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Research Progress of Hydrate-based CO₂ Separation and Capture from Gas Mixtures

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Abstract: Hydrate-based CO₂ separation and capture from gas mixtures containing CO₂ has gained growing attention as one new technology of gas separation, and it is of important significance for reducing anthropogenic CO₂ emissions. The previous studies of the technology include the thermodynamics and kinetics of the hydrate formation/dissociation, hydrate formation additives, analytical methods, separation and capture progress, equipments and application. Presently, the technology is still in the experimental research stages, and there are few reports of industrial application. This review examines research progress in the hydrate formation process and analytical methods with special focus on laboratory studies, including the knowledge developed in analog computation, laboratory experiments, and industrial simulation. By comparing the various studies, we propose original comments and suggestions on further developing the hydrate-based CO₂ separation and capture technology.

Keywords: gas hydrate, carbon dioxide, separation and capture, research progress

1. Introduction

Carbon dioxide (CO₂) is one of the most important anthropogenic greenhouse

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gases (GHG). Between 1970 to 2004, its annual emissions have grown by about 80%, from 21 to 38 gigatonnes (Gt), and CO₂ represented 77% of total anthropogenic GHG emissions in 2004^[1]. According to predictions by the International Panel on Climate Change (IPCC), CO₂ concentration may reach 570 ppm in the atmosphere by the year 2100, causing the mean global temperature to rise approximately 1.9°C^[2]. To prevent global climate deterioration, fossil energy alternatives such as nuclear, biomass, solar energy, etc., are being developed. However, these energy sources cannot replace the fossil fuels to meet our needs, and any rapid change to non-fossil energy resources may result in large disruptions to the existing energy supply infrastructure. Therefore, fossil fuels continue to be the major energy supply in the near future because of their availability, competitiveness and ease of transport. Thus, a highly effective technology of CO₂ separation and capture from fossil fuels uses need to be further researched and developed in order to meet CO₂ reduction targets. The major CO₂ separation technologies that are commercially used involve chemical absorption, physical adsorption, cryogenic separation and membrane separation. However, conventional technologies have intensive energy consumption, chemical degradation, low capacity, etc.^[3]. Therefore, some researches dedicate efforts to developing new technologies, gas hydrates separation technology, chemical looping technology, electro-chemical cells separation technology^[4].

Gas hydrates are non-stoichiometric compounds composed of water molecules and small gas molecules. Examples of gas hydrates include methane (CH₄), carbon dioxide (CO₂), nitrogen (N₂), hydrogen (H₂), sulfur dioxide (SO₂), hydrogen sulfide (H₂S), ethane (C₂H₆), propane (C₃H₈), *iso*-butane (*i*-C₄H₁₀), ethylene (C₂H₄), propylene (C₃H₆)^[5, 6]. Water molecules (hosts) connect with each other by hydrogen-bonds to form cavities, and small gas molecules (guests) are stabilized in the cavities by Van der Waals interaction forces^[7]. Currently, the most common gas hydrate structures include structure I (sI), structure II (sII), structure H (sH) and semi-clathrate (sc)^[8, 9]. In general, the gas hydrate structure is mainly determined by size of the gas molecule if a single gas acts as a single guest. However, the structure is also affected by the composition and/or pressure when gas mixtures with multiple

components act as guests^[10]. The structures of sI and sII hydrates were first determined by single crystal X-ray crystallography in the early 1950's. After the structures were discovered, van der Waals and Patteeuw were the first two people to describe the hydrates in terms of stability and composition^[11].

In 1810, Humphrey Davy first reported gas hydrates in the Bakerian lecture to the Royal Society^[12]. Hammerschmidt suggested that it was methane hydrate blocking gas pipelines rather than ice in 1934^[13]. However, researchers investigated the hydrates existing in nature until 50 years later^[7, 14]. The effects of gas hydrates on energy and environmental applications have been being intensively researched since the early 1990s. The applications include production and transportation of gas in subsea flow assurance, the potential energy recovery from naturally occurring gas hydrates deposits, the storage of new fuels (natural gas or hydrogen) in hydrate materials, the role of gas hydrates in environmental safety (stability of seafloor and climate change), gas separation and purification from gas mixtures, and desalination of sea water^[8, 15-17].

Hydrate-based gas separation is based on the selective partitioning of the ingredients in hydrate phase and in gas phase^[3, 18-20]. At the same temperature, different gases have their individual equilibrium hydrate formation pressures. The gas with relatively low equilibrium hydrate formation pressure at a certain temperature is expected to preferentially entrap in water cavities to form gas hydrate with higher thermodynamic stability, and it results in a gas-rich hydrate phase while the residual gas phase is gas-poor^[21-23]. Relative to the other gas separation technologies, the gas hydrate separation technology has the following advantages: (1) simple process, (2) low investment, (3) low material and energy loss, and (4) environmental friendly^[24]. The previous studies focused on the separation of CO₂, CH₄^[25-32], H₂^[33-35], N₂^[36], oil gas^[37, 38], and other greenhouse gases^[39-44]. The main research contents include kinetics and thermodynamics of gas hydrate formation/dissociation, separation and capture process, analytical methods, and equipments and applications. For example, the studies of CO₂ separation focus on the equilibrium condition of hydrate formation, hydrate formation additive/promoter approaches, and separation equipment and

process. This review paper examines research progress in the hydrate formation process and analytical methods with special focus on laboratory studies of hydrate-based CO₂ separation, and the contents include the following parts: equilibrium hydrate formation conditions, additives for forming CO₂ hydrates, molecular-level measurements of the hydrates containing CO₂, process and apparatus, cost and comparison, and conclusions.

2. Equilibrium Hydrate Formation Conditions

2.1 Computation of equilibrium formation conditions

Phase equilibrium conditions of hydrate formation for gas mixture-water (or solution in presence of additive/or promoter) systems need to be measured before conducting studies of CO₂ hydrate separation. In 1964, Saito et al. first used the van der Waals and Platteeuw model (vdWP model) to systematically predict hydrate formation temperatures and pressures^[11, 45, 46]. Then, the approach was extended by Parrish and Prausnitz^[47]. Later, the model was substantially simplified by John and Holder^[48]. During the last 30 years, the vdWP model coupled with the simplified Parrish and Prausnitz algorithm were widely used to predict the equilibrium hydrate formation temperatures and pressures^[7, 49-55].

In fact, all prediction models are established based on parameters (e.g. gas fugacity, Langmuir constant) and correlations between the parameters. There are five major methods to determine the correlations. The first is the K-value method, which utilizes the vapor-solid equilibrium constants to predict hydrate formation conditions^[56, 57]. The second is a gas-gravity plot developed by Katz^[58]. The gas-gravity is defined as the apparent molecular weight of a gas mixture divided by the apparent molecular weight of air. The method is a simple graphical technique and it is useful for an initial estimate of hydrate formation conditions. The hydrate formation chart is made according to the limited experimental data and calculations based on the K-value method. But, the statistical accuracy analysis (Sloan^[59]) showed that the method is inaccurate, and different gas mixtures can lead to about 50% deviation in predicted pressure for the same gas gravity. However, the copious amounts of

experimental data have been collected in the past 60 years, and a more accurate gas-gravity plot may be developed based on the data. Therefore, Holder et al.^[60] and Makogon^[61] developed empirical correlations for selected pure gases, and this is the third method. Kobayashi et al.^[62] developed a new empirical equation for hydrate formation conditions of natural gases. However, the empirical equations have their limitation of temperature and pressure, and the method of the gas-gravity plot is seldom used for predicting the equilibrium conditions of gas hydrates containing CO₂. The fourth method for determining correlations between parameters involves a chart of permissible expansion, and it is based on the range of the permissible expansion, that a natural gas can undergo without possibility of hydrate formation. The chart of permissible expansion is drawn based on the gas-gravity chart using the Joule-Thomson cooling curve^[58]. The method is suitable for rough design of throttling in valves, chokes where gas expansion normally occurs. However, it is not suitable for natural gases containing more CH₄. An average error of 10% can be obtained in general. The fifth is a statistical thermodynamic approach, developed by van der Waals and Platteeuw^[11], predicting the equilibrium hydrate formation temperatures and pressures on the criterion $\Delta\mu_{\text{H}} = \Delta\mu_{\text{W}}$ at equilibrium^[60]. Thus, from a statistical mechanics point of view, those constants that can impact the chemical potentials between the hypothetical empty and fully filled hydrate lattice become key for the approach^[11, 63-65].

The Langmuir constant is quite important, and different models have been developed to obtain more accurate values of the Langmuir constant, for example, Kihara potential model^[66-68]. Parrish and Prausnitz developed a correlation using the Kihara potential and experimental data of the hydrate formation, and the accuracy of the correlation is approximately 0.2%^[47]. The parameters of the Kihara potential model are empirically regressed from the experimental data of the cavity occupancy and the phase equilibrium. Although the Kihara potential models can reproduce the experimental data, its capability for extrapolation is generally poor. For instance, Parrish-Prausnitz model^[47] and CSMHYD program^[7] can only predict phase

equilibria below 40-50 MPa. Thus, the models cannot predict the structure changes in mixture hydrates (e.g., the transition from sI to sII in CH₄-C₂H₆ hydrate^[10]). Furthermore, Tee et al.^[69] found that the Kihara potential surface calculated from the experimental data was inconsistent with that calculated from the second virial coefficient and viscosity data, and the inconsistency was due to the pre-treatment of the model overrating the occupancy fraction of non-spherical guests in a small cage^[51, 70], i.e., the Kihara potential model needs further optimization, especially in accurately describing the interaction between guest and water molecules. Accurate intermolecular potential between a guest molecule and a water molecule can be directly obtained by ab initio quantum chemical method, and the intermolecular potential is considered to be strongly angle dependent^[71-75]. The ab initio potential model can be used for predicting the hydrate number and the cage occupancies. Duan et al.^[76] successfully used an atomic site-site Lennard-Jones formula plus an electrostatic term to fit the ab initio intermolecular potential energy surface of CO₂-H₂O complex to account for the angle dependent molecular potential angle. They improved the model and predicted the equilibrium pressure of CO₂-hydrate in a wide T-P range with absolute average deviation less than 3%.

The best method for determining the hydrate formation conditions is to experimentally measure the hydrate formation at the temperature, pressure and composition of interest. However, it is impossible to satisfy the infinite numbers of the conditions for which measurement are needed. Thus, the hydrate formation prediction methods need to interpolate between the measurements. But, such experimental measurements are both time consuming and expensive. Therefore, a comprehensive artificial neural network model (ANN model) was developed to enable the user to accurately predict hydrate formation conditions for a given gas mixture without having to make experimental measurements^[77].

Previous studies about predicting CO₂ hydrate phase equilibrium are summarized in Table 1. The most recent predictions are rooted in the vdWP theory for hydrates^[11]. Although the methods mentioned above have their individual characteristics on predicting the equilibrium conditions for forming or dissociating the different gas

hydrates, they all have their limitations. To solve these problems, an integrated method combined with the above different methods must be developed.

2.2 Experimental equilibrium conditions

The experimental equilibrium condition is generally determined by two events during the hydrate formation: (1) initial occurrence or just disappearance of hydrate particles, and (2) a sharp decrease in pressure or a sharp increase in temperature. For the first, the pressure must be elevated above the hydrate equilibrium value, and then the hydrate formation leads to a certain meta-stable pressure. Then, the system is heated slowly or depressd slightly to dissociate hydrate and to ensure no meta-stability. Thus, the endpoint of hydrate dissociation is ensured to be reproducible and is taken as the upper limit of formation meta-stability^[7]. Carson and Katz further verified the principle to judge the hydrate equilibrium point^[56]. For the second, when the gas is enclosed in the hydrate, the system pressure decreases, or the disappearance of the last hydrate often accompanies a decrease of the slope of the pressure vs. the temperature trace. By this means, the hydrate formation equilibrium conditions can be obtained by measuring the intersection point of the cooling or heating isochore. Therefore, three primary methods (isothermal, isobaric and isochoric, respectively) were developed.

For the isothermal method, the system is first set at a pressure higher than the expected equilibrium pressure to form hydrates, and the system pressure must be kept by an external reservoir for addition or withdrawal of gas. The pressure is reduced gradually after the hydrate formation. The equilibrium pressure can be obtained by the visual observation of the hydrate disappearance. Thus, the method requires an apparatus with windows mounted in both back and front ^[7, 15, 78-85].

For the isobaric method, the system pressure is first maintained constant by an external reservoir for addition of gas, then, the temperature is decreased until a significant addition of gas is noted from the external reservoir, which indicates the hydrate formation. Then, the temperature is slowly increased to dissociate the hydrates. During the process of hydrate dissociation, the system pressure must be kept constant. As the last hydrate disappears, the point is taken as the equilibrium

temperature of the hydrate formation at the constant pressure. Similar to the isothermal method, the isobaric method must use an apparatus with windows. Figure 1 is a typical P - T diagram of the three-phase and four-phase equilibrium in the system of $\text{CO}_2/\text{H}_2\text{O}$ by the method^[79].

The isochoric method describes how the pressure in a closed vessel changes with the temperature and the phase transition. The temperature is first lowered from the vapor-liquid (V-L) region, and the isochoric cooling leads the pressure to slightly decrease. At a certain temperature, the hydrate forms, causing a remarkable pressure drop. Then, the temperature is slowly increased to dissociate the hydrates, resulting in the pressure rising quickly. Then, we can find one point that is the intersection of the hydrate dissociation trace with the initial cooling trace, and the point is taken as the equilibrium point for the hydrate dissociation. The isochoric method is commonly used for the hydrate formation at high pressure, as it does not need to be visually observed.

Based on the isochoric method, a method of isochoric step-heating (T-cycle method) was developed^[19, 86-89]. The experimental results obtained by this method are quite reliable and repeatable. However, it takes more than 24 hours for a measurement^[86]. Herri and Kwaterski^[90] improved the isochoric step heating method by sampling small quantities of gas and liquid during the heating procedure, and analyzing them by gas chromatography, ionic chromatography and refractive index measurement. By the mass balance, the improved method (a modified step heating method) allows one to determine the gas and hydrate compositions.

Differential scanning calorimetry (DSC) has also been used to determine binary phase (solid/solid or solid/liquid) equilibrium data in various fields^[91]. Recently, DSC was applied to determine the equilibrium condition of hydrate^[92-94]. The key is calibrating temperature by measuring the melting temperatures of pure materials and then computing a correction function by taking into account the deviation between the measurements and the known melting temperatures at different heating rates within a special temperature range. Once the temperature calibration is complete, the DSC software can automatically correct the measured temperature according to the

correction function. The method of DSC requires a careful calibration, and the sample mass and heating rate must be chosen within reasonable limits.

Table 2 shows previous hydrate equilibrium measurements involving pure CO₂ or gas mixtures containing CO₂ in pure water, or electrolyte solution, or porous media systems. Presently, the hydrate equilibrium measurements mainly relate to the sequestration of pure CO₂ in the seafloor, while CO₂ separation and capture pertains to gas mixtures containing CO₂. However, due to the equilibrium equipment limitations, the measurements are operated at a relatively narrow range of pressure. The equilibrium data at higher pressure (for example, >100 MPa) still needs computation models. As mentioned in section 2.1, more accurate prediction needs more experimental data. The ANNs method should be further developed because it integrates four different models and saves computational time at a wide range of temperatures and pressures^[95-98].

3. Additives for Forming CO₂ Hydrates

In pure water, CO₂ hydrate needs high pressure and low temperature to form, and the extreme operation conditions lead to high costs in industrial application. The hydrate formation rate is quite slow. Therefore, additives that can moderate the hydrate formation conditions and promote hydrate formation are developed in the process of forming CO₂ hydrates.

The additives are classified into thermodynamic and kinetics types. The thermodynamic additives have the tendency to moderate the equilibrium conditions to higher temperature or lower pressure, and they often consist of organic compounds, including Tetrahydrofuran (THF), Propane (C₃H₈), Cyclopentane (CP), and Tetra-n-butyl-Ammonium (Bromide, or Fluoride, or Chloride) (TBAB, or TBAF, TBACl). Kinetic additives accelerate the hydrate formation and they typically consist of surfactants including Sodium Dodecyl Sulfate (SDS), and Dodecyl Trimethyl Ammonium Chloride (DTAC)^[7, 99].

Tetrahydrofuran (THF) solution has proved to be capable of significantly reducing the hydrate formation pressure at a given temperature^[100-102]. Kang et al.,^[100]

Linga et al.,^[101] and Hashimoto et al.^[102] found that the equilibrium pressure of hydrates for both CO₂/N₂ CO₂/H₂ mixtures in the presence of THF solution was considerably lower than that without the additive, and THF of 1.0 mol% proved to be the optimal concentration for CO₂ separation from the mixture^[22, 100]. However, THF can form sII THF-hydrates, competing with CO₂ for occupying large cavities (5¹²6⁴)^[22, 103]. Therefore, THF cannot remarkably improve the gas consumption and CO₂ separation efficiency although it can moderate the conditions of forming gas hydrates for either CO₂/N₂ or CO₂/H₂^[104]. Kumar et al.^[105] compared the hydrate equilibrium conditions for CO₂/H₂ and CO₂/H₂/C₃H₈, and found that a 3.2 mol% C₃H₈ added to a CO₂/H₂ mixture reduced the pressure by approximately 50%. They verified that the adding of C₃H₈ into the CO₂/H₂ mixture reduced the hydrate phase equilibrium pressure without comprising the CO₂ recovery and found that H₂ existed in both sI hydrates formed by CO₂/H₂ mixture and sII hydrates formed by CO₂/H₂/C₃H₈ mixture (C₃H₈ of 2.6 mol%) by Raman spectra^[106]. Cyclopentane (CP) can also reduce the hydrate phase equilibrium pressure. Zhang et al.^[107, 108] found that the equilibrium of ternary CO₂/H₂/CP hydrates was significantly lower than that of ternary CO₂/H₂/THF at a vapor-phase CO₂ mole fraction of 0.3204. However, because the CO₂/H₂/CP forms sII hydrate and CP occupies the large cavities of 5¹²6⁴ preferentially, CO₂ can only compete with H₂ to occupy the small cavities of 5¹², reducing the selectivity of CO₂ over H₂ in the hydrate phase^[108]. TBAB in water forms a semi-clathrate hydrate at moderate conditions. In the semi-clathrate hydrate system, the anions (Br⁻) are strongly incorporated with the host water lattice and a single TBA cation (TBA⁺) occupies four cavities, leaving dodecahedral cavities for small gaseous molecules^[9, 88, 109-112]. Arjmandi et al.^[88], Oyama et al.^[113] and Duc et al.^[24] found that the equilibrium conditions for binary CO₂/TBAB hydrates were considerably lower than those for pure CO₂ hydrate. Furthermore, the hydrate phase equilibrium pressure shifts to lower with the increase of the TBAB concentration^[32, 114, 115]. TBAB of 0.29 mol% is considered as the optimum to recover CO₂ from either flue gas or IGCC synthesis gas because TBAB of more than 0.29 mol% makes no more contribution to the CO₂ recovery^[19, 23, 88, 116, 117]. However, adding TBAB reduces the gas

consumption because the TBA^+ occupies the big cavities in the sc hydrates. Therefore, there is some controversy over the use of TBAB as gas hydrate promoter. Besides, both TBAF and TBACl can also reduce the hydrate equilibrium conditions^[118-121]. The TBAF is rarely used because it is much more expensive than TBAB although the effect of reducing pressure of TBAF is superior to that of TBAB.

SDS is widely used as a kinetic additive. Zhong and Rogers^[122] studied the SDS effects on gas hydrate formation and found the hydrate formation rate can be increased multiple orders of magnitude in presence of SDS solution or related surfactant solution. Tajima et al.^[123], Li and Chen^[124], Rossi et al.^[125], and Torre et al.^[126] further verified that the SDS of CMC has the best effect on enhancing the hydrate formation rate.

However, either the thermodynamic additives or the kinetic additives cannot resolve all the problems (extreme condition, low gas consumption, low hydrate formation rate and low CO_2 recovery) of hydrate-based CO_2 separation and capture from the gas mixtures. Therefore, researchers focus on the synergistic effect of thermodynamic additives and kinetics additives. Li et al.^[117] added DTAC into the 0.29 mol% TBAB solution to investigate hydrate-based CO_2 capture from the flue gas and considerably improved the formation conditions, the formation rate and CO_2 recovery. Ricaurte et al.^[127] used THF in combination with SDS to investigate CO_2 removal from CH_4/CO_2 gas mixture by hydrate formation and found that the combinational additive decreased the hydrate formation pressure and improved the selectivity of CO_2 capture. The combination with two thermodynamic additives or two kinetic additives is also studied. Ding^[128] used SDS associated with an anionic fluorosurfactant (FS-62) (FS-62/SDS:100/1000 ppm) as a joint additive to hydrate-based CO_2 capture from CO_2/N_2 mixture, but its effect on raising the gas consumption was limited. However, Li et al.^[19] found that the adding of CP into the 0.29 mol% TBAB solution could considerably improve hydrate-based CO_2 separation from IGCC synthesis gas, and the result was further verified by powder X-ray diffraction (PXRD) spectra^[18].

In fact, the additives are still in the course of screening, i.e., which kind of

additive is the best for hydrate-based CO₂ separation and capture from the gas mixtures is still undetermined. Currently, THF and TBAB are two of the most popular thermodynamic additives. Much work is needed to further screen the additive, especially to screen one that can remarkably enhance the gas uptake.

4. Molecular-Level Measurements of the Hydrates Containing CO₂

The information (identification of the hydrate structure type, lattice parameters, guest occupancy and position in the cavity) of the hydrates structure (containing CO₂) can be accurately obtained using molecular-level measurement methods, including diffraction and spectroscopic methods. The hydrates containing CO₂ are measured in the forms of protecting samples under liquid nitrogen (LN) (only for spectroscopic methods) or in situ. For the in situ measurement, the original formed hydrates are detected, through a silica window with high-purity silica or a sapphire window, by a set of fiber optics or microprobe equipped in the spectrograph. For samples, the hydrate samples are firstly handled and quickly transferred in dry LN vapor before being mounted for detection in a pre-cooled stage.

4.1 Diffraction methods

The diffraction methods consist of X-ray diffraction (XRD) and neutron diffraction. The earliest and most comprehensive diffraction method is X-ray diffraction (XRD)^[49, 129, 130]. The hydrate structure, lattice constants and composition of hydrates containing CO₂ can be determined from crystal XRD data at a certain temperature^[131-134]. Through XRD analysis confirmed that CO₂ molecules were confirmed to trap in the small 5¹² cavities of the CO₂/THF binary sII hydrates^[103]. In a ternary system, the XRD patterns showed that CO₂ molecules occupy both sI and sII CO₂/H₂/C₃H₈ hydrates at 5 MPa and 253.15 K^[106]. For binary systems, e.g. CO₂/H₂ or CO₂/N₂, the XRD patterns showed that the gas hydrates were exemplary sI crystal structures^[135]. However, the hydrates structures might shift with the change of CO₂ in the binary systems. The CO₂/N₂ gas mixture containing CO₂ of 3 – 20 mol% formed sI hydrates while that containing CO₂ of 1 mol% formed sII hydrate by analyzing the

XRD patterns.^[136] In 0.29 mol% TBAB solution in the presence of CP, CO₂ occupied sII and sc hydrates cavities. It is worthwhile to note that for samples detection, due to the high sensitivity of the XRD measurement, the samples must be well handled to remain flat on the sample disk.

Neutron diffraction studies are able to determine the positions of the guest and the host in a hydrate crystal, to trace the structural changes during the hydrate formation, and to measure the extent of guest-host interactions in a hydrate lattice^[137-142]. However, few studies on CO₂ hydrate via neutron diffraction are specially reported. Henning et al.^[139, 143] observed complete conversion from the hexagonal ice to the sI type CO₂ hydrate as the temperature of the sample was slowly increased through the melting point of D₂O.

4.2 Spectroscopic methods

Two main types of spectroscopy have been used to investigate the hydrates containing CO₂: Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy.

Raman spectroscopy is a good way to identify the hydrate structure and composition because the Raman peak is determined by the inter-atomic vibration^[144-146]. Hydration number and relative cavity occupation can also be measured via Raman spectroscopy^[103, 147-152]. Figure 2 shows a typical Raman spectrum of CO₂^[153]. The split peaks (located at 1276 cm⁻¹ and 1384 cm⁻¹, respectively) are caused by Fermi resonance effect corresponding to C-O symmetric stretching (ν_1) and O-C-O bending ($2\nu_2$) mode of CO₂ molecules. Due to the various conditions of measurements and hydrate structures, the Raman shifts of CO₂ molecules may be changes in a small range^[103, 106, 154]. The Raman peaks of molecules of CH₄, N₂, H₂ are around 2910 cm⁻¹, 2325 cm⁻¹ and 4120 cm⁻¹, corresponding to their vibration modes of ν_1 sym C-H stretching, ν_1 sym N-N stretching, H-H oscillation (pure molecular vibration). Thus, it is quite simple to identify CO₂ from CO₂/CH₄, CO₂/N₂, and CO₂/H₂ gas mixtures via Raman spectra^[102, 106, 154-158].

NMR can be used to identify the hydrate structure and quantify the relative cavity occupancy. Presently, the study of NMR on hydrate-based CO₂ separation focuses on the spectrum of ¹H, ¹²⁹Xe and ¹³C^[159-162]. Among all the studies, ¹H NMR has been used for ethane, propane, and isobutene hydrates^[159]; ¹²⁹Xe NMR has been used for identifying ratios of xenon atoms in small and large cavities^[160-162]; and ¹³C NMR has been applied to study hydrates of CO₂, CH₄ and C₃H₈^[149, 163-165]. Seo et al.^[166] and Seo and Lee^[136] found, based on the ¹³C NMR spectra for CO₂, CO₂ molecules occupied the large cavities of sI, and as the CO₂ increased in the CO₂/N₂ vapor phase, the role of stabilizing both small and large cavities was transformed from N₂ to CO₂ molecules.

5. Process and Apparatus

5.1 Process

The processes of hydrate-based CO₂ separation and capture from gas mixtures are investigated. During the process, the gas continuously dissolves into the solution and forms gas hydrates in a reasonable condition, resulting in the decrease of the pressure in the system. Thus, the gas from the supply vessel must be introduced into the system to maintain the pressure. Hydrate formation is an exothermic process, causing the system temperature a slight rise when forming large amount of hydrates. Once the hydrate formation rate decreases, the system temperature returns to the setting temperature because of the heat transfer. The CO₂ separation efficiency changes with the continuous consumption of the gas in the process according to the formula of $\frac{n_{CO_2}^H}{n_{CO_2}^{feed}}$ and $\frac{n_{CO_2}^H n_{other}^G}{n_{CO_2}^G n_{other}^H}$ (n is the number of mole, the superscripts of H and G express hydrate phase and gas phase, respectively. The subscripts of CO_2 and $other$ express CO₂ and other component, respectively.)^[167].

Duc et al.^[24] conducted experiments to separate CO₂ from a CO₂/N₂ mixture in the presence of TBAB at a suitable operation condition, and they proposed a continuous multi-stage separation process. However, hydrate-based CO₂ separation becomes more difficult and the CO₂ recovery becomes lower with the decrease of

CO₂ concentration in the gas mixtures, and the separation process with single hydrate method cannot separate CO₂ from gas mixtures such as flue gas or fuel gas completely and efficiently^[168]. Thus, various hybrid processes were proposed. In the hybrid processes, CO₂ was first separated by the hydrate method, leaving lean-CO₂ gas mixtures to be separated by other methods such as chemical adsorption, cryogenic separation, and membrane separation. Linga et al.^[167] proposed a hybrid process that combined the hydrate method and membrane separation method for separating CO₂ from flue gas and fuel gas, respectively. Xu et al.^[169] conducted experiments to separate CO₂ from IGCC synthesis gas by a hybrid process of two-stage hydrate separation in combination with a chemical absorption separation. Surovtseva et al.^[170] designed a process combined cryogenic and hydrate method to capture CO₂ from IGCC flue gases. Pure CO₂ (>95%) could be obtained by the above hybrid processes, which were considered to be more efficient and economic compared to conventional CO₂ separation methods^[104, 167, 169-171]. However, two problems retard even pilot-scale application of the hybrid processes: the gas hydrate capacity per volume of water (L) and the hydrate formation rate per unit of time (h).

The hydrate based CO₂ separation process does not use large absorber towers or steam-reboiled regenerators, so both the capital and operating costs of the process are primarily in refrigeration and compression systems. Before designing parameters for the process, researchers must focus on some parameters and key processes:

- 1) Hydrate number of the hydrate: the number of water molecules required for removing a mole of CO₂ has a great effect on the heat removal requirements in the reactor, and therefore the size of the refrigeration system.
- 2) Slurry Concentration: the amount of free water circulating in the system must be heated and cooled, and this also affects the size of the refrigeration system.
- 3) Temperature of the reactor: the performance of the system is greatly affected by the temperature in either CO₂ removal or heat transfer.

SIMTECHE designed a test apparatus for a plant of coal feed 5 Kt per day. The mixed gases and conditioned water were metered to a reactor, mixing with the reactants, and the reactants flowed through a tail tube (ID: 4.8 mm). At the conditions

of around 10 MPa and 269 K and at the feed rates of CO₂ (0.94 mole/min) and H₂O (28 mole/min), the test result shown that the hydrate production rate were 0.271 mole/min which matched the design requirement^[172]. However, being subject to hydrate formation way, CO₂ separation efficiency and gas-liquid-hydrate separation in a special pressure vessel, there yet no really mature hydrate-based CO₂ separation process is applied in industry, even in a small-scale pilot application. Thus, we have a long way to go to achieve the final goal of hydrate-based CO₂ separation and capture from the gas mixtures in industry, especially for the aspects of the gas-liquid-hydrate separation process, improvement of the CO₂ separation efficiency, optimization of the process parameters.

5.2 Apparatus

Various apparatus were also developed along with proposing the processes for CO₂ separation and capture, and the development of the apparatus mainly focuses on the innovation about a mode of hydrate formation and design of a continuous flow reactor. The modes of hydrate formation generally include stirring, bubbling, and spraying which can well mix the gas and water or solution. Szymcek et al.^[173] designed a pilot-scale continuous-jet hydrate reactor (CJHR). A multiple capillary was mounted in the CJHR to maximize the surface area of interaction between reactants during the hydrate formation. Furthermore, the new design overcame the product-limit aspects of hydrate production, decreasing the amounts of unconverted CO₂ and H₂O. Li et al.^[174] also invented a set of batch-flow apparatus to capture CO₂ from the flue gases. The water (or solution) was jetted into the reactor filled with gases. The hydrate slurry formed in the reactor flowed into a decomposing tank via a special device. Xu et al.^[23] designed a visual bubble reactor and conducted experiments of CO₂ capture from CO₂/H₂ mixture. The visual bubble reactor had a volume of 40 L (4 m in height and 0.01 m² in area), which was around 100 times as big as the general reactor in the laboratory. Via the reactor, while the gas bubbles move from the bottom to the top, the whole gas bubbles could convert to gas hydrates. Castellani et al.^[175] developed a new apparatus to capture CO₂. The water (or solution)

and the gas mixtures are sprayed from the top and the bottom into the reactor via arranged nozzles. Linga et al.^[176] designed a new apparatus in which stirring and bubbling were combined together to enhance the contact of gases with water. Via the new apparatus, the hydrate formation rate, the gas uptake and the CO₂ recovery from the flue gases or the fuel gases are considerably improved compared to the results that were obtained in a smaller scale stirred tank reactor^[101, 171]. Yang et al.^[177, 178] developed a set of continuous flow reactors (Figure 4) for CO₂ hydrate formation based on a block flow diagram of the SIMTECHE CO₂ capture process (Figure 3). Using the continuous flow reactor, the effects of the gas carrier, the fluid velocity, the slurry concentration, and the temperature on the hydrates formation rate are investigated. The results indicated the reactor brought vigorous inter-phase mixing, reducing the heat and mass transfer resistances, and ultimately ensuring the global reaction rate to approach the intrinsic CO₂ hydrate formation rate under industrially relevant processing conditions.

Although it has been subject to the gas-solid-liquid separation in special pressure vessel and the low CO₂ recovery, the continuous CO₂ separation process is still immature. Furthermore, no complete set of equipment has been developed and utilized for CO₂ hydrate-based separation and capture until now. Therefore, it is imperative to further develop the process associated with developing apparatus for hydrate-based CO₂ separation and capture.

6. Cost and Comparison

Reduction of anthropogenic CO₂ emissions into the atmosphere can be obtained by different means, which have been summarized by Professor Yoichi Kaya of the University of Tokyo and can be expressed as follows^[179]:

$$CO_2^{\uparrow} = POP \times \frac{GDP}{POP} \times \frac{BTU}{GDP} \times \frac{CO_2^{\uparrow\uparrow}}{BTU} - CO_2^{\downarrow} \quad (1)$$

Where CO_2^{\uparrow} is the total CO₂ released to the atmosphere, POP is population, GDP/POP is per capita gross domestic product and is a measure of living,

BTU/GDP is energy consumption per unit of GDP and is a measure of energy intensity, $CO_2^{\uparrow\uparrow}/BTU$ is the amount of CO_2 released per unit of energy consumed and is a measure of carbon intensity, and CO_2^{\downarrow} is the amount of CO_2 stored/sequestered in biosphere and geo-sphere sinks. Reducing the population or the standard of living is not likely to be considered. Therefore, only three methods including reducing energy intensity, reducing carbon intensity and carbon storage are employed. Geo-sphere sinks have the capabilities to store large quantities of CO_2 in geologic time scale of thousands of years, and the most important issue that limits the use of the geological sinks as mitigation options is cost^[180].

The cost of disposing of CO_2 consists of four factors, including separation (i.e. capture/separation of CO_2 from combustion gases), compression, pipelining and injection (e.g. pumping and disposal wells). Capture/separation costs represent the largest financial impediment among the four factors, accounting for approximately three fourths of the total costs. Hence, it is necessary to develop efficient, cost-effective transportation and capture/separation technologies to allow large-scale use of geologic sinks. New CO_2 separation technologies such as gas hydrate and membrane are developed under the driving force.

Spencer et al.^[181] first proposed a relatively comprehensive economic analysis on the basis of a hybrid process of on-stage hydrate in conjunction of chemical absorption proposed by SIMTCHE. The engineering basis of the analysis was divided into four parts: on-stream factor, major equipment costs estimated from ASPEN “Icarus”, installation factor, and contingencies. In the process, two-stage hydrate separation were carried out at 22 °F and 108 to 625 psia. Under the condition of 90% removal of CO_2 , the cost for capturing one tonne CO_2 from the flue gas was about 18 dollars. The cost was much lower than those by chemical absorption, membrane, cryogenic separation and solid physical adsorption. According to Wong et al.’s analysis, the range for the cost of capturing CO_2 from flue gas using amine absorption is \$30 –\$50 per tonne (t) of CO_2 , and the costs for the other technologies such as solid physical adsorption (including pressure swing adsorption (PSA) and temperature

swing adsorption (TSA)), cryogenic separation, membranes, hybrid membrane/Amine processes, electrical swing adsorption (ESA) and sorbents energy transfer system are higher [179, 182]. The gas hydrate technology has the certain advantage on economy, however, there are some barriers to the technology, including the ability to release CO₂ from the hydrate in an energy efficient manner, efficient capture of CO₂, stale pre-hydrate, and trace contaminants interfere with hydrate formation. The barriers limit the further development of the gas hydrate separation technology. Until now, there are quite few publications reporting on the process of CO₂ separation by gas hydrate and the relevant cost analysis. Thus, in order to evaluate the CO₂ separation cost by the gas hydrate, the further development of the gas hydrate including kinetics and thermodynamics is necessary as well as the CO₂ hydrate separation process and equipments.

7. Conclusions

The hydrate-based CO₂ separation and capture from the gas mixtures containing CO₂ is considered as one new technology to reduce anthropogenic CO₂ emissions, and it is being extensively studied. In this work, we comprehensively discuss the hydrates containing CO₂ formation equilibrium condition, hydrate formation promoter, molecular-level measurement method, the hydrate-based CO₂ separation process and the relative equipments based on the previous studies.

The present computation models are mainly based on van der Waals-Platteeuw model and are developed according to the various revisions of relevant parameters. Although the models are considered to be increasingly accurate, they still have individual limitations such as the limitation of pressure range and the dependency on the experimental data. ANNs, a new computation model consisting of the four conventional models has been developed to save computation time and to obtain more accurate predictions. The experimental data of equilibrium conditions for hydrates containing CO₂ or gas mixtures are obtained in different systems, including pure water, solutions with additives, and solutions with electrolytes in different measurement

methods. The numerous data are the basis for hydrate-based CO₂ separation and capture.

Neither thermodynamic additives nor kinetic additives can resolve all the problems of hydrate-based CO₂ separation, thus, the combination additives are developed. It was found the combination additives of THF and SDS, TBAB and CP, THF and C₃H₈, etc., can considerably improve the CO₂ separation compared to the single additives. However, until now, there is no conclusion to determine which kind of additive is the best for hydrate-based CO₂ separation and capture from the gas mixtures

The hydrate structures, compositions and the cage occupancies can be identified by diffraction methods and microscopic methods. However, due to the limitation of sampling, the molecular-level measurements are difficult to be conducted. Thus, it is necessary to develop new apparatus or new ways to make the measurement simpler.

Because the equilibrium condition becomes extreme as the CO₂ decreases in the gas mixture such as CO₂/H₂ or CO₂/N₂, it is quite difficult to thoroughly separate and capture CO₂ from the gas mixtures by the hydrate method. Thus, the integrated separation technologies such as hydrate/chemical absorption, hydrate/membrane and hydrate/cryogenic are developed, and the experimental results indicate almost all the CO₂ can be completely separated and captured. But, being subject to the hydrate formation way, CO₂ separation efficiency and gas-liquid-hydrate separation in a special pressure vessel, there no mature hydrate-based CO₂ separation process that is applied in industry, even in a small scale-scale pilot application

New apparatuses that can promote the gas hydrate formation are developed, including a new type of reactor, continuous flow reactor, etc. The objective of developing a new apparatus is expected to bring the hydrate-based CO₂ separation from the experiment to industrial practice. However, the present apparatus does not yet match the requirement.

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FIGURE AND TABLE CAPTIONS**Figure caption**

FIGURE 1. *P-T* diagram of the three- and four-phase equilibria in the system carbon dioxide–water

FIGURE 2. Raman spectra of solvated CO₂ and CO₂ hydrates. The black dotted lines are located at the solvated CO₂ peak positions to show the peak shift associated with hydrate formation

FIGURE 3. Block flow diagram of the SIMTECHE CO₂ capture process (for IGCC applications)

FIGURE 4. Basic layout of flow rate reactors in the ETM system

Table caption

Table 1. List of equilibrium conditions predictions for hydrates containing CO₂ via computation models

Table 2. List of experimental measurements of equilibrium conditions for hydrates containing CO₂

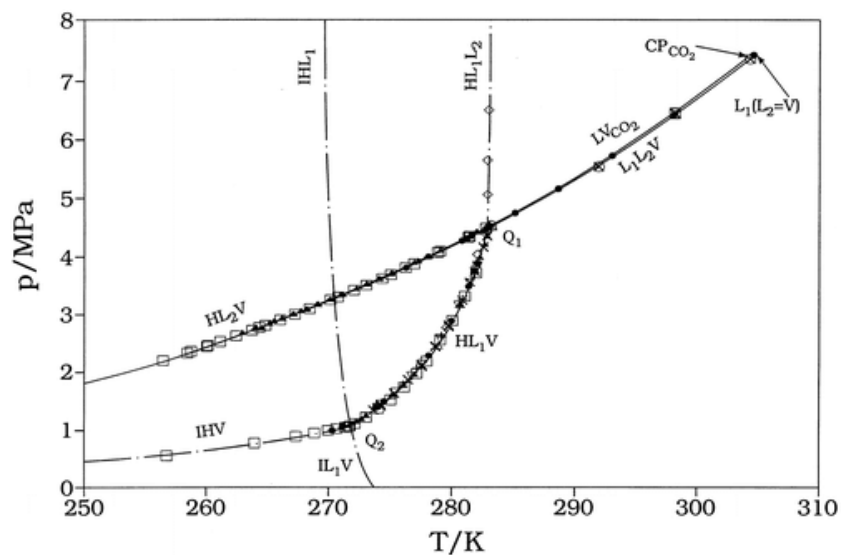


Fig. 1, P - T diagram of the three- and four-phase equilibria in the system carbon dioxide–water: □ Comparison of the results reported by Wendland et al.^[79] (·) with literature data (Kuenen and Robson^[183] (⊗); Deaton and Frost^[184] (×); Unruh and Katz^[185] (+); Larson^[186] (□); Takenouchi and Kennedy^[187] (◐); Robinson and Mehta^[188] (△); Vlahakis et al.^[189] (▲); Ng and Robinson^[190] (◇); Nakayama et al.^[191] (□); Adisasmito et al.^[85] (▼).

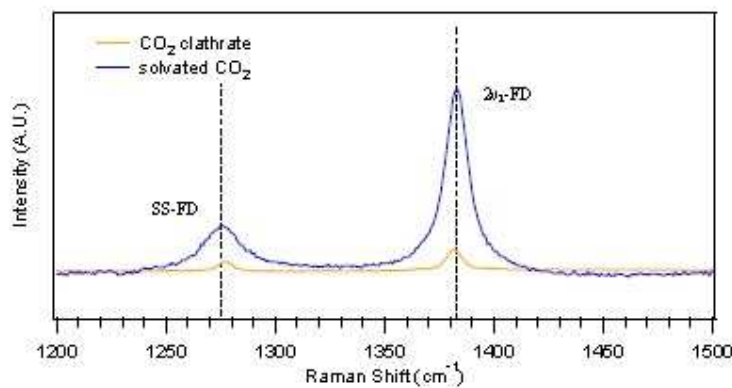


Fig. 2. Raman spectra of solvated CO₂ and CO₂ hydrates. The black dotted lines are located at the solvated CO₂ peak positions to show the peak shift associated with hydrate formation^[153].

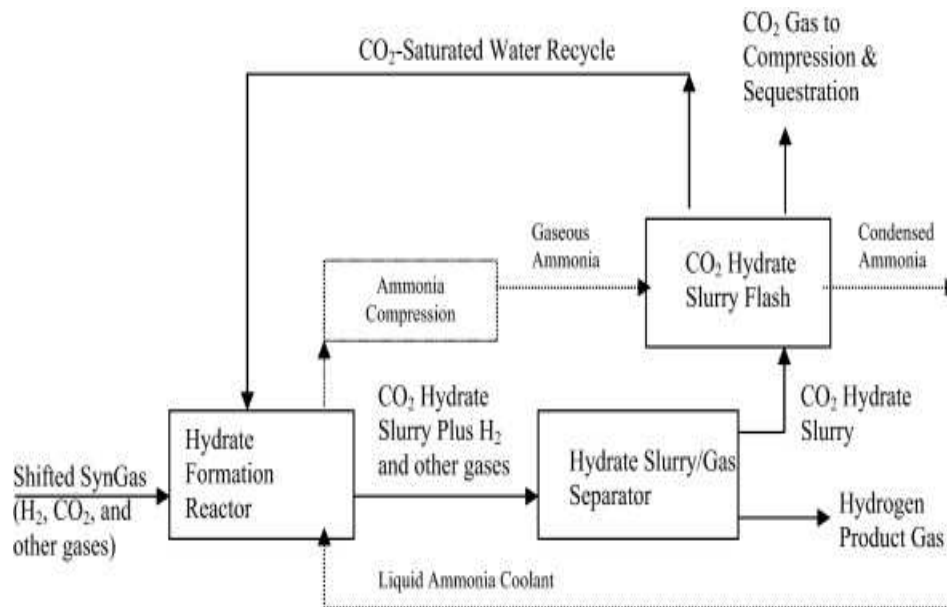


Fig. 3. Block flow diagram of the SIMTECHE CO₂ capture process (for IGCC applications)^[177].

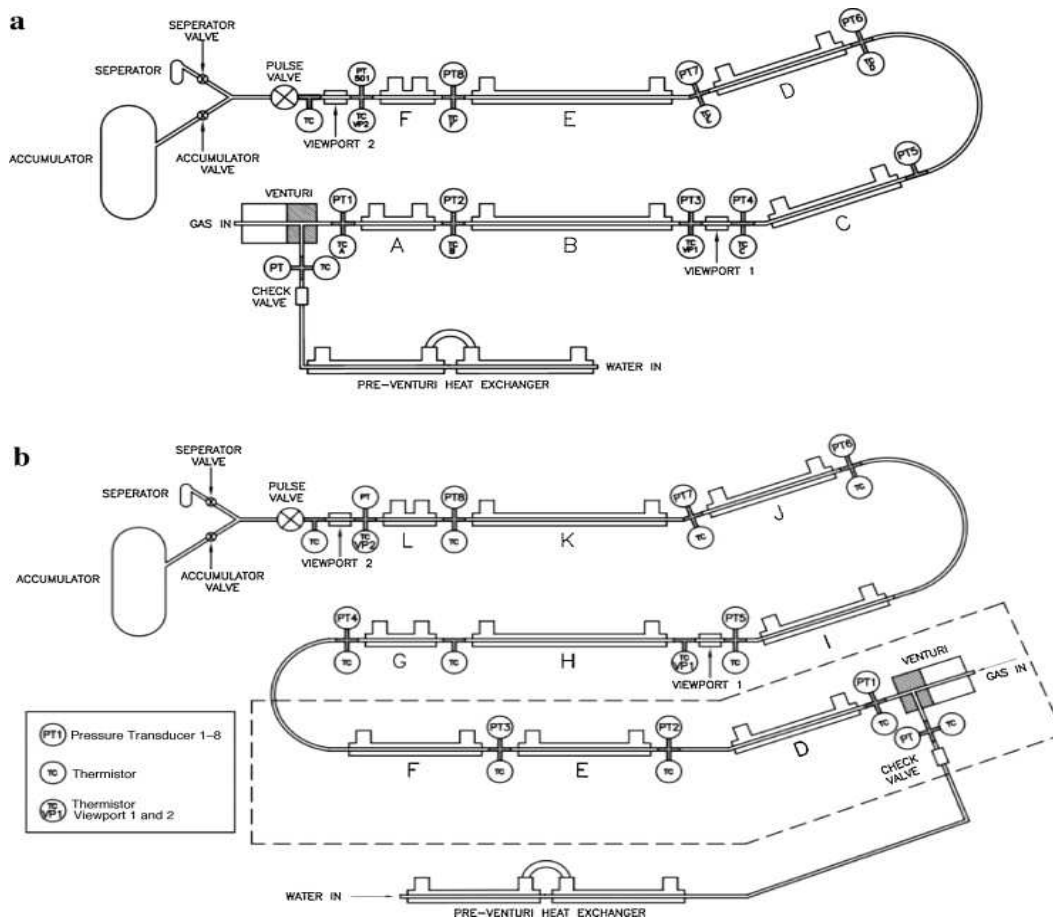


Fig. 4. Basic layout of flow rate reactors in the ETM system^[177].

Table 1. List of equilibrium conditions predictions for hydrates containing CO₂ via computation models.

Authors	Temperature (K)	Pressure (MPa)	Study	N [†]
Deaton & Frost ^[184]	273-283	1.3-4.3	K-charts, giving the vapor-solid equilibria for natural gases (including pure gases or gas mixtures) at lower than 273.15 K and higher than 273.15 K.	19
Carson & Katz ^[56]	277-283	2.0-4.5	Katz method, using vapor-solid equilibrium constants to predict the hydrate formation conditions. Katz correlation is not recommended above 100-150 MPa, depending on the composition of the gas mixtures.	15
Katz ^[58]	273-322	0.2-42.0	Method of gas-gravity plots which relate the hydrate formation pressure and temperature to gas gravity. The method was useful for an initial estimate of hydrate formation conditions and the prediction is rough.	128
Van der Waals & Platteeuw ^[11]			Van der Waals-Platteeuw model which was based on a statistical thermodynamic approach, accounting for the interactions between gas molecules and water molecules forming gas hydrates.	
Larson ^[186]	257-283	0.5-4.5	Predicted the equilibrium hydrate formation conditions of CO ₂ hydrates.	45
Miller & Smythe ^[192]	151-193	0-0.000022	Dissociation pressure of CO ₂ hydrate with equations for CO ₂ hydrate dissociation pressures and vapor pressures.	8
Robinson & Mehta ^[188]	274-283	1.3-4.5	The conditions for initial hydrate formation in system of CO ₂ /C ₃ H ₈ /H ₂ O over a wide concentration range for the hydrate-water-rich liquid-gas phase region were measured and predicted in terms of solid-vapor K-factor.	7
Falabella ^[193]	148.8-240.4	0.02-0.1	At a low pressure range, hydrates of CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ and CO ₂ are involved. Van der Waals-Platteeuw model was employed to predicting the equilibria associated with experimental measurements.	5
Ng & Robinson ^[78, 190]	279-284	2.7-14.5	A modification of the Parrish and Prausnitz program, predicting hydrate forming conditions for pure gases in presence of up to 20 wt%	9

[†] Number of measurements

			methanol solutions.	
Holder et al. ^[60]			Empirical correlations developed in different forms and with various numbers of parameters.	
Adisasmito et al. ^[85]	273-288	1.2-11.0	Verifying the work done by Unruh and Katz and by Berecz and Balla-Achs by experimental measurement.	9
Englezos ^[63]	269-281	1.1-4.3	Because the solubility of CO ₂ in salt solutions cannot be computed accurately using rigorous thermodynamic models, thus CSMHYD in conjunction with Trebble-Bishnoi equation is adopted to predict the incipient CO ₂ hydrate formation pressure in NaCl solutions and the average deviation is around 7.2%.	57
Dholabhai et al. ^[83]	273-279	1.3-2.5	Coupling model of statistical thermodynamic model of van der Waals and Platteeuw with coefficient models. Equilibrium conditions of CO ₂ hydrate in pure water and single and mixed electrolytes.	4
Englezos & Hall ^[194]	275-283	1.5-4.2	CSMHYD model predicting and measuring CO ₂ hydrate formation pressure in electrolyte, water-soluble polymers and montmorillonite.	6
Breland & Englezos ^[195]	275-280	1.6-3.0	Isothermal pressure search method is employed to measure the incipient equilibrium data for CO ₂ hydrate in glycerol solutions (10, 20, 30 mass%).	2
Tohidi et al. ^[81]	268-284	1.0-5.0	The model based on a thermodynamic approach, in which an equation of state is combined with a modified Debye-Huckel electrostatic term, with only on adjustable parameter for the water-rich phase. Predicting phase equilibrium conditions for CO ₂ hydrates in presence of saline water.	
Nakano et al. ^[82]	289-294	100-500	The high-pressure phase equilibrium for CO ₂ in pure water and saturated liquid CO ₂ and Raman spectrum of CO ₂ hydrate.	13
Fan & Guo ^[196]	264-284	0.5-5.0	Hydrate phase equilibrium for CO ₂ /CH ₄ , CO ₂ /C ₂ H ₆ , CO ₂ /N ₂ , CO ₂ /CH ₄ /C ₂ H ₆ /N ₂ in pure water and 10 mass% NaCl solution.	13
Wendland et al. ^[79]	270-305	0.5-7.0	Equilibrium conditions for CO ₂ /H ₂ O system focusing on three- and four-phase equilibria including fluid, hydrate and Ice phases. The experimental data are correlated with the equations of Clausius-Clapeyron type.	9
Seo & Lee ^[80, 197]	272-284	1.5-5.0	The three phase equilibria for aqueous containing	26

Duan & Sun ^[76, 198]	253-293	0.5-200	<p>CO₂ and CH₄ were predicted. The vapor and liquid phases were treated with SRK-EOS incorporated with the second-order modified Huron-Vidal (MHV2) mixed rule and hydrate phase with van der Waals-Platteeuw model.</p> <p>Ab initio potential model predicting initial hydrate formation conditions for CH₄ and CO₂. Compared to the models employing Kihara potential or Lennard-Jones potential, atomic site-site potentials was more accurate either in low pressure or in high pressure.</p>	20
Li & Englezos ^[199]	298-313	5.0-11.0	<p>SAFT equation of state was employed for the correlation and prediction of vapor-liquid equilibrium of eighteen binary mixtures. The predicted values were agree with the experimental data except for the H₂O/CH₃OH/CH₄ at low CH₃OH concentration in liquid phase of 60 wt.%</p>	4
Bahadori & Vuthaluru ^[200]	265-298	1.2-40.0	<p>A novel correlation based on the extracted data from Katz gas-gravity charts was proposed to predicting the hydrate formation conditions for gases with weights of 16-29, the absolute deviation in average around 0.18%.</p>	44
Zeng & Li ^[201]	270-282	0.8-4.0	<p>PC-SAFT in conjunction with van der Waals-Platteeuw model and capillary Kelvin model was employed to predict CH₄ and CO₂ hydrates formation equilibrium conditions in porous media. The deviations for CH₄ hydrate and CO₂ hydrates were 1.66% and 2.76%, respectively.</p>	18
Sloan ^[7]	277-283	Up to 400 MPa	<p>Presenting an alternative set of K-values for Katz method which are dependent upon gas composition and hydrate structures, the valid pressure up to 400 MPa.</p>	20
Karamoddin & Varaminian ^[97]	260-330	0-5.0	<p>A method using PR equation of state and different mixing rules for predicting hydrate formation conditions for binary mixtures of CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, CO₂ and H₂S. The interaction parameters were optimized by using two phase equilibrium data (VL_w), and then the optimized parameters were used for three phase equilibrium (VL_wH) calculations.</p>	63
Elgibaly & Elkamel ^[77]	250-320	0.001-1000	<p>Firstly proposing ANN compositional models to predicting hydrate formation conditions based on K-value method and gas-gravity chart method.</p>	2387

Eslamimanesh et al. ^[202]	279-295	0-120	<p>The ANN models consist of four models. The predicted results were more accurate than those obtained by the conventional models. The new model have to be updated by being retrained by using extra collected data.</p> <p>A thermodynamic model is proposed for representation/prediction of phase equilibria of semi-clathrate hydrates of the CO₂, CH₄, or N₂+tetra-n-butylammonium bromide (TBAB) aqueous solution. The van der Waals–Platteeuw (vdW–P) solid solution theory is used, revised with two modifications for evaluations of Langmuir constants and vapor pressure of water in the empty hydrate lattice, in which these values are supposed to be a function of TBAB concentration in aqueous solution. The Peng–Robinson (PR-EoS) equation of state along with re-tuned parameters of Mathias–Copeman alpha function is applied for calculation of the fugacity of gaseous hydrate former. For determination of the activity coefficient of the non-electrolyte species in the aqueous phase, the Non-Random Two-Liquid (NRTL) activity model is used.</p>	40
Eslamimanesh et al. ^[203]	276-294	2-500	<p>The model based on conventional Clapeyron model. Considered that the effect of pressure on molar volume of gas hydrate could not ignored, the “Clausius-Clapeyron” equation was improved from $\frac{dP}{dT} = \frac{\Delta H_H}{T\Delta V}$ to $\frac{dP}{dT} = \frac{\Delta H_H + nx\Delta H_S}{T\Delta V}$</p>	40
Shuker et al. ^[95]	270-295	0-2.5	<p>NN model was employed to predict hydrate formation conditions for pure gases and gas mixtures. The ANNs model was relatively accurate for a given gas mixture and without having to do experimental measurements compared to the previous models of K-factor, HYDOFF, CSMHYD and HYSYS.</p>	20

Heydari et al. ^[96]	273-296.5	0.3-29.0	ANN models were used for prediction of hydrate formation temperature. The results included the calculation relative error and R ² values between the experimental data and ANN predictions. The results showed that the ANN models could be improved based on the more collected data in a wider range of temperature and pressure.	167
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Table 2. List of experimental measurements of equilibrium conditions for hydrates containing CO₂.

Author(s)	System	Study
Hashimoto et al. ^[102]	H ₂ /CO ₂ /THF/water	Phase equilibria and Raman spectroscopic analysis for gas hydrate
Shin et al. ^[103]	CO ₂ /3M1B/water	Thermodynamic stability, spectroscopic identification and cage occupation of binary CO ₂ hydrates
	CO ₂ /THF/water	
Kang & Lee ^[21]	CO ₂ /DXN/water	Phase equilibrium measurements for CO ₂ recovery from flue gas using gas hydrate
	CO ₂ /N ₂ /water	
	CO ₂ /N ₂ /THF/water	
Dholabhai et al. ^[84]	CO ₂ /water	CO ₂ hydrate equilibrium conditions in aqueous solutions
	CO ₂ /electrolytes/water	
Dholabhai & Bishonoi ^[204]	CO ₂ /Methanol/water	Hydrate equilibrium conditions in aqueous electrolyte solutions
	CO ₂ /CH ₄ /electrolytes/water	
Matsui et al. ^[205]	CO ₂ /C ₂ H ₆ /water	Phase equilibrium for binary hydrate systems
	CO ₂ /CF ₄ /water	
Makino et al. ^[206]	CO ₂ /CP/water	Phase equilibrium and structural transition in the CO ₂ /CP mixed hydrates
Yang et al. ^[207]	CO ₂ /Doda glass/water	Characteristics of CO ₂ hydrate formation and dissociation in glass beads and silica gel
	CO ₂ /Silica gel/water	
Li et al. ^[116]	CO ₂ /H ₂ /TBAB/water	Phase equilibrium conditions for CO ₂ /H ₂ /TBAB/water mixed gas hydrate
Kumar et al. ^[105]	CO ₂ /H ₂ /C ₃ H ₈ /water	Hydrate phase equilibrium conditions for CO ₂ /H ₂ /C ₃ H ₈ /water mixed gas hydrate
Belandria et al. ^[208]	CO ₂ /N ₂ /water	Experimental and predicted hydrate phase equilibrium conditions for CO ₂ /N ₂ /water gas hydrate
Lee et al. ^[209]	CO ₂ /Electrolyte/water	Phase equilibria and kinetic behavior of CO ₂ hydrate in electrolyte and porous media solutions
Sabil et al. ^[210]	CO ₂ /porous media/water	
Maekawa ^[211]	CO ₂ /THF/water	Hydrate equilibrium conditions for CO ₂ hydrates in presence of Alcohols, Glycols, and Glycerol
	CO ₂ /Alcohols/water	
	CO ₂ /Glycols/water	
Kim et al. ^[155]	CO ₂ /Glycerol/water	Hydrate-based CO ₂ capture for pre-combustion process in IGCC plant
	CO ₂ /H ₂ /TBAB/water	
Lin et al. ^[212]	CO ₂ /TBAB/water	Hydrate phase equilibrium and dissociation enthalpy for CO ₂ /TBAB hydrate
Li et al. ^[120]	CO ₂ /TBAB(TBACl, TBAF)	Hydrate phase equilibrium for CO ₂ hydrate in presence of TBAB, TBACl, TBAF
Kang et al. ^[100]	CO ₂ /N ₂ /THF/water	Hydrate phase equilibrium for CO ₂ /N ₂ /THF hydrate
Zhang et al. ^[108]	CO ₂ /H ₂ /CP/water	Thermodynamic analysis of hydrate-based pre-combustion capture of CO ₂
Sugahara et al. ^[213]	CO ₂ /H ₂ /water	Hydrate phase equilibria for CO ₂ /H ₂ hydrate

Park et al. ^[214]	CO ₂ /N ₂ /Silica gel/water	Hydrate phase equilibrium and NMR analysis for CO ₂ /N ₂ /Silica gel hydrate
Mayoufi et al. ^[215]	CO ₂ /TBPB/water	Hydrate phase equilibria for TBPB hydrate and CO ₂ /TBPB hydrate
Mayoufi et al. ^[216]	CO ₂ /TBMAC/water	Hydrate phase equilibrium for CO ₂ /TBMAC hydrate
Lee et al. ^[22]	CO ₂ /H ₂ /THF/water	Hydrate phase equilibrium, gas consumed and CO ₂ separation efficiency in the process of pre-combustion capture of CO ₂
Lee et al. ^[118]	CO ₂ /CH ₄ /N ₂ /water	Thermodynamic stability, spectroscopic identification, and gas storage capacity of CO ₂ /CH ₄ /N ₂ hydrate
Nakano et al. ^[82]	CO ₂ /water/liquid CO ₂	High-pressure phase equilibrium and Raman spectroscopic analysis for CO ₂ hydrate
Ohgaki et al. ^[217]	CO ₂ /CH ₄ /water	Hydrate phase equilibrium for CO ₂ /CH ₄ gas hydrate and replacement of CH ₄ by CO ₂
Bruusgaard et al. ^[218]	CO ₂ /CH ₄ /water	Hydrate phase equilibrium for CO ₂ /CH ₄ hydrate
Adisasmito et al. ^[85]	CO ₂ /CH ₄ /water	PVT studies on dissociation conditions of CO ₂ /CH ₄ hydrate
Belandria et al. ^[219]	CO ₂ /CH ₄ /water	Phase equilibria in the CO ₂ /CH ₄ /H ₂ O system has measured by the method of isochoric pressure-search method in the conditions of 233-373 K and up to 60 Mpa.
Beltran & Servio ^[220]	CO ₂ /CH ₄ /water CO ₂ /CH ₄ /neohexane-emulsion	PVT studies on dissociation conditions and composition measurement of gas phase
Fan et al. ^[221]	CO ₂ /CH ₄ /SDS/water	Experimental and modeling studies on the hydrate formation of CO ₂ and CO ₂ -rich gas mixtures
Deschamps & Dalmazzone ^[222]	CO ₂ /N ₂ /TBAB/water CO ₂ /CH ₄ /TBAB/water	Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N ₂ , CO ₂ , N ₂ /CO ₂ and CH ₄ /CO ₂
Fan et al. ^[223]	CO ₂ /H ₂ /TBAB/water CO ₂ /H ₂ /THF/water	Efficient Capture of CO ₂ from Simulated Flue Gas by Formation of TBAB or TBAF Semiclathrate Hydrates
Meysel et al. ^[224]	CO ₂ /N ₂ /TBAB/water	Incipient equilibrium conditions for the formation of semi-clathrate hydrates from quaternary mixtures of (CO ₂ /N ₂ /TBAB/H ₂ O)
Mohammadi et al. ^[225]	CO ₂ /N ₂ /TBAB/water	Experimental data for the hydrate dissociation conditions for the system comprising mixtures of CO ₂ (0.151/0.399 mole fraction) + N ₂ (0.849/0.601 mole fraction) + TBAB (0.05/0.15/0.30 mass fraction) in the conditions of 277.1-293.2 K and up to 16.21 Mpa.
Kamata et al. ^[32]	CO ₂ /H ₂ S/TBAB/water	A high-pressure vessel of separation gas from gas mixture Molar compositions of carbon dioxide (and hydrogen) in the gas phase in equilibrium with gas hydrate and aqueous
Belandria et al. ^[226]	CO ₂ /H ₂ / water	phases were measured for various (H ₂ t CO ₂) gas mixtures t water systems in the temperature range of 273.6-281.2 K at

pressures up to ~9 MPa. The compositions of the gas phase were measured using an isochoric technique, in combination with the ROLSI capillary gas-phase sampling and a gas chromatography technique.
