



Review

CO₂ Gas hydrate for carbon capture and storage applications – Part 1

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ABSTRACT

Gas hydrates are solid crystalline compounds formed by water and gas molecules through molecular interactions, typically at low temperatures and high pressures. While gas hydrates are generally known as flow assurance challenges for the oil and gas industries (e.g., pipeline blockages), numerous studies have shown the potential application of gas hydrate in carbon capture and storage (CCS).

Due to the more thermodynamic stability of CO₂ hydrate compared to other industrial emission gas components like nitrogen, CO₂ hydrates have emerged as a viable mechanism for CO₂ capture. Moreover, a large volume of CO₂ can be stored securely in the stable structure of gas hydrates, providing an additional benefit for CO₂ storage in geological formations. Thus, gas hydrates can be suggested as a technology for mitigating CO₂ emissions.

Notwithstanding the CO₂ hydrate advantages in CCS, they may also present some challenges, particularly in terms of flow assurance. For example, CO₂ hydrate formation during CO₂ transportation can cause a serious pipeline blockage. Therefore, the fundamental understanding of gas hydrates is crucial for CCS. In the first part of this review, the principle on gas hydrates (especially CO₂ hydrates) and CO₂ hydrate-based carbon capture are discussed.

1. Introduction

Gas hydrates are solid crystalline compounds that contain water molecules and suitably sized guest molecules. Clathrate hydrates form through the physical combination of water and guest molecules under certain pressure and temperature conditions (i.e., typically low temperatures and elevated pressures). The water molecules form cages through hydrogen bonding (an attractive interaction of a hydrogen atom with an electronegative atom such as oxygen) and trap guest molecules. The guest molecules can rotate inside the cavities as there is no bonding

between water and guest molecules. In contrast to inorganic hydrates (e.g., CaCl₂·6H₂O), gas hydrates are non-stoichiometric crystalline compounds with different hydration numbers (i.e., hydration number is the mole fraction ratio of water to guest molecules).

The gas hydrate flow assurance-related area was the principal hydrate research to prevent or minimise the risk of hydrate blockage in the pipeline. However, due to its unique advantages, gas hydrate is now considered for various applications, such as gas storage (i.e., high gas storage capacity), seawater desalination, carbonated solid foods, refrigeration, gas separation, energy production from hydrate

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reservoirs, etc. Certainly, the application of CO₂ hydrate can be utilised for CO₂ capture and storage applications through carbon capture and storage (CCS) process to promote sustainable economic growth. The simple procedure of CO₂ capture using hydrate makes it sustainable technology compared to other traditional technologies. Furthermore, CO₂ gas hydrate can be exploited for permanent storage of CO₂ in geological formations through CH₄-CO₂ replacement in the permafrost gas hydrate reservoir. Notwithstanding the importance of CO₂ hydrate application for CO₂ capture and storage, there is still a challenge to reduce the risk of CO₂ hydrate formation during transportation (i.e., CO₂ is normally captured from the large point sources and transported via pipelines or ship to store in a safe place).

This review paper includes two parts which provides a fundamental understanding of advances in gas hydrates chemistry and technologies that are potentially applicable and relevant in CCS. Due to the global attention and interest in CCS, the research, advances, and developments in sustainable hydrate-based technologies are growing fast. Therefore, this review focuses on hydrate-based technologies particularly relevant for CCS.

Fig. 1 shows the graphical content for the sections and topics that are covered in both part 1 and part 2. In Part 1, the importance of carbon management and sequestration is firstly discussed. Part 1 then aims to review the gas hydrate chemistry and properties (focused on CO₂ hydrate). Carbon capture is the first stage in the CCS chain. Therefore, the last section of part 1 provides a fundamental understanding of the most recent advances and research in hydrate-based carbon capture technologies.

2. Importance of carbon management

One of the essential biochemical cycles for sustaining life on Earth is carbon cycle. Carbon is the main component that exchanges among the biosphere, hydrosphere, geosphere, pedosphere, and atmosphere (Fig. 2). The long-term process of carbon movement, as well as carbon sequestration to the carbon sinks, can be described by the carbon cycle [1]. About one-quarter of the carbon released by human activities sinks into the land and ocean each year [2]. The excessive carbon emissions caused by human activities, such as modifying land use and mining fossil carbon from the geosphere, have disrupted the biological carbon cycle

[1,3].

The two main forms of carbon in the atmosphere are carbon dioxide and methane. These gases are highly effective at trapping heat in the atmosphere, leading to global warming [4]. Compared to carbon dioxide, methane has a stronger greenhouse effect per unit of volume. However, methane is more short-lived than carbon dioxide, and its concentration in the atmosphere is much lower. Therefore, the impact of carbon dioxide as greenhouse effect is more significant [5].

Since the Industrial Revolution began in 1760, the atmospheric concentration of CO₂ and other greenhouse gases has been rising exponentially and has now reached a critical level [6–8]. According to studies from the International Energy Outlook, worldwide energy consumption was approximately 549 quadrillion Btu in 2012 and is predicted to continue to rise to 815 quadrillion Btu in 2040, an increase of 48 % [9]. For the next several decades, fossil fuels will remain the cornerstone of global energy. It is essential to implement appropriate measures to control CO₂ emissions resulting from the combustion of fossil fuels for power generation [9,10].

Anthropogenic activities, such as cement and steel production, deforestation, and fossil-fuel combustion for power and transportation, have disrupted the natural equilibrium by adding excessive carbon dioxide to the atmosphere [11–13]. The level of carbon dioxide concentration in 2020 has increased by 52 % since the Industrial Revolution. As a consequence of increased carbon dioxide emissions, marine chemistry has been significantly altered due to carbon dioxide dissolution in the water, increasing the acidity of the ocean surface by 30 % [14–16]. Based on a NASA GIS study in 2019, the climate change model developed by the assessment of greenhouse gases (MAGICC) predicts that, if the current fossil fuel-intensive emission trajectory continues, the global average temperature rise will be greater than 4 °C by the end of the century [2].

The impacts of higher temperatures and consequently higher rates of evaporation can be summarized as more severe heat waves and drought, a higher risk of terrestrial vegetation destruction, possible lack of food supplies, ocean warming and acidification (with about 90 % of all heat and 25 % of carbon dioxide transferred into the ocean), and rising sea levels caused by the melting of North Sea ice [2,14,15].

The current concentration of carbon dioxide is approximately 410 ppm [2]. Various studies have shown that a target carbon dioxide

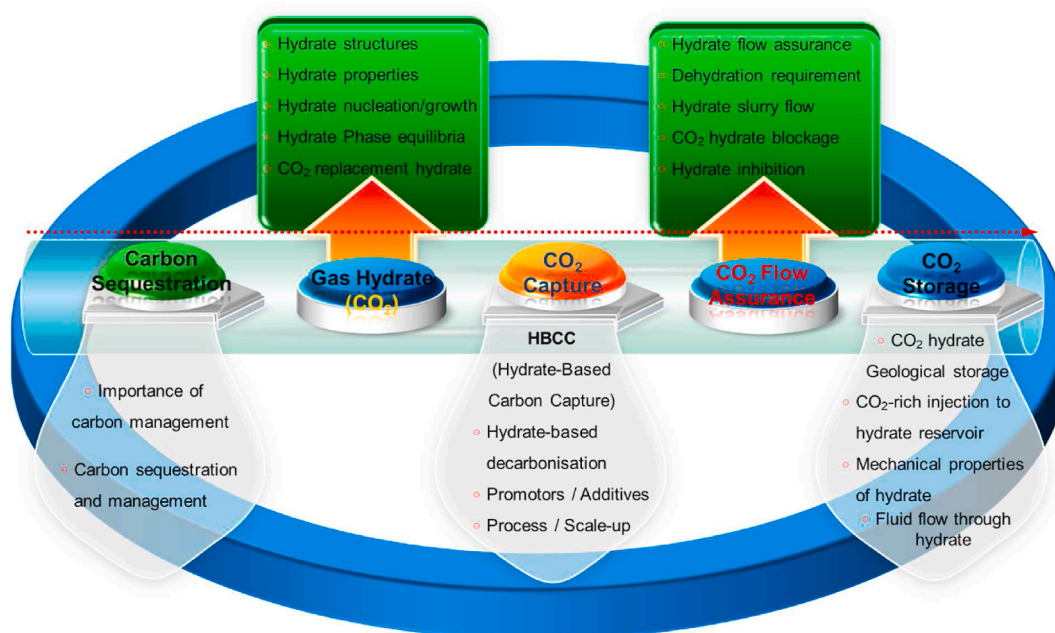


Fig. 1. A graphical representation summarizing the key concepts explored in this review.

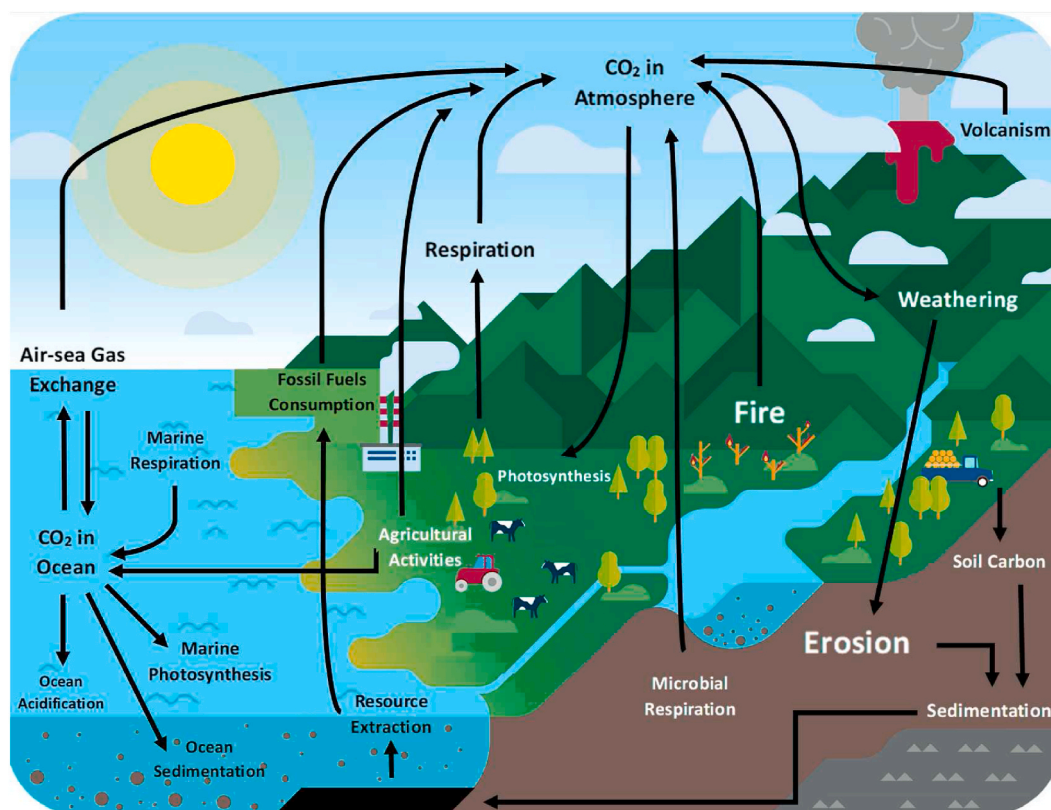


Fig. 2. The movement of carbon occurs among the atmosphere, hydrosphere, biosphere, and pedosphere over a range of timeframes, varying from hours to centuries.

concentration of 450 ppm is needed to stabilize the average global temperature rise at 2 °C by the end of 2100. It is estimated that between 40 % and 70 % of total carbon dioxide emissions must be reduced by 2050 to maintain the optimum carbon dioxide concentration [2,10,17]. Therefore, it is crucial to avoid any delays in executing countermeasures to manage carbon emissions. Note that, based on the current situation, CO₂ management can be defined as a procedure that seeks a cure rather than preventing the problem.

3. Gas hydrate

3.1. Gas hydrate structures

Gas hydrates consist of various cages/cavities which are polyhedral described by nomenclature $n_i m_i$ where n_i is the number of edges in polygon type i and m_i is the number of n_i type polygon. The combination of varying hydrate cavities results in the formation of various hydrate

structures. Canonical clathrate hydrates and semi-clathrate hydrates are the two main hydrate categories. While canonical clathrate hydrates do not have direct host-guest interaction, there are directional guest-host interactions in the semi-clathrate hydrates. They have many similar properties as described in the following sections.

3.1.1. Clathrate hydrates

The guest molecules are not bonded to water molecules in the canonical clathrate hydrates. They can rotate through the van der Waals forces inside the hydrogen-bonded water lattice. Structure-I (sI), structure-II (sII), and structure-H (sH) are three main hydrate structures (Fig. 3). These structures consist of various cavities, including pentagonal dodecahedron (5^{12}), tetrakaidecahedron ($5^{12}6^2$), hexakaidecahedron ($5^{12}6^4$), irregular dodecahedron ($4^35^66^3$), and icosahedron ($5^{12}6^8$), as shown in Fig. 4.

Structure-I hydrate is a cubic crystal structure with space group $Pm\bar{3}n$ and forms from small molecules with size of 0.4–0.55 nm (e.g., C₁,

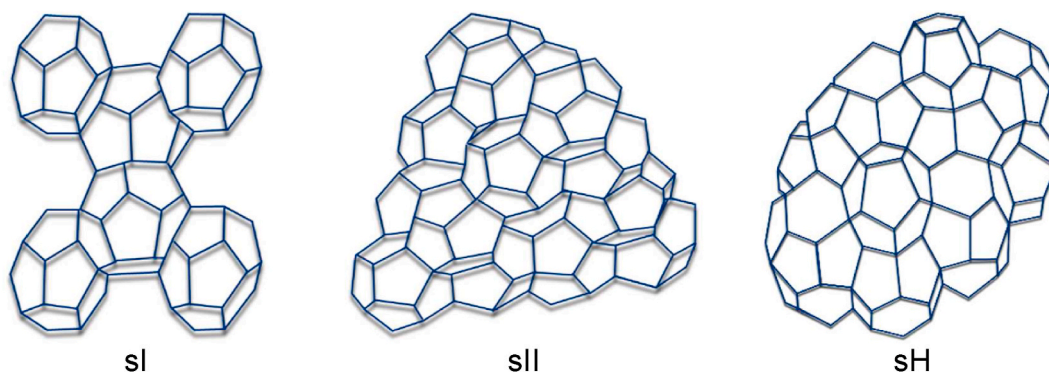


Fig. 3. Clathrate hydrate structures: Structure I (sI), Structure II (sII), and Structure H (sH). The structures are taken from Ref. [18].

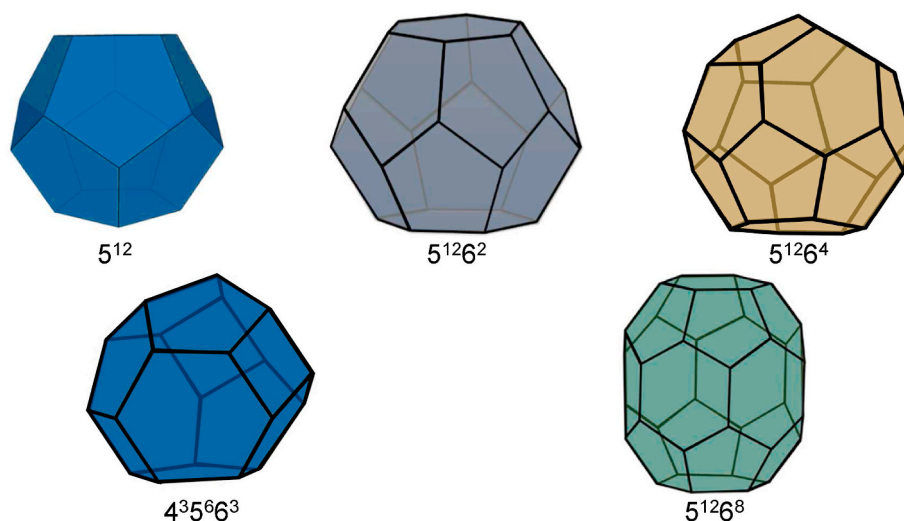


Fig. 4. Clathrate hydrate cavities: pentagonal dodecahedron (5^{12}), tetrakaidecahedron ($5^{12}6^2$), hexakaidecahedron ($5^{12}6^4$), irregular dodecahedron ($4^35^66^3$), and icosahedron ($5^{12}6^8$).

C_2) [18,19]. Cubic sI with a unit cell size of 12 \AA is composed of 46 water molecules forming six large cages ($5^{12}6^2$, comprising 12 pentagons and two hexagons) and two small cages (5^{12} , comprising 12 pentagons). In sI hydrates, 5^{12} cavities join only through vertices without direct face sharing. The 5^{12} cavities are placed in a position where they fill the space between each set of two $5^{12}6^2$ cavities in a column [20,21].

The molecules with an intermediate size of 0.6–0.7 nm (e.g., C_3 , C_4) form sII hydrate in the form of cubic crystal structure with space group $Fd3m$ [18,19]. Some small molecules (e.g., N_2 and O_2) with a size of less than 0.4 nm can also form sII hydrates [18]. A unit cell of sII hydrates with a size of 17.3 \AA is composed of 136 water molecules forming 16 small cages (5^{12}) and eight large cages ($5^{12}6^4$). In the cubic sII hydrate, 5^{12} cavities share their faces in which $5^{12}6^4$ are placed in empty spaces [20].

Structure-H (sH) with space group $P6/mmm$ consists of 34 water molecules forming three small cages (5^{12}), two medium cages ($4^35^66^3$), and one large cage ($5^{12}6^8$) [19]. While a single guest molecule can form stable sI and sII hydrates, two guest molecules (including one large guest molecule and one small guest molecule, e.g., methane + neohexane) are required to form a stable sH [22,23]. Larger guest molecules fill the large cage, and small guest molecules stabilize the two smaller cages of sH [24].

While some single guest molecules such as methane usually form sI, they can form sII (or even sH) hydrates under certain pressure-temperature conditions. For example, sII methane hydrate at 250 MPa and sH methane hydrate at 600 MPa were reported [25]. Shu et al. (2011) reported a structural transition from sI methane to sII methane with space group $Fd3m$ at 120 MPa and sH methane with space group $P6_3/mmc$ at 600 MPa [26]. They reported decomposition of methane hydrate at high pressure above 3 GPa and formation of orientationally $Fm3m$ structure methane and ice with space group $Pn3m$ [26]. The formation of sII methane hydrate and coexistence of sI and s-II in the binary guest mixture of methane and ethane have also been reported [27–29]. In the real multicomponent natural gas systems, various hydrate structures or phases can form in the order of thermodynamic stability [30–33]. Heterogeneous and coexisting hydrate phases have been also rereported in the natural gas system [34].

3.1.2. Semi-clathrate hydrates

Water molecules and small gases such as methane and CO_2 can form semi-clathrate hydrates. Unlike clathrate hydrates, semi-clathrate hydrates are crystalline compounds consisting of water and ionic or non-ionic compounds that can form with or without gas molecules. The

ionic substances are considered as both host and guest molecules that can physically attach to the water crystalline lattice through the hydrogen bond. The semi-clathrate hydrates are more stable than clathrate [35,36]. Since semi-clathrate hydrates are thermally stable at atmospheric pressure, they have many applications, including refrigeration fields [37,38], gas separation [39,40], and energy storage [41–45].

Various quaternary ammonium and phosphonium salts can form semi-clathrate hydrate. While tetra-*n*-butylammonium (TBA) and tetra-*n*-butylphosphonium (TBP) are the most common ionic elements used to form semi-clathrate hydrates [46–51], some other ionic elements have been reported such as tetra-iso-pentylammonium, tri-*n*-butyl sulfonium, and tetra iso-amyl ammonium [52,53]. These ionic semi-clathrate hydrates are classified as a quaternary ammonium salt (QAS) and phosphonium salt hydrates. The equilibrium temperature of these semi-clathrate hydrates can be as high as 280 K–290 K at atmospheric pressure [54–58].

Four basic semi-clathrate hydrate structures were reported, including orthorhombic structure (space group $Pbmm$), tetragonal structure (space group: $P4_2/mmm$), tetragonal structure (space group $P4_2/m$), and cubic structure ($Pm3n$) [52]. These structures consist of different cages, such as pentagonal dodecahedral, tetrakaidecahedral, and pentakaidecahedral [59]. For example, TBA and TBP substances can enter the combined four cages, including two tetrakaidecahedra and two pentakaidecahedra [60,61].

Tetra-*n*-butylammonium bromide (TBAB) is one of the examples of TBA salt that has been used widely to form semi-clathrate in the form of $C_{16}H_{36}N^+ \cdot Br^- \cdot 38H_2O$. In this semi-clathrate hydrate, the anions substances (e.g., Br^-) can physically attach to the water crystalline lattice to construct the cavities. On the other hand, while the tetra-*n*-butylammonium substances (cations substances) can enter the cavities by broking of cage structure, TBAB semi-clathrate hydrates can engage small gas molecules such as C_1 [62], CO_2 [63], H_2 [64], and H_2S [65] through the empty dodecahedral cages [62].

While some researches show the promotion effect of TBAB in CO_2 hydrate formation [66–72], TBAB may have an inhibitor effect at low concentration [73–77]. At a very high concentration of TBAB or in the presence of other quaternary ammonium salts, TBAB may not be involved in creating semi-clathrate hydrate (i.e., free ions of TBA^+ and Br^-) and act as an inhibitor [73,74]. Furthermore, the inhibition effect of diluted TBAB solution on CO_2 gas hydrate formation was reported due to the impact of surface adsorption of TBA^+ on water alignment at the gas water interface [78]. Temperature also affects the inhibition/promotion

effect of TBAB, i.e., while TBAB shows the inhibition effect in difluoromethane (HFC-32) + TBAB + water system above 289.4 K, it promotes the hydrate formation below 289.4 K [75].

The alkylamine hydrate is another class of semi-clathrate hydrates. The early studies of alkylamine hydrate were done by Pickering [79] together with some other studies related to alkylamine semi-clathrate hydrates [80–82]. The only exception to alkylamine semi-clathrate is tert-butylamine which occupies 17-hedra ($4^3 5^9 6^2 7^3$) through canonical hydrate clathrate [83]. While the amine group in the alkylamine molecules can do hydrogen bonds to the water lattice, the alkyl chain functional groups stabilize the cavity [81]. Although the pure alkylamine forms semi-clathrate hydrates, the structural transition of semi-clathrate alkylamine hydrate to the canonical hydrates (e.g., sII hydrate) in the presence of secondary guest molecules (e.g., C_1 , H_2) has been reported [84–87]. The alkylamine molecules are important because they could be potentially used for the CO_2 capture process using hydrate technology [88]. The CO_2 molecules are attracted to the alkylamine molecules due to the attraction forces between the carbon in CO_2 molecules and the negative charge in heteroatom nitrogen in the alkylamine molecules. This attraction force is relatively stronger than the attraction forces between CO_2 and oxygen in the water molecules [88]. Therefore, alkylamine molecules in the hydrate lattice can attract more CO_2 molecules.

3.2. CO_2 hydrate

3.2.1. CO_2 clathrate hydrate structures

CO_2 can form both clathrate and semi-clathrate hydrates. Structure of CO_2 hydrate has been studied using X-ray diffraction [89–91], NMR spectroscopy [92], neutron powder diffraction [93,94], IR spectroscopy [95], and Raman spectroscopy [96,97]. These studies indicate sI CO_2 hydrate is the most stable hydrate structure. In sI hydrate, CO_2 molecule mainly occupies the large cages ($5^{12}6^2$) while it can occupy small cages (5^{12}), i.e., molecular size of CO_2 is close to the size of 5^{12} cage, making it difficult to fit in small cages. Molecular dynamic simulation shows a rich orientation landscape of CO_2 molecules in sI [98]. Powder X-ray Diffraction show 99 % large cage occupancy and 69 % small cage occupancy in CO_2 sI hydrate [90]. CO_2 sI hydrate with the space group $Pm3n$ can have different hydration numbers between 5.75 (if all cages are filled) and 7.67 (if only the large cages are filled) [89,99]. In fact, some cages may not be filled with CO_2 (particularly small cages, 5^{12}); therefore, a higher hydration number (>6) has been reported [89,92, 100–102].

Although CO_2 forms a stable sI, a transient formation of sII CO_2 hydrate with the growth of sI CO_2 hydrate was reported using neutron diffraction [103] and FTIR spectroscopy [104]. While sII transition occurs when some sI formers are mixed (e.g., $CH_4 + C_2H_6$), CO_2 doesn't form sII with another sI former [105]. However, sII hydrates form when CO_2 is mixed with other sII formers, such as propane [106]. The sII hydrate formation in the systems including $CO_2 + N_2 +$ tetrahydrofuran (THF) [40], $CO_2 + H_2 +$ THF [107], $CO_2 + CH_4 + N_2$ [108], $CO_2 + CH_4 +$ THF [109,110], $CO_2 +$ THF [96], and $CO_2 + N_2$ [111] was also reported.

CO_2 can also form sH hydrate as a co-guest. X-ray diffraction, Raman spectroscopy, and NMR indicate that CO_2 are trapped in the $4^3 5^6 6^3$ cages and help the formation of sH hydrate in the $CH_4 + CO_2 +$ Neohexane system [112,113]. The enclathration of CO_2 in sH hydrates has been also reported in $N_2 + CO_2 +$ Neohexane [114], $CH_4 +$ flue gas ($CO_2 + N_2$) + Neohexane [113], $CO_2 + N_2 +$ methylcyclopentane [115], $CO_2 +$ methylcyclopentane [116,117], $CH_4 + CO_2 + N_2 +$ methylcyclopentane [118], $N_2 + CO_2 +$ 3,3-dimethyl-1-butanol [119], and $CO_2 +$ 3,3-dimethyl-2-butanone [120]. Although enclathration of CO_2 in sH hydrates was reported [92,114], a few studies showed that CO_2 is not a good help gas for some sH former (e.g., 3-methyl-1-butanol) [121,122].

In CO_2 -rich systems, the mole fraction of CO_2 significantly affects the stability of sH hydrate formation and may cause the structural transition [118,119,123]. The structural transition of sH to sI in the CO_2 -rich

systems has been reported in the $CH_4 + CO_2 +$ Neohexane system [112, 123]. Uchida et al. pointed out that while the increase of CO_2 fraction reduces the stability of sH hydrates in the $CH_4 + CO_2 +$ Neohexane system, it increases the thermodynamic stability of sI [112].

3.2.2. CO_2 semi-clathrate hydrate structures

Tetra-*n*-butyl-ammonium salts (e.g., bromide (TBAB) [42,124,125], chloride (TBAC) [126,127], fluoride (TBAF) [128,129], nitrate ($TBANO_3$) [130,131]) and tetra-*n*-butyl phosphonium salts (e.g., bromide (TBPB) [132,133], and chloride (TBPC) [40]) have been studied for engagement of CO_2 to semi-clathrate hydrates either in the pure CO_2 system or flue gas system ($CO_2 + N_2$).

X-ray diffraction and Raman spectroscopy show the tetragonal hydrate structure formation with TBAC and orthorhombic hydrate structure formation with TBPB and TBPC [40]. TBAB, which is the most popular ionic substance, can form polymorphic phases consisting of orthorhombic and tetragonal hydrate structures in the CO_2 system [39]. In-situ Raman studies reveal that orthorhombic structures form at the onset of TBAB + CO_2 semi-clathrate hydrate formation, while tetragonal hydrate structures can form to make polymorphic phase [134]. In addition to the cation, the structure of semi-clathrate hydrate also depends on the type of anion [135], e.g., the CO_2 capture capacity in the TBAC + CO_2 hydrate structure is more than in the TBAB + CO_2 hydrate structure because CO_2 molecules can encapsulate in a planar distribution in the pentagonal dodecahedral cages [59]. CO_2 can occupy pentagonal dodecahedral cages as shown by X-ray diffraction in the TBAB + $CO_2 +$ water system [59].

3.2.3. CO_2 hydrate nucleation

Hydrate nucleation depends on many factors including composition, mixing rate, impurities/additives, driving force, and history effect [136–144]. Molecular dynamic simulations show that a high aqueous CO_2 concentration and adsorption of sufficient CO_2 molecules around hydration cages are the key factors in CO_2 hydrate nucleation [145]. Molecular dynamic simulations also show that higher guest concentration leads to a more structured hydration shell for the guest [146]. However, CO_2 hydrate formation from amorphous solid water and crystalline CO_2 is reported indicating CO_2 vapour pressure is not required for hydrate crystallization [147]. Formation of critical nucleation with a critical cluster size/radius is the first step of hydrate nucleation that is described by various mechanisms as summarized in Fig. 5. The classical nucleation theory calculates the hydrate nucleation point using Gibbs free energy analysis by assuming bulk-like properties of hydrate nucleus [148]. This theory assumes that hydrate nucleation can occur in the gas-liquid interface or supersaturated liquid water [149].

The microscopic view of hydrate nucleation and unknown hydrate structures in the classical approach leads to errors in free energy calculation and hydrate nucleation point. Therefore, other theories are developed by considering of intermolecular interactions between water and gas molecules. Labile cluster nucleation hypothesis suggests that the interaction between water molecules and dissolved gas in aqueous phase makes the labile clusters surrounding the gas molecules [150]. This theory says hydrate nucleation will occur when both type of cavities for sI or sII are formed. The interface nucleation theory was also proposed based on labile clusters formation only on the vapour side of gas-water interface [151]. In this theory, when gas molecules are adsorbed to the interface and moved to the right position, the partially open cages are formed and then completed.

Molecular dynamic simulation of CO_2 hydrate nucleation shows another mechanism called local structuring nucleation [152]. In this theory, CO_2 molecules are arranged locally by the thermal fluctuation rather than arrangement of water molecules. This local arrangement of gas molecules induces the ordering of water molecules that leads to hydrate nucleus formation.

The study of amorphous precursors in CO_2 hydrate nucleation using

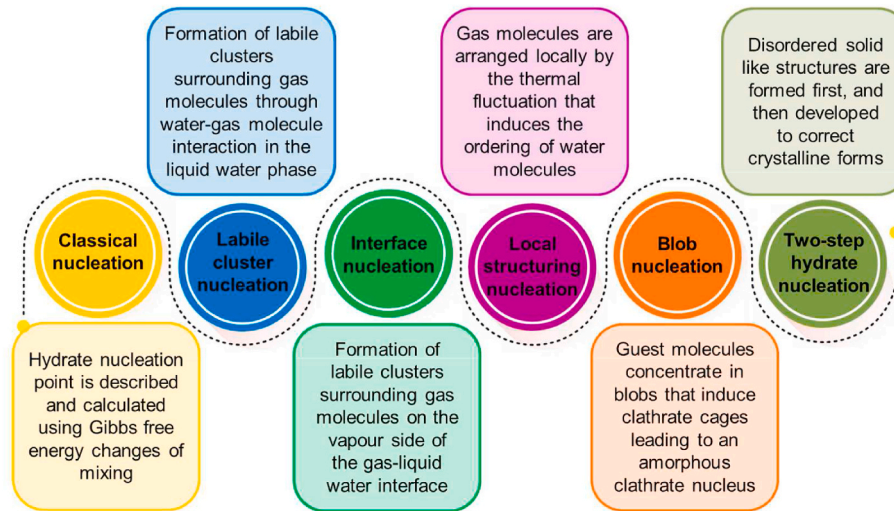


Fig. 5. Various gas hydrate nucleation mechanisms.

molecular dynamic simulation proposed the blob nucleation mechanism [153]. In blob nucleation mechanism, guest molecules concentrate in blobs which are in equilibrium with solution. These blobs induce the cages that lead to an amorphous clathrate nucleus. This theory uses both features of local structuring and labile cluster mechanisms [153].

In the two-step mechanism hydrate nucleation, the disordered solid-like structures start to form as an amorphous phase [154]. This intermediate state is then processed to evolve correct hydrate structure. Moreover, some researchers proposed multiple pathways for hydrate nucleation including direct nucleation [155–157]. In addition to different hydrate nucleation mechanisms, various models have been introduced to describe CO₂ hydrate nucleation based on different theories, including crystallization [158], classical nucleation [159], and phase field theory [160,161]. One model was proposed by Natarajan et al. to predict the induction time by crystallization considerations [158]. In this model, the induction time is an exponential dependence of driving force (fugacity difference). Another model was proposed by Kvamme established based on phase field theory to describe CO₂ hydrate nucleation rate [160].

3.2.4. CO₂ hydrate growth

Growth kinetics of CO₂ hydrate can be studied experimentally by observing the changes in the concentration of dissolved CO₂ in water and the rate of hydrate formation. The rate of CO₂ hydrate growth is influenced by several factors, including the concentration of dissolved CO₂, CO₂ concentration of the gas mixture, diffusion of water and guest molecules, temperature, pressure, mixing, heat transfer, and the presence of chemicals/additives. At low concentrations of dissolved CO₂, growth rate of CO₂ gas hydrate is slow, but it increases with increasing CO₂ concentration. Lower temperatures and higher pressures also increase the growth rate of CO₂ hydrate. It has been demonstrated that while decreasing of temperature can significantly increase the CO₂ hydrate growth rate, the pressure has little effect on growth rate [162].

The growth of CO₂ gas hydrate is a complex process that involves several stages. First, small crystals of CO₂ hydrate are formed through a process called nucleation as described before. Next, these crystals grow as additional water molecules and CO₂ are added to the crystal lattice. Finally, the crystals may merge to form larger crystals through the agglomeration process. Various mathematical models have been developed to describe the kinetics of gas hydrate growth, which are based on different controlling mechanisms, including heat transfer, mass transfer, and intrinsic kinetics.

In the hydrate growth models with heat transfer rate dominated, temperature has a highest impact on CO₂ hydrate growth rate which is

controlled by conductive and convection heat transfer [163,164]. Uchida et al. proposed a model (Equation (1)) for CO₂ hydrate film growth which is controlled by temperature gradient [165].

$$\vartheta\lambda^{-1} = (L\rho_c r_c)^{-1} \Delta T \quad \text{Equation 1}$$

where ϑ is rate of CO₂ hydrate film, λ is the thermal conductivity, L is latent heat of the hydrate formation, ρ_c is CO₂ hydrate density, and ΔT is the temperature difference. Peng et al. also demonstrated that CO₂ hydrate growth rate depends on temperature and NaCl concentration [166].

In the mass transfer dominated hydrate growth rate, CO₂ gas dissolution is the rate-dominated step. Zhou and Ferreira proposed Equation (2) for mass growth rate of CO₂ hydrate (G) which is controlled by mass transfer [167] (k_l is CO₂ mass transfer coefficient from bulk liquid to the crystal, ρ_{sol} is solution density, A_h is hydrate layer area, $x_b^{CO_2}$ and $x_{int}^{CO_2}$ are the CO₂ mole fraction in the bulk liquid and liquid-crystal layer in equilibrium respectively).

$$G = k_l \rho_{sol} A_h (x_b^{CO_2} - x_{int}^{CO_2}) \quad \text{Equation 2}$$

Intrinsic kinetics of CO₂ hydrate can be also investigated by eliminated the effect of mass and heat transfer using stirred tank reactor [168–170]. In intrinsic model, the fugacity difference between CO₂ dissolved gas and three-phase equilibrium ($f - f_{eq}$) is proposed as an overall driving force for hydrate crystallization [170]. The chemical potential difference or mole difference was also introduced as a driving force [171,172]. Clark and Bishnoi used Equation (3) to describe the intrinsic kinetics of CO₂ hydrate [168] ($R_y(t)$ is reaction rate, K^* is overall rate constant around hydrate particle, and μ_2 is second moment of particle size distribution).

$$R_y(t) = \pi K^* \mu_2 (f - f_{eq}) \quad \text{Equation 3}$$

When mass and heat transfer resistance are negligible, the overall rate constant (K^*) is approximately equal to intrinsic rate constant of hydrate formation. Clark and Bishnoi reported the intrinsic rate constant of CO₂ hydrate in the range of 3.214×10^{-3} – 6.423×10^{-3} (mole/m²Pa s) [168].

Heat transfer, mass transfer, and intrinsic kinetics cannot be ignored and may control the CO₂ hydrate growth simultaneously [173]. Ota et al. described the kinetics of CO₂ gas hydrate by considering both controls mechanisms of mass transfer and intrinsic kinetics [174]. One such model is introduced by Sarshar et al. which describes the growth of CO₂ hydrate crystals in terms of heat transfer, mass transfer, and intrinsic kinetics [175].

3.2.5. CO₂ hydrate properties

Thermophysical properties and bulk properties of CO₂ hydrate are essential for studying gas hydrate in the sediment and simulating carbon sequestration using gas hydrate. CO₂ hydrate density is required for accurate modelling and simulation of carbon injection into cold saline aquifers or deep ocean storage of CO₂, where the density of CO₂ hydrate plays an essential role in determining the final distribution of CO₂. To measure the density of CO₂ hydrate and understand its relationship with temperature and pressure, several steps are involved. Initially, the structure and composition of CO₂ hydrate are determined through experimental techniques like X-ray diffraction or theoretical techniques such as Monte Carlo Simulation. This provides crucial information about the lattice parameter and composition which are required for density estimation. Subsequently, the density of CO₂ hydrate can be estimated by considering factors such as cage occupancy and the temperature-pressure dependence of unit-cell parameters. By analysing how these parameters vary with temperature, the density-temperature/pressure relationship of CO₂ hydrate can be determined. Density of CO₂ hydrate measured by different techniques at some conditions are listed in Table 1.

As mentioned, to estimate CO₂ hydrate density, it is essential to know the lattice parameter and composition. As pressure increases, CO₂ molecules tend to fill both small and large cages in sI. While hydrostatic pressure causes lattice compression and decreasing hydration number, the lattice parameter increases with temperature due to thermal expansion. The lattice parameter of CO₂ hydrate as a function of pressure and temperature is shown in Fig. 6. As shown in Fig. 6 (a), lattice parameter of CO₂ hydrate can increase from 11.83 Å at 8 K to 11.97 Å at 270 K at atmospheric pressure.

Some other thermos-physical properties of CO₂ hydrate reported in the literature are listed in Table 1. While molecular dynamic simulation was used to estimate the dissociation heat of CO₂ hydrate [127], experimental techniques using a calorimeter and Clausius Clapeyron equation have been used to measure the dissociation heat as listed in Table 1. Dissociation heat of CO₂ hydrate could be in the range of 50–70 kJ mol⁻¹, and is directly related to pressure, temperature, and hydration number. The hydration number of CO₂ hydrate as a function of temperature at different pressure is also plotted in Fig. 7 (b). The results reveal that the hydration number decreases at low temperature and high pressure, indicating that CO₂ molecules tend to fill both small and large cages in sI.

Furthermore, heat capacity of hydrate is a vital parameter to control the CO₂ hydrate dissociation when the thermal dissociation of hydrate occurs in the sediment. While there are several data for the heat capacity of hydrates (e.g., methane) [190], there are limited data for CO₂ hydrate. The specific heat capacity of CO₂ hydrate predicted by PVTsim is shown in Fig. 7 (a), which is in the range of values predicted by Mathews et al. [191]. Ning et al. also used molecular dynamics to predict the specific heat capacity of CO₂ hydrate between ~2100–2700 (J Kg⁻¹ K⁻¹) [188] which is much higher than Mathews et al. [191]. Therefore,

Table 1

Reported thermo-physical properties of CO₂ hydrate.

Hydration Number	Density (Kg/m ³)	Dissociation Heat (KJ/mole)	Temperature (K)	Pressure (bara)	Method	Reference
6.2	1140		173		X-ray diffraction	Udachin et al. [89]
6.5	1105		268	1	X-ray diffraction	Takeya et al. [91]
5.75	1126.2–1179.9		150–280	40–500	Monte Carlo Simulation	Ferdows and Ota [127],
7.67	1050.1–1093.3					
7.3	1090–1110	35.57	285.15	300	Heat Exchange	Aya et al. [176]
7.3	1110	58.2–61.5	273–283	1	Clausius Clapeyron	Bozzo et al. [177]
5.9–6		66.6–69.6	277.15–281.15	19.9–33.4	Clausius Clapeyron	Fournaison et al. [178]
5.75–6.4		58.2–62.5	274.15–282.15	13.7–38.6	Clausius Clapeyron	Anderson [99]
		56.85–75.37	273.15–282.06	10.5–36	Clausius Clapeyron	Sabil et al. [179]
6.21		57.66	273.15		Clapeyron	Yoon et al. [102]
6.6–7.9		63.1–70.8	275.3–279.9	15.9–28.6	Clapeyron	Lirio et al. [180]
		50.3–58.4	276–280	17–31	Clapeyron	Ohgaki et al. [181]
7.23		65.22 ± 1.03	273.65	1	Calorimetry	Kang et al. [182]

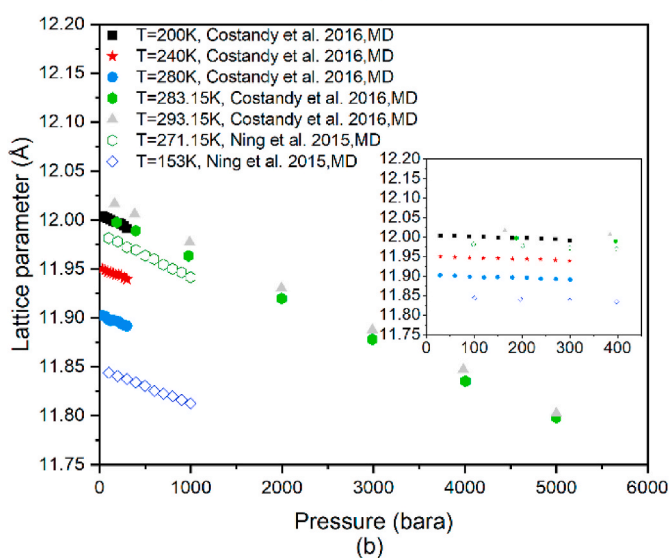
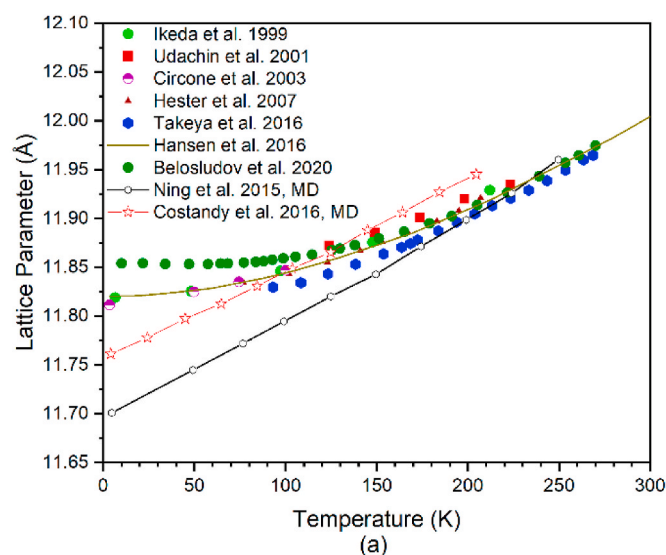


Fig. 6. Lattice parameter of CO₂ hydrate (a) as a function of temperature at atmospheric pressure [89,91,183–189] (b) as a function of pressure at constant temperature [188,189]. (MD: molecular dynamic).

further research is required to experimentally measure CO₂ hydrate heat capacity.

Interfacial properties in CO₂-water-hydrate system, including contact angle and interfacial tension (IFT), play an essential role in hydrate nucleation, crystallization, and growth. The experimental observation

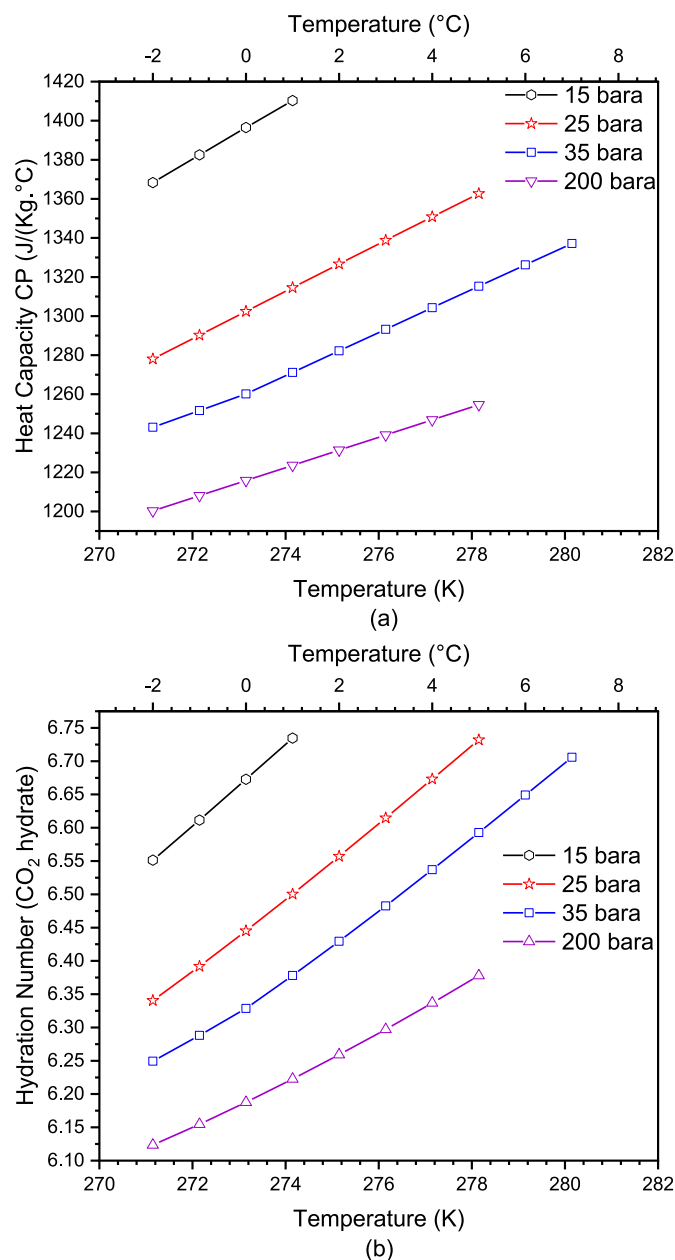


Fig. 7. Specific heat capacity (C_p) and hydration number for CO₂ sI hydrate predicted by PVTsim using the SRK-CPA equation of state.

using the pendant drop method indicates that the summation of interfacial tension between liquid CO₂ and CO₂ hydrate and between water and CO₂ hydrate is less than between water and liquid CO₂ [192]. Further studies about the effect of IFT on the kinetics of CO₂ hydrate reveal that hydrate growth rate increases as IFT decreases [193]. Interfacial phenomena have also a crucial role in hydrate inhibition where thermodynamic hydrate inhibitors (e.g., methanol) can change the solubility of CO₂ and hydrocarbon components [194,195].

3.2.6. Phase equilibria: CO₂ hydrate

Various experimental and numerical methods have been used to explore the equilibrium condition of CO₂ hydrate. The hydrate dissociation point can be determined using various techniques [196] including visual observation or graphical analysis through isochoric [197], isothermal [198], or Isobaric [199] process using autoclave cell [30], differential scanning calorimetry [200], and microfluidic device [201]. Among the different techniques to measure hydrate dissociation point,

nonvisual techniques combined with step heating in the isochoric approach is the most popular technique [202]. In this method, the hydrate dissociation point is measured by the intersection of cooling and heating curves which can be determined by measuring a few equilibrium points. However, Aminnaji et al. (2021) indicated that various clear heating curve slopes could be observed in the multicomponent systems due to the presence of various hydrate structures, therefore, the step heating method could result in the wrong equilibrium dissociation point [30,196].

Furthermore, numerical modelling using equation of state (EoS) has been used to predict gas hydrate equilibrium state [203]. A multiphase flash using CPA combined with Peng–Robinson was used to describe the fluid phases and vapour-liquid-hydrate equilibrium [204]. It is concluded that CPA can better predict the phase equilibria of CO₂ hydrate [205]. In fact, the CPA considers the chemical/quasi-chemical associative hydrogen bonds contribution through the associating sites and strength. Particularly, for CO₂ hydrate modelling, the guest-guest interactions should not be ignored in CPA due to the rich orientation landscape of CO₂ molecules in structure I hydrate [98].

To predict hydrate equilibrium using EoS, it is required to calculate the chemical potential and fugacity of molecules in the hydrate phase. This is achieved by various models that calculate the molecule-cell interaction potential while assuming spherically symmetric conditions, i.e., Zhang et al. compared the accuracy of vdW-P model, Parrish–Prausnitz model, John–Holder mode, and Chen–Guo model for the prediction of CO₂ gas hydrate equilibrium curve [206]. However, density functional theory (DFT) calculations for CO₂ gas hydrates shows that CO₂ molecule - cell interaction potential is anisotropic and asymmetric. Therefore, spherical approximations for guest molecule-hydrate interaction may not be sufficient for CO₂ hydrates [207].

Molecular dynamics (MD) simulation has been also used to measure the phase equilibrium [208]. MD was used to study CO₂ hydrate growth/dissociation and the mechanism involved in the guest involvement or replacement in the hydrate crystals [209–212]. Three phase equilibrium of hydrate + liquid water + liquid CO₂ was analysed from 2 MPa to 500 MPa using the MD simulation [213]. It is pointed out that a positive deviation from Lorentz-Berthelot combining rules must be considered for accurate prediction [213]. Different water and CO₂ molecular models (TIP4P/Ice, TIP4P/2005, SPC/E, SPC/Fw) were also examined to predict CO₂ hydrate stability and dissociation [214]. The growth and equilibrium temperature of CO₂ hydrate up to 100 MPa were also analysed using MD simulation [215]. It is demonstrated that although sI hydrate is stable at below 100 MPa, the emergence of unstable medium-sized 4¹5¹⁰6² cages may affect the CO₂ hydrate growth [215].

Figs. 8 and 9 show experimental data illustrating the phase equilibrium and hydrate phase boundary for CO₂+water system at low and high pressure, respectively. The CO₂ liquid-gas equilibrium line and ice melting equilibrium line divide the global phase diagram of CO₂ into different sections that are equilibrated with CO₂ hydrate. The trend of CO₂ hydrate equilibrium curve depends on the presence of other phases, i.e., as shown in Fig. 8, the quadruple points of Q₁ and Q₂ change this trend significantly.

As shown in Fig. 9, the re-entrant phenomenon of CO₂ hydrate is observed at a very high pressure. An equilibrium temperature of 294 K at 328 MPa is reported as a maximum temperature that CO₂ hydrates can form [222]. At very high pressure, the hydrate structure shrinks due to the reduction in the size of hydrate cages, so they become too small to stabilize the gas molecules. Hydrate re-entrant behaviour of CO₂ is also indicated at high pressure by MD simulation [213]. The s-I CO₂ clathrate hydrate can be stable up to 0.7–0.8 MPa as shown in Fig. 9. However, above this pressure, s-I CO₂ hydrate is no longer stable and a new high-pressure phase (filled ice-like framework) forms between 0.8 and 1 GPa [223].

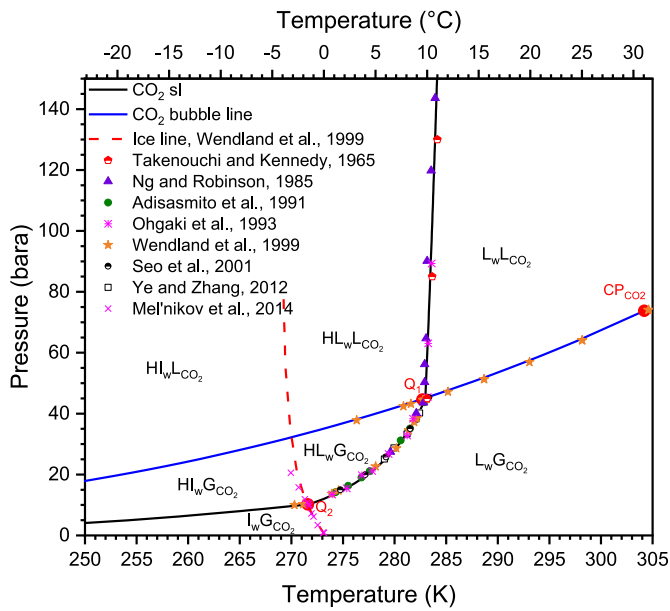


Fig. 8. Hydrate phase boundary and phase equilibrium for CO₂+water up to 150 bara. Black and blue solid lines are CO₂ hydrate phase boundary and CO₂ liquid-vapour equilibrium predicted by PVTsim. Dashed red line is ice melting equilibrium line for water saturated with CO₂ [216]. The other equilibrium data points are taken from Refs. [181,197,216–221]. H=CO₂ hydrate, L_{CO2}=Liquid CO₂, G_{CO2}=Gas CO₂, L_w = liquid water, I_w = Ice water, CP = critical point, Q = quadruple point. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

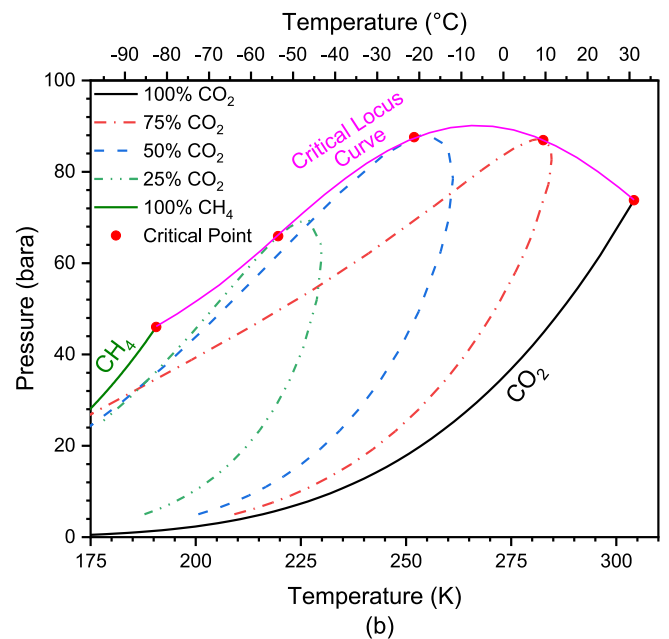
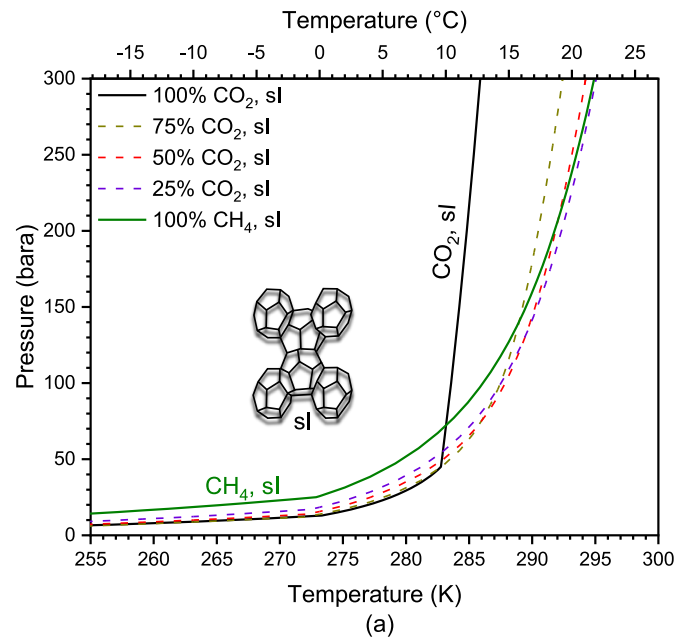


Fig. 10. (a) Hydrate phase boundary and (b) Phase envelop for mixture of CO₂ and CH₄ predicted by PVTsim.

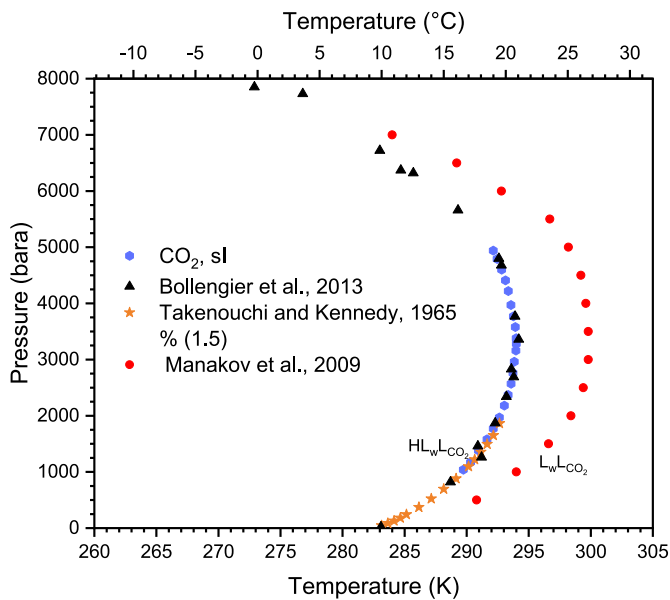


Fig. 9. Hydrate phase boundary for the system of CO₂+water up to 8000 bara. The equilibrium data points are taken from Refs. [222,223,218,224].

3.2.7. Phase equilibria: CO₂ replacement in methane hydrate

Phase equilibria and hydrate phase boundary of CO₂ with other gas components (e.g., methane and nitrogen) are discussed in this section. Fig. 10 shows the hydrate phase boundary and phase envelope of CO₂+CH₄ gas mixture at different compositions. Hydrate phase boundary shifts to the lower pressure at a particular temperature by adding more stable guest molecules (e.g., adding more CO₂ to CH₄). At lower pressure, hydrate pressure formation of CO₂ is lower than CH₄ at a particular temperature. It indicates that HL_wL_{CO2} molecules are more

thermodynamically stable than CH₄ molecules in hydrate sl. In contrast, at higher pressure where CO₂ is liquid, the hydrate pressure formation of CO₂ becomes more than CH₄ at a particular temperature. This has come up with the idea of CO₂ injection into the hydrate reservoir to be replaced with methane in the clathrate cages. This process of methane replacement with CO₂, which is an exothermic process [225], not only helps with carbon storage but also induces methane production from gas hydrate reservoir. Injection of flue gas (CO₂-N₂ mixture) into the hydrate reservoir shows some promising advantages over pure CO₂ injection [226]. So, various studies have investigated the thermodynamic process [227] and hydrate stability zone of flue gas with methane [228–232]. A comparison of hydrate phase boundaries for CH₄, CO₂, N₂, and a mixture of flue gas is shown in Fig. 11.

3.2.8. CO₂ hydrate in the presence of other components

The syngas, flue gas, and biogas usually consist of other components

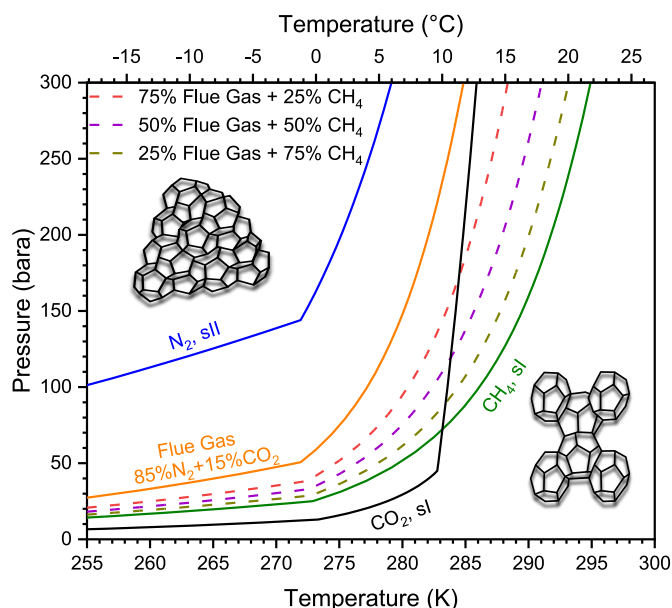


Fig. 11. Hydrate phase boundary for CH_4 , CO_2 , N_2 , and flue gas predicted by PVTsim.

such as NO_x (nitrogen oxides), SO_2 (sulfur dioxide), O_2 (oxygen), CO (carbon monoxide), H_2S (hydrogen sulfide), H_2O , Hg (Mercury), As (Arsenic), Ar (Argon), H_2 (hydrogen), etc. Those impurities that can form a more thermodynamically stable hydrate than CO_2 shift the hydrate phase boundary of CO_2 hydrate to the lower pressure. For example, the molecular dynamic simulation shows that the clathrate hydrate of H_2S and SO_2 is more stable than CO_2 hydrate, therefore, a high content of these impurities can reduce the efficiency of carbon capture and storage by hydrate technology [233]. The molecular dynamic simulation also shows that while SO_2 tends to encage the large cages, H_2S tends to encage the small cages [233] which have been confirmed by others [234–236]. The Laser Raman Spectroscopy shows SO_2 molecules can be encaged in both small and large cages in CO_2 hydrate lattice and increase the stability of CO_2 hydrates [237]. In contrast, those impurities that are less stable than CO_2 hydrate shift the hydrate phase boundary to the higher pressure. For example, N_2 , O_2 , and Ar hydrates are less thermodynamically stable than CO_2 hydrates.

Fig. 12 shows the phase boundary of some pure components that potentially exist in the flue gas. The hydrate phase equilibria of CO_2 rich system in the presence of some impurities (e.g., N_2 , CH_4 , O_2 , Ar , and CO) were measured experimentally and modelled using CPA by Chapoy et al. [238]. The hydrate phase boundary of binary systems of CO_2 – N_2 and CO_2 – CH_4 (or a mixture of CO_2 + N_2 + CH_4) in the water or brine were also experimentally measured and predicted by Herri et al. [239], Zheng et al. [240,241], Legoix et al. [242], Zang et al. [243], Li et al. [244], and Chazallon and Pirim [245].

Impurities in the flue gas can form different hydrate structures. Both nitrogen [246] and Argon [247] are known to form hydrate structure II. The neutron powder diffraction also confirms the formation of oxygen structure II hydrate [248]. In contrast, hydrogen sulphide and methane tend to occupy the tetrakaidecahedrons ($5^{1,2}6^2$) and dodecahedrons (5^{12}) cages, respectively, and they form structure I hydrate [249,250]. In-situ Raman spectroscopy shows that the selectivity of CO_2 capture in structure II is lower than in structure I in CO_2 + N_2 system [245].

Phase equilibrium of CO_2 hydrate has also been investigated in the presence of other components, such as cyclopentane and hydrogen. The hydrate phase equilibrium of CO_2 and cyclopentane is experimentally measured and modelled by Babakhani et al. [251]. They reported that various hydrate structures (structures I and II) can form in CO_2 +cyclopentane mixture [251]. The CO_2 + H_2 hydrate has also been

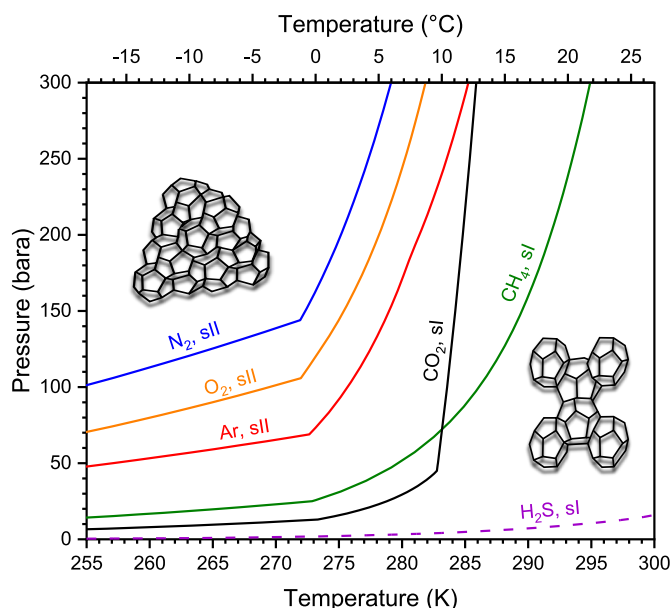


Fig. 12. Hydrate phase boundary for pure methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), Oxygen (O_2), argon (Ar), and hydrogen sulphide (H_2S) predicted by PVTsim.

studied due to its different applications, including increasing gas recovery by injection of CO_2 + H_2 mixture into the hydrate reservoir [252–254], hydrogen hydrate storage [255], and CO_2 separation [256]. Xie et al. showed that the small concentration of H_2 and N_2 enhances the effectiveness of CO_2 replacement in methane hydrate reservoir [257]. The Raman, neutron, and x-ray show that pure hydrogen form structure II hydrate [258]. However, Xie et al. demonstrated that H_2 can be encaged both in 5^{12} and $5^{1,2}6^2$ cages in the form of CO_2 + H_2 structure I [259, 260]. They reported the coexisting of CO_2 and H_2 in the large cavity of structure I ($5^{1,2}6^2$) [259]. It is also reported that several hydrogen molecules can occupy the cages in the hydrate structures [261]. Skiba et al. experimentally measured the hydrate phase equilibria of the CO_2 + H_2 mixture and the hydrogen solubility at different H_2 concentration [262].

It has been shown that the impurities of N_2 and CH_4 can reduce CO_2 storage capacity due to the change in the hydrate stability zone [263]. The impurities and hydrates can also change the fluid properties. The solubility measurement under the hydrate-liquid-vapour equilibrium has been investigated by many researchers for various CO_2 +impurities systems, including CO_2 + CH_4 [264,265], CO_2 + N_2 [266], and CO_2 + CH_4 + C_2H_6 [267]. An experimental investigation and thermodynamic models were implemented by Chapoy et al. to investigate the effect of impurities such as N_2 , O_2 , and Ar on the phase behaviour of CO_2 hydrate [268]. They reported that these impurities can change some thermophysical properties of pure CO_2 by decreasing the density (up to 35 %) and water dissolution (10–30 % lower than pure CO_2) [268]. There are some other impurities (e.g., metal nanoclusters [269], nanoparticles [270], TBAB [271], THF [272], etc.) that could be deliberately used to change the hydrate stability region or promote CO_2 hydrate formation, which are discussed in next section.

4. Hydrate-based carbon capture

CO_2 capture could be undertaken in pre-combustion, oxy-fuel combustion, or post-combustion. In pre-combustion, CO_2 is removed from fuels before utilisation. For example, the process involves the partial oxidation of coal using air or oxygen to produce a synthesis gas composed of hydrogen, carbon monoxide, and a small amount of methane. In a gas clean-up stage, CO is converted to CO_2 , resulting in a

synthesis gas with CO₂ and H₂ concentrations of around 40 % and 50 %, respectively. The CO₂ is then removed from the gas resulting in H₂-rich gas [273,274].

In oxy-fuel combustion (combustion in an oxygen-enriched atmosphere) exhaust gas with high concentrations of CO₂ and water vapour with minimum nitrogen are produced. This high content of CO₂ gas can be removed through the CO₂ drying and compression. However, to produce oxygen for combustion, the air separation process is required, i. e., oxygen purity of approximately 95 % [275].

On other hand, post-combustion technologies are often preferred for existing conventional power units [276]. In this process, carbon capture process is employed after fuel combustion to remove CO₂ from the low concentration of CO₂. For example, a typical exhaust gas from coal-based power plants consists of N₂, CO₂, O₂, H₂O, and some impurities (e.g., SO₂, and NO₂). The CO₂ partial pressure and concentration (e.g., 13–15 %) are low in the flue gas, therefore, it results in a low driving force for carbon capture [275,277,278]. The processes of CO₂ separation in oxy-fuel combustion, post-combustion, and pre-combustion are shown in Fig. 13. The aforementioned approaches for carbon capture have different physical and chemical processes as shown in Fig. 14.

Among the various techniques, hydrate-based carbon capture (HBCC) is one of the carbon capture technologies, which is discussed in this section.

4.1. Hydrate-based decarbonisation fundamentals

Hydrate-based CO₂ separation is a promising technology that uses gas hydrates to separate CO₂ from gas mixtures [19,279]. Hydrate-based technology can also be applied to separate other gases such as Xenon from Noble Gas Mixtures [280]. The process involves the formation of CO₂ hydrates, followed by dissociation, effectively separating CO₂ from a gas mixture (Fig. 15). Due to the differences in the phase equilibria of

CO₂ in the presence of the other gases, CO₂ is trapped in the hydrates and CO₂ separation can occur effectively [281]. This process typically occurs at low temperature and high-pressure [282]. The amount of CO₂ that can be accommodated in the CO₂ hydrates depends on several factors, such as pressure, temperature, and the composition. For example, Raman spectroscopy was used to investigate the trapping efficiency of HBCC technology for CO₂-N₂ and CO₂-CO [283]. The findings indicated a higher efficiency for CO₂-N₂ mixture at low CO₂ concentration.

This method offers several opportunities, including a cost-effective (low capital investment) and energy-efficient alternative to traditional methods [284,285]. Moreover, applying the hydrates as a transport medium for CO₂ is another economic benefit [286,287]. Low energy requirements of HBCC and the possibility of using waste heat sources to feed and drive the process attract lots of attention in research society [288,289]. In a method developed by Obara & Tanaka (2021), the waste heat from nuclear power plants has been used to operate a hydrate heat cycle [288].

Further application of the HBCC is in natural gas processing, in which this technology can be used to remove CO₂ from natural gas streams to enhance purity [290,291]. This application is also extended to separating CO₂ from fuel or flue gases emitted from power plants, cement factories, and other industrial sources [226,279,292,293].

One of the challenges in HBCC is how to increase the rate of hydrate formation. The importance of intricate interaction between CO₂ and water molecules in the hydrate structure can dictate the efficiency of CO₂ capture process. Different scale study of HBCC is critical in enhancing our understanding of this process. By exploring at micro to meso-scale, the research community can gain insights into fundamental governing mechanisms, including hydrate formation, growth, and dissociation. In terms of CO₂ hydrate promoters, experimental data on micron-scale crystallographic features are lacking, creating a gap between single scales such as macroscopic temperature-pressure variations

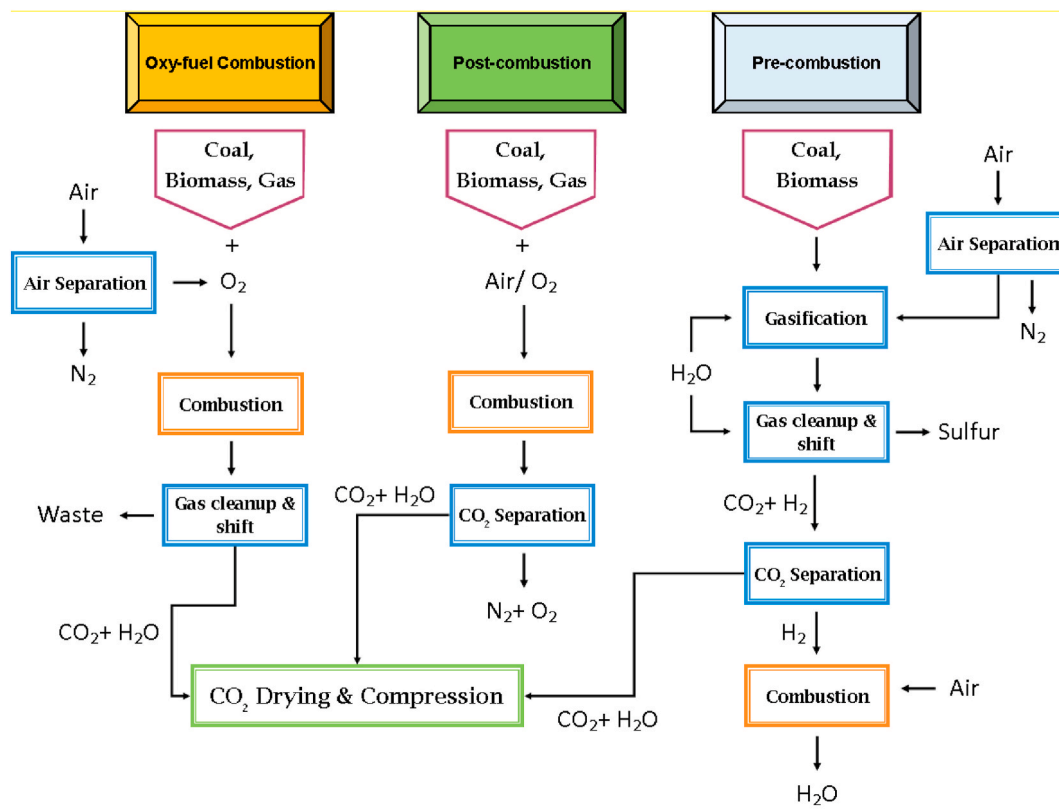


Fig. 13. CO₂ separation in oxy-fuel combustion, post-combustion, and pre-combustion.

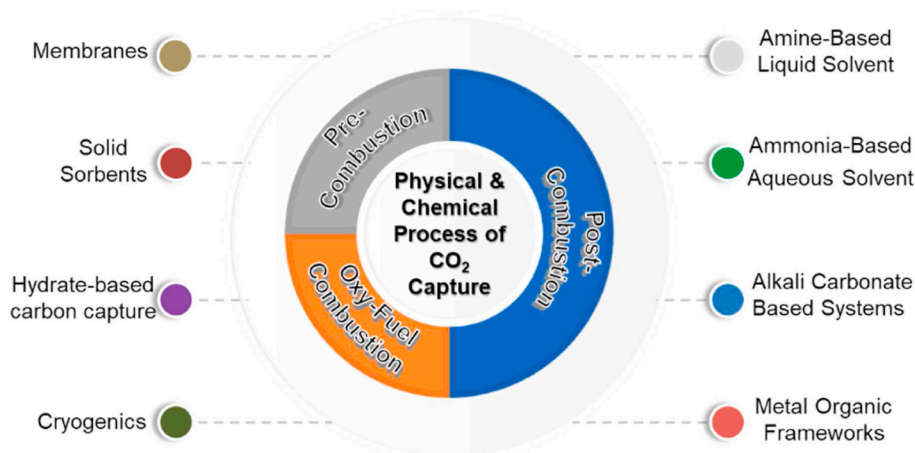


Fig. 14. Various physical and chemical processes involved in CO₂ capture.

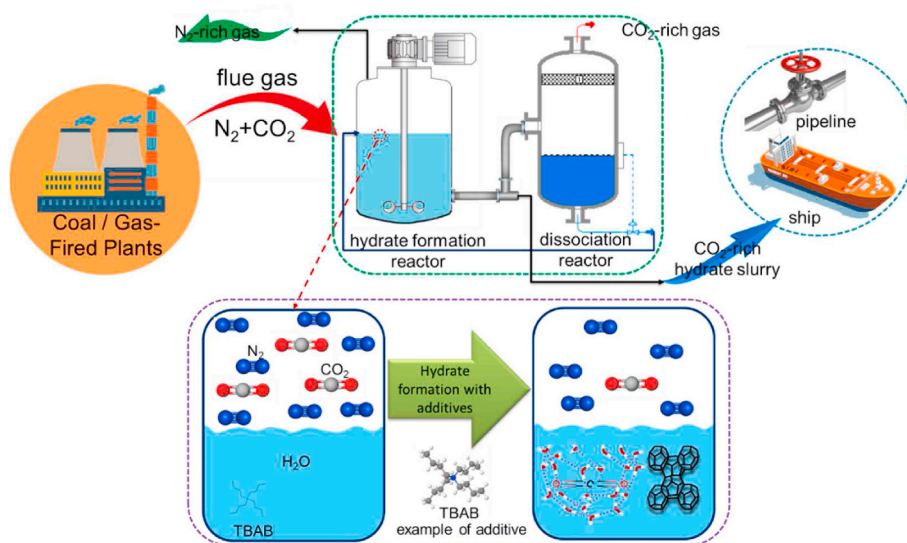


Fig. 15. Schematic process for hydrate-based CO₂ capture from flue gas.

[294] and molecular-scale spectroscopic features [295]. Nanobubbles have been investigated as an alternative approach, particularly in the context of natural gas hydrates [296]. These nanoscale gas-filled bubbles have the potential to enhance the nucleation process through heterogeneous mechanisms. Additionally, their presence can impact the selectivity of gas hydrates. Introducing hydrophobic and hydrophilic surfaces can also effectively facilitate nanobubble generation, leading to rapid hydrate formation [297–299]. However, the operational challenges associated with nanobubble hydrate systems have constrained the accuracy of this approach.

The significant challenge in the micro and meso-scale studies of CO₂ hydrates is due to the limitations of the current experimental and computational techniques. It is required to develop novel experiments, along with innovative computational models. To achieve this, multidisciplinary research collaborations are greatly important.

Enhancing the discussion on hydrate-based decarbonisation fundamentals with recent advancements delivers a clearer picture of the potential and challenges in hydrate-based CO₂ separation technologies. The addition of novel materials and methodologies offers promising paths to improve the efficiency and feasibility of CO₂ capture, a critical step toward sustainable environmental solutions.

A study by Liu et al. (2021) delved into the kinetics of the CO₂ hydrate formation in the presence of acid-dissolvable organic matters,

suggesting that the marine sediment's organic composition significantly influences CO₂ sequestration efficiency [300]. Moreover, the interaction between metal-organic frameworks (MOFs) and CO₂ gas hydrates heralds a transformative era for CO₂ capture and methane storage techniques [301]. MOFs, characterised by their large specific surface areas and pore sizes, present an unparalleled scaffold that significantly advances the thermodynamics and kinetics of CO₂ hydrate formation. This synergy expands the selection of materials within hydrate-based applications and highlights the fundamental role of rigorous research into MOF-CO₂ hydrate interactions. Such research could help develop more proficient CO₂ capture approaches and storage solutions. The attractive findings from studies on MOFs coupled with hydrates call for a concerted effort across scientific disciplines. This multidisciplinary approach is necessary to deepen our comprehension of these complex systems and to plan innovative and eco-friendly strategies for CO₂ management.

Additionally, leveraging the synergy between MOFs and hydrates, particularly for CH₄ storage, has showcased extensive potential, indicating an enhanced capacity for CH₄ containment under milder conditions compared to traditional methods [301]. The unique physicochemical properties of MOFs facilitate the formation of hydrates, thus increasing the volumetric and gravimetric storage densities. This harmonious integration of MOFs with gas hydrates lays the groundwork

for novel approaches that could revolutionise the energy sector. As global energy demands burgeon, these findings catalyse the hunt for sustainable energy practices, ensuring that CH₄, a critical component of natural gas, is utilised efficiently and responsibly. The empirical evidence from various studies propels this field toward the threshold of innovation, where sustainable practices meet the escalating energy needs of tomorrow.

Expanding the understanding of material effects on CO₂ hydrate formation, Yan et al. (2018) assessed the role of graphene oxide (GO) nanoparticles, showcasing their efficacy in promoting CO₂ hydrate formation under varied temperature and pressure conditions [302]. The ability of GO nanoparticles to substantially moderate induction time and enhance gas consumption presents a novel method to improve the kinetics of hydrate formation, highlighting the importance of nano-materials in developing competent CCS solutions.

Liu et al. (2022) investigated the carbonation behaviour of calcium silicate hydrate (C–S–H) [303], delivering a deeper understanding of C–S–H's potential for CO₂ capture through a detailed analysis of its carbonation kinetics and the evolution of carbonation products. The study highlights the role of environmental and material properties in influencing carbonation, offering insights into CO₂ sequestration using cementitious materials.

Addressing the role of saline conditions, Mok et al. (2023) investigated the NaCl-induced improvements in CO₂ selectivity during hydrate formation [304]. Their results highlight the nuanced impact of salts on both the thermodynamic and kinetic aspects of hydrate formation, emphasising the significance of considering saline water's influence on CO₂ sequestration strategies. The application of molecular dynamics simulations to study CO₂ hydrate growth in salt-containing electrolyte solutions by Wang et al. (2023) offered critical insights into how salt ions and thermodynamic conditions affect hydrate growth rates [305]. This study provides a fundamental understanding of seawater's CO₂ hydrate generation mechanism, guiding the future development of CO₂ sequestration technologies via hydrate formation in marine environments.

In rounding off the discussion on hydrate-based decarbonisation fundamentals, the potential of this technology stretches beyond current applications. Advances in understanding the microscopic and macroscopic mechanisms of hydrate formation hold the promise of optimising CO₂ capture processes to meet the constraints of environmental sustainability. As we continue exploring the complex dynamics of CO₂ and CH₄ hydrates, particularly in the presence of MOFs and other novel materials, bridging the gap between laboratory-scale research and large-scale applications is crucial. The challenge lies in translating these elaborate interactions and kinetic behaviours into commercially viable solutions that can contribute to global efforts to reduce carbon footprints. This interest is not just a scientific endeavour but a collaborative mission that calls for aligning research, industry, and policy-making to connect the full potential of hydrate-based technologies for a greener future.

4.2. Hydrate-based decarbonisation scale-up

Scaling up hydrate-based decarbonisation from laboratory experiments to industrial-scale operations presents opportunities and challenges. The scale-up process involves both technical and economic challenges, such as the thermodynamic understanding of the process for operation at high pressure and low temperature and the equipment and energy cost. One of the critical opportunities lies in its energy efficiency compared to other CCS technologies. The moderate operating temperature and pressure in HBCC make this process a potentially cost-effective solution for large-scale industrial applications [306]. The challenges in scaling up HBCC processes can be categorised into four areas.

1. Technical challenges: gas hydrate formation requires precise control over temperature and pressure conditions. The main technical

challenge in this process is to maintain these thermodynamic conditions on a large scale [307]. Developing novel materials and processes that can facilitate hydrate formation under milder conditions is a crucial area of future research. For instance, using promoters or additives, such as surfactants, can lower the pressure and temperature requirements for hydrate formation [308,309]. The other technical challenge is the hydrates blockage in the equipment. Research is needed to develop effective anti-agglomerants and strategies for hydrate management to ensure the smooth operation of HBCC. Further, hydrate-forming performance in gas-dispersion reactors depends on gas dispersion quality and heat-discharge capacity, both of which can deteriorate with scale-up [310]. Stirred-tank reactors face a major scale-up disadvantage due to a significant increase in required stirrer-driving power. In contrast, multiple-tube reactors can be scaled up more efficiently by increasing the number of tubes or tube diameter without drastically increasing flow velocity [310]. However, these findings by Mori (2015) are based on simplified models and do not account for potential issues like wall fouling or hydrate crystal formation, which could obstruct operation.

2. Economic challenges: The cost of implementing and operating a HBCC process on a large scale still needs to be comprehensively investigated. However, the costs for this process are relatively high due to the need for specialised equipment and energy required to maintain the necessary conditions for hydrate formation [310]. More recent research points to promising improvements. For instance, Nguyen (2022) [311] and Rezaei (2022) [312] provide more optimistic projections. Nguyen (2022) estimates the cost of HBCC to be 20–40 US\$/tonnes of CO₂ avoided with an energy penalty of 15 %, making it potentially competitive with conventional absorption methods [311].
3. Efficiency Challenges: While HBCC demonstrates effectiveness on a small scale, it remains to be seen how efficient the process would be when scaled up [307]. Further research is necessary to ascertain the potential efficiency of large-scale operations.
4. Environmental Challenges: Although HBCC is a promising technology, there are concerns about the potential environmental impact of large-scale operations [313]. These concerns include the potential for CO₂ leaks and the effects on local ecosystems. This challenge will be applied to any other CCS process.

The design and optimisation of HBCC is also a critical area of research. This involves the development of mathematical models and simulation tools to predict hydrate behaviour and guide the design of efficient and robust systems. Integrating HBCC with other processes, such as power generation or industrial processes, can enhance its feasibility and efficiency. Research is needed to explore such integration opportunities and assess their technical and economic viability. In conclusion, the scale-up of HBCC is a complex and multifaceted process that requires research efforts linking science and engineering knowledge.

4.3. Advances to promote the process of HBCC

Chemical additives/promoters can enhance the process of CO₂ separation in HBCC. Hydrate promoters can increase gas consumption and hydrate production rate [314]. They work by altering the thermodynamical conditions, allowing hydrate formation at lower pressures and higher temperatures [315]. Chemical methods use thermodynamic and kinetic additives like tetrahydrofuran (THF) [316], tetrabutylammonium bromide (TBAB) [317], and cyclopentane (CP) [318] to moderate phase equilibrium. TBAB has been highlighted as an eco-friendly additive that reduces energy consumption and boosts CO₂ hydration. The orthorhombic TBAB.38H₂O.nCO₂ ionic clathrate is reported as the most effective lattice structure for CO₂ capture [319]. Kinetic additives such as sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), and cetyltrimethylammonium bromide (CTAB) are also

commonly employed [320,321]. Some additives have both thermodynamic and kinetic properties, i.e., 1,3-dioxolane (DIOX) shows the dual-action additive for the formation of hydrate [322,323]. Molecular dynamic simulation shows that promoters such as urea increases the CO₂ mass transfer and catalyses the cage formation [324]. Furthermore, some plants and fungi are reported to increase the kinetic formation of bio clathrate CO₂ [325].

Some non-ionic surfactants including Span80, Tween80, Span20 and Tween20 have also the ability to increase the hydrate growth rate [326]. They reduce the surface tension, promoting the dispersion of gas bubbles in the water phase [279]. This increases the contact area between the gas and water, facilitating the formation of hydrates and enhancing the efficiency of CO₂ separation.

Phan and Striolo (2023) employed molecular dynamics to study the effect of chemical additives, particularly aziridine, pyrrolidine, and THF, on CO₂ hydrate growth and dissociation [308]. They demonstrated that aziridine, while not reducing the nearly 30 wt% CO₂ storage capacity of the hydrates, outperformed the others in accelerating growth rates. Crucial to their findings was the correlation between the kinetics of CO₂ hydrate growth and factors such as the free energy barrier for CO₂ desorption and the binding energy of additives. The investigation also encompassed nitrogen-containing heterocyclic compounds at pressures of 25.5 bar and temperatures ranging from 269.1 to 289.1 K, where they showed promise as thermodynamic promoters. However, their effectiveness in shifting coexistence curves was less than THF. Mid-infrared (MIR) fiber-optic evanescent field sensing technique was also used to characterise IR absorption of some additives (e.g., THF and SDS) and their promoting effect [327]. Liu et al. (2023) investigated CO₂ capture by hydrates and reported that TBAB, CP, and THF enhance hydrate formation and CO₂ capture [328].

Hassan et al. (2020) investigated CO₂ hydrate formation in integrated gasification combined cycle (IGCC) conditions [329]. Using an isochoric system, they determined hydrate formation through CO₂ solubility in water. The study demonstrated increased CO₂ uptake with the expansion of ΔP , and combined promoter type T1-5 and T3-2 showed the best results, achieving 5.95 and 5.57 mmol of CO₂ per g of H₂O, respectively.

The prevailing trend in the field is the combination of different chemical promoters for CO₂ hydrate formation, potentially offering a more effective and efficient approach to CO₂ capture. As a response to the increasing interest in leveraging chemical promoters for CO₂ hydrate, Wang et al. explored the idea of combining different promoters to capitalise on their varying functionalities [271]. They investigated the impact of 0.244 g L⁻¹ SDS, 0.288 g L⁻¹ TBAB, and 0.33 g L⁻¹ nano graphite, both individually and in combination. Among the combined systems, SDS-TBAB yielded the best-promoting effect. Zhang et al. focused on exploring the impact of anionic surfactant SDS and cationic surfactant dodecyltrimethylammonium chloride (DTAC) on the kinetics of CO₂-TBAB hydrate formation, a crucial substance known for moderating CO₂ hydrate phase equilibrium but with a downside of decreasing CO₂ gas uptake [330]. The researchers utilised a batch reactor for conducting experiments with initial CO₂/N₂ gas mixtures, using 10-wt% TBAB and varied SDS concentrations (0–1500 ppm) and DTAC concentrations (0–0.6 wt%). The study metrics included induction time, normalised gas uptake, split fraction, and separation factor. Results indicated that SDS accelerated hydrate formation most effectively, while DTAC showed superior CO₂ separation performance. The study concluded with the need for further research on the mechanism of the blockage effects and the role of surfactant micelles on the kinetics of CO₂-TBAB hydrate formation.

The physical and chemical properties of the chemical additives is one the key important factors in CO₂ gas uptake during hydrate formation. For example, those additives with a strong polar ionic cause a formation of dense hydrate layer at the interface which results in decreasing of CO₂ gas diffusion and reducing CO₂ gas uptake [331]. On the other hand, the dissolution characteristics of weak polar or non-polar additives affect

the CO₂ gas uptake [331]. The liquid to the gas ration is also another factor in CO₂ gas uptake. It was demonstrated that the CO₂ storage capacity is maximised at 8.25 M liquid water–gas ratio which led to CO₂ gas uptake of ~9.1 L at standard condition [332].

One of the key mechanical methods used in HBCC is pressure control. By carefully controlling the pressure conditions under which hydrates form and dissociate, it is possible to optimise the CO₂ separation process. Temperature control is another critical mechanical method. Moreover, flow control is a critical aspect of HBCC. By controlling the flow rate of the gas and water, it is possible to optimise the contact between them, enhancing the formation of hydrates. Flow control can also help prevent the formation of large hydrate chunks that can cause blockage.

Mixing is a mechanical method that enhance the efficiency of HBCC. Mixing can be achieved through various means, such as agitation or static mixers. The mechanical method aims to enhance mass/heat transfer by introducing mechanical disturbances. However, conventional hydrate reactors like stirring [333], spraying [334], and bubbling reactors [335] could not meet the demands of large-scale hydrate formation and gas separation process. Some new reactor designs like a pilot-scale continuous jet hydrate reactor [336] and a high-speed spray device in the pipeline reactor [337] have been developed, aiming to enhance the gas–liquid interface and promote rapid formation of the gas hydrate. In a recent development, Xue (2023) conducted a study using a 15 L pilot-scale jet impingement stream reactor to separate CH₄ from CO₂ in biogas [338]. The reactor achieved a peak space velocity of 557 h⁻¹ and a maximum gas uptake of 1.00 mol L⁻¹ at 4.0 MPa. A CH₄ concentration of 50.0 % was increased to 70.0 % after the first stage of hydration separation and to 95.1 % after four-stage separation. CH₄ recovery rate and CO₂ capture ratio were found to be 58.8–78.2 % and 52.0–75.8 % in one stage, respectively.

While various mechanical methods have been used to enhance HBCC, there is still much room for improvement. Future research should focus on developing more efficient and reliable pressure, temperature, flow, and mixing control methods.

4.4. From laboratory to industrial scale: a scale-up framework

Scale-up of HBCC from laboratory to industrial scale presents a unique set of challenges. One of the primary challenges is the energy consumption. The energy required for hydrate formation/dissociation can be substantial, especially at industrial levels. This energy demand can pose a significant challenge. Moreover, the energy used in the process, if derived from non-renewable sources, could contribute to the very problem the technology is trying to solve.

In a study by Rezaei (2022), HBCC was integrated with membrane separation and amine-absorption techniques to design hybrid CO₂/H₂ separation processes [312]. The economic analysis, based on different flow rates and the application of various hydrate promoters, showed that combining hydrate formation and membrane separation resulted in the most cost-effective process, mainly when TBAB was used as a hydrate promoter. This combination resulted in a total cost of \$29.47 per ton of captured CO₂. Despite the increase in energy consumption for hydrate formation when TBAB was used, its high separation efficiency significantly reduced the overall cost of the process.

Dashti and Lou (2018) developed a model for estimating energy requirements in different stages of HBCC, taking into account the influence of various chemical additives [339]. The application of this model demonstrated that chemical additives, specifically THF, substantially reduced the total energy consumption through impacts on CO₂ hydrate formation and dissociation pressures and temperatures, as well as hydration kinetics.

Recent research has shown significant advances in scaling up HBCC. As highlighted by Surovtseva et al. (2011), an innovative CO₂ capture technology applied to integrated gasification combined cycle (IGCC) power plants effectively combines cryogenic condensation and hydrate formation, significantly reducing CO₂ concentration from 75 mol% to 7

mol% in a two-stage process [340]. This method demonstrated considerable effectiveness as up to 80 mol% of CO₂ could be captured.

Dashti et al. (2021) established a foundational approach for large-scale implementation of the HBCC process through the development of reactor-scale models [341]. Two distinct models were developed: a basic model, which focuses on estimating the role of mass and heat transfer during the dissolution phase, and an improved model that incorporates both dissolution and hydrate formation processes. The improved model identifies mass transfer as the rate-controlling mechanism, a significant insight that influences reactor operation strategy. Moreover, comparing these two models highlighted the substantial impact of the consumption/reaction term on the reactor profiles, further emphasising the necessity of considering hydrate formation for realistic process simulation. Using time-dependent boundary conditions for the bulk gas, the improved model was successfully applied to batch operations and scaled up using parameters such as volume, time, and length.

Safe and efficient CO₂ storage is critical to any CCS technology, including HBCC. Developing and implementing effective storage solutions is a complex task involving considerations related to geology, engineering, safety, and regulation. Furthermore, the transition from laboratory to industrial scale often involves dealing with issues related to the handling and storing large volumes of CO₂. Lastly, there are challenges related to integrating HBCC into existing industrial processes. These systems must be designed and operated to be compatible with existing infrastructure and operations. Despite these challenges, the potential benefits of HBCC make it a promising avenue for future research and development.

4.5. Advantaged and limitations of HBCC

HBCC presents a range of advantages, drawing attention to carbon sequestration technology. Foremost, it offers a higher storage density compared to conventional storage methods. One volume of hydrate structure can store approximately 160 vol of CO₂. The technology also provides a safer storage medium as CO₂ hydrates are more stable than gaseous or supercritical states, reducing the risk of accidental leaks. HBCC has flexibility in application; it can be used on power plant flue gases, industrial emissions, and even direct air capture. Additionally, it potentially facilitates the CO₂ transportation via pipeline, a practice already employed for natural gas. Finally, gas hydrate technology may enable the use of CO₂ in enhanced oil recovery.

Despite these advantages, the widespread application of HBCC is hindered by significant challenges. One of the main challenges is the slow kinetics of hydrate formation and decomposition. In practice, this sluggishness in the kinetics can potentially hinder the time effectiveness of the process. The formation of hydrates requires specific conditions, which may be energy-intensive to maintain. Moreover, separating CO₂ from other flue gas constituents using hydrates is not sufficiently efficient, requiring additional stages of gas treatment such as scrubbing with amines to remove contaminants like SO₂ and NO_x. The use of additives to promote hydrate formation is another concern, as these can have environmental implications. Lastly, the technology's readiness and commercial viability are still uncertain. The need for established large-scale demonstration projects for HBCC has resulted in a substantial shortage of data relevant to large-scale operation. As such, the economic assessments of this process mainly rely on theoretical or laboratory-scale studies.

CRedit authorship contribution statement

Morteza Aminnaji: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M Fahed Qureshi:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Hossein Dashti:** Writing – review & editing, Writing – original draft, Validation, Investigation,

Formal analysis, Data curation. **Alfred Hase:** Writing – review & editing, Validation, Methodology, Conceptualization. **Abdolali Mosalanejad:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Amir Jahanbakhsh:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Masoud Babaei:** Writing – review & editing, Validation, Methodology, Conceptualization. **Amirpiran Amiri:** Writing – review & editing, Validation, Methodology, Conceptualization. **Mercedes Maroto-Valer:** Writing – review & editing, Validation, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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