



HAL
open science

Zeolitic ice: A route toward net zero emissions

Ahmed Omran, Nikolay Nesterenko, Valentin Valtchev

► **To cite this version:**

Ahmed Omran, Nikolay Nesterenko, Valentin Valtchev. Zeolitic ice: A route toward net zero emissions. Renewable and Sustainable Energy Reviews, 2022, 168, pp.112768. <10.1016/j.rser.2022.112768>. <hal-03725296>

HAL Id: hal-03725296

<https://hal.science/hal-03725296v1>

Submitted on 8 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Zeolitic Ice: A Route Toward Net Zero Emissions

Ahmed Omran^a, Nikolay Nesterenko^b, Valentin Valtchev^{c,*}

^{a,*}Normandie Université, ENSICAEN, UNICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

^bTotalEnergies One Tech Belgium, Zone Industrielle C, 7181, Seneffe, Belgium

^cNormandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

*To whom correspondence should be addressed:

(Valentin Valtchev) valentin.valtchev@ensicaen.fr; Tel: +33 (0)2 31 45 27

Abstract

In COP 26, the international community reaffirmed its ambitious targets to reduce carbon emission to mitigate climate change according to Paris Agreement. To achieve that target, a proper combination of energy efficiency and integration of renewables should be applied to ensure a smooth energy transition that balances the increasing demand and environmental commitments. Natural gas can work as a transition fuel between the polluting fossil fuels, and zero-emission renewables such as hydrogen. Carbon capture and sequestration is another important aspect that allows reducing already existing and future carbon emissions that arise from industrial processes. However, the storage and purification of natural gas, CO₂ and H₂ is still challenging and represents an overhead cost that slows down the energy transition process. This review discusses the use of "zeolitic ice" or clathrate hydrates as an environmentally benign material to help the energy transition process. Having structural topologies and properties that are identical to some zeolites and zeolitic clathrasils, those green materials showed unique properties that enable their utilization in different purposes related to the energy transition, such as gas separation, desalination, fuel cells, and others. The review especially focuses on their possible role to purify and safely store gases such as CH₄, CO₂, and H₂, which are in the heart of energy transition. Amongst the objectives of the overview is to present different possible uses of clathrates, their benchmark against existing technologies, and the possibility to integrate them into current technologies with special focus on their application for energy storage and CCS.

Keywords:

Energy transition, Hydrogen storage, Methane storage , Clathrate hydrate, Semi-clathrate hydrate , Water-energy nexus, Zeolitic ice, DOE targets

sectionfont

1 Introduction

The IRENA (International Renewable Energy Agency) has defined the energy transition pathway that involves transforming the global energy mix from entirely fossil fuel-based to zero-carbon by 2050 [1]. To achieve that ambitious target, it is crucial to reduce CO₂ emissions and integrate renewable sources into the energy sector globally [2]. The polluting effects of natural gas are about half of the other fossil fuels. Therefore, natural gas is considered a transition fuel that possesses a well-established technology that can mitigate CO₂ emission while renewable energies and hydrogen economy mature both technologically and economically [3]. However, this bridging role of natural gas should be considered only as a "temporary" role because natural gas still emits CO₂ emissions [4]. In addition, the carbon emission of the natural gas processing and storage should be reduced as much as possible either through process optimization or post-processing to produce useful products [5]. Although natural gas processing and transportation are well-established, long-term storage and utilization of discrete and remote gas resources is still a challenge, an issue that is related to appropriate gas storage. Current global storage capacity is estimated to accommodate only 2% of the global annual natural gas production. This deficiency may result in an energy crisis whenever the supply chain is

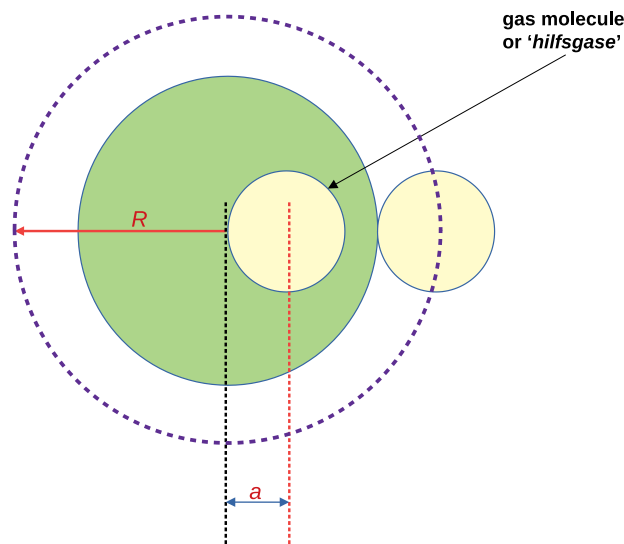


Figure 1: Barrer's model to calculate the intercalation heats of clathrates (adapted from [6]).

disturbed [7]. Moreover, the main overhead capital cost of the natural gas processing process comes from the purifi-

cation process that targets the removal of acid gases and N_2 from natural gas [8]. Thus, viable and economical carbon capture and sequestration (CCS) should be coupled with the process to ensure efficiency. When it comes to hydrogen economy as a main part of the renewable energy sources, there is a significant development in the production side from both renewable and natural gas [9]. However, the bottleneck of successful hydrogen incorporation into the energy mix is connected mainly to proper and compact hydrogen storage [10].

In general, clathrates are inclusion compounds formed when guests of specific sizes (CH_4 , CO_2 , H_2 , Na, etc) are engaged in various host molecules (H_2O , SiO_2) or elements (Si, Ge, C, etc.) under appropriate temperature and pressure conditions [11]. According to those conditions, one or multiple guest molecules can be entrapped in the host cavity. When the host molecules are mainly silica or water, clathrates from the well-known zeolitic clathrasils or gas hydrates, respectively [12]. The two classes are structurally analogous because both materials have a framework of several cages with voids occupied by guest species **Table 1** [13].

Using simple models such as **Figure 1**, early statistical thermodynamic interpretation of van der Waals and Platteeuw could provide satisfactory information about the non-stoichiometric nature of clathrate and the stabilizing action of guest gas as well as successfully expected the conditions under which clathrates phases are formed in most cases [6, 14, 15]. R.M. Barrer -the founding father of zeolite chemistry with a gas permeability unit named after him [16]- extended van der Waals work and dedicated a series of his early publications for those inclusion materials [6, 17–19]. Moreover, he had pointed out their structural and properties similarities to zeolites in several others as illustrated in **Figure 2** [17, 20]. Based on those similarities and the success of zeolites inclusion compounds in catalysis and gas separation [21], one can anticipate that gas clathrates can have promising industrial and technological applications especially in the context of energy transition. In that particular context, gas clathrates offer the potential for environmentally benign purification and storage of natural gas, CO_2 , and H_2 , as shown in **Figure 2**. Clathrate hydrates are non-stoichiometric nanoporous crystalline structures that are mainly composed of host water molecules [14, 15]. Connected by hydrogen bonding, those host molecules are forming three-dimensional cavities which enclose guest gas molecules. Under certain pressure and temperature conditions, they can exist in nature or be artificially synthesized. Different hydrate structures are stabilized by the encapsulation of gases such as CO_2 , H_2S , CH_4 , H_2 , or organic solvent such as tetrahydrofuran (THF), cyclopentane, or cyclooctane (Cyclo-O). Recently, gas hydrates have been the subject of intensive research related to a wide range of energy transition applications. The existence of clathrates has been known for a long time. A description of chlorine gas crystal structure was reported by Sir Humphrey Davy back in 1810[23]. However, clathrate hydrates attracted more attention particularly with the rise of the oil and gas industry in 20th [24]. In particular, the research at that period focused mainly on flow assurance and how to secure pipelines from being blocked by hydrates. Such blockage can interrupt the production from offshore reservoirs and the associated economic and safety concerns [25].

Table 1: Clathrate types of Hydrates and Clathrasils

Clathrate Hydrate Type	I	II	H
Space group	$Pm\bar{3}n$	$Fd\bar{3}m$	$P6/mmm$
Cages	$5^{12}, 5^{12}6^2$	$5^{12}, 5^{12}6^4$	$5^{12}, 4^35^66^3, 5^{12}6^8$
Hydrate Lattice Parameter(n.m)	a= 1.2	a= 1.73	a= 1.22 , c= 1.01
Guests (Hydrates)	CH ₄ , CO ₂	H ₂ , CH ₄ (0.25 GPa[22])	CH ₄ -Cyclooctane
Clathrasil IZA code	MEP	MTN	DOH
Clathrasile Lattice Parameter(n.m)	a= 1.346	a= 1.99	a= 1.378 , c= 1.119
Guests (Clathrasils)	CH ₄ , N ₂ , CO ₂	CH ₄ ,N ₂ Ar, (CH ₃) ₃ N	N ₂ , (CH ₂) ₅ NH

In recent decades, gas hydrates showed increasing potential for various industrial applications such as energy storage

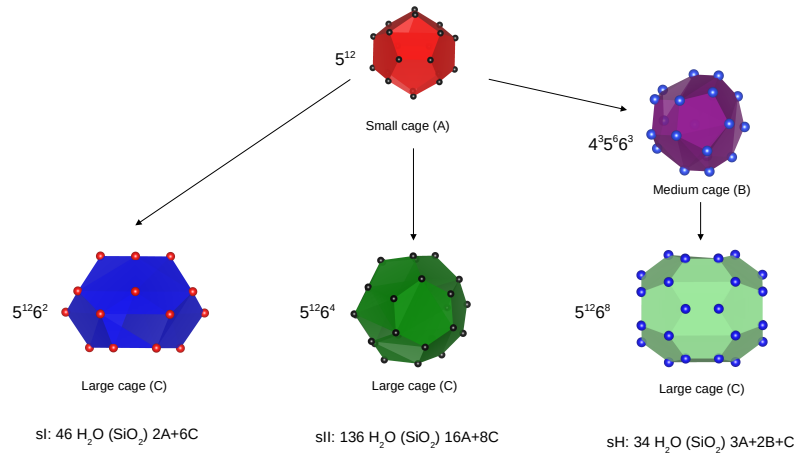


Figure 2: Summary of common clathrasil and gas hydrate cage structures.

[26], gas separation [27, 28], CO₂ capture and sequestration (CCS) [29], desalination [30, 31] and fuel cells [32, 33] as shown in **Figure 3**. With the energy transition toward renewables, low-carbon and unconventional energy, electrification, and decarbonization to reduce greenhouse gases (GHGs) emissions, recent studies on gas hydrates are distributed between the following main areas: (1) the traditional field of natural gas flow assurance, (2) gas hydrate natural occurrence and the associated environmental impact and (3) possible technological applications of hydrates.

Traditionally, gas clathrate is a problem of great concern in the field of natural gas processing as it may interrupt the

gas flow from offshore to onshore and affect drilling process safety [34]. Concerning clathrate's natural occurrence, the recently discovered enormous hydrates reserves, usually filled with methane, can present affordable clean energy sources and balance between the increasing energy demand and the environmental impact of using other fossil fuels such as oil and coal [35, 36]. *Clathrate gun hypothesis* refers to possible uncontrolled methane release from clathrates in oceans due to the increased temperature [37]. In such a scenario, this methane release can accelerate global warming which destabilizes more clathrate structures and invoke further warming[37, 38].

Finally, hydrates applications for green energy transition and sustainable development represent another growing area of interest. In that context, cages can be utilized for safe energy storage. With a volumetric capacity of methane that can reach about 160-180 V/V [39, 40], they can also be used to store and transport other gases of economic interest such as CO₂, N₂ and H₂ in economically feasible *P-T* conditions is one of the highly promising areas[41]. CH₄-CO₂ replacement in the enormous methane hydrate reservoirs is another important application that became the focus of recent research studies [42]. The interest in that technology comes from the fact that it could achieve the double benefit of simultaneous energy recovery and carbon fingerprint reduction via permanently storing CO₂ of flue gases in the deep ocean. In fact, clathrate applications can not only be regarded as "stand-alone", but also they can be integrated within exciting technologies such as LNG or biogas production.

However, despite the wide range of applications, the extensive industrial use of hydrate faces challenges such as slow kinetics, lack of clear understanding of phenomena such as self-preservation [43], memory effect [44] and different possibilities of cage occupancy [45]. The clathrate properties need to be further understood to resolve those problems, by combining both theoretical and experimental studies. In fact, evaluating the various interactions between the host water crystal and the enclathrated guest molecules is an indispensable part of clathrates research. There are several detailed reviews [46–50] and early comprehensive pioneering books [23, 51] for different aspects of hydrate research. Instead of duplicating that, this paper selectively reviews the most important contributions and current state of the art of theoretical calculations, experimental studies, and industrial research, focusing on the application side. More precisely, it aims to exhibit the current problems hindering the energy transition industrial application of clathrates from scientific and engineering perspectives and propose solutions for those challenges.

2 Gas Clathrate Structures and Properties

The structure-property relationship within the domain of gas hydrate depends on the nature of guest molecules and various temperature and pressure conditions. This relation has a great influence on the practical application of clathrates and their impact on the environment. To illustrate, parameters such as the ability to control gas hydrate synthesis and crystallization kinetics using different methods, additives, reactor, and process design are crucial for reducing the operational cost and increasing their industrial applicability. This section will discuss different structures and properties

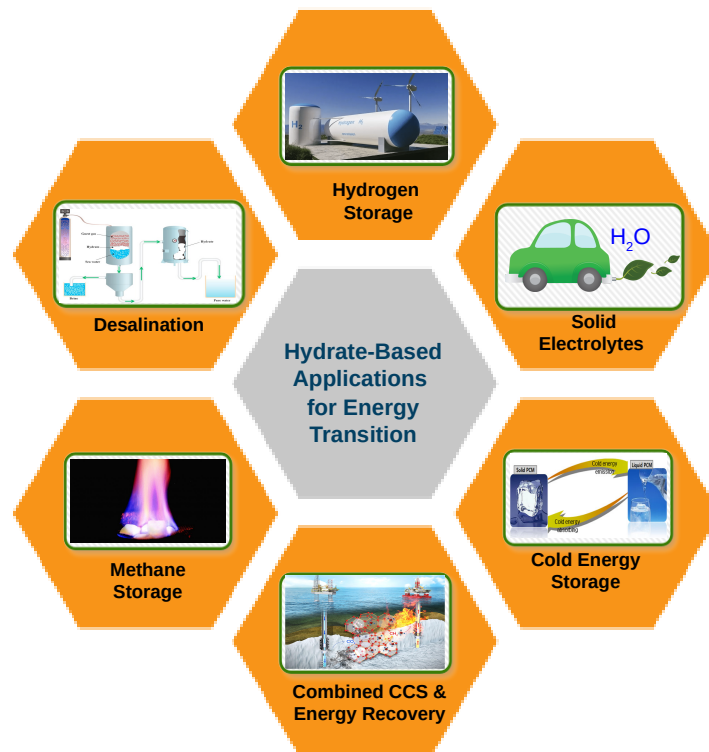


Figure 3: Gas hydrates potential technological applications for the energy transition.

of clathrate hydrates, which can give important insights into their applications.

2.1 Hydrate Structures

Although usually formed under high pressure, a combination of both experimental work and theoretical calculations in recent decades has enabled us to precisely determine the structure of those materials. Experimental techniques such as in situ NMR [52, 53], X-ray diffraction [54, 55] and Raman Spectroscopy [56, 57] provided us with important information such as the nature of host structure, cage occupancy, and guest molecules motion in the cages. For example, Okuchi *et al* used in situ NMR single-crystal XRD (SXRD) was used to get the atomic coordinates and geometries that are not provided by the conventional spectroscopic techniques [58, 59]. However, it has limited use due to the complexity of finding a suitable size clathrate single crystal. To solve that, experimental techniques can be coupled with theoretical studies to define the clathrate structure [60] or even anticipate new phases that are difficult to synthesize [61, 62]. The different nature and interactions between guest or "helpsgase" [63] and host molecules are crucial to understand the thermodynamic stability of different clathrates. While early theory has considered only the guest-host interactions while ignoring others [46], recent studies showed that guest-guest and host-host interactions

can also affect hydrate formation and stability[64, 65]. In general, water clathrates can be classified into two main categories: (1) clathrate hydrate and (2) ionic clathrates.

2.1.1 Clathrate Hydrates

Clathrate hydrates are nanoporous inclusion crystalline material with weak, non-directional van der Waal's attraction forces between the encaged hydrophobic guest molecules and the host water crystal that form a hydrogen-bonding network around them. The most common ones are sI, sII, and sH as summarized in **Figure 2**. They attracted more attention due to the presence of methane as a guest in all three structures depending on the formation pressure [22].

The presence of pentagonal dodecahedra (5^{12}) or small cages are common in all three structures. While sI is dis-

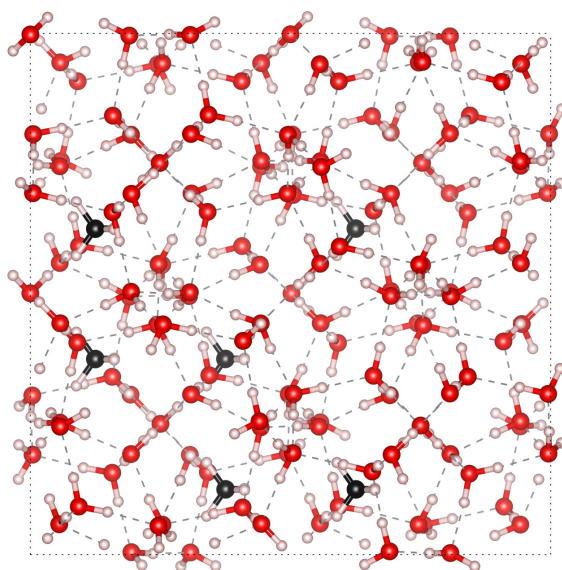


Figure 4: Structure II of pure methane hydrate can be formed at 0.25 GPa [22]. Hydrogen atoms are shown in pink, oxygen in red, carbon is black, and hydrogen bonds are with dashed lines.

tinguished by the presence of large cages of tetrakaidecahedra ($5^{12}6^2$) that may host gases such as CO_2 or CH_4 , sII have larger hexakaidecahedra ($5^{12}6^4$) cages that can host large solvent molecules such as THF [23, 66, 67]. Finally, sH contains medium irregular dodecahedra ($4^35^66^3$) medium cages in addition to the large icosahedra ($5^{12}6^8$) cages which can accommodate larger molecules such as cyclooctane [68]. It should be noted that smaller guest size does not always result in sI hydrate. For example, although they have relatively small kinematic diameter, hydrogen and nitrogen are naturally formed sII clathrate at elevated pressure [69]. The hydrate structure is controlled by not only by guest size but also P - T conditions. For example, increasing the pressure to 250 MPa, methane hydrate can form sII hydrate rather than structure I [22] as shown in **Figure 4**.

Cage occupancy is another important factor to determine clathrate properties and storage capacity [70]. Large and

small cage occupancies depend on the type of guest molecules as well as P - T formation conditions. While increased cage occupancies can improve clathrate stability, it is not a pre-condition to get a stable clathrate host structure [71]. For instance, pure sII hydrogen hydrate can store about 5.3 wt% at elevated pressures. In the case of binary H_2 -THF sII with stoichiometric THF amount of 5.56 mol%, the large cages are completely occupied by THF and the maximum hydrogen storage capacity is about 1 wt% only but at relatively much lower pressure [72].

2.1.2 Semi-clathrate hydrate

Although their existence can be dated to 1893, this important class of zeolitic ice structures that has potential application in gas separation [73], energy storage and CCS [74–76]. This kind of clathrate is usually called "ionic clathrate" due to the fact that hydrophobic cations or anions are encapsulated by host cages while a counter ion is incorporated into the host water framework. In other words, the walls of cages are partially removed or replaced by anions or guest molecules in addition to the hydrophobic inclusion that exists in clathrate hydrates [32]. They can be distinguished from clathrate hydrates by exhibiting partial hydrogen bonding between the guest species and the water host cages in addition to van der Waals interactions. These latter properties result in a relatively high thermal stability in atmospheric conditions, enhanced ionic and hydrogen conductivity making them ideal candidates for applications such as solid electrolytes.

Numerous strong acids form semi-clathrates in which anion guests are encapsulated into the acidic host lattice. For example, $HAsF_6$ and HPF_6 forms sVII, which has only $4^6 6^8$ cages and is distinguished by high melting point and high ionic conductivity [77]. Acidic clathrate such as $HBF_4 \cdot 5.75 H_2O$ or $HClO_4 \cdot 5.5 H_2O$ can form the cubic sI clathrate. In these structures, the anions can occupy both large and small cages. HPF_6 can also form sI too, but in this case, it occupies the large cages ($5^{12} 6^2$), only leaving the small cages empty. In contrast to sVI semiclathrate, sI compounds have relatively lower melting points [78]. Similarly, SF_6 neutral molecule has been shown to form sII occupying the large cages of $5^{12} 6^4$ [77]. On the other hand, some ionic clathrate hydrates show strong or weak basicity by encapsulating cationic guests while the host lattice charge is balanced by anions such as OH^- , F^- , and Br^- . The base-containing semi-clathrate are more diverse than acidic ones with a general formula of $R_4N^+ X^-$ where ($R=CH_3$, nC_3H_7 , nC_4H_9 , and others) while ($X=OH^-$, F^- , Cl^- , Br^- , and others [79]).

Quaternary ammonium salts (QAS) are the most common type of these clathrates and are distinguished by a high melting point that can reach $31^\circ C$ [80]. For example, tetra- n -butyl ammonium bromide (TBAB) has the bromide anions constructing the cage along with host water. At the same time, the hydrophobic cation fills the cage without H-bonding to the host water molecules. In the latter case, all the dodecahedral cages are empty, providing potential storage sites for other guest molecules [81–83]. The thermal stability at ambient conditions along with the non-volatile nature of salts represent a great advantage when it comes to hydrogen storage.

3 Role of Zeolitic Ice for Energy Transition

In this section, we will focus on two of the main applications of gas hydrates: solid energy storage (SES) and CO₂ capture and sequestration (CCS). There is intensive research for both applications. The IPCC and Paris agreement suggested that to tackle the impacts of global warming, the carbon emissions have to be reduced systematically to zero by 2050 [84, 85]. In general, gas storage can be classified into two main categories according to the state in which the gas (for example, CH₄, CO₂ or H₂) is stored: (1) physisorption (physical storage) in which the gas is stored in molecular form, and physical adsorbed on the material surface and interact with the host material with van der Waals forces and (2) chemisorption (chemical storage) in which the gas is dissociating form ionic or covalent bond with the host.

The current CO₂ capture techniques such as adsorption, cryogenic separation, and membranes have been widely investigated. However, their economic feasibility is challenged by their high energy consumption and technical difficulties such as non-consistent performance and increased differential pressure. Thus, they are not suitable yet for industrial-scale applications, at least in the short and medium terms. When it comes to energy storage, a useful benchmark for those materials can be obtained from the United States Department of Energy (DOE), which sets some criteria for both methane and hydrogen storage for onboard applications. The purpose of this section is to focus on CCS, methane, and hydrogen storage in clathrates and compares them to other existing technologies.

3.1 Methane Storage

Methane clathrate formations can be from both natural and synthetic routes. Naturally occurring gas hydrates have been accumulated long geological periods in permafrost regions and mostly on the more accessible submarine continental margins representing a low carbon energy source and possible CO₂ storage sinks. Although there is considerable uncertainty about the methane hydrate reserves, the amount of methane gas is expected to be more than all other carbonaceous fuel reserves combined. One can refer the reader to some comprehensive reviews for gas hydrate reservoirs [35, 36]. We focus here on synthetic gas hydrates (SGH) as an emerging technology.

Natural gas can be stored in underground inventories such as salt caverns and depleted oil or gas reservoirs. This technique, which depends on the natural occurrence, is distinguished by the ease of gas recovery, but it may possess some environmental risks. Apart from storing natural gas in underground inventories, the main natural gas storage and transportation technologies are CNG (compressed natural gas), LNG (liquified natural gas), ANG (adsorbed natural gas), and SGH (synthetic gas hydrates). Storing and transporting methane in its native gaseous state via tanks and pipeline networks (PLG) require high volume and can be less economically feasible when it comes to discrete gas resources such as shale gas and biogas [86]. On the other hand, CNG can reduce the storage volume, but it needs expensive multistage compression, high-pressure tanks that exhibit safety concerns, and poor volumetric capacity. Thus,

CNG is not applicable when it comes to large-scale natural gas storage [87]. Storage and transportation of natural gas in liquid form or LNG have been expanded rapidly to become the most convenient technology for industrial-scale and transoceanic transportation. This can be attributed to the fact that a single cubic meter of LNG can contain as high as 600 m³ STP conditions. Although currently, LNG tankers are roaming around the world to transport methane, the technology possesses some drawbacks. First, it needs big reserves and long-term commitment to install expensive facilities and associated infrastructure such as cold insulation and cryogenic tanks (i.e., high CAPEX). Then, it also has a high operational cost (OPEX) coming from the energy demand for cooling methane to -161 °C, boil-off gases re-compression, and regasification at the customer end. Furthermore, the technique is not flexible to store methane for long periods such as several months or years due to the high OPEX [88, 89]. The recent pandemic and geopolitical developments disturbed gas supply and resulted in unprecedented natural gas prices increase and highlighted the need for long-term storage technologies [90]. In general, the calculation of MOFs' storage capacity calculations commonly reported in the literature were based on a single crystal assumption. Such a calculation methodology is far from practical as it ignored the packing efficiency effect. Thus, the calculations of actual or deliverable gravimetric and volumetric gas uptakes based on bulk powder are significantly lower. Furthermore, other factors like re-usability, mechanical stability, thermal conductivity, and the high cost of the material are significant challenges that impede the use of MOFs for some onboard and all industrial-scale methane storage [91, 92].

SGH can be a promising alternative or complementary technology that can be integrated with existing infrastructure to improve the current technologies. First, SGH has very competitive safety and eco-friendly advantages due to factors such as the presence of water and lower storage temperature and pressure conditions. Such factors are reflected in the non-explosive and well-controlled storage and recovery processes. Moreover, unlike chemical storage, the methane hydrate storage process depends on the physical interactions such as vdW force and thus the storage is almost fully reversible. Finally, they are economically attractive due to the simple modular synthesis arrangements and moderate storage conditions. Several studies showed that the SGH plant can have about half the cost of LNG one of the same capacity. In addition, it is that it can reduce methane transportation costs by a quarter compared to LNG [93]. However, despite the above advantages, the industrial applications of hydrate-based technologies (HBTs) are still limited. The reasons behind that can be the slow kinetics, poor heat, and mass transfer, uncertainties of scale-up storage capacities.

To solve the above problems specific additives or promoters are added during hydrate synthesis. The role of promoters can be either catalyzing the kinetics of hydrate formation (kinetic hydrate promoter or KHI) or reducing the thermodynamic requirements (thermodynamic hydrate promoter or THP). However, understanding the crystallization processes -and more specifically the nucleation process- during hydrate formation is crucial to develop a suitable ki-

netic model for hydrates synthesis[94]. In general, the hydrate crystallization process can be divided into three main stages: gas dissolution, nucleation, and growth. First, the gas dissolves in the aqueous medium until enough guest molecules are adsorbed in the liquid phase to start nucleation. Nucleation is usually very slow and is distinguished by its stochastic nature [95]. Two types of *microscopic nucleation* may occur (1) homogeneous nucleation or "labile cluster hypothesis" in which the crystal formation starts directly from the liquid phase and (2) heterogeneous nucleation in which the process starts on the surface of "nucleation sites" [96, 97]. On the other hand, *macroscopic nucleation* can be spotted experimentally due to the exothermic nature of the hydrate formation reaction. This temperature increase is associated with rapid pressure drop due to gas enclathration [98]. Based on that, the macroscopic induction time or "lag time" can be determined. Such a time then can be spotted by the above thermodynamic changes and the appearance of detectable hydrate crystals [23, 99]. In the last stage, catastrophic crystal growth is distinguished by a very rapid increase in the particle size as the gas becomes more concentrated in cages than in vapor[100]. At the end of that stage, the reaction is controlled by mass transfer or gas diffusion through the 'hydrate film' at the liquid-gas interface [101].

Another important phenomenon that is closely related to the understanding of the nucleation process is called the "memory effect"[51, 102, 103]. When a hydrate undergoes decomposition, the resulting solution can form hydrate more readily. In other words, it needs a relatively shorter induction time compared to a fresh solution used to make hydrate [44, 104]. The sI methane clathrate showed the highest methane uptake among all clathrate structures with volumetric storage that can reach 170 V/V relatives to STP, as shown in **Figure 5**. Early investigation of Vysniauskas and Bishnoi for sI methane hydrate formation kinetics showed that it depended on P - T conditions, gas-liquid interfacial area, and degree of supercooling [102]. After that, there were many other investigations for sI methane clathrate such as those Englezos *et al.* [105], and Kim *et al* [106]. A common observation of these studies is that at the gas-water interfaces, hydrate films grow laterally along with the interface, and it is crucial to increase the surface area of gas-water contact to enhance both mass and heat transfer. Indirect methane hydrate formation can start from ice and could result in a high yield. However, this approach may not be economic due to the high energy spending and longer time associated with the ice formation [107].

To solve the problem of slow kinetics, KHP is added to reduce the time required for hydrate synthesis without influencing thermodynamic requirements. In other words, the hydrate structure, as well as the P - T condition of hydrate formation, are not affected. Surfactants (anionic, cationic, and non-ionic) are commonly used for that purpose[108]. In particular, the anionic surfactant sodium dodecyl sulfate (SDS) is predominant and has extensively been studied in different concentrations [109–111]. Close to its critical micelle concentration (CMC), SDS can relatively increase the hydrate formation rate significantly [112]. Micelles formation increases methane concentration in the aqueous phase and thus enables the nucleation to start earlier [111]. Here, it's worth mentioning that selection of the suitable surfactants should take into account their Krafft temperatures. The Krafft temperature is the minimum temperature

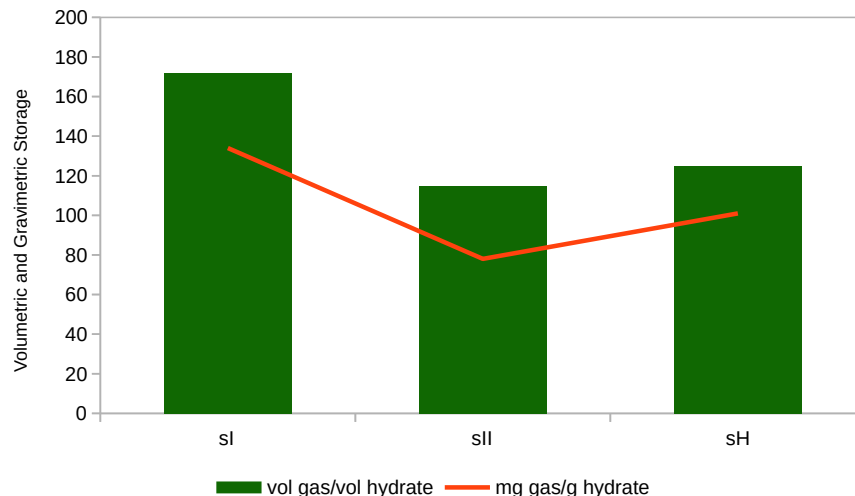


Figure 5: The estimated volumetric and gravimetric storage of common methane clathrate hydrate structures.

from which the micelle formation takes place. Surfactants are usually employed above their Krafft points otherwise hydrated surfactant crystals are formed [113]. To illustrate, Du *et al.* found that hydrate formation at 274 K has been little affected by dodecyltrimethylammonium chloride (DTAC) whose Krafft point below 273 K compared SDS, dodecylamine hydrochloride (DAH), and dodecyltrimethylammonium chloride (DTAC) whose Krafft points near room temperature [114]. Moreover, Zhang *et al.* explained that SDS increases the hydrate particles' surface area and the gas-liquid interfacial area while reducing surface tension [115]. Increasing the carbon chain length of sodium alkyl sulfates showed the same kinetic promotion behavior of SDS under similar conditions but required much less concentration than SDS [116, 117]. However, the utilization of surfactants for the hydrate-based process has a serious drawback related to foaming which is a serious problem in gas processing. This has been particularly observed during hydrate dissociation and scale-up experiments [118–120]. Moreover, it has been seen the presence of surfactants at certain concentrations may have inhibiting effect probably due to the presence of sodium ions. The intrinsic water network around that hard cation collapses due to the hydrogen bond breaking and strong binding between the ion and water molecules [121, 122]. In addition to not being environmentally friendly, such drawbacks hinder the industrial applicability of this class of promoters.

In order to overcome those drawbacks, two other classes of kinetics promoters were suggested: amino acids and porous materials. It has been found that amino acids increase the rate of hydrate formation at a certain concentration [123]. Although the rate is less than SDS in some cases, the final methane uptakes are still comparable in both cases [124]. Amino acids are promising biodegradable materials that can work as hydrate promoters. Low dosage hydrophobic or aromatic amino acids such as tryptophan and methionine or have shown better performance than hydrophilic or aliphatic ones such as KHP for methane hydrate synthesis [122, 125].

Porous materials such as those from carbon origin (such as activated carbon and carbon nanotubes) or silica origin (silica gel, silica sand, hollow silica, and nano-silica), zeolites, and MOFs has been proposed as KHP [126]. In general, these materials can be utilized in two different ways: (1) in low concentrations as a nucleation site for heterogeneous nucleation to reduce the induction time [127] and (2) as host for hydrate using the confinement effect [128]. In the first approach, the porous material increases the surface area by adding another interface (or third surface) that facilitates crystallization and gas diffusion [129]. For example, hollow silica was also examined in many studies and showed kinetic improvement. However, it needed the addition of SDS to get acceptable results when the conditions tested were near ambient conditions [130]. Xiaoya *et al.* has tested for LTA-type zeolite (3A and 5A) for methane hydrate formation and concluded that 3A has better promoting effect. However, a reasonable gas storage capacity above 120 V/V could be only achieved in presence of SDS [131, 132]. Kim *et al.* showed zeolite 13X (FAU-type) at 0.01 wt% concentration showed higher gas consumption than SDS and LTA-type zeolite, making it the most promising zeolite as KHP. The author attributed that to the small particle size and large pore diameter of 13X compared to the other zeolites studied [133]. In addition to being cheap and eco-friendly, the above zeolites are used in low concentrations and can be easily separated.

On the other hand, the porous material in the second approach can act as a medium for hydrate synthesis within the confinement approach. It has been found that high-pressure phases and reactions were found to occur in confined spaces in pressures that are magnitudes lower than required for bulk ones [134, 135]. For example, Siangsai *et al.* investigated the effect of activated carbon (AC) particle size on methane hydrate kinetics. They found that in the size range of (841–1680 μm) showed higher conversion while the highest recovery could be achieved in the range of (250–420 μm) [136]. Celzard *et al.* took advantage of activated carbon nanopore space to synthesize methane hydrate at mild conditions of (3.5 MPa and 2°C) and faster kinetics than nature [137]. It is also suggested that hydrophobic MOFs (ZIF-8) can show a high yield of methane hydrate uptake by combining methane hydrate formation and adsorption of methane in the interior pore spaces [138]. Borchardt *et al.* reviewed such an approach in detail and showed that in addition to hydrophobicity and pore size, water loading R_w (g H₂O/g soild) plays a crucial role in the uptake yield and kinetics [126]. The approach is very promising as those materials may act as both KHP and THP. However, several factors need to be examined in that approach for possible scale-up application. For example, there is packing efficiency that needs to be taken into account, additional cost to handle those materials, and the considerable loss in the gravimetric capacity.

KHP does not affect with thermodynamic conditions of hydrate formation. For that, another type of promoter is required. THP works to move the hydrate formation P - T conditions to a more moderate range and thus lowering the energy requirements. Depending on the nature of promoter and thermodynamic conditions, different hydrate structures can be obtained. For example, THF can direct hydrate synthesis toward sII formation. It is also reported to

work in synergy with SDS to improve the kinetics [139–142]. Other sII formers such as acetone [143], cyclopentane [144], dioxane [145], and others were reported in the literature [146]. On the other hand, sH formation needs larger molecules to stabilize the large cage of $5^{12}6^8$. Common sH formers are neohexane [54], methyl cyclohexane [147], cyclooctane [148]. Theoretically, sH can store gases such as CH_4 , CO_2 , or H_2 in both small and medium cages and may result in high storage capacity. A more comprehensive review of various promoters studies (KHP and THP) can be found in the literature [108]. The main drawback of using THP is the significant reduction in methane uptake compared to sI. The main reason behind that decrease is that those promoters occupy the sII or sH large cages while stabilizing the structure. However, the reduction of formation conditions closer to ambient temperatures can significantly offset that storage capacity reduction. For example, compression cost was found to be around three-quarters of the total cost of SGH formation in a pilot-scale reactor [149]. Increasing the methane formation temperature from 274.2 K to 293.2 will reduce 80% of the cooling cost as estimated by Veluswamy *et al.* [150]. The main drawback of sII and sH promoters are the potential environmental hazards and higher costs. In particular, solvent loss or volatility that requires additional solvent amount represents a big overhead on the OPEX.

3.2 HBCS and Simultaneous Methane Recovery

Due to various factors, such as the increasing world population, the associated global energy demand has been steadily rising, which has impacted immense pressure on dwindling fossil fuel resources. Simultaneously, environmental problems such as climate change start to affect the global economy and social stability. Consequently, the international legislation that emphasizes the importance of reducing carbon fingerprints is increasingly enforced worldwide [84, 111]. Capturable CO_2 sources can be generally divided into two main groups (1) low concentration such as air [151] and (2) high concentration such as flue gases. Although there are many advances in capturing CO_2 directly from the air [152], intensive research activities are focused on capturing it directly from the flue gas sources. The major sources of flue CO_2 gas emission are pre-combustion, post-combustion, and oxyfuel processes. The latter aims to increase the CO_2 concentration via burning the fuel in pure oxygen, which will result in easier CO_2 capture.

There are several methods to capture CO_2 from flue gases [153]. The most common ones are adsorption, absorption, cryogenic separation and membrane separation. Although each technique has some advantages, it also shows some drawbacks. For example, membrane separation is expensive with an estimated cost of 24-48\$ per ton depending on working conditions [154]. Moreover, while inorganic ones do not perform well in terms of reliability and cost control, organic membranes can not simultaneously reach high selectivity and high permeability. Generally, membranes are affected by the flue gas composition and lack sustainable performance and aging resistance [155]. Adsorbent-based systems with high surface areas such as MOFs and zeolites can reduce the cost to around 14\$ per ton [156, 157]. However, their sustainability can be affected by impurities, the humidity of flue gas, and complicated unit operations due

to the low-temperature requirements and pressure drop. Absorption is the most common method for removing acid gases from flue gas streams, especially in gas processing plants [158]. Despite its ability to reach high CO₂ capture capacity and high separation efficiency, it has some problems such as solvent degradation, safety risk associated with high pressure in the absorber, and high energy requirement of solvent regeneration as typical regeneration is at 120°C [159]. As shown in **Figure 6**, the same problem of high energy consumption persists with cryogenic separation [160] of CO₂ as cooling and pressurization may consume approximately 600 kW per ton of CO₂ on average [161].

Carbon sequestration has received relatively less attention compared to carbon capture [162]. Different carbon seques-

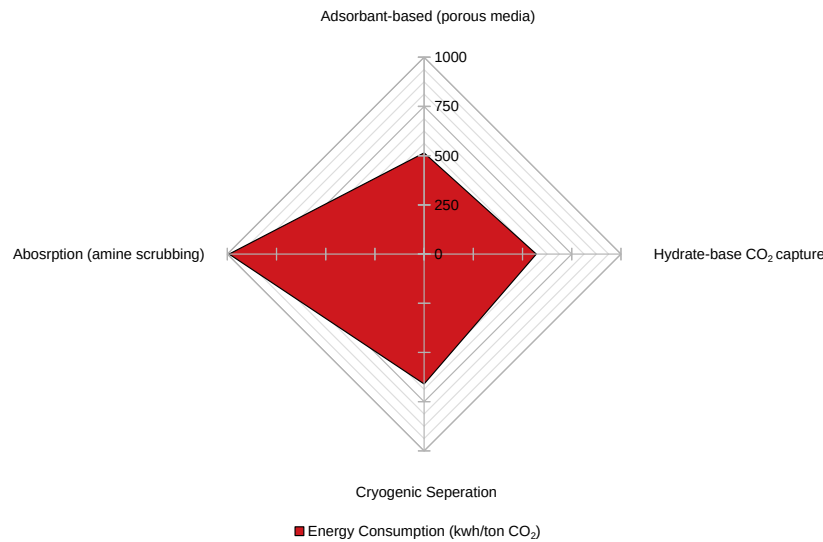


Figure 6: Estimated energy consumption (kw h per ton CO₂) of different carbon capture technologies. Hydrate-based technology combines both capture and sequestration methods in a single step. The figure is reproduced from Yu *et al.*[154].

tration options include but are not limited to saline aquifers, depleted and current oil and gas reservoirs, deep ocean storage, and mineral carbonation. However, many factors such as geohazard risks of the available sites and environmental, economic, social, and political factors should be considered [162]. Thus, *hydrate-based carbon capture and sequestration (HBCS)* has been proposed recently to overcome some of the above drawbacks of other methods while combining both capture and sequestration in a single step [163, 164]. Additionally, the recently discovered tremendous reserves of hydrates, mostly methane hydrates or natural gas hydrates (NGH), represent a huge opportunity for an affordable energy source [35, 36]. The most practical NGH extraction techniques are thermal stimulation, chemical inhibitor injection, and depressurization. However, each of these methods has its advantages and deficiencies. To illustrate, CH₄ is encapsulated in a delicate crystal that can rapidly decompose in an uncontrolled or even explosive fashion under depressurization or thermal stimulation which can be a serious safety concern. In addition, methane is a high global warming potential (GWP) and can contribute to the "clathrate gun hypothesis" mentioned earlier [37].

Accordingly, the utilization of naturally occurring gas hydrates should be associated with a proper hazard analysis

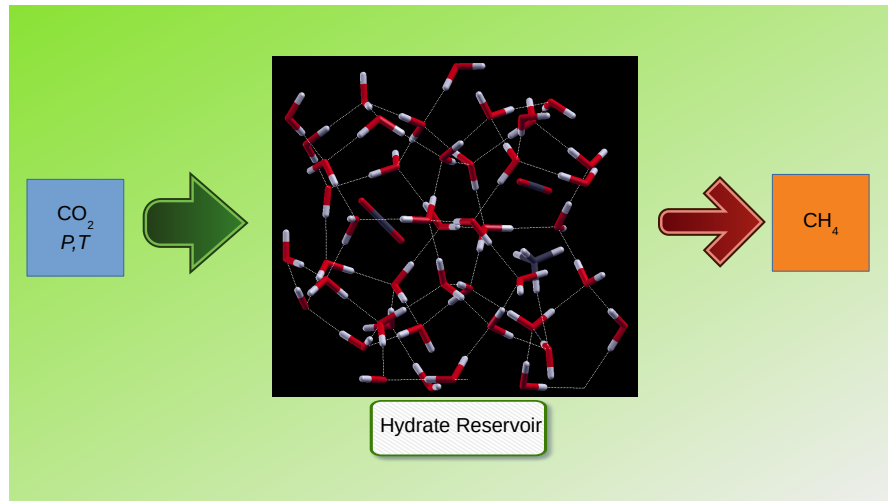


Figure 7: Schematic representation of methane clathrate replacement with CO_2 .

of the environmental impact. To solve the problem of uncontrolled methane release, a suitable guest molecule can be employed to replace methane in the hydrate structure. In that context, it is suggested that CO_2 can replace methane in natural gas hydrate reservoirs. The formation of the more stable but geological similar CO_2 hydrates possesses a double-benefit elegant solution involving both energy recovery and combustion product sequestration as illustrated in **Figure 7**. Such a technique will reduce the associated greenhouse gases (GHGs) emissions [42]. In principle, the exchange possibility has already been confirmed through experimental and theoretical studies [165]. From a thermodynamics point of view, the change in Gibbs free energy (ΔG) of CH_4 - CO_2 replacement in the hydrate is negative, which declares that the reaction is spontaneous without involving latent heat [166]. Thus, this exchange between injected CO_2 and methane hydrate is more economic than gas recovery via decomposition only. In addition, the thermodynamic equilibrium conditions (P, T) are more moderate in the case of CO_2 compared to CH_4 [167]. Furthermore, the process has been applied, and NGH exploitation via the CH_4 - CO_2 replacement method has been used in the northern slope of Alaska since 2012 [168, 169]. The technique has many advantages and can be both economically feasible and environmentally friendly. First, it is ecofriendly as it retains the current geological structures without change. In fact, the CO_2 clathrate is more stable than the CH_4 clathrate which has been already stayed for many geological eras. Then, the exchange process is safer than mining processes from Hazard, and Operability Analysis (HAZOP) point of view. Finally, it is economically attractive as there is no need to treat the tremendous amount of water usually associated with gas hydrate dissociation. Despite the above, there is an inherited uncertainty in the economic feasibility due to the lack of enough information about the methane reserves, mechanism, and rate of the exchange reaction [170].

3.3 Hydrogen Storage

The hydrogen economy is a very important element in the energy transition. In this economy, hydrogen is proposed to be used extensively as the primary energy carrier. Hence, the development of hydrogen production from both natural gas (grey and blue hydrogen) and renewables (green hydrogen) is of great importance. However, safe and practical hydrogen storage represents the major bottleneck for a sustainable hydrogen economy [171]. While conventional gaseous state storage systems as pressurized hydrogen gas need very high pressure and expensive infrastructure, liquid hydrogen needs extensive refrigeration and re-compression of boil-off gas to keep the temperature near 20 K. It is very important to evaluate the specific energy consumption and CO₂ to evaluate the storage efficiency. Consequently, the above requirements pose safety and cost problems to both, onboard and large-scale applications, and do not satisfy the core objectives for a hydrogen economy [172].

Thus, solid-state storage systems have a great potential to store hydrogen in a safe, compact, and feasible manner, making it an increasingly attractive technology for hydrogen storage [173]. When they are benchmarked with chemisorption such as metal hydrides or physisorption such as metal-organic frameworks (MOFs), hydrogen hydrates possess the potential to be environmentally benign, safe, and cheap material for hydrogen storage [50]. While hydrogen storage in MOFs suffers from uptake reduction when scale-up due to packing efficiency loss as described above, zeolites and activated carbon need to work at about 77 K [174]. Chemical storage is successful in storing hydrogen at a significantly higher temperature near ambient conditions. However, it needs high energy to break the chemical bond and restore hydrogen. For example, to restore hydrogen from hydrocarbon or ammonia, it needs to undergo reforming at a high energy cost. Hydrides that seem to be the closest to attaining DOE targets need a high temperature to retrieve hydrogen [175]. To illustrate, aromatic hydrogenation reactions are highly exothermic and thermodynamically favorable with the aromatic benzene ring enthalpy being $\Delta H_R = -68.73$ kJ/mol H₂. At the same time, the dehydrogenation is endothermic with the high energy demand of 64–69 kJ/mol H₂ [176, 177]. Liquid-organic hydrogen carriers (LOHC) partially solve that problem via reducing the dehydrogenation enthalpy catalytic processes [178]. However, both hydrides and LOHC face common challenges such as safety, eco-toxicity, solid-based or liquid-based infrastructure for transportation, cost of catalyst or metal, and difficulty producing enough pure H₂ over a long life cycle.

In 1999, Dyadin *et al.* could utilize differential thermal analysis (DTA) to prove that pure hydrogen clathrates synthesized at ≈ 15 kbar are of sII clathrate (CS-II). While they anticipated H₂/H₂O ratio (R) as high as 1/3 [179], Mao *et al.* characterized sII hydrogen clathrate *in situ* by different spectroscopic methods at 145 K and 1 atm and proved that R can be $\sim 1/2$ [180]. Unlike Villard's rule $R \sim 1/6$ in which each cage can be only occupied by a single guest [23], those higher ratios prove multiple hydrogen occupancy in both small and large cages of sII. It has been estimated that a small (5¹²) cage can hold two hydrogen molecules while the large (5¹²6⁴) cages can encapsulate 4 hydrogen molecules at high pressures. With such occupancy taken into account, the pure hydrogen clathrate can exhibit a hydrogen storage

capacity of 5.3 wt% or 1.8 kW.h/kg [181, 182].

H₂-THF binary clathrates have been widely investigated as THF eases the thermodynamic requirement to acceptable ranges of 7-8 MPa. However, that extra stability was at the expense of a storage capacity that significantly dropped [70, 183]. Lee *et al.* suggested tuning the THF concentration to allow hydrogen molecules to be enclathrated in the large cages of sII without compromising the moderate *P-T* requirements. The systematic reduction of THF concentration from 5.56 mol% to 0.2 mol% resulted in a storage capacity increase from 2.09 to 4.03 wt% at 120 bar and 270 K [184]. However, tuning phenomena is controversial in the literature. While few studies could obtain tuned H₂-THF clathrates such as Sugahara *et al.* who modified the synthesis method at ~ 70 MPa and 255 K [185], many other researchers reported that such results could not be reproduced and only ~ 1.0 wt% hydrogen storage could be obtained regardless of the THF concentration [186–188]. Therefore, increasing the hydrogen clathrate gravimetric and volumetric capacity in feasible *P-T* conditions remains an open area for further research. Due to their relatively higher thermal stability compared to clathrate the the the the hydrates, semi-clathrate were also studied for hydrogen storage. However, they showed lower storage capacity compared to H₂-THF binary clathrates [189]. To solve those problems, the second generation of gaseous THP promoters has been proposed to exploit the hydrate structure storage potential in small and large cages. For instance, Park *et al.* showed that N₂ can allow hydrogen multiple occupancies in sII clathrate in the presence of THF and pyrrolidine (PRD) [190]. Similarly, SF₆ and CO₂ as promoters allowed hydrogen to be stored in large cages [191]. Another ambitious direction was to use light alkane (C₁-C₃) to form hydrogen clathrate with high calorific value at affordable formation and storage conditions. According to Mao *et al.*, such a combination is expected to fulfill the US Department of Energy (DOE) energy density targets [180]. Recently, our group used *ab initio* calculations to prove that CH₄ or CO₂ can play the role of thermodynamic promoter, allowing double occupancy of methane and hydrogen in 5¹²6² large cages of sI. This double occupancy has not only enhanced the hydrogen diffusion but also pushed sI binary H₂-CH₄ volumetric and gravimetric storage capacity to meet DOE requirements [192]. Those results agreed well with previous experimental observations [193]. It has been demonstrated that different H₂-CH₄ hydrates (sI and sII) could be synthesized by varying the thermodynamic conditions [194, 195]. PXRD and Raman spectroscopy analysis of those binary clathrates showed that either sI or sII could be obtained depending on (1) *P-T* conditions, (2) initial composition, and (3) hydrate synthesis time. Interestingly, the thermodynamic requirements of such hydrates were more relaxed compared to pure H₂ or even tuned H₂-THF hydrates [196].

Similarly, ethane has been reported to form binary clathrate with hydrogen. Theoretical calculations showed that C₂H₆ can form both cubic structures (sI and sII) at 250 K with hydrogen storage capacity of 2.5wt%, and 3.5 wt%, respectively [197]. Ghaani *et al.* reported using propane as a co-guest with hydrogen that can also reduce the thermodynamic requirements [198]. Ahn *et al.* found that for H₂-CH₄-C₂H₆ system, multiple H₂ cage occupancies in all cages of hythane hydrates of sI and sII could be achieved via guest-exchange reaction. In that approach, a double

hydrogen occupancy in small cages was obtained in the formed hydrate whether it is sI or sII [41]. More recently, Moon *et al.* optimized the hydrogen concentration needed to achieve the maximum possible hydrogen storage capacity in moderate thermodynamic conditions. However, despite those promising multiple hydrogen occupancies, the GC (Gas chromatography) results indicated that most of the hydrate cages to be filled either by methane or ethane rather than hydrogen with a composition of (51.74:17.98:30.2) mol% for (CH₄:C₂H₆:H₂) in hydrate at the best case [199].

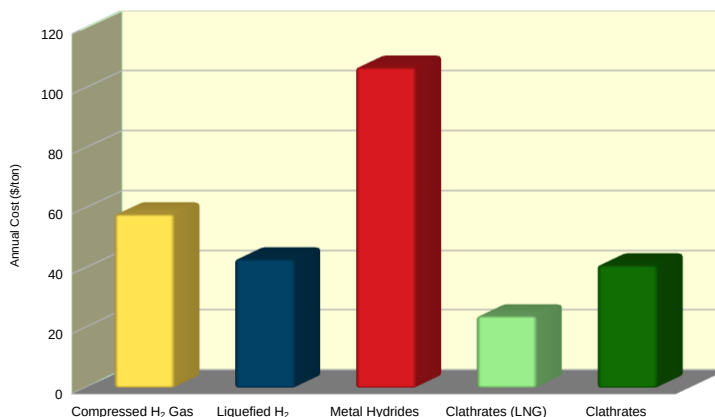


Figure 8: The estimated cost of different hydrogen storage technologies. Clathrat storage cost is assumed with a volumetric capacity of 3.03 wt% [200].

3.4 Other Hydrate-based Applications

There are many other hydrate-based applications for the energy transition as shown in **Figure 9**. In the *energy-water nexus*, water and energy are closely interlinked. While water can be considered as an energy source, energy is needed to transport or desalinate water. The latter is a big global challenge due to climate change and the intensive energy consumption for water desalination [201]. Thus, there is an urgent need to develop innovative technologies that can reduce such requirements and make use of waste heat from industrial sources. One clear example of that wasted energy is the cold energy of LNG re-gasification. The LNG received at the terminal at -162 °C is normally heated to 25 °C by employing seawater which is dumped back to the sea wasting the LNG cold energy. Such an amount of cold energy is huge as one tonne of LNG is estimated to require 214 kWh of cold energy removal [202]. One of the best options to utilize such wasted energy is hydrate-based desalination or (HyDesal). HyDesal work as stand-alone or in hybrid arrangement with other desalination technique to reduce the energy consumption and cost of the desalination process[30]. Such an approach can not only help to reduce the desalination energy requirements but also in GHGs capture. To illustrate, using proper hydrate former such as CH₄, CO₂, C₃H₈ at selected *P-T* range, water molecules form clathrate hydrate around gas molecules separating themselves from salty solution [23, 203]. For example, Babu *et al.* optimized the desalination conditions to reach ~ 35% and salt rejection of ~ 88 % for simulated seawater solution [204]. Although known from the 1940s, its commercialization faces some challenges related to reactor design to

form and separate hydrate from salts and also the lack of commercial feasibility studies [203, 205].

There is increasing energy demand for space cooling along with climate change [47, 202]. Therefore, there is a

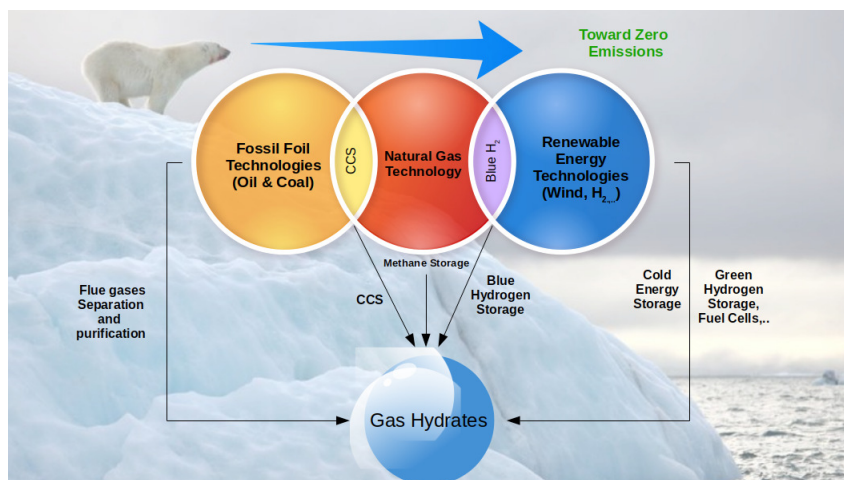


Figure 9: Schematic illustration of current and possible hydrate-based applications for energy transition.

growing demand to explore for the best phase change material (PCM) candidates that can efficiently take benefit of the cold energy released from the production sectors (e.g. energy from renewable sources, cheap off-peak electricity, oil and gas industry waste heat, and LNG regasification in terminals) for storage and transport applications. In that context, semi-clathrate hydrates (SCHs) are ideal candidates because of their suitable phase change temperature (5–27 °C), thermal stability (melting point can vary from -66 up to 31 °C), latent heat of fusion (190-220 kJ/kg) and relatively better heat transfer efficiency compared to clathrate hydrates [32, 206] which is suitable for various cooling requirements [207]. The process usually starts with cooling the system to form a hydrate, which is an exothermic process. The cold energy stored then could be consumed through depressurization or receiving heat from the external environment or a combination of both. CO₂ (or mixed CO₂-THF) hydrates were well-demonstrated for such an approach [208]. However, CO₂ is corrosive acid gas that will require expensive infrastructure. Although semi-clathrate hydrates can overcome those drawbacks, a more comprehensive economic assessment for the energy cycle is missing in the literature. Moreover, SCHs either in their acidic or basic ionic form showed exceptional thermal stability, ionic and proton conductivity. Such unique properties enable them to compete with solid electrolytes such as Nafion. More comprehensive research studies are highly desired to evaluate the unique physicochemical properties of such materials [32, 209, 210].

4 Engineering and Economic Challenges and Perspectives

Hydrate technologies for economic gas storage give promises due to the moderate production and storage condition and the ease of gas recovery compared to other means of energy storage and transportation [211]. Few studies targeted the life-cycle of NGH for transportation or mobile storage. For instance, Nogami and Oya showed that NGH is more economic in the medium distance for 1000-6000 km distance compared to LNG, CNG, or PLG. However, for longer distances, LNG is still the optimum choice [212]. Furthermore, Nakai made a comprehensive life cycle assessment (LCA) for NGH for trucks and shipping purposes and concluded that it can reduce the cost by about 20% compared to the LNG plant of 1-1.5 MTPA (Million Tonnes per Annum) [213]. Other cost analysis studies showed that NGH could reduce the capital cost by at least 25%-48% relative to LNG [86].

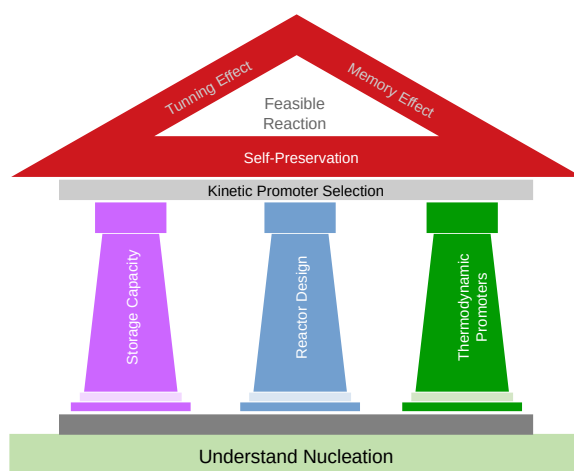


Figure 10: Future perspectives of hydrate research toward industrial application.

The recent sharp increases in natural gas and LNG prices due to the pandemic and recent geopolitical development revealed the need for long-term or static storage of methane especially from discrete and small gas resources (shale gas, biogas, flue gases) [90]. In that context, NGH showed a superior advantage over other technologies. In particular, it offers a high gravimetric and volumetric capacity of methane in a much controlled and safer manner compared to LNG or CNG. The safety of such a method is inherited from lower storage pressure (2-5 bar compared to 10 or MPa for CNG) and non-explosive nature due to the presence of water in excess. Economically, it can be feasible for static medium and long time storage with a relatively high storage temperature (-20°C compared to 162°C) and less boil-off gas (BOG) re-compression requirements [88, 172]. Such unusual stability of methane clathrates even outside its zone of thermodynamic stability can be attributed to the hydrate self-preservation phenomenon [214]. For instance, an early study by Gudmundsson *et al.* showed that natural gas hydrates (92 mol% methane, 5 mol % ethane, and 3 mol% propane) can be stored in a deep freezer (-5 to -18°C) for 10 days at atmospheric pressure without significant

loss of methane [215]. In a more recent study, Mimachi *et al.* showed that NGH pellets could successfully stored for 3 months at 253 K under atmospheric pressure [216]. Stability can be improved and storage can be extended for years in case of CH₄-THF sII clathrates [217]. However, this higher stability and longer storage period comes on the expense storage capacity that has been significantly reduced. To address that point, Takeya *et al.* suggested coating CH₄ hydrates with THF or cyclopentane (CP). In case of cyclopentane-coated methane hydrate, the authors found that the hydrates remained stable for extended periods at a temperature higher than the equilibrium temperature and under atmospheric pressure [218].

Clathrate hydrates do not only reduce the cost compared to conventional storage for large-scale storage but also open the door for small and medium-size methane storage from discrete or remote resources. These resources such as shale gas, coal mine gas, offshore and onshore flue gases are not suitable for LNG which needs huge capital investment and tremendous reserves, and long-term contracts. It is important to stress here that NGH technology is complementary rather than competitive with existing technologies. In fact, NGH technology is best working in and hybrid mode due to their simple modular construction and operation which reduce the investment threshold by allowing to taking profit from the existing facilities and infrastructure [154].

In general, NGH processing technology consists of a formation step, followed by dewatering of non-converted water, cooling and depressurizing of excess gas, and finally pelletizing the hydrate for storage. While safety, storage conditions, and economics are the big advantage of NGH technology, the formation or synthesis step is the main engineering and economic obstacle that prevent the widespread of such technology [93, 212, 219]. The hydrate formation suffers from slow kinetics and severe operating condition, especially for pure methane (sI) [220]. To solve that problem, it is crucial to understand the nucleation process to shorten the induction time. The use of a carefully selected kinetic promoter (KHP) can reduce the lag time and the overall hydrate synthesis duration. In that aspect, the KHP should avoid the drawback of foaming without compromising the gas uptake. In addition to not being expensive, the selected KHP should be also eco-friendly and recyclable or degradable. The promising material in that aspect are nanoparticles [221], amino acids [222, 223], and porous materials at low concentrations [224]. The latter can be also used as the main storage medium allowing clathrates to grow inside pores at mild *P-T* conditions which is pretty similar to the THP effect [225]. Using liquid THP can reduce the hydrate formation requirements and increase the stability of formed hydrates [217]. However, the environmental impact of this promoter needs to be carefully assessed. If used in optimal concentrations, the use of those promoters can compromise between the reduced storage capacity and cooling requirement and hence minimize the overall process cost.

Recently, the use of gaseous THP such as light hydrocarbons (C₁-C₃) [226] showed promising results for both methane and blue hydrogen storage. Moreover, one the of the biggest advantages of hydrates is that they are insensi-

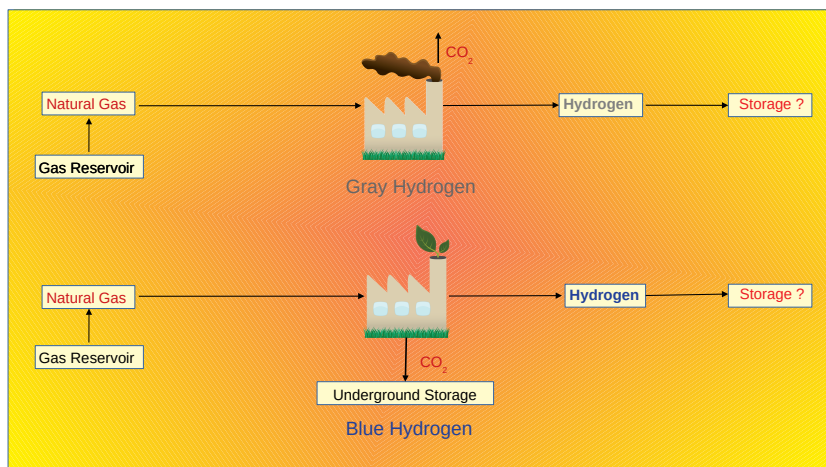


Figure 11: Schematic representation of gray and blue hydrogen.

tive to impurities. On the contrast, acid gases such as CO₂ and H₂S can also reduce the thermodynamic requirements of methane hydrate formation [227, 228]. For example, Gudmundsson *et al.* could store NGH of methane, ethane, and propane in a normal deep freezer temperature (255.2-268.2 K) for 10 days under a pressure [215]. Overcoming the slow kinetic problem needs also innovative reactor design to enhance the gas-liquid contact, mass and heat transfer to the extent that industrial-scale application can be feasible. Current research studies in that direction, packed bed reactors [229], horizontal reactors with metallic packing [148] showed promising results. So to summarize, research perspectives for methane hydrate studies include but not limited to (1) understanding nucleation, self-preservation, structural transformation and memory phenomena, (2) proper selection of KHP, innovative (3) practical reactor design, (4) removal or optimization of THP, (5) explore the possibility of salty water and increasing pressure conditions toward the atmospheric pressure to improve the process economics and finally (6) perform detailed LCA studies.

In the case of carbon capture and sequestration (CCS), hydrate-based carbon capture and sequestration (HBCS) is a promising technique based on a simple process that is not affected by a pressure gradient, contaminants, and humidity. Moreover, the recovery or regeneration can be achieved simply by depressurization or thermal exchange at ambient conditions. This makes it energy-efficient and thus cost-effective carbon capture technology with estimated energy consumption below 0.60 kWh per ton CO₂ [154]. Although slow kinetics is still a problem, the thermodynamic requirements are much lower compared to NGH or hydrogen hydrates. Combining carbon capture and sequestration in a single process is a unique feature that favors HBCS over other carbon capture technologies. On the other hand, higher thermodynamic requirements are needed to maintain decent separation efficiency when the feed mixture has a lower CO₂ concentration. There are two possible solutions for that problem: (1) multistage HBCS and (2) hybrid hydrate CO₂ capture methods. The latter is more favored as it takes advantage of both HBCS and the conventional

carbon capture method such as membrane or cryogenic separation to lower the energy requirements [230–232].

Safety and environment are priorities in the hydrogen storage process. In that aspect, hydrogen clathrate has a clear advantage over other physical and chemical storage methods. While storing hydrogen in solid clathrate is compact and needs relatively low storage pressure, storing hydrogen in reasonable amounts at its gaseous form needs a very large volume and/or high-pressure tanks which is a serious safety challenge. Moreover, it shows less CO₂ emission compared to other physical storage in both liquid and gas forms. Both economics studies show the net energy gain from hydrogen storage is competitive with chemical storage due to the less energy required to recover hydrogen [172]. On the other hand, hydrogen clathrate still faces many challenges. First and foremost, it needs very high thermodynamic requirements in terms of high pressure and low temperature. Such a challenge can be solved by blending hydrogen with natural gas to form "Hythane" in which hydrogen storage can be in a reasonable *P-T* range with multiple hydrogen cage occupancies [233]. However, further investigation is still needed to evaluate that approach especially in terms of kinetic studies and uncertainty of storage capacity.

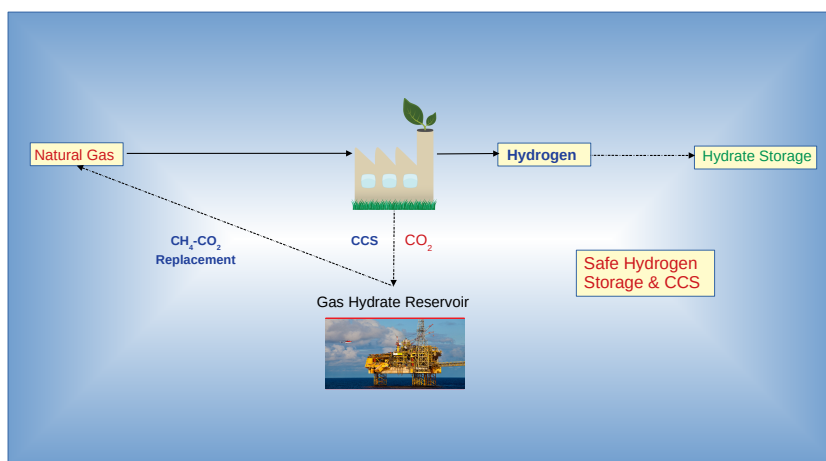


Figure 12: Schematic representation of possible hydrate-based blue hydrogen.

As mentioned above for desalination, the use of wasted cold energy such as those of LNG facilities can make hydrogen clathrates very competitive with the well-established hydrogen hydride or compressed hydrogen [234]. Currently, fuel cells and hydrogen hydride are the most common options for onboard hydrogen storage. While the first requires a low temperature as low as 200 K, the latter assumes a storage capacity of about 5.06 wt% hydrogen. These two conditions can be, at least theoretically, met by hydrogen clathrates [200]. However, overall cost estimates for onboard hydrogen clathrate are still needed for better evaluation. **Figure 10** summarizes future research areas required to enable the industrial application of gas hydrates for the energy transition.

One of the strong points of zeolitic ice technologies is their ability to be integrated with existing infrastructure and processes improving them toward greener energy transition. Having already highlighted the role of gas hydrates for methane storage, CCS, and hydrogen storage above, one can suggest an integrated approach that can enhance the environmental feasibility of blue hydrogen production or hydrate-based blue hydrogen (HBBH). Natural gas (composed mainly of methane) is currently the primary source of hydrogen production through catalytic reactions. It is estimated that 75% of the globally produced methane is utilized for hydrogen production via processes such as steam reforming (SRM) [235] or dry reforming (DRM) [5]. Currently, the state of art hydrogen production is "gray hydrogen" which comes from steam methane reforming (SMR). Green hydrogen which refers to the hydrogen produced from clean renewable energy sources still has not had enough supply or competitive cost compared to gray hydrogen despite the rapid decrease of renewables costs[236]. To overcome the problem of GHG emissions coming from gray hydrogen, an increasing number of researchers promoted the idea of "blue hydrogen" as shown in **Figure 11**. The relatively new concept adds CCS to the SMR process and used to be described zero or low GHG emission technology[237]. A common gap in those 3 hydrogen production approaches (green,gray and blue), the three technologies lack a clear method for safe hydrogen storage. Such a gap is very important as it can be the bottleneck for the hydrogen economy. To illustrate, Dawood **et al.** proposed that, in addition to production and utilization, safety and storage are two

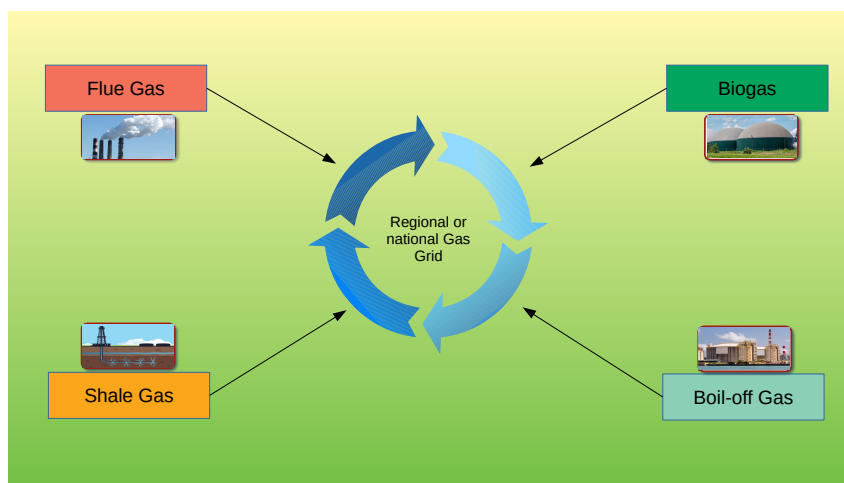


Figure 13: Gas Hydrate can make use of discrete gas resources by lowering the investment barrier.

important corners for hydrogen-based energy systems [238]. Although blue hydrogen technology is claimed to have a good balance between economic feasibility and GHG emissions, the steps of CO₂ capture and sequestration are two independent sub-processes. In addition, the storage is described to be in geological structures such as a saline aquifer with 800 m depth. However, a recent complete LCA by Howarth & Jacobson showed that blue hydrogen reduces carbon dioxide emission by only 9-12% less than gray hydrogen. The reason behind that is the lower amount

of carbon dioxide emissions are compensated by fugitive methane emissions due to the use of natural gas to power for the carbon capture. For heating purposes, it has been found that the greenhouse gas footprint of blue hydrogen is 20% greater than natural gas or coal [239]. A major part of those drawbacks can be avoided if hydrates are utilized for methane and CO₂ capture and sequestration in addition to hydrogen storage as shown in **Figure 12**. In principle, CO₂ storage can be used to recover natural gas with a double benefit of energy recovery and CCS. Resistant to contaminants, clathrate hydrates can be used to capture flue gas and fugitive methane emissions at a reasonable cost.

Finally, this review demonstrated the potential of HBT integration with existing processes for the efficient energy transition. Being flexible and implementable at a low cost, HBTs can facilitate large scale gas transportation and storage. Moreover, they can provide lower entrance barriers to utilize remote and discrete energy sources which are not feasible to transport through other gas transportation means as illustrated at **Figure 13**. In analogy to CCS, clathrate hydrates can be also used for methane and other GHGs capture and sequestration. Last but not least, they can be used to safely store hydrogen at a lower cost.

5 Conclusions

This review sheds light on increasing research interest for hydrate-based technologies (HBTs) in various fields related to energy transition and decarbonization. The main properties of hydrate (both clathrates and semi-clathrates) have been introduced to show their uniqueness and potential for industrial applications. First, we showed the advantages of NGH for methane storage and benchmarked them with existing technologies such as PLG, CNG, and LNG. NGH is suitable for medium-distance transportation, both small and large volume stationary methane storage, especially for long time storage. We concluded that NGH technology is very flexible and can be utilized in synergy with other existing methane storage technology which enables us to make use of the current infrastructure. Hydrates can also be an interesting opportunity for CCS with HBCS combining both carbon capture and sequestration in a single step. Moreover, that technique can be used for methane recovery as we showed in the CH₄-CO₂ replacement process. Then, we introduced hydrogen clathrate as a compact, safe, and environmentally benign option with a great potential for static hydrogen storage.

We have also shown the role of clathrate in the energy-water nexus with applications such as desalination. We also addressed the engineering and economic challenges that hinder the industrial application of HBTs. In our opinion, future research should focus on improving heat and mass transfer via reactor design, optimum selection and concentration of kinetic and thermodynamic hydrate promoters, and possible hybrid HBTs. Above all, detailed life-cycle economic studies will help evaluate those proposed solutions. Finally, we presented some conceptual examples of possible hydrate technology integration into the existing energy processes to enhance their performance. Presenting

the current status of research, major challenges, and proposed solutions, we hope this review will attract scientists and enterprises' attention to that exciting field to reach the energy transition and low carbon economy.

6 Author Contributions

A.O."investigation; writing original draft; "N.N. "Writing-review & editing ,conceptualization, supervision"; V.V. "Writing -review & editing ,conceptualization, supervision"

7 Conflicts of interest

There are no conflicts to declare.

8 Acknowledgments

This work was supported by the Industrial Chair ANR-TOTAL "NanoClean Energy" [ANR-17-CHIN-0005-01].

References

- [1] Tanay Sidki Uyar. *Accelerating the Transition to a 100% Renewable Energy Era*, volume 74. 2020.
- [2] Xavier Garcia-Casals, Rabia Ferroukhi, and Bishal Parajuli. Measuring the socio-economic footprint of the energy transition. *Energy Transitions*, 3(1-2):105–118, 2019.
- [3] C Gürsan and V. de Gooyert. The systemic impact of a transition fuel: Does natural gas help or hinder the energy transition? *Renew. Sustain. Energy Rev.*, 138(March 2020):110552, 2021.
- [4] Eleanor Stephenson, Alexander Doukas, and Karena Shaw. "Greenwashing gas: Might a 'transition fuel' label legitimize carbon-intensive natural gas development?". *Energy Policy*, 46(2012):452–459, 2012.
- [5] Ahmed Omran, Sun Hee Yoon, Murtaza Khan, Minhaj Ghouri, Anjaneyulu Chatla, and Nimir Elbashir. Mechanistic insights for dry reforming of methane on Cu/Ni bimetallic catalysts: DFT-assisted microkinetic analysis for coke resistance. *Catalysts*, 10(9):1–16, 2020.
- [6] R. M. Barrer and W. I. Stuart. Non-stoichiometric clathrate compounds of water. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, pages 172–189, 1957.

- [7] Herib Blanco and André Faaij. A review at the role of storage in energy systems with a focus on Power to Gas and long-term storage. *Renew. Sustain. Energy Rev.*, 81(May 2017):1049–1086, 2018.
- [8] Lars Peters, A. Hussain, M. Follmann, T. Melin, and M. B. Hägg. CO₂ removal from natural gas by employing amine absorption and membrane technology-A technical and economical analysis. *Chem. Eng. J.*, 172(2-3):952–960, 2011.
- [9] Hazzim F. Abbas and W. M.A. Wan Daud. Hydrogen production by methane decomposition: A review. *Int. J. Hydrogen Energy*, 35(3):1160–1190, feb 2010.
- [10] Suman Dutta. A review on production, storage of hydrogen and its utilization as an energy resource. *J. Ind. Eng. Chem.*, 20(4):1148–1156, 2014.
- [11] Pramod Warriar and Carolyn A. Koh. Structure-Property-Comparisons of Clathrasils and Gas Hydrates. *Trans. Indian Inst. Met.*, 72(8):2229–2237, 2019.
- [12] Koichi Momma. Clathrate compounds of silica. *J. Phys. Condens. Matter*, 26(10):103203, 2014.
- [13] Juli Anna Dolyniuk, Bryan Owens-Baird, Jian Wang, Julia V. Zaikina, and Kirill Kovnir. Clathrate thermo-electrics. *Mater. Sci. Eng. R Reports*, 108:1–46, 2016.
- [14] J. H. Van Der Waals. The statistical mechanics of clathrate compounds. *Trans. Faraday Soc.*, 52:184–193, 1956.
- [15] J. H. van der Waals and J. C. Platteeuw. Clathrate solutions. In I. Prigogine, editor, *Adv. Chem. Phys.*, volume II, pages 1–57. John Wiley & Sons. Inc., 1958.
- [16] Lovat V. C. Rees. Richard Maling Barrer. 16 June 1910–12 September 1996. *Biogr. Mem. Fellows R. Soc.*, 44:37–49, 1998.
- [17] R. M. Barrer and D J Ruzicka. Non-stoichiometric clathrate compounds of water. Part 2. Formation and properties of double hydrates. *Trans. Faraday Soc.*, 58:2239–2252, 1962.
- [18] R. M. Barrer and D J Ruzicka. Non-stoichiometric clathrate compounds of water. Part 3.-Inclusion Energies and Constants in the small Cavities of Structure II BY. *Trans. Faraday Soc.*, 58:2253–2261, 1962.
- [19] R. M. Barrer and D. J. Ruzicka. Non-stoichiometric clathrate compounds of water. Part 4. - Kinetics of formation of clathrate phases. *Trans. Faraday Soc.*, 58:2262–2271, 1962.
- [20] R M Barrer. Zeolite inclusion complexes. *J. Incl. Phenom.*, 1(2):105–123, 1983.

- [21] Svetlana Mintova, Jean Pierre Gilson, and Valentin Valtchev. Advances in nanosized zeolites. *Nanoscale*, 5(15):6693–6703, 2013.
- [22] Jinfu Shu, Xiaojia Chen, I. Ming Chou, Wenge Yang, Jingzhu Hu, Russell J. Hemley, and Ho Kwang Mao. Structural stability of methane hydrate at high pressures. *Geosci. Front.*, 2(1):93–100, 2011.
- [23] E. Dendy Sloan and Carolyn Ann Koh. *Clathrate hydrates of natural gases, third edition*. CRC Press, third edition, 2007.
- [24] Yu A. Dyadin, I. S. Terekhova, T. V. Rodionova, and D. V. Soldatov. Half-century history of clathrate chemistry. *J. Struct. Chem.*, 40(5):645–653, 1999.
- [25] Xiangfang Li, Wenyuan Liu, Shujie Liu, Jinqiu Hu, Yufeng Nan, Tian Tian, and Yunjian Zhou. A prevention and control method for natural gas hydrate in pipe strings during deepwater gas well production tests. *Nat. Gas Ind. B*, 7(1):82–92, 2020.
- [26] Seokyeon Moon, Sujin Hong, Yunseok Lee, Jae S. Lee, Yun Ho Ahn, and Youngjune Park. Enhancing Hydrogen Cluster Storage in Clathrate Hydrates via Defect-Mediated Lattice Engineering. *J. Phys. Chem. C*, 2021.
- [27] Ali Eslamimanesh, Amir H Mohammadi, Dominique Richon, Paramespri Naidoo, and Deresh Ramjugernath. Application of gas hydrate formation in separation processes: A review of experimental studies. *J. Chem. Thermodyn.*, 46:62–71, 2012.
- [28] Gyeol Ko, Joonseop Lee, and Yongwon Seo. Separation efficiency and equilibrium recovery ratio of SF₆ in hydrate-based greenhouse gas separation. *Chem. Eng. J.*, 405(September 2020):126956, 2021.
- [29] Wonjung Choi, Woojin Go, Yohan Lee, Junghoon Mok, and Yongwon Seo. Mechanism and kinetics of guest exchange in sII hydrate – Flue gas replacement as revealed by experimental and computational approaches for hydrocarbon recovery and CO₂ sequestration. *Chem. Eng. J.*, (October):128119, 2020.
- [30] Sang Hyun Lee and Kyungtae Park. Conceptual design and economic analysis of a novel cogeneration desalination process using LNG based on clathrate hydrate. *Desalination*, 498(114703):1–16, 2021.
- [31] Ponnivalavan Babu, Chandradeep Bollineni, and Nagu Daraboina. Energy Analysis of Methane-Hydrate-Based Produced Water Desalination. *Energy and Fuels*, 35(3):2514–2519, 2021.
- [32] Kyuchul Shin, Jong Ho Cha, Yongwon Seo, and Huen Lee. Physicochemical properties of ionic clathrate hydrates. *Chem. - An Asian J.*, 5(1):22–34, 2010.

- [33] Timothy A. Strobel, Yongkwan Kim, Gary S. Andrews, Jack R. Ferrell, Carolyn A. Koh, Andrew M. Herring, and E. Dendy Sloan. Chemical-clathrate hybrid hydrogen storage: Storage in both guest and host. *J. Am. Chem. Soc.*, 130(45):14975–14977, 2008.
- [34] Kyuchul Shin, Konstantin A. Udachin, Igor L. Moudrakovski, Donald M. Leek, Saman Alavi, Christopher I. Ratcliffe, and John A. Ripmeester. Methanol incorporation in clathrate hydrates and the implications for oil and gas pipeline flow assurance and icy planetary bodies. *Proc. Natl. Acad. Sci. U. S. A.*, 110(21):8437–8442, 2013.
- [35] Timothy A et al Minshull. Hydrate occurrence in Europe :A review of available evidence. *Mar. Pet. Geol.*, 111:2735–2764, 2020.
- [36] Roy Andrew Partain and Constantinos Yiallourides. Hydrate occurrence in Europe: Risks, rewards, and legal frameworks. *Mar. Policy*, 121(104122):1–10, 2020.
- [37] Mark Maslin, Matthew Owen, Simon Day, and David Long. Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology*, 32(1):53–56, 2004.
- [38] Nikolaus Froitzheim, Jaroslaw Majka, and Dmitry Zastrozhnov. Methane release from carbonate rock formations in the Siberian permafrost area during and after the 2020 heat wave. *Proc. Natl. Acad. Sci. U. S. A.*, 118(32):2020–2022, 2021.
- [39] E Dendy Sloan. Gas hydrates: Review of physical/chemical properties. *Energy and Fuels*, 12(2):191–196, 1998.
- [40] A Drobyshev, A Aldiyarov, V Kurnosov, K Katpaeva, E Korshikov, D Sokolov, A Shinbayeva, and A Timchenko. Physical modeling of the formation of clathrate hydrates of methane. *Low Temp. Phys.*, 41(6):429–434, 2015.
- [41] Yun Ho Ahn, Seokyeon Moon, Dong Yeun Koh, Sujin Hong, Huen Lee, Jae W. Lee, and Youngjune Park. One-step formation of hydrogen clusters in clathrate hydrates stabilized via natural gas blending. *Energy Storage Mater.*, 24(March 2019):655–661, 2020.
- [42] Salvatore F. Cannone, Andrea Lanzini, and Massimo Santarelli. A Review on CO₂ Capture Technologies with Focus on CO₂-Enhanced Methane Recovery from Hydrates. *Energies*, 14(2):387, 2021.
- [43] Xuemei Lang, Caijuan Zheng, Shuanshi Fan, Yanhong Wang, Gang Li, Shenglong Wang, and Chi Yu. “Similar self-preservation” and decomposition kinetics of tetrahydrofuran-hydrogen hydrate particles. *Int. J. Hydrogen Energy*, 47(13):8457–8466, 2022.

- [44] John A. Ripmeester and Saman Alavi. Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect. *Curr. Opin. Solid State Mater. Sci.*, 20(6):344–351, 2016.
- [45] Ioannis N. Tsimpanogiannis and Ioannis G. Economou. Monte Carlo simulation studies of clathrate hydrates: A review. *J. Supercrit. Fluids*, 134(December 2017):51–60, 2018.
- [46] Fernando De Azevedo Medeiros, Iuri Soter Viana Segtovich, Frederico Wanderley Tavares, and Amadeu K. Sum. Sixty Years of the van der Waals and Platteeuw Model for Clathrate Hydrates - A Critical Review from Its Statistical Thermodynamic Basis to Its Extensions and Applications. *Chem. Rev.*, 120(24):13349–13381, 2020.
- [47] Zhenyuan Yin, Junjie Zheng, Hyunho Kim, Yutaek Seo, and Praveen Linga. Hydrates for cold energy storage and transport: A review. *Adv. Appl. Energy*, 2(March):100022, 2021.
- [48] J. O. Abe, A. P.I. Popoola, E. Ajenifuja, and O. M. Popoola. Hydrogen energy, economy and storage: Review and recommendation. *Int. J. Hydrogen Energy*, 44(29):15072–15086, 2019.
- [49] Mohammad Reza Ghaani, Judith M. Schicks, and Niall J. English. A review of reactor designs for hydrogen storage in clathrate hydrates. *Appl. Sci.*, 11(2):1–16, 2021.
- [50] Aliakbar Hassanpouryouzband, Edris Joonaki, Mehrdad Vasheghani Farahani, Satoshi Takeya, Carolyn Ruppel, Jinhai Yang, Niall J. English, Judith M. Schicks, Katriona Edlmann, Hadi Mehrabian, Zachary M. Aman, and Bahman Tohidi. Gas hydrates in sustainable chemistry. *Chem. Soc. Rev.*, 49(15):5225–5309, 2020.
- [51] Y.F Makogon. *Hydrates of Hydrocarbons*. Pennwell Publishing Co., 1997.
- [52] Seungmin Lee, Sungwon Park, Youngjun Lee, and Yongwon Seo. Thermodynamic and ^{13}C NMR spectroscopic verification of methane-carbon dioxide replacement in natural gas hydrates. *Chem. Eng. J.*, 225:636–640, 2013.
- [53] Jong Won Lee, Jonghyub Lee, and Seong Pil Kang. ^{13}C NMR spectroscopies and formation kinetics of gas hydrates in the presence of monoethylene glycol as an inhibitor. *Chem. Eng. Sci.*, 104:755–759, 2013.
- [54] Satoshi Takeya, Konstantin A Udachin, Igor L Moudrakovski, Robin Susilo, and John A Ripmeester. Direct space methods for powder X-ray diffraction for guest-host materials: Applications to cage occupancies and guest distributions in clathrate hydrates. *J. Am. Chem. Soc.*, 132(2):524–531, 2010.
- [55] Byeongwan Lee, Kyuchul Shin, Sanehiro Muromachi, Igor L. Moudrakovski, Christopher I. Ratcliffe, and John A. Ripmeester. Enhanced methane storage in clathrate hydrates induced by antifreezes. *Chem. Eng. J.*, 418(January):129304, 2021.
- [56] Amadeu K. Sum, Robert C. Burruss, and E. Dendy Sloan. Measurement of clathrate hydrates via Raman spectroscopy. *J. Phys. Chem. B*, 101(38):7371–7377, 1997.

- [57] Davi Éber Sanches de Menezes, Amadeu K Sum, Arnaud Desmedt, Pedro de Alcântara Pessôa Filho, and Maria Dolores Robustillo Fuentes. Coexistence of sI and sII in methane-propane hydrate former systems at high pressures. *Chem. Eng. Sci.*, 208(115149):1–11, 2019.
- [58] Michael T. Kirchner, Roland Boese, W. Edward Billups, and Lewis R. Norman. Gas hydrate single-crystal structure analyses. *J. Am. Chem. Soc.*, 126(30):9407–9412, 2004.
- [59] Konstantin A. Udachin, Christopher I. Ratcliffe, and John A. Ripmeester. Single crystal diffraction studies of structure I, II and H hydrates: Structure, cage occupancy and composition. *J. Supramol. Chem.*, 2(4-5):405–408, 2002.
- [60] Yingying Huang, Keyao Li, Xue Jiang, Yan Su, Xiaoxiao Cao, and Jijun Zhao. Phase Diagram of Methane Hydrates and Discovery of MH-VI Hydrate. *J. Phys. Chem. A*, 122(28):6007–6013, 2018.
- [61] Xiaoxiao Cao, Yingying Huang, Xue Jiang, Yan Su, and Jijun Zhao. Phase diagram of water-methane by first-principles thermodynamics: Discovery of MH-IV and MH-V hydrates. *Phys. Chem. Chem. Phys.*, 19(24):15996–16002, 2017.
- [62] J. S. Loveday, R. J. Nelmes, M. Guthrie, D. D. Klug, and J. S. Tse. Transition from cage clathrate to filled ice: The structure of methane hydrate III. *Phys. Rev. Lett.*, 87(21):215501–1–215501–4, 2001.
- [63] M von Stackelberg and W Meinhold. Feste Gashydrate III. Mischhydrate. *Zeitschrift für Elektrochemie*, 58:40–45, 1954.
- [64] Ravi Radhakrishnan and Bernhardt L. Trout. A new approach for studying nucleation phenomena using molecular simulations: Application to CO₂ hydrate clathrates. *J. Chem. Phys.*, 117(4):1786–1796, 2002.
- [65] Qiao Shi, Pinqiang Cao, Zhengde Han, Fulong Ning, Hao Gong, Yue Xin, Zhisen Zhang, and Jianyang Wu. Role of Guest Molecules in the Mechanical Properties of Clathrate Hydrates. *Cryst. Growth Des.*, 18(11):6729–6741, 2018.
- [66] M. V. Stackelberg and H. R. Müller. On the structure of gas hydrates. *J. Chem. Phys.*, 19(10):1319–1320, 1951.
- [67] Thomas C. W. Mak and Richard K. McMullan. Polyhedral Clathrate Hydrates. X. Structure of the Double Hydrate of Tetrahydrofuran and Hydrogen Sulfide. *J. Chem. Phys.*, 42(8):2732–2737, 1965.
- [68] John A. Ripmeester, John S. Tse, Christopher I. Ratcliffe, and Brian M. Powell. A new clathrate hydrate structure. *Nature*, 325:135–136, 1987.
- [69] Claire Petuya, Françoise Damay, Bertrand Chazallon, Jean Luc Bruneel, and Arnaud Desmedt. Guest Partitioning and Metastability of the Nitrogen Gas Hydrate. *J. Phys. Chem. C*, 122(1):566–573, 2018.

- [70] Ali Rasoolzadeh and Alireza Shariati. Hydrogen hydrate cage occupancy: A key parameter for hydrogen storage and transport. *Fluid Phase Equilib.*, 494:8–20, 2019.
- [71] Andrzej Falenty, Thomas C. Hansen, and Werner F. Kuhs. Formation and properties of ice XVI obtained by emptying a type sII clathrate hydrate. *Nature*, 516(7530):231–233, 2014.
- [72] Louw J. Florusse, Cor J. Peters, Joop Schoonman, Keith C. Hester, Carolyn A. Koh, Steven F. Dec, Kenneth N. Marsh, and E. Dendy Sloan. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science* (80-.), 306(5695):469–471, 2004.
- [73] Yasushi Kamata, Yukiyasu Yamakoshi, Takao Ebinuma, Hiroyuki Oyama, Wataru Shimada, and Hideo Narita. Hydrogen sulfide separation using tetra-n-butyl ammonium bromide semi-clathrate (TBAB) hydrate. *Energy and Fuels*, 19(4):1717–1722, 2005.
- [74] Sanehiro Muromachi. CO₂ capture properties of semiclathrate hydrates formed with tetra-n-butylammonium and tetra-n-butylphosphonium salts from H₂ + CO₂ mixed gas. *Energy*, 223:120015, 2021.
- [75] Antonin Chapoy, Ross Anderson, and Bahman Tohidi. Low-pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. *J. Am. Chem. Soc.*, 129(4):746–747, 2007.
- [76] Ali Davoodabadi, Ashkan Mahmoudi, and Hadi Ghasemi. The potential of hydrogen hydrate as a future hydrogen storage medium. *iScience*, 24(1):101907, 2021.
- [77] Dietrich Mootz, Ernst Josef Oellers, and Michael Wiebcke. First Examples of Type I Clathrate Hydrates of Strong Acids: Polyhydrates of Hexafluorophosphoric, Tetrafluoroboric, and Perchloric Acid. *J. Am. Chem. Soc.*, 109(4):1200–1202, 1987.
- [78] Jong Ho Cha, Kyuchul Shin, Sukjeong Choi, Sangyong Lee, and Huen Lee. Maximized proton conductivity of the HPF₆ clathrate hydrate by structural transformation. *J. Phys. Chem. C*, 112(35):13332–13335, 2008.
- [79] Dyadin, Yu A. and K. A. Udachin. Clathrate polyhydrates of peralkylonium salts and their analogs. *J. Struct. Chem.*, 28(44):394–432, 1987.
- [80] Sungwon Park, Seungmin Lee, Youngjun Lee, and Yongwon Seo. CO₂ capture from simulated fuel gas mixtures using semiclathrate hydrates formed by quaternary ammonium salts. *Environ. Sci. Technol.*, 47(13):7571–7577, 2013.
- [81] Wataru Shimada, Takao Ebinuma, Hiroyuki Oyama, Yasushi Kamata, Satoshi Takeya, Tsutomu Uchida, Jiro Nagao, and Hideo Narita. Separation of gas molecule using tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals. *Japanese J. Appl. Physics, Part 2 Lett.*, 42(2 A):2–5, 2003.

- [82] Wataru Shimada, Motoo Shiro, Hidemasa Kondo, Satoshi Takeya, Hiroyuki Oyama, Takao Ebinuma, and Hideo Marita. Tetra-n-butylammonium bromide-water (1/38). *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 61(2):65–66, 2005.
- [83] Qiang Sun, Jinzhao Zhang, Yang Luo, Xuqiang Guo, and Aixian Liu. Separation of methane-ethylene via forming semi-clathrate hydrates with TBAB. *J. Nat. Gas Sci. Eng.*, 34:265–268, 2016.
- [84] Carl-friedrich Schleussner, Joeri Rogelj, Michiel Schaeffer, Tabea Lissner, Rachel Licker, Erich M Fischer, Reto Knutti, Anders Levermann, Katja Frieler, and William Hare. Science and policy characteristics of the Paris Agreement temperature goal. *Nat. Publ. Gr.*, (July), 2016.
- [85] Hideaki Kobayashi, Akihiro Hayakawa, K. D.Kunkuma A. Somarathne, and Ekenechukwu C. Okafor. Science and technology of ammonia combustion. *Proc. Combust. Inst.*, 37(1):109–133, 2019.
- [86] Hari Prakash Veluswamy, Asheesh Kumar, Yutaek Seo, Ju Dong Lee, and Praveen Linga. A review of solidified natural gas (SNG) technology for gas storage via clathrate hydrates. *Appl. Energy*, 216(February):262–285, 2018.
- [87] B. P. Prajwal and K. G. Ayappa. Evaluating methane storage targets: From powder samples to onboard storage systems. *Adsorption*, 20(5-6):769–776, 2014.
- [88] Laura A. Pellegrini, Stefania Moioli, Fabio Brignoli, and Camilla Bellini. LNG technology: The weathering in above-ground storage tanks. *Ind. Eng. Chem. Res.*, 53(10):3931–3937, 2014.
- [89] Younggy Shin and Yoon Pyo Lee. Design of a boil-off natural gas reliquefaction control system for LNG carriers. *Appl. Energy*, 86(1):37–44, 2009.
- [90] Matúš Mišík. The EU needs to improve its external energy security. *Energy Policy*, 165(April), 2022.
- [91] Yang Peng, Vaiva Krungleviciute, Ibrahim Eryazici, Joseph T. Hupp, Omar K. Farha, and Taner Yildirim. Methane storage in metal-organic frameworks: Current records, surprise findings, and challenges. *J. Am. Chem. Soc.*, 135(32):11887–11894, 2013.
- [92] Eyas Mahmoud, Labeeb Ali, Asmaa El Sayah, Sara Awni Alkhatib, Hend Abdulsalam, Mouza Juma, and Ala'A H Al-Muhtaseb. Implementing metal-organic frameworks for natural gas storage. *Crystals*, 9(8):1–19, 2019.
- [93] H. Kanda. Economic study on natural gas transportation with natural gas hydrate (NGH) pellets. *Int. Gas Union World Gas Conf. Pap.*, 4:1990–2000, 2006.

- [94] Behzad Partoon and Jafar Javanmardi. Effect of Mixed Thermodynamic and Kinetic Hydrate Promoters on Methane Hydrate Phase Boundary and Formation Kinetics. *J. Chem. Eng. Data*, 58:501–509, 2013.
- [95] Zhen Pan, Yi Wu, Liyan Shang, Li Zhou, and Zhien Zhang. Progress in use of surfactant in nearly static conditions in natural gas hydrate formation. *Front. Energy*, 14(3):463–481, 2020.
- [96] Niall J English and J M D MacElroy. Perspectives on molecular simulation of clathrate hydrates: Progress, prospects and challenges. *Chem. Eng. Sci.*, 121:133–156, 2015.
- [97] Sebastien Bergeron, Juan G. Beltrán, and Phillip Servio. Reaction rate constant of methane clathrate formation. *Fuel*, 89(2):294–301, 2010.
- [98] Hari Prakash Veluswamy and Praveen Linga. Macroscopic kinetics of hydrate formation of mixed hydrates of hydrogen/tetrahydrofuran for hydrogen storage. *Int. J. Hydrogen Energy*, 38(11):4587–4596, 2013.
- [99] Hari Prakash Veluswamy, Gaurav Bhattacharjee, Junxiong Liao, and Praveen Linga. Macroscopic kinetic investigations on mixed natural gas hydrate formation for gas storage application. *Energy and Fuels*, 34(12):15257–15269, 2020.
- [100] Kazuya Ozawa and Ryo Ohmura. Crystal Growth of Clathrate Hydrate with Methane plus Partially Water Soluble Large-Molecule Guest Compound. *Cryst. Growth Des.*, 19(3):1689–1694, 2019.
- [101] Craig J. Taylor, Kelly T. Miller, Carolyn A. Koh, and E. Dendy Sloan. Macroscopic investigation of hydrate film growth at the hydrocarbon/water interface. *Chem. Eng. Sci.*, 62(23):6524–6533, 2007.
- [102] A. Vysniauskas and P. R. Bishnoi. A kinetic study of methane hydrate formation. *Chem. Eng. Sci.*, 38(7):1061–1072, 1983.
- [103] Y.F. Makogon. *Hydrates of Natural Gas*. PennWell Books Tulsa, Oklahoma, 1981.
- [104] John A Ripmeester and Saman Alavi. Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect. *Curr. Opin. Solid State Mater. Sci.*, (20):344–351, 2016.
- [105] P. Englezos, N. Kalogerakis, P. D. Dholabhai, and P. R. Bishnoi. Kinetics of gas hydrate formation from mixtures of methane and ethane. *Chem. Eng. Sci.*, 42(11):2659–2666, 1987.
- [106] S. S. Kim, H. C., Bishnoi, P. R., Heidemann, R. A., Rizvi. Kinetics of methane hydrate decomposition. *Chem. Eng. Sci.*, 42(7):1645–1653, 1987.
- [107] M. Z. Faizullin, A. V. Vinogradov, and V. P. Koverda. Formation of clathrate hydrates under crystallization of gas-saturated amorphous ice. *Int. J. Heat Mass Transf.*, 65:649–654, 2013.

- [108] Qazi Nasir, Humbul Suleman, and Yasir A. Elsheikh. A review on the role and impact of various additives as promoters/ inhibitors for gas hydrate formation. *J. Nat. Gas Sci. Eng.*, 76(December 2019):103211, 2020.
- [109] Hesam Najibi, Morteza Mirzaee Shayegan, and Hassan Heidary. Experimental investigation of methane hydrate formation in the presence of copper oxide nanoparticles and SDS. *J. Nat. Gas Sci. Eng.*, 23:315–323, 2015.
- [110] Zhen Pan, Zhiming Liu, Zhien Zhang, Liyan Shang, and Shihui Ma. Effect of silica sand size and saturation on methane hydrate formation in the presence of SDS. *J. Nat. Gas Sci. Eng.*, 56(February):266–280, 2018.
- [111] Xiao-Yan Deng, Ying Yang, Dong-Liang Zhong, Xi-Yue Li, Bin-Bin Ge, and Jin Yan. New Insights into the Kinetics and Morphology of CO₂ Hydrate Formation in the Presence of Sodium Dodecyl Sulfate. *Energy & Fuels*, 35(17):13877–13888, 2021.
- [112] Y. Zhong and R. E. Rogers. Surfactant effects on gas hydrate formation. *Chem. Eng. Sci.*, 55(19):4175–4187, 2000.
- [113] Naoki Ando, Yui Kuwabara, and Yasuhiko H. Mori. Surfactant effects on hydrate formation in an unstirred gas/liquid system: An experimental study using methane and micelle-forming surfactants. *Chem. Eng. Sci.*, 73:79–85, 2012.
- [114] Jianwei Du, Huijuan Li, and Liguang Wang. Effects of ionic surfactants on methane hydrate formation kinetics in a static system. *Adv. Powder Technol.*, 25(4):1227–1233, 2014.
- [115] J. S. Zhang, Sangyong Lee, and Jae W. Lee. Kinetics of methane hydrate formation from SDS solution. *Ind. Eng. Chem. Res.*, 46(19):6353–6359, 2007.
- [116] Young Ah Kwon, Jong Mok Park, Kwang Eun Jeong, Chul Ung Kim, Tae Wan Kim, Ho Jeong Chae, Soon Yong Jeong, Jin Heong Yim, Young Kwon Park, and Ju dong Lee. Synthesis of anionic multichain type surfactant and its effect on methane gas hydrate formation. *J. Ind. Eng. Chem.*, 17(1):120–124, 2011.
- [117] Yan He, Meng-Ting Sun, Chen Chen, Guodong Zhang, Kun Chao, Yan Lin, and Fei Wang. Surfactant-based Promotion to Gas Hydrate Formation for Energy Storage. *J. Mater. Chem. A*, 2019.
- [118] Gaurav Bhattacharjee, Vivek Barmecha, Omkar S. Kushwaha, and Rajnish Kumar. Kinetic promotion of methane hydrate formation by combining anionic and silicone surfactants: Scalability promise of methane storage due to prevention of foam formation. *J. Chem. Thermodyn.*, 117:248–255, 2018.
- [119] Gaurav Pandey, Gaurav Bhattacharjee, Hari Prakash Veluswamy, Rajnish Kumar, Jitendra S. Sangwai, and Praveen Linga. Alleviation of Foam Formation in a Surfactant Driven Gas Hydrate System: Insights via a Detailed Morphological Study. *ACS Appl. Energy Mater.*, 1(12):6899–6911, 2018.

- [120] W. X. Pang, G. J. Chen, A. Dandekar, C. Y. Sun, and C. L. Zhang. Experimental study on the scale-up effect of gas storage in the form of hydrate in a quiescent reactor. *Chem. Eng. Sci.*, 62(8):2198–2208, 2007.
- [121] Ngoc N. Nguyen and Anh V. Nguyen. Hydrophobic Effect on Gas Hydrate Formation in the Presence of Additives. *Energy and Fuels*, 31(10):10311–10323, 2017.
- [122] Ngoc N. Nguyen, Mirza Galib, and Anh V. Nguyen. Critical Review on Gas Hydrate Formation at Solid Surfaces and in Confined Spaces—Why and How Does Interfacial Regime Matter? *Energy & Fuels*, 34(6):6751–6760, 2020.
- [123] Burla Sai Kiran, Tulluru Bhavya, and Pinnelli SR Prasad. Synergistic and antagonistic effects of amino acids in clathrate hydrates of greenhouse gases. *Chem. Eng. J. Adv.*, 7(February):100117, 2021.
- [124] Jyoti Shanker Pandey, Yousef Jouljamal Daas, and Nicolas von Solms. Screening of amino acids and surfactant as hydrate promoter for CO₂ capture from flue gas. *Processes*, 8(124):1–23, 2020.
- [125] Ahmad A.A. Majid, Joshua Worley, and Carolyn A. Koh. Thermodynamic and Kinetic Promoters for Gas Hydrate Technological Applications. *Energy and Fuels*, 35(23):19288–19301, 2021.
- [126] Lars Borchardt, Mirian Elizabeth Casco, and Joaquin Silvestre-Albero. Methane Hydrate in Confined Spaces: An Alternative Storage System. *ChemPhysChem*, 19(11):1298–1314, 2018.
- [127] Maninder Khurana, Zhenyuan Yin, and Praveen Linga. A review of clathrate hydrate nucleation. *ACS Sustain. Chem. Eng.*, 5(12):11176–11203, 2017.
- [128] Praveen Linga, Nagu Daraboina, John A. Ripmeester, and Peter Englezos. Enhanced rate of gas hydrate formation in a fixed bed column filled with sand compared to a stirred vessel. *Chem. Eng. Sci.*, 68(1):617–623, 2012.
- [129] Ahmed Omran, Nikolay Nesterenko, and Valentin Valtchev. Revealing Zeolites Active Sites Role as Kinetic Hydrate Promoters: Combined Computational and Experimental Study. *ACS Sustain. Chem. Eng.*, June 2022. Article ASAP.
- [130] Katipot Inkong, Hari Prakash Veluswamy, Pramoch Rangsunvigit, Santi Kulprathipanja, and Praveen Linga. Innovative Approach to Enhance the Methane Hydrate Formation at Near-Ambient Temperature and Moderate Pressure for Gas Storage Applications. *Ind. Eng. Chem. Res.*, 58(49):22178–22192, 2019.
- [131] Xiao Ya Zang, Shuan Shi Fan, De Qing Liang, Dong Liang Li, and Guang Jin Chen. Influence of 3A molecular sieve on tetrahydrofuran (THF) hydrate formation. *Sci. China, Ser. B Chem.*, 51(9):893–900, 2008.

- [132] Xiao Ya Zang, De Qing Liang, Shuan Shi Fan, and Cui Ping Tang. Influence of 5A-type zeolite powder on tetrahydrofuran hydrate formation and dissociation process. *Acta Phys. - Chim. Sin.*, 25(6):1047–1052, 2009.
- [133] Jun-Ho Hyun Nam-Jin Kim, Sung-Seek Park, Sang-Woong Shin and Wongee Chun. An experimental investigation into the effects of zeolites on the formation of methane hydrates. *Int. J. Energy Res.*, 39:26–32, 2015.
- [134] Mirian E. Casco, Joaquín Silvestre-Albero, Anibal J. Ramírez-Cuesta, Fernando Rey, Jose L. Jordá, Atul Bansode, Atsushi Urakawa, Inma Peral, Manuel Martínez-Escandell, Katsumi Kaneko, and Francisco Rodríguez-Reinoso. Methane hydrate formation in confined nanospace can surpass nature. *Nat. Commun.*, 6, 2015.
- [135] Sohaib Mohammed, Hassnain Asgar, Milind Deo, and Greeshma Gadikota. Interfacial and Confinement-Mediated Organization of Gas Hydrates, Water, Organic Fluids, and Nanoparticles for the Utilization of Sub-surface Energy and Geological Resources. *Energy and Fuels*, 35(6):4687–4710, 2021.
- [136] Atsadawuth Siangsai, Pramoch Rangsunvigit, Boonyarach Kitiyanan, Santi Kulprathipanja, and Praveen Linga. Investigation on the roles of activated carbon particle sizes on methane hydrate formation and dissociation. *Chem. Eng. Sci.*, 126:383–389, 2015.
- [137] A. Celzard and J. F. Maréché. Optimal wetting of active carbons for methane hydrate formation. *Fuel*, 85(7-8):957–966, 2006.
- [138] Mirian E Casco, Fernando Rey, José L Jordá, Svemir Rudić, François Fauth, Manuel Martínez-Escandell, Francisco Rodríguez-Reinoso, Enrique V Ramos-Fernández, and Joaquín Silvestre-Albero. Paving the way for methane hydrate formation on metal-organic frameworks (MOFs). *Chem. Sci.*, 7(6):3658–3666, 2016.
- [139] Qiang Zhang, Junjie Zheng, Baoyong Zhang, and Praveen Linga. Coal mine gas separation of methane via clathrate hydrate process aided by tetrahydrofuran and amino acids. *Appl. Energy*, 287(September 2020):116576, 2021.
- [140] P S R Prasad, K Shiva Prasad, and N K Thakur. Laser Raman spectroscopy of THF clathrate hydrate in the temperature range 90-300 K. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 68(4):1096–1100, 2007.
- [141] Alexandr Talyzin. Feasibility of H₂-THF-H₂O clathrate hydrates for hydrogen storage applications. *Int. J. Hydrogen Energy*, 33(1):111–115, 2008.
- [142] Marvin Ricaurte, Christophe Dicharry, Daniel Broseta, Xavier Renaud, and Jean Philippe Torré. CO₂ removal from a CO₂-CH₄ gas mixture by clathrate hydrate formation using THF and SDS as water-soluble hydrate promoters. *Ind. Eng. Chem. Res.*, 52(2):899–910, 2013.

- [143] Behzad Partoon, Khalik M. Sabil, Hariz Roslan, Bhajan Lal, and Lau Kok Keong. Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates. *Fluid Phase Equilib.*, 412:51–56, 2016.
- [144] Dong Liang Zhong, Nagu Daraboina, and Peter Englezos. Recovery of CH₄ from coal mine model gas mixture (CH₄/N₂) by hydrate crystallization in the presence of cyclopentane. *Fuel*, 106:425–430, 2013.
- [145] Alondra Torres Trueba, Laura J. Rovetto, Louw J. Florusse, Maaïke C. Kroon, and Cor J. Peters. Phase equilibrium measurements of structure II clathrate hydrates of hydrogen with various promoters. *Fluid Phase Equilib.*, 307(1):6–10, 2011.
- [146] Tatsuo Maekawa. Equilibrium conditions for clathrate hydrates formed from methane and aqueous propanol solutions. *Fluid Phase Equilib.*, 267(1):1–5, 2008.
- [147] Ekta Chaturvedi, Nitish Prasad, and Ajay Mandal. Enhanced formation of methane hydrate using a novel synthesized anionic surfactant for application in storage and transportation of natural gas. *J. Nat. Gas Sci. Eng.*, 56(May):246–257, 2018.
- [148] Namrata Gaikwad, Gaurav Bhattacharjee, Omkar S. Kushwaha, Jitendra S. Sangwai, Praveen Linga, and Rajnish Kumar. Effect of Cyclooctane and L-Tryptophan on Hydrate Formation from an Equimolar CO₂-CH₄ Gas Mixture Employing a Horizontal-Tray Packed Bed Reactor. *Energy and Fuels*, 34(8):9840–9851, 2020.
- [149] Brinchi Lucia, Beatrice Castellani, Federico Rossi, Franco Cotana, Elena Morini, Andrea Nicolini, and Mirko Filippini. Experimental investigations on scaled-up methane hydrate production with surfactant promotion: Energy considerations. *J. Pet. Sci. Eng.*, 120:187–193, 2014.
- [150] Hari Prakash Veluswamy, Sharad Kumar, Rajnish Kumar, Pramoch Rangsunvigit, and Praveen Linga. Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: Application to natural gas storage. *Fuel*, 182:907–919, 2016.
- [151] Mihrimah Ozkan. Direct air capture of CO₂: A response to meet the global climate targets. *MRS Energy Sustain.*, (0123456789):1–6, 2021.
- [152] Eloy S. Sanz-Pérez, Christopher R. Murdock, Stephanie A. Didas, and Christopher W. Jones. Direct Capture of CO₂ from Ambient Air. *Chem. Rev.*, 116(19):11840–11876, 2016.
- [153] Clas Ekström, Frank Schwendig, Ole Biede, Flavio Franco, Günther Haupt, Gelein de Koeijer, Charalambos Papapavlou, and Petter E. Røkke. Techno-Economic Evaluations and Benchmarking of Pre-combustion CO₂ Capture and Oxy-fuel Processes Developed in the European ENCAP Project. *Energy Procedia*, 1(1):4233–4240, 2009.

- [154] Yi-Song Yu, Xianwei Zhang, Jian-Wu Liu, Yohan Lee, and Xiao-Sen Li. Natural gas hydrate resources and hydrate technologies: a review and analysis of the associated energy and global warming challenges. *Energy Environ. Sci.*, 2021.
- [155] Yuan Zhang, Jaka Sunarso, Shaomin Liu, and Rong Wang. Current status and development of membranes for CO₂/CH₄ separation: A review. *Int. J. Greenh. Gas Control*, 12:84–107, 2013.
- [156] Anshuman Sinha and Matthew J. Realff. A parametric study of the techno-economics of direct CO₂ air capture systems using solid adsorbents. *AIChE J.*, 65(7):1–8, 2019.
- [157] Luogang Wu, Jiaqi Liu, Hua Shang, Shishuai Li, Jiangfeng Yang, Libo Li, and Jinping Li. Capture CO₂ from N₂ and CH₄ by zeolite L with different crystal morphology. *Microporous Mesoporous Mater.*, 316(December 2020):110956, 2021.
- [158] Dennis Y.C. Leung, Giorgio Caramanna, and M. Mercedes Maroto-Valer. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.*, 39:426–443, 2014.
- [159] Friday O. Ochedi, Jianglong Yu, Hai Yu, Yangxian Liu, and Arshad Hussain. Carbon dioxide capture using liquid absorption methods: a review. *Environ. Chem. Lett.*, 19:77–109, 2021.
- [160] Dennis Y.C. Leung, Giorgio Caramanna, and M. Mercedes Maroto-Valer. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.*, 39:426–443, 2014.
- [161] G. Göttlicher and R. Pruschek. Comparison of CO₂ removal systems for fossil-fuelled power plant processes. *Energy Convers. Manag.*, 38(SUPPL. 1):173–178, 1997.
- [162] Mohammed D. Aminu, Seyed Ali Nabavi, Christopher A. Rochelle, and Vasilije Manovic. A review of developments in carbon dioxide storage. *Appl. Energy*, 208(September):1389–1419, 2017.
- [163] Khalik Mohamad Sabil and Behzad Partoon. Recent advances on carbon dioxide capture through a hydrate-based gas separation process. *Curr. Opin. Green Sustain. Chem.*, 11:22–26, 2018.
- [164] Xiaolin Wang, Fengyuan Zhang, and Wojciech Lipiński. Research progress and challenges in hydrate-based carbon dioxide capture applications. *Appl. Energy*, 269(114928):1–26, 2020.
- [165] A. Falenty, J. Qin, A. N. Salamatın, L. Yang, and W. F. Kuhs. Fluid composition and kinetics of the in situ replacement in CH₄-CO₂ hydrate system. *J. Phys. Chem. C*, 120(48):27159–27172, 2016.
- [166] Jinxiang Liu, Yujie Yan, Jiafang Xu, Shujuan Li, Gang Chen, and Jun Zhang. Replacement micro-mechanism of CH₄ hydrate by N₂/CO₂ mixture revealed by ab initio studies. *Comput. Mater. Sci.*, 123:106–110, 2016.

- [167] Ross Anderson, Maria Llamedo, Bahman Tohidi, and Rod W. Burgass. Experimental measurement of methane and carbon dioxide clathrate hydrate equilibria in mesoporous silica. *J. Phys. Chem. B*, 107(15):3507–3514, 2003.
- [168] Ray Boswell, David Schoderbek, Timothy S. Collett, Satoshi Ohtsuki, Mark White, and Brian J. Anderson. The Iñik Sikumi field experiment, Alaska North Slope: Design, operations, and implications for CO₂-CH₄ exchange in gas hydrate reservoirs. *Energy and Fuels*, 31(1):140–153, 2017.
- [169] T. S. Collett, R. E. Lewis, W. J. Winters, M. W. Lee, K. K. Rose, and R. M. Boswell. Downhole well log and core montages from the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope. *Mar. Pet. Geol.*, 28(2):561–577, 2011.
- [170] A. N. Salamatin, A. Falenty, and W. F. Kuhs. Diffusion Model for Gas Replacement in an Isostructural CH₄-CO₂ Hydrate System. *J. Phys. Chem. C*, 121(33):17603–17616, 2017.
- [171] Michel Noussan, Pier Paolo Raimondi, Rossana Scita, and Manfred Hafner. The role of green and blue hydrogen in the energy transition—a technological and geopolitical perspective. *Sustain.*, 13(1):1–26, 2021.
- [172] Pietro Di Profio, Simone Arca, Federico Rossi, and Mirko Filippini. Comparison of hydrogen hydrates with existing hydrogen storage technologies: Energetic and economic evaluations. *Int. J. Hydrogen Energy*, 34(22):9173–9180, 2009.
- [173] Hari Prakash Veluswamy, Rajnish Kumar, and Praveen Linga. Hydrogen storage in clathrate hydrates: Current state of the art and future directions. *Appl. Energy*, 122:112–132, 2014.
- [174] Jinxiang Dong, Xiaoyan Wang, Hong Xu, Qiang Zhao, and Jinping Li. Hydrogen storage in several microporous zeolites. *Int. J. Hydrogen Energy*, 32(18):4998–5004, 2007.
- [175] Huy Quoc Nguyen and Bahman Shabani. Review of metal hydride hydrogen storage thermal management for use in the fuel cell systems. *Int. J. Hydrogen Energy*, 46(62):31699–31726, 2021.
- [176] Qi Long Zhu and Qiang Xu. Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage. *Energy Environ. Sci.*, 8(2):478–512, 2015.
- [177] Rajesh B. Biniwale, S. Rayalu, S. Devotta, and M. Ichikawa. Chemical hydrides: A solution to high capacity hydrogen storage and supply. *Int. J. Hydrogen Energy*, 33(1):360–365, 2008.
- [178] Purna Chandra Rao and Minyoung Yoon. Potential liquid-organic hydrogen carrier (Lohc) systems: A review on recent progress. *Energies*, 13(6040):1–23, 2020.

- [179] Yuri A. Dyadin, Eduard G. Larionov, Andrei Yu Manakov, Fridrich V. Zhurko, Evgeny Ya Aladko, Tamara V. Mikina, and Vladislav Yu Komarov. Clathrate hydrates of hydrogen and neon. *Mendeleev Commun.*, 9(5):209–210, 1999.
- [180] Wendy L Mao, Ho kwang Mao, Alexander F. Goncharov, Viktor V. Struzhkin, Quanzhong Guo, Jingzhu Hu, Jinfu Hu, Russell J. Hemley, Maddury Somayazulu, and Yusheng Zhao. Hydrogen clusters in clathrate hydrate. *Science (80-.)*, 297(5590):2247–2249, 2002.
- [181] Wendy L. Mao and Ho Kwang Mao. Hydrogen storage in molecular compounds. *Proc. Natl. Acad. Sci. U. S. A.*, 101(3):708–710, 2004.
- [182] Niall J. English and Christian J. Burnham. Intra-cage structure, vibrations and tetrahedral-site hopping of H₂ and D₂ in doubly-occupied 51264 cages in sII clathrate hydrates from path-integral and classical molecular dynamics. *Appl. Sci.*, 11(54):1–9, 2021.
- [183] Keisuke Katsumasa, Kenichiro Koga, and Hideki Tanaka. On the thermodynamic stability of hydrogen clathrate hydrates. *J. Chem. Phys.*, 127(044509):1–8, 2007.
- [184] Huen Lee, Jong Won Lee, Do Youn Kim, Jeasung Park, Yu Taek Seo, Huang Zeng, Igor L. Moudrakovski, Christopher I. Ratcliffe, and John A. Ripmeester. Tuning clathrate hydrates for hydrogen storage. *Mater. Sustain. Energy A Collect. Peer-Reviewed Res. Rev. Artic. from Nat. Publ. Gr.*, 434(April):285–288, 2010.
- [185] Takeshi Sugahara, Joanna C. Haag, Pinnelli S.R. Prasad, Ashleigh A. Warntjes, E. Dendy Sloan, Amadeu K. Sum, and Carolyn A. Koh. Increasing hydrogen storage capacity using tetrahydrofuran. *J. Am. Chem. Soc.*, 131(41):14616–14617, 2009.
- [186] Timothy A. Strobel, Craig J. Taylor, Keith C. Hester, Steven F. Dec, Carolyn A. Koh, Kelly T. Miller, and E. D. Sloan. Molecular hydrogen storage in binary THF-H₂ clathrate hydrates. *J. Phys. Chem. B*, 110(34):17121–17125, 2006.
- [187] Fokko M. Mulder, Marnix Wagemaker, Lambert Van Eijck, and Gordon J. Kearley. Hydrogen in porous tetrahydrofuran clathrate hydrate. *ChemPhysChem*, 9(9):1331–1337, 2008.
- [188] Jr. Yorihiro Nagai, Hiroki Yoshioka, Masaki Ota, Yoshiyuki Sato, Hiroshi Inomata, Richard L. Smith. Binary Hydrogen-Tetrahydrofuran Clathrate Hydrate Formation Kinetics and Models. *AIChE J.*, 54(11):3007–3016, 2008.
- [189] Hari Prakash Veluswamy, Rajnish Kumar, and Praveen Linga. Hydrogen storage in clathrate hydrates: Current state of the art and future directions. *Appl. Energy*, 122:112–132, 2014.

- [190] Seongmin Park, Dong Yeun Koh, Hyery Kang, Jae W. Lee, and Huen Lee. Effect of molecular nitrogen on multiple hydrogen occupancy in clathrate hydrates. *J. Phys. Chem. C*, 118(35):20203–20208, 2014.
- [191] Tomohiro Hasegawa, Paul E. Brumby, Kenji Yasuoka, and Amadeu K. Sum. Mechanism for H₂ diffusion in sII hydrates by molecular dynamics simulations. *J. Chem. Phys.*, 153(5):054706–1–054706–9, 2020.
- [192] Ahmed Omran, Nikolai Nesterenko, and Valentin Valtchev. Ab initio mechanistic insights into the stability, diffusion and storage capacity of sI clathrate hydrate containing hydrogen. *Int. J. Hydrogen Energy*, 47(13):8419–8433, 2022.
- [193] R. Gary Grim, Prasad B. Kerkar, Michele Shebowich, Melissa Arias, E. Dendy Sloan, Carolyn A. Koh, and Amadeu K. Sum. Synthesis and characterization of sI clathrate hydrates containing hydrogen. *J. Phys. Chem. C*, 116(34):18557–18563, 2012.
- [194] Sergei S. Skiba, Eduard G. Larionov, Andrey Y. Manakov, Boris A. Kolesov, and Viktor I. Kosyakov. Investigation of hydrate formation in the system H₂-CH₄-H₂O at a pressure up to 250 MPa. *J. Phys. Chem. B*, 111(38):11214–11220, 2007.
- [195] R V Belosludov, R K Zhdanov, O S Subbotin, H Mizuseki, Yoshiyuki Kawazoe, and V R Belosludov. Theoretical study of hydrogen storage in binary hydrogen-methane clathrate hydrates. *J. Renew. Sustain. Energ.*, 6:053132, 2014.
- [196] Yuuki Matsumoto, R Gary Grim, Naveed M Khan, Takeshi Sugahara, Kazunari Ohgaki, E Dendy Sloan, Carolyn A Koh, and Amadeu K Sum. Investigating the thermodynamic stabilities of hydrogen and methane binary gas hydrates. *J. Phys. Chem. C*, 118(7):3581–3589, 2014.
- [197] R. V. Belosludov, R. K. Zhdanov, O. S. Subbotin, H. Mizuseki, M. Souissi, Y. Kawazoe, and V. R. Belosludov. Theoretical modelling of the phase diagrams of clathrate hydrates for hydrogen storage applications. *Mol. Simul.*, 38(10):773–780, 2012.
- [198] Mohammad Reza Ghaani, Satoshi Takeya, and Niall J. English. Hydrogen storage in propane-hydrate: Theoretical and experimental study. *Appl. Sci.*, 10(24):1–10, 2020.
- [199] Seokyeon Moon, Yunseok Lee, Dongju Seo, Seungin Lee, Sujin Hong, Yun-Ho Ahn, and Youngjune Park. Critical hydrogen concentration of hydrogen-natural gas blends in clathrate hydrates for blue hydrogen storage. *Renew. Sustain. Energy Rev.*, 141(September 2020):110789, 2021.
- [200] Anshul Gupta, Gino V. Baron, Patrice Perreault, Silvia Lenaerts, Radu George Ciocarlan, Pegie Cool, Paulo G.M. Mileo, Sven Rogge, Veronique Van Speybroeck, Geert Watson, Pascal Van Der Voort, Maarten

- Houllberghs, Eric Breynaert, Johan Martens, and Joeri F.M. Denayer. Hydrogen Clathrates: Next Generation Hydrogen Storage Materials. *Energy Storage Mater.*, 41(June):69–107, 2021.
- [201] R. G. Raluy, L. Serra, and J. Uche. Life cycle assessment of desalination technologies integrated with renewable energies. *Desalination*, 183(1-3):81–93, 2005.
- [202] Tianbiao He, Zheng Rong Chong, Junjie Zheng, Yonglin Ju, and Praveen Linga. LNG cold energy utilization: Prospects and challenges. *Energy*, 170:557–568, 2019.
- [203] Ponnivalavan Babu, Abhishek Nambiar, Tianbiao He, Iftekhar A. Karimi, Ju Dong Lee, Peter Englezos, and Praveen Linga. A Review of Clathrate Hydrate Based Desalination to Strengthen Energy-Water Nexus. *ACS Sustain. Chem. Eng.*, 6(7):8093–8107, 2018.
- [204] Ponnivalavan Babu, Abhishek Nambiar, Zheng Rong Chong, Nagu Daraboina, Mohammad Albeirutty, Omar A Bamaga, and Praveen Linga. Hydrate-based desalination (HyDesal) process employing a novel prototype design. *Chem. Eng. Sci.*, 218:115563, 2020.
- [205] Kyung Chan Kang, Praveen Linga, Kyeong nam Park, Sang June Choi, and Ju Dong Lee. Seawater desalination by gas hydrate process and removal characteristics of dissolved ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , B^{3+} , Cl^- , SO_4^{2-}). *Desalination*, 353:84–90, 2014.
- [206] A. Khafaei, A., & Kamran-Pirzaman. Experimental Study of Semiclathrate Hydrates Formation TBAOH, TBAF, and TBAC in the Presence of SDS and Tween Surfactants as a Cold Thermal Energy Storage System for Air Conditioning Applications. *J. Chem. Eng. Data*, 66(7):2901–2910, 2021.
- [207] P. Zhang, Z. W. Ma, and R. Z. Wang. An overview of phase change material slurries: MPCs and CHS. *Renew. Sustain. Energy Rev.*, 14(2):598–614, 2010.
- [208] Sandrine Marinhas, Anthony Delahaye, and Laurence Fournaison. Solid fraction modelling for CO_2 and CO_2 -THF hydrate slurries used as secondary refrigerants. *Int. J. Refrig.*, 30(5):758–766, 2007.
- [209] Jong Ho Cha, Kyuchul Shin, Sukjeong Choi, and Huen Lee. Ionic conductivity enhancement due to coguest inclusion in the pure ionic clathrate hydrates. *J. Phys. Chem. C*, 112(28):10573–10578, 2008.
- [210] Arnaud Desmedt, Frank Stallmach, Ruediger E. Lechner, Dominique Cavagnat, Jean Claude Lassègues, François Guillaume, Joseph Grondin, and Miguel A. Gonzalez. Proton dynamics in the perchloric acid clathrate hydrate $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$. *J. Chem. Phys.*, 121(23):11916–11926, 2004.
- [211] Xiaolin Wang, Fengyuan Zhang, and Wojciech Lipiński. Carbon dioxide hydrates for cold thermal energy storage: A review. *Sol. Energy*, 211(September):11–30, 2020.

- [212] T. Nogami, N. Oya, H. Ishida, and H. Matsumoto. Development of natural gas ocean transportation chain by means of natural gas hydrate (NGH). *6th Gas Hydrates Int. Conf. [ICGH] (Vancouver, Br. Columbia, 7/6-10/2008) Proc.*, (Icgh), 2008.
- [213] Satoo Nakai. Development of natural gas hydrate (NGH) supply chain. *Int. Gas Union World Gas Conf. Pap.*, 4:3040–3049, 2012.
- [214] Satoshi Takeya, Hiroko Mimachi, and Tetsuro Murayama. Methane storage in water frameworks: Self-preservation of methane hydrate pellets formed from NaCl solutions. *Appl. Energy*, 230(July):86–93, 2018.
- [215] J. S. Gudmundsson, Mahmut Parlaktuna, and A. A. Khokhar. Storing natural gas as frozen hydrate. *SPE Prod. Facil.*, 9(1):69–73, 1994.
- [216] Hiroko Mimachi, Masahiro Takahashi, Satoshi Takeya, Yoshito Gotoh, Akio Yoneyama, Kazuyuki Hyodo, Tohoru Takeda, and Tetsuro Murayama. Effect of Long-Term Storage and Thermal History on the Gas Content of Natural Gas Hydrate Pellets under Ambient Pressure. *Energy and Fuels*, 29(8):4827–4834, 2015.
- [217] Gaurav Bhattacharjee and Praveen Linga. Amino Acids as Kinetic Promoters for Gas Hydrate Applications : A Mini Review. 2021.
- [218] Satoshi Takeya, Sanehiro Muromachi, Akio Yoneyama, Keiichi Hirano, Kazuyuki Hyodo, and John A. Ripmeester. Superheating of Structure I Gas Hydrates within the Structure II Cyclopentane Hydrate Shell. *J. Phys. Chem. Lett.*, 13(9):2130–2136, 2022.
- [219] Gregor Rehder, Robert Eckl, Markus Elfgen, Andrzej Falenty, Rainer Hamann, Nina Kähler, Werner F. Kuhs, Hans Osterkamp, and Christoph Windmeier. Methane hydrate pellet transport using the self-preservation effect: A techno-economic analysis. *Energies*, 5(7):2499–2523, 2012.
- [220] Gaurav Bhattacharjee, Hari Prakash Veluswamy, Rajnish Kumar, and Praveen Linga. Rapid methane storage via sII hydrates at ambient temperature. *Appl. Energy*, 269(March):115142, 2020.
- [221] Syed Y. Nahri, James L. Nielsen, and Yuanhang Chen. Effect of nanoparticles on the nucleation and agglomeration rates of hydrate growth using THF–water clathrates. *Pet. Sci.*, 17(2):467–476, 2020.
- [222] Parisa Naeiji, Akram Arjomandi, and Farshad Varaminian. Journal of Natural Gas Science and Engineering Amino acids as kinetic inhibitors for tetrahydrofuran hydrate formation : Experimental study and kinetic modeling. *J. Nat. Gas Sci. Eng.*, 21:64–70, 2014.
- [223] H. Fakharian, H. Ganji, A. Naderi Far, and M. Kameli. Potato starch as methane hydrate promoter. *Fuel*, 94:356–360, 2012.

- [224] Avinash V. Palodkar and Amiya K. Jana. Clathrate hydrate dynamics with synthetic- and bio-surfactant in porous media: Model formulation and validation. *Chem. Eng. Sci.*, 213:115386, 2020.
- [225] Mirian E. Casco, Joaquín Silvestre-Albero, Anibal J. Ramírez-Cuesta, Fernando Rey, Jose L. Jordá, Atul Bansode, Atsushi Urakawa, Inma Peral, Manuel Martínez-Escandell, Katsumi Kaneko, and Francisco Rodríguez-Reinoso. Methane hydrate formation in confined nanospace can surpass nature. *Nat. Commun.*, 6, 2015.
- [226] Seokyo Moon, Yunseok Lee, Dongju Seo, Seungin Lee, Sujin Hong, Yun-Ho Ahn, and Youngjune Park. Critical hydrogen concentration of hydrogen-natural gas blends in clathrate hydrates for blue hydrogen storage. *Renew. Sustain. Energy Rev.*, 141(September 2020):110789, 2021.
- [227] Zachary T. Ward, Connor E. Deering, Robert A. Marriott, Amadeu K. Sum, E. Dendy Sloan, and Carolyn A. Koh. Phase equilibrium data and model comparisons for H₂S hydrates. *J. Chem. Eng. Data*, 60(2):403–408, 2015.
- [228] Ponnivalavan Babu, Ting Yang, Hari Prakash Veluswamy, Rajnish Kumar, and Praveen Linga. Hydrate phase equilibrium of ternary gas mixtures containing carbon dioxide, hydrogen and propane. *J. Chem. Thermodyn.*, 61:58–63, 2013.
- [229] P. Linga and M. A. Clarke. A review of reactor designs and materials employed for increasing the rate of gas hydrate formation. *Energy and Fuels*, 31(1):1–13, 2017.
- [230] Vafa Feyzi and Vahid Mohebbi. Hybrid Hydrate-Membrane Post-combustion CO₂Capture: A Conceptual Process Design and Analyses. *Ind. Eng. Chem. Res.*, 59(29):13132–13142, 2020.
- [231] Daria Surovtseva. *Department of Chemical Engineering Clean Gas Technologies Australia CO₂ Separation by Cryogenic and Hydrate*. PhD thesis, Curtin University of Technology, 2010.
- [232] Daria Surovtseva, Robert Amin, and Ahmed Barifcani. Design and operation of pilot plant for CO₂ capture from IGCC flue gases by combined cryogenic and hydrate method. *Chem. Eng. Res. Des.*, 89(9):1752–1757, 2011.
- [233] Yun-Ho Ahn, Seokyo Moon, Dong-Yeun Koh, Sujin Hong, Huen Lee, Jae W Lee, and Youngjune Park. One-step formation of hydrogen clusters in clathrate hydrates stabilized via natural gas blending. 2019.
- [234] Toshio Shibata, Hiroshi Yamachi, Ryo Ohmura, and Yasuhiko H. Mori. Engineering investigation of hydrogen storage in the form of a clathrate hydrate: Conceptual designs of underground hydrate-storage silos. *Int. J. Hydrogen Energy*, 37(9):7612–7623, 2012.

- [235] Luning Chen, Zhiyuan Qi, Shuchen Zhang, Ji Su, and Gabor A Somorjai. Catalytic hydrogen production from methane: A review on recent progress and prospect. *Catalysts*, 10(8), 2020.
- [236] Alexandra M Oliveira, Rebecca R Beswick, and Yushan Yan. A green hydrogen economy for a renewable energy society. *Curr. Opin. Chem. Eng.*, 33:100701, 2021.
- [237] Sonja van Renssen. The hydrogen solution? *Nat. Clim. Chang.*, 10(9):799–801, 2020.
- [238] Furat Dawood, Martin Anda, and G M Shafiullah. Hydrogen production for energy: An overview. *Int. J. Hydrogen Energy*, 45(7):3847–3869, 2020.
- [239] Robert W Howarth and Mark Z Jacobson. How green is blue hydrogen? *Energy Sci. Eng.*, 9(10):1676–1687, 2021.