power increase investment costs, and the safety of the container is also affected by the long-term action of the ultrasonic waves.

3) Supergravity technology

Supergravity means the acceleration of substance is much larger than 9.8 m²/s. A powerful centrifugal force field is generated by high-speed rotating packing materials to simulate a supergravity environment that increases gas-liquid interface and strengthens multiphase flow and reaction processes [51-52]. Fig.9 is a structural diagram of

a supergravity rotating packed bed.

Bai *et al.* [53] studied the formation process of CO₂ hydrate in a static supergravity reactor. The structure of the experimental device is shown in Fig.10. The most obvious feature of this reactor is that there is no moving part, its supergravity field is generated by the vortex flow of CO₂ gas. The experimental results showed that under the action of supergravity, the gas-liquid-solid is fully contacted, the formation rate of CO₂ hydrate continued to increase with the increase of supergravity factor.

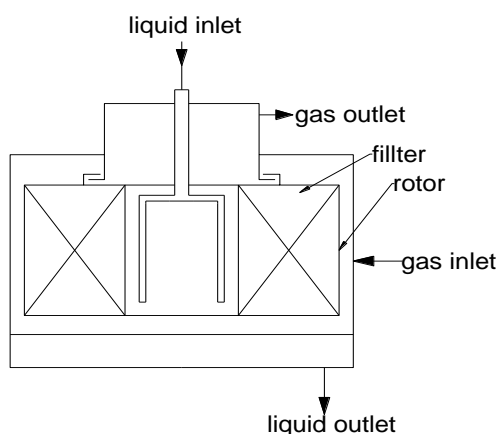


Fig.9 Supergravity rotating packed bed

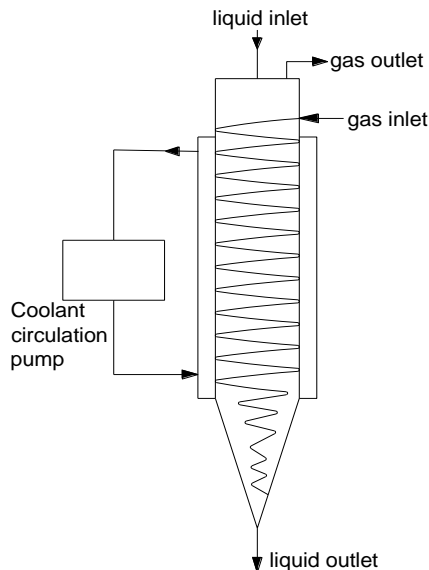


Fig.10 Static supergravity reactor structure

The method of supergravity rotating packed bed also has obvious shortcomings. The supergravity rotating packed bed requires complicated structure, reliable airtightness and additional energy consumption. Static supergravity technology promotes the gas hydrate formation process, however, there are some problems such as the low gas conversion rate and large energy consumption need to be solved.

4) Impinging stream technology

Impinging stream technology can be applied to the field of gas hydrates due to the strong multiphase heat and mass transfer performance [54].

The structure of the impinging stream hydration reactor is shown as Fig.11 [55]. Gas is introduced into the reactor through the gas inlet, and the ice-water mixture is introduced through the feed port when the charge pressure reaches a certain value. The fluid in the reactor forms impinging stream through reverse rotation of the high-speed stirring rod, promoting the mixing of the gas and liquid as well as the formation of the hydrate.

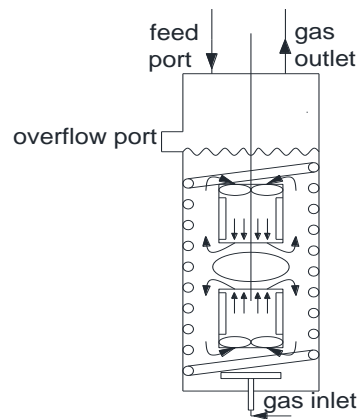


Fig.11 Structure of the impinging stream hydration system

The problems of impinging stream technology lie in the nonuniform mixing or transmission and large energy consumption. Currently, application of impinging stream technology in the large industry system is still immature [56].

5) Magnetic field technology

Guangzhou Institute of Energy Conversion (GIEC) did some comprehensive study in the magnetic field [57, 58] as shown in Fig.12 and found that under the magnetic field, the R141b hydrate formation was effectively improved, including shortening the induction time and accelerating the hydrate nucleation rate.



Fig.12 Magnetic field hydration reactor schematic

All these hydrate formation methods, especially stirring, spraying, and bubbling, can enhance the heat and mass transfer performance during hydration greatly, but none of them is mature enough in engineering application.

2.2. Additives

Except for the mechanical mixing, another method of enhancing CO₂ hydration is the use of additives [59]. Kalogerakis *et al.* [60] found that in the hydrate reaction system, additives can effectively reduce the surface tension of water-gas, increase the gas solubility and diffusion coefficient in the liquid phase, further they can shorten the induction time, accelerate nucleation and the heat and mass transfer so as to promote hydrate formation [61]. In summary, the researched additives include the following types: surface active agents, small organic molecule compounds, porous medium, and ionic compound etc [62]. Some typical additives are introduced as following:

2.2.1. TBAB

TBAB is a kind of frequently used surfactant promoting hydrate formation in many literatures, and it can significantly decrease the equilibrium pressure of hydrate formation. TBAB is a kind of thermodynamic additive. The TBA⁺ in the TBAB molecular structure has a high solubility of CO₂, which facilitates the dissolution of the CO₂ gas [63-66]. Up to now, many works have been done to promote the CO₂ hydration using TBAB [67-74].

Amir *et al.* [75] found in the system of CO₂/H₂/TBAB, the phase equilibrium temperature and pressure changed from 278.4K, 10.5MPa to 288.6K, 4.07MPa after adding 30wt% TBAB. Lin *et al.* [67] studied the phase equilibrium and dissociation enthalpy for hydrate mixture of CO₂ + TBAB. The results showed that the presence of TBAB reduced about 70% to 90% of normal CO₂ hydrate phase equilibrium pressure, moreover, pressure reduction degree was related on the TBAB concentration. From the Fig.13 [70], the phase equilibrium pressure of CO₂ hydrate decreased with the increasing of TBAB concentration significantly. Yang *et al.* [76] found that 5% TBAB + 5% THF is better than TBAB in reducing CO₂ hydrate phase equilibrium pressure and induction time. Youssef *et al.* [77] studied the single CO₂ and CO₂+TBAB hydrate formation in oil-in-water emulsion. The results showed the heat capacity of the new system (consists of oil in water emulsion+TBAB+CO₂) increased to 142 kJ·kg⁻¹ which is higher than that of classical O/W emulsion.

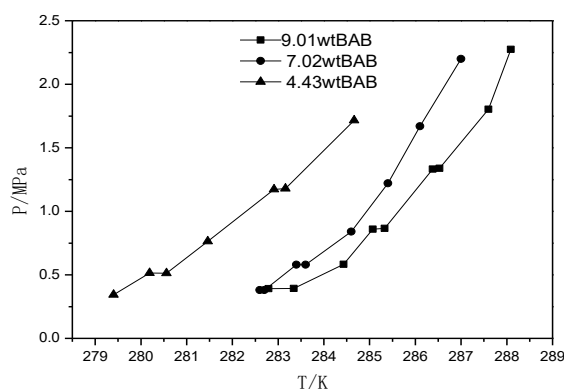


Fig.13. ^[70] Phase equilibrium curves of CO₂ hydrate at different TBAB concentrations

2.2.2. THF

THF is another typical thermodynamic additive. CO₂-THF hydrate is a kind of S II hydrate with a enthalpy slightly higher than that of ice^[4]. Additionally, THF can significantly reduce the CO₂ hydrate phase equilibrium pressure, as well as improve the equilibrium temperature ^[69]. Sandrine *et al.* ^[78] found THF can reduce the CO₂ hydrate phase equilibrium pressure to 1MPa but have no influence on its available enthalpy. Daraboina *et al.* ^[79] found that in the system of CO₂/ N₂/SO₂, 1mol% of THF can reduce the CO₂ hydrate phase equilibrium pressure from 7.25 MPa to 0.15 MPa at 273.75 K and reduce the induction time to 5 min. However, both the hydrate formation rate and gas consumption were reduced. Lee *et al.* ^[80] measured the phase equilibrium conditions for the CH₄ and CO₂ hydrations under the action of THF, and found the enhancement effect of THF on the formation of hydrates. Contradictorily, Veluswamy *et al.* ^[81, 82] and Liu *et al.* ^[83] indicated that THF could not promote CO₂ hydrate formation but could promote the CH₄ hydrate formation.

Fig. 14 ^[84] is the H-L-V (hydrate-liquid-vapor) equilibria diagram for water-CO₂ and water-THF-CO₂ systems. The results showed that THF could effectively reduce the CO₂ hydrate phase equilibrium pressure and increase its phase equilibrium temperature. Meanwhile, increasing the mass concentration of THF can create more moderate formation conditions. Khalik *et al.* ^[85] found that THF extended the CO₂ hydrate phase equilibrium region by elevating the hydrate equilibrium temperature. Similar results were found by Torre *et al.* ^[86] and Mingjun Yang *et al.* ^[87]. Zhu *et al.* ^[88] found that in the [APM1m] [Br] ionic solution with a 0.01mole% of THF, the CO₂ hydrate phase equilibrium pressure can decrease to 1 MPa, means THF can effectively promote the CO₂ hydration in the ionic liquids.

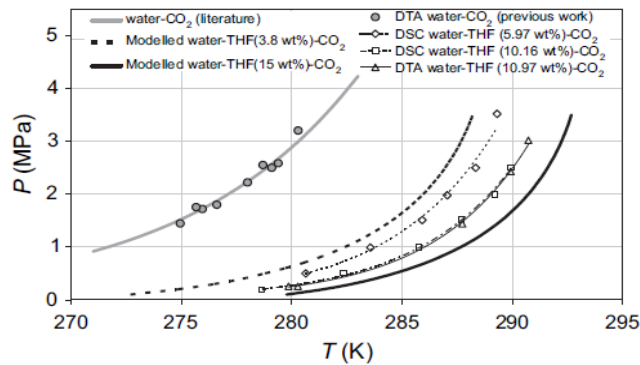


Fig.14.^[84] Diagram of HLV equilibria for water-CO₂ and water-THF-CO₂ systems.

2.2.3. SDS

Sodium dodecyl sulfate (SDS) has excellent kinetic promoting effect on hydrate formation^[89-93], especially on methane hydrate formation^[94-97]. CHI *et al.*^[98] found that the nucleation rate can be accelerated with the increasing of SDS concentration. However, when the SDS concentration is higher than 2000 ppm, the solution will change into a kind of turbid suspension^[99], Torre and Ricaurte *et al.*^[79] suggested that the concentration of SDS should be above 1500 ppm in order to guarantee the good dissolution of CO₂. Oignet *et al.*^[100] showed that CO₂ hydrate slurry with the 1500–2000 ppm SDS had the pseudoplastic behaviour when hydrate fraction was at the range of 0~15.5 vol%. They also found that flow viscosity of water-CO₂-SDS hydrate was lower than that of water-CO₂ hydrate. The characteristics of pseudoplastic behaviour is described in the following paragraphs. Liu *et al.*^[83] and Torre *et al.*^[86] studied the characteristics of CO₂ hydration in combination of SDS and THF. Their results showed that the additive mixture was more effective than a single additive during the CO₂ hydration.

Even more, Yu *et al.*^[101-102] studied the effect of SDS, SDBS and their mixed solution (1:2) on the formation of CO₂ hydrate. Results showed that CO₂ hydration was promoted after adding SDS, SDBS, and their mixture. And the additive mixture promoted CO₂ hydration better than SDS or SDBS individually.

As shown in Fig.15, the presence of single SDS had no noticeable effect on CO₂ hydration formation. This is opposite to the findings given by Yu *et al.*^[101-102] and Liu *et al.*^[75], but is agreed by Zhang and Lee^[103] and Jiang^[104], who considered single SDS is not able to promote the CO₂ hydrate formation. The further researches need to be done to explore the effect mechanism of SDS on CO₂ hydrate formation.

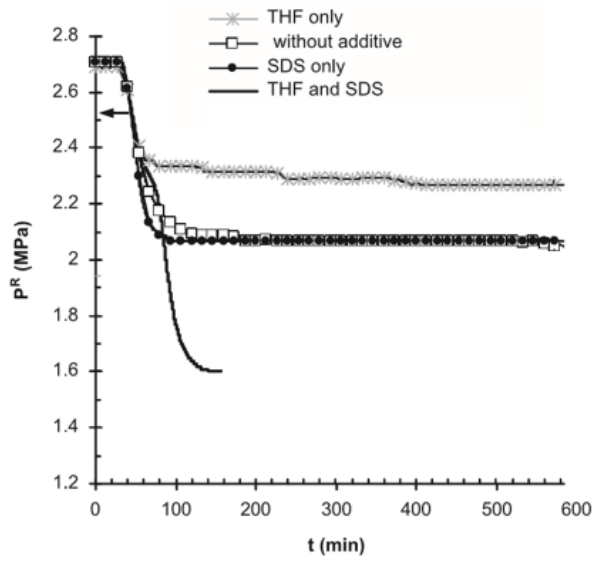


Fig.15 Comparison of four different kinetic curves obtained with and without additives.

2.2.4. Other additives

There are other types of additives, such as ionic additives, nanoparticles [105, 106], and porous media [107-109], etc. The ionic additives including NaCl, KCl, CaCl₂ and MgCl₂ are commonly used [110, 111], and porous medias include glass beads, molecular sieve, and quartzite [112], etc. Moreover, several studies have been carried out on the effects of some nanoparticles on CO₂ hydration. These researches are summarized and showed in the Tab.1.

Tab.1 Effect of nanoparticles to CO₂ hydration.

authors	types of nanoparticles	research results
Liu [53]	Cu nanoparticles and Al ₂ O ₃ nanoparticles	Cu nanoparticles and Al ₂ O ₃ nanoparticles both have a promotion effect on the induction time and gas consumption of CO ₂ hydrate
Mohammadi [112]	Ag nanoparticles+ SDS	the mixture of SDS and Ag nanoparticles promote the CO ₂ storage capacity
Mohammadi [113]	ZnO nanoparticles	the rate of CO ₂ hydrate growth accelerated and the amount of the stored gas enhanced in the presence of ZnO nanoparticles.
Said [114]	SiO ₂ nanoparticles	SiO ₂ nanoparticles had the most effective enhancement on CO ₂ gas consumption, particularly at a concentration of 0.3 wt%.
Zhou [115]	graphite nanoparticles	the induction time decreased and the maximum CO ₂ consumption increased in the presence of graphite nanoparticles

Qu ^[116]	nano-SiO ₂	dry water with 5% of nano-SiO ₂ has the largest gas storage rate of 167v/v
Fa ^[83]	Graphene oxide	the induction time decreased and the amount of the stored gas increased

All these additives can enhance the CO₂ hydrate formation, but none of these additives has employed in cool storage industry, further study still need to be carried out.

2.4. A novel CO₂ hydrate slurry formation apparatus

A novel CO₂ hydrate slurry formation apparatus based on CO₂ trans-critical cycle is presented in Fig.16.

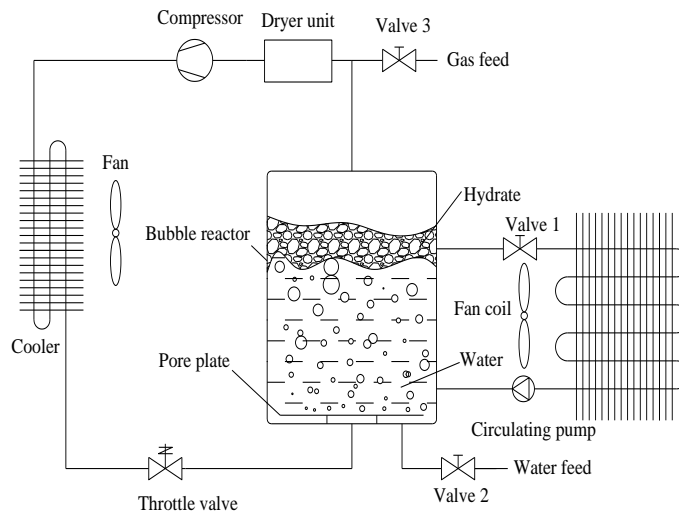
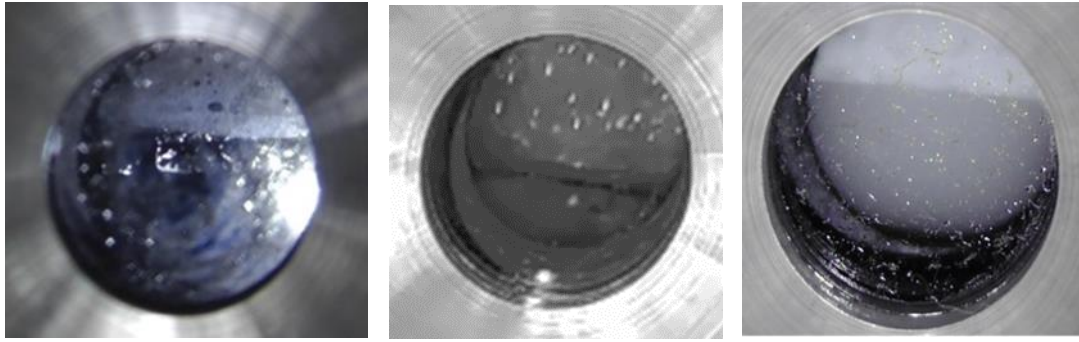


Fig.16 schematic diagram of a novel CO₂ hydrate enhancement formation apparatus

In this apparatus, CO₂ trans-critical refrigeration cycle is adopted to continuously produce hydrate slurry in the bubble reactor. The process can be described as follows: after getting through the throttle valve, CO₂ gas turns into a low-temperature and low-pressure vapor-liquid two-phase fluid and then goes into the bubble reactor through the pore plate at the bottom. As a result, liquid CO₂ decreases the temperature of solution and creates a condition suitable for CO₂ hydrate formation. Simultaneously, liquid CO₂ evaporates and absorbs the heat released by CO₂ hydrate formation. Afterward the redundant CO₂ gas is drawn away and compressed by the compressor, its temperature and pressure increase during compression, then it is cooled by the cooler, finally it goes back to the throttle valve again. This process is repeated within a closed loop system. Dense CO₂ hydrate slurry are produced in this apparatus as shown in Fig.17.



a) preliminary stage of growth b) intermediate stage of growth c) finish stage of growth

Fig.17 Growth of CO₂ hydrate in the novel CO₂ hydrate slurry formation apparatus

The pore plate can maximize the gas–liquid interfacial area, and increase the turbulence strength to peel off the hydrate film and therefore the CO₂ bubbles can directly contact with water. The system can quickly remove the hydrate formation heat in the reactor and continuously intensify CO₂ hydrate slurry formation. This novel apparatus is now under test by the team of Xie and some promising results have been presented. They found that when initial water was at 15°C and charge pressure was at the range of 3.6~4.2MPa in the reactor, the cool storage performance can be improved greatly with the increasement of the charge pressure^[117-119]. The increase of charge pressure can result in the decrease of precooling time and supercooling degree, faster growth rate and denser hydrate. The maximum values of hydrates average growth rate, total cool storage amount, average cool storage rate and cool storage efficiency were 154g.min⁻¹, 3.791MJ, 99.5kJ.min⁻¹ and 4.91^[117], respectively.

3. FLOW and HEAT TRANSFER PROPERTIES

3.1. Flow behaviours

Fluids rheological behaviour can be described by the relation between the shear stress τ and its shear rate $\dot{\gamma}$ [错误!未定义书签。]:

$$\tau = f(\dot{\gamma}) \quad (1)$$

As shown in Tab.2, the fluids can be classified according to the different yield stress τ_0 and rheological index n . k is fluids viscosity coefficient.

Tab.2 Classification of different fluids rheological behaviours

	$\tau_0 = 0$	$\tau_0 \neq 0$
$n = 1$	Newtonian: $\tau = k\dot{\gamma}$	Bingham-plastic: $\tau = \tau_0 + k\dot{\gamma}$

$$0 < n < 1$$

$$\text{Pseudo-plastic: } \tau = k\dot{\gamma}^n$$

$$\text{Herschel-Bulkley: } \tau = \tau_0 + k\dot{\gamma}^n$$

$$n > 1$$

$$\text{Dilatant: } \tau = k\dot{\gamma}^n$$

Different fluids rheological curves are presented in Fig.18.

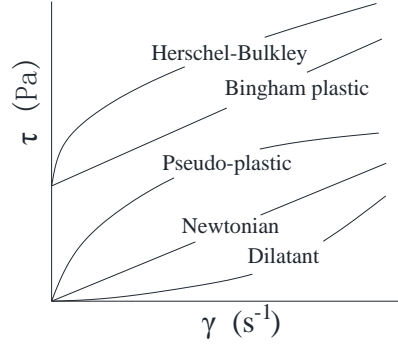


Fig.18 Fluids rheological curves

Fluids rheological behaviour of CO₂ hydrate slurry can be calculated using Ostwald viscometer^[68]. The calculation of fluids rheological behaviour is shown in equation (2) ~ (6).

$$\frac{Q}{\pi R^3} = \frac{1}{\tau_w^3} \int_0^{\tau_w} \tau^2 \dot{\gamma} d\tau \quad (2)$$

Where Q is the volume flow rate (m³/s), τ_w is the wall shear stress (Pa) and R is the pipe radius (m). Based on the Ostwald viscometer method, the shear stress and the shear rate are defined as.

$$\tau_w = \frac{D \Delta P}{4 L} \quad (3)$$

$$\dot{\gamma}_w = \frac{8u}{D} \frac{3n+1}{4n} \quad (4)$$

Where, D , L , ΔP , and u represent respectively the pipe diameter (m), length (m), pressure drop (Pa) and the fluid velocity (m.s⁻¹). The rheological index n is defined as:

$$n = \frac{d \ln \tau_w}{d \ln \frac{8u}{D}} \quad (5)$$

Finally, the fluid viscosity μ_{app} is obtained by the following equation:

$$\mu_{app} = \frac{\tau_w}{\dot{\gamma}_w} \quad (6)$$

Many researchers studied fluids rheological behaviours of CO₂ hydrate slurry. They found that CO₂ hydrate slurry are non-Newtonian fluids that retain this character even at very low mass concentrations of CO₂ hydrate^{[120-}

^{122]}. Fluids rheological behaviour of CO₂ hydrate slurry in cool storage application are summarized in Tab.3.

Tab.3 Fluids rheological behaviours of CO₂ hydrate slurry (HB mean Herschel-Bulkley).

authors	additives	method	volume fraction /vol%	Rheological behaviours	Apparent viscosity /mPa·s
Oyama <i>et al.</i> ^[123]	none	Magnetic (stress)	—	μ_{app} increase before nucleation, decrease after nucleation	—
Delahaye <i>et al.</i> ^[66]	none	Viscometer method	0~5	Dilatant fluids	$\dot{\gamma}_w = 400s^{-1}$, $\mu_{app} = 4\sim 42mPa \cdot s$
			5~10	HB-type fluids (with a dilatant trend);	
			10	Bingham plastic	
			10~20	HB-type fluid (with a pseudo-plastic trend)	
Hu <i>et al.</i> ^[错误!未定义书签。]	none	Viscosity meter	Mass concentration: 7.8%~45%	μ_{app} increase before nucleation, decrease after nucleation	2.0~3.4mpa·s
Delahaye <i>et al.</i> ^[124]	Caflon (0.1w%)	Viscometer method	4~10	Newtonian	$\dot{\gamma}_w = 600s^{-1}$, $\mu_{app} = 8.2\sim 15mPa \cdot s$
Chen ^[125]	TBAB (0.125~0.4 wt%)	Viscometer method	2.75~6.34	pseudo-plastic	$\dot{\gamma}_w = 600s^{-1}$, $\mu_{app} = 10\sim 14mPa \cdot s$
Jerbi <i>et al.</i> ^[126]	none	Viscometer method	0~22	Bingham plastic	$\dot{\gamma}_w = 400s^{-1}$, $\mu_{app} = 3\sim 8mPa \cdot s$
Liu <i>et al.</i> ^[127]	TBAB THF	Viscometer method	Mass concentration: 15%	Herschel-Bulkley (H-B) dilatant fluid	—

Liu [128]	TBAB (0.25wt%)	Viscome- ter method	8.2~23.1	$\dot{\gamma}_w < 610s^{-1}$: HB-type fluid (with a pseudo-plastic trend) $\dot{\gamma}_w > 640s^{-1}$: dilatant	$\dot{\gamma}_w = 600s^{-1}$, $\mu_{app} = 8.5\sim 10.6mPa \cdot s$
Jerbi <i>et al.</i> [129]	SDS (1500~2000 ppm)	Viscome- ter method	10~15	HB-type fluid (with a pseudo- plastic trend)	$\dot{\gamma}_w = 400s^{-1}$, $\mu_{app} = 8.34\sim 15mPa \cdot s$

Tab.3 showed that CO₂ hydrate slurry have the low fluid velocity, lower than that of ice slurry and TBAB slurry [44]. Jerbi *et al.* [130] studied that fluid velocity of CO₂ hydrate slurry decreased by 73% with 15 vol% CO₂ hydrate in a stirring reactor, because of the shear rate increased by the stirring and the pseudoplastic behaviour. As shown in Fig.19, Benedict *et al.* [131] found that Pressure drop decreased with the increase of CO₂ hydrate mole fraction at the different inlet temperate. The pressure drop was changed from 973 to 295 kPa.

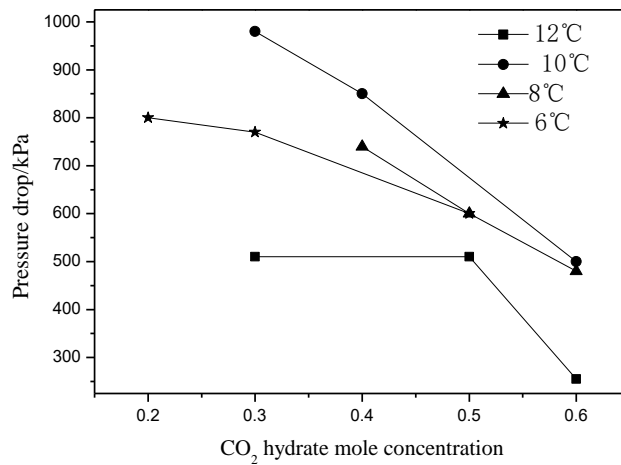


Fig. 19^[131] Pressure drop variation with CO₂ hydrate mole fraction

3.2. Heat transfer characteristics

The study of heat transfer characteristics is an important direction of CO₂ hydrate slurry research. Heat transfer characteristics of CO₂ hydrate slurry is quite different from that of water. The equation (7) can calculate the total heat transfer coefficient of CO₂ hydrate slurry in the plate heat exchanger [133].

$$\frac{1}{h_{tot}} = \frac{1}{h_{hot}} + \frac{1}{h_{cold}} + \frac{\delta}{\lambda} \quad (7)$$

Where h_{tot} , h_{hot} and h_{cod} are total heat transfer coefficients, hot side and cold side heat transfer coefficients in

the heat exchanger respectively; δ and λ are the wall thickness and thermal conductivity of the heat exchanger.

h_{hot} and h_{cold} could be calculated using the equation $Nu = aRe^b Pr^c$. Prandtl index number c is generally taken as $1/3$. Equation (7) can be inferred to Equation (8).

$$1/h_{tot} = \frac{D}{\lambda_{cold}} * \frac{1}{aRe_{cold}^b Pr_{cold}^{1/3}} + \frac{D}{\lambda_{hot}} * \frac{1}{aRe_{hot}^b Pr_{hot}^{1/3}} + \frac{\delta}{\lambda} \quad (8)$$

a and b are calculated by the iterative method and a, b can be calculated as $0.49, 0.63$. The equation for hot side is obtained by equation (9):

$$Nu_{hot} = 0.49Re^{0.63} Pr^{1/3} \quad (9)$$

Due to the influence of the latent heat, the equation for cold side need to correct, the final equation for cold side is as following:

$$Nu_{cold} = 0.338Re^{0.667} Pr^{1/3} \left(1 + \frac{\Delta\omega\Delta H}{Cp\Delta T}\right)^{0.037} \quad (10)$$

Where $\Delta\omega$ is the mass concentration change of CO_2 hydrate slurry, ΔT is the temperature difference, Cp and ΔH are respectively the specific heat and latent heat of CO_2 hydrate slurry. Finally, h_{tot} can be obtained by submitting equation (9) and equation (10) into equation (7).

Hu *et al.* [134] studied the heat transfer coefficient and fluid velocity with 15% hydrate mass concentration, and they found that the CO_2 hydrate slurry has better heat transfer characters than water, and the heat transfer coefficient is $3658 \text{ W}/(\text{m}^2 \cdot \text{K})$. Oignet *et al.* [129] studied the thermal behaviour of CO_2 hydrate slurry based on a heating tube method. The results showed that the convective heat transfer coefficients (CHTC) of 14wt% CO_2 hydrate slurry is $3,500 \text{ W}/(\text{m}^2 \cdot \text{K})$, which is 2.5 times that of liquid water. It could be due to the better homogenization of the CO_2 hydrate slurry. CHTC and fluid viscosity increased with the increasing of CO_2 hydrate slurry mass concentrations.

3.3. Particle size distribution of hydrate

The performance of CO_2 hydrate slurry not only depends on various flow parameters such as hydrate mass concentration, Reynolds number and heat transfer coefficient in macroscopic view, but also the crystal size distribution in microcosmic view [66, 67]. The particle size distribution of CO_2 hydrate slurry needs to develop in order to further study the CO_2 hydrate formation [132-134]. Some studies suggested that the particle size distribution could influence the thermo-physical properties of ice slurry. Different particle size distribution of ice and hydrate slurry are showed in the Tab.4.

Tab.4 Different particle size distribution

authors	solute	Ways of generation	Mean diameter/ μ m	distribution
Matthew et al. ^[16, 133]	CO ₂ hydrate	stirring	4~6	gamma
Myriam et al. ^[135]	TBAB hydrate	stirring	10~100	—
Delahaye et al. ^[60]	Ice	crystallizer	48~73	log-normal
Delahaye et al. ^[60]	THF hydrate	crystallizer	33~59	log-normal
Inada et al. ^[136]	Ice	stirring	100~400	normal
Pascal et al. ^[137]	TBPB hydrate	stirring	75~160	—
Song et al. ^[138]	CO ₂ hydrate	crystallizer	70~150	log-normal

34 With particle size smaller than that of ice and TBAB hydrate slurry, CO₂ hydrate slurry has the better heat
35 transfer coefficients than those of ice slurry or TBAB hydrate slurry. It is a promising candidate in cool storage
36 because of the lower fluid viscosity and higher heat transfer coefficients for CO₂ hydrate slurry.

37 **4. CHALLENGES and TECHNOLOGY PERSPECTIVES**

38 Different kinds of CO₂ hydration enhancement methods, such as mechanic mixing (stirring, spraying, bub-
39 bling, etc.) and additives (TBAB, THF, SDS, etc.), as well as the flow and heat transfer properties of CO₂ hydrate
40 slurry are reviewed in this paper. In order to promote the industrialization of CO₂ hydrate slurry in cool storage,
41 some suggestions are presented as following:

42 1) Among all kinds of mechanical mixing methods, stirring is already well investigated, but it has some
43 drawbacks such as additional investment, too much energy costs and inconvenience in continuous production
44 of CO₂ hydrate slurry which hindering large-scale application (e.g. Industrial use).

45 Comparing to stirring, spraying can greatly enhance the contact interface between water and CO₂ mole-
46 cules, resulting in short induction time and energy saving. However, as the water enters the hydrate reactor by
47 spraying, the formed CO₂ hydrate tends to be less compactness.

48 As for bubbling, it increases the contact interface of water and CO₂ molecules and greatly accelerates the
49 CO₂ hydrate formation rate. However, some measures should be taken to avoid the blocking of the diffuser
50 intake by nearby hydrate.

51 The physical fields (magnetic field, sound wave field, etc.) can also promote the formation of CO₂ hydrate,

52 but the study is immature, so further research should be carried out on the basis of theory and experiments.

53 By comparing the characteristics of different mechanical mixing methods, the prospect of bubbling is the
54 most promising which need further research. Moreover, some novel mechanical methods, such as fluidized
55 bed, hypergravity, ultrasonic, impinging streams, are worth to be studied further to develop new types of hy-
56 drate reactors.

57 2) Additives, such as TBAB, THF, SDS, or their mixtures, are widely investigated. Their hydrate promotion
58 mechanisms, such as reducing the phase equilibrium pressure and increasing the hydrate formation rate are
59 still not fully understood. The phase equilibrium and formation dynamics of CO₂ hydrate should be deeply
60 studied. It is the key to finding ways to promote the application of CO₂ hydrate in cool storage.

61 3) CO₂ hydrate is a non-Newtonian fluid with excellent flow and heat transfer characteristics. Its flow and
62 heat transfer properties need to be further studied through experiments and simulations for better utilization.

63 A novel CO₂ hydrate slurry formation apparatus is introduced. In this apparatus, CO₂ trans-critical refrigera-
64 tion cycle is adopted to continuously produce hydrate slurry in the bubble reaction tank charged with water. This
65 simple system can quickly and compactly produce CO₂ hydrate slurry, so it has great potential to be applied in the
66 cool storage engineering of CO₂ hydrate slurry.

67 According to the above conclusions, the research on CO₂ hydrate slurry in cool storage applications is still
68 immature. More study including growth kinetics, phase equilibrium as well as flow and heat transfer should be
69 carried out in the future.

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74 **Nomenclature**

a A constant

b A constant

c A constant

D Pipe diameter, m

*h*_{tot} Total heat transfer coefficient, W·(m²·K)⁻¹

h_{cold}	Cold side heat transfer coefficient, $\text{W}\cdot(\text{m}^2\cdot\text{K})^{-1}$
h_{hot}	Hot side heat transfer coefficient, $\text{W}\cdot(\text{m}^2\cdot\text{K})^{-1}$
L	Mole number, mol
n	The rheological index
Nu	Nusselt number
Pr	Prandtl number
Q	Volume flow rate, $\text{m}^3\cdot\text{s}^{-1}$
R	Outer Radius, m
Re	Reynolds, number
u	Velocity, $\text{m}\cdot\text{s}^{-1}$
$\dot{\gamma}$	shear rate, s^{-1}
δ	Thickness, m
η	Crystal hole ratio, %
λ	Thermal conductivity, $\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$
μ	Coefficient of viscosity, Pa·s
μ_{app}	Apparent viscosity, Pa·s
τ	Shear stress, Pa
τ_o	Yield stress, Pa
τ_w	Wall shear stress, Pa
$\Delta\omega$	Solid fraction, %
ΔP	Pressure drop, Pa
ΔH	Latent heat, $\text{kJ}\cdot\text{kg}^{-1}$
C_p	Thermal capacity, $\text{kJ}\cdot(\text{kg}\cdot\text{K})^{-1}$
ΔT	Mean logarithmic temperature difference, K

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