



Review of natural gas hydrates as an energy resource: Prospects and challenges[☆]



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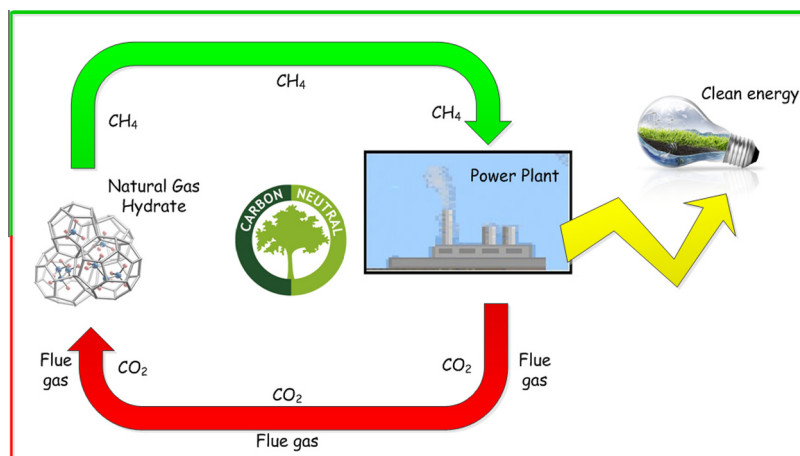
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HIGHLIGHTS

- A comprehensive review of natural gas hydrates as a resource is presented.
- CH₄–CO₂ displacement mechanism is reviewed and challenges are outlined.
- Prospects and future directions for methane recovery from natural gas hydrates are discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 October 2014

Received in revised form 23 December 2014

Accepted 28 December 2014

Available online 4 February 2015

Keywords:

Gas hydrates
Natural gas
Energy recovery
Energy resource
Methane hydrates
Unconventional gas

ABSTRACT

Natural gas is the cleanest burning fossil fuel and has been identified as a strong candidate for energy resource compared to oil and coal. Natural gas hydrate is an energy resource for methane that has a carbon quantity twice more than all fossil fuels combined and is distributed evenly around the world. Several field trials on energy production from hydrate resources have been conducted, and their outcomes revealed the possibility of energy production from hydrate resources. In this paper, we review various studies on resource potential of natural gas hydrate, the current research progress in laboratory settings, and several recent field trials. Possible limitation in each production method and the challenges to be addressed for large scale production are discussed in detail. Whilst there are no technology stoppers to exploit or produce methane from hydrates, specific technological breakthroughs will depend on the effective management of the sand and water during production, as well as the appropriate mitigation of environmental risks.

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[☆] This article is based on a four-page proceedings paper in Energy Procedia Volume 61 (2015). It has been substantially modified and extended, and has been subject to the normal peer review and revision process of the journal, Applied Energy.

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1. Introduction

Global energy demand is expected to increase significantly in the coming decades as human society grows. In the Reference Case of the 2013 International Energy Outlook by the US DOE, it has been projected that the global energy consumption will rise by 56% from 524 quadrillion BTU in 2010 to 820 quadrillion BTU in 2040 [1]. The main contributors to this increase in demand stems from non-OECD developing economies led by China and India, where demand is projected to rise by 112% from 2010 to 2040 [1].

While it is expected that more energy can be harnessed from the renewables and nuclear source as time progresses, the amount generated may still be far from meeting the vast increase in energy demand. It is projected that more than 76% of energy will come from carbon based source (gas, oil and coal) at 2040 despite growth in other renewable sources [2]. Amongst these 3 carbon based energy sources, natural gas is poised to increase at the highest rate (1.7% per year) as compared to the other source of fossil energy (0.9% p.a. for liquid fuel and 1.3% p.a. for coal) [1,3].

Asia is expected to be the main contributor to CO₂ emissions in the years to come due to higher energy demand – emissions from India, China and the rest of Asia ex-Japan are foreseen to grow annually at 2.3%, 2.1% and 1.9% respectively mainly from the combustion of carbon based energy sources [1,4]. Following such trend, the concerns about CO₂ emissions and climate change are expected to grow significantly and take centre-stage in the coming decades. As natural gas generates the lowest amount of CO₂ per unit of energy as compared to the other fossil fuels, replacing coal with natural gas as a primary energy source will become one possible mitigation measure to reduce CO₂ emissions in the foreseeable future [5].

Almost 80% of global natural gas demand is met by conventional sources with unconventional sources coming into prominence in recent years [6]. Projections of future developments indicate that a significant portion of future natural gas will be supplied by unconventional sources – tight gas, shale gas and coal bed methane. Estimates of technically recoverable conventional and unconventional reserves are fairly optimistic – a 2011 estimate by the International Energy Agency (IEA) indicated that globally recoverable resources were sufficient for 250 years following

current consumption rate. However, a large degree of uncertainty remains with regard to the accuracy of such figures. For example, the US Energy Information Administration (EIA) reduced its estimate of technically recoverable shale gas reserves in the United States from 827 trillion cubic feet (TCF) in 2011 to 482 TCF in 2012 [7].

Natural gas hydrates (NGH) are natural gas resources that have remained stable for millions of years which have been found since 1960s [8–10]. These ice-like solid compounds containing hydrocarbons are present in marine and permafrost environments. Gas hydrate resources have a more diverse distribution geographically and exist in a far greater amount than both conventional and other unconventional resources combined, which ignited the interest of various research groups around the world. The research activities on natural gas hydrates based on publications, subject area and countries are summarized in Fig. 1. As can be seen in Fig. 1A, the research activity on natural gas hydrates began to gain attention after the 1960s and has been on an increase ever since. After several field test activities done around 1995, there has been an exponential growth on the research publications over the past 20 years from different subject area. The summary of published research work according to country (Fig. 1B) shows that a total of 82 countries have been involved in research works on hydrate area, with more than 50% of these published works originated from the top 3 countries: the United States, China and Japan.

Prior to this work, reviews on energy recovery from natural gas hydrates (NGH) have been conducted by numerous groups from different perspectives. A perspective on the global natural gas hydrate resources is available in the literature [11]. A review specifically for CH₄-CO₂ exchange pertaining to laboratory studies on the thermodynamic and kinetic properties of the replacement process has also been conducted [12]. The representative reservoir models and their application on various recovery techniques have been summarized recently in the literature [13]. Recent reviews have also summarized the research progress on NGH in different countries around the world, which encompass the permafrost and marine NGH exploration, laboratory scale research progress on basic hydrate science and production responses [14,15]. In summary, these reviews were done on a very specific area of interest. Therefore, this paper aims to provide a holistic review that touches

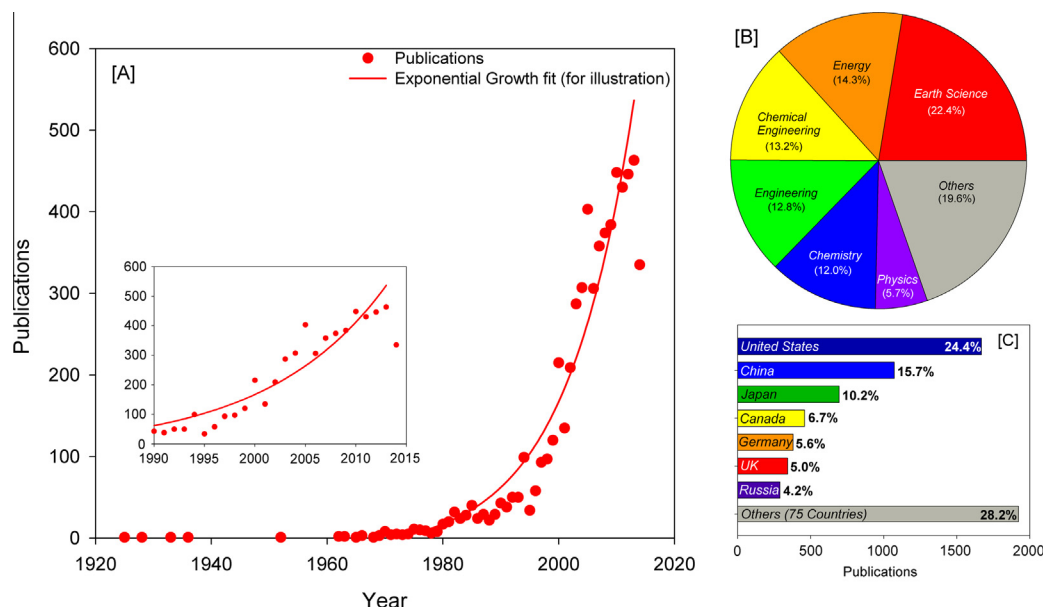


Fig. 1. (A) A histogram of the progress of research activity on “natural gas hydrates” or “methane hydrates” (data obtained from Scopus database on 03-October-2014, data presented till the year 2013); (B) subject area distribution of publications; (C) country wise distribution of publications.

upon all the aspects like production, environmental impact, strategy, state-of-the-art and also the review of the field test done so far including the latest Nankai Trough and Alaska tests. Finally we propose future directions and identify the challenges ahead for the natural gas hydrate research.

2. Gas hydrates

2.1. Structure

The chemical structure and stability of natural gas hydrates have been relatively well investigated. Gas hydrates are formed under certain sets of high pressure and low temperature conditions, outside of which the gas and water species typically remain in separate phases. Three main structures of gas hydrates – cubic structure I (sI), cubic structure II (sII) and the hexagonal structure (sH) have been identified [16–19]. In each structure, water molecules arrange in different patterns, forming cavities of different diameters (ranging from 7.82 Å in sII 5¹² cage to 11.58 Å in sH 5¹²6⁸ cage [18]) to reside gas molecules. The size, pressure and temperature conditions, and chemical nature of gas molecules determine which hydrate structure forms [18].

2.2. Hydrates in nature

There are two main origins of the natural hydrocarbon gases that form natural gas hydrates – biogenic or thermogenic. Biogenic natural gases are formed from CH₄-generating microbes (methanogens), which can be characterized by their high methane purity ($C_1/C_{2+} > 100$) [20–22]. On the other hand, thermogenic natural gases are formed from the decomposition of organic matter from fossil origin. Apart from methane as the major constituent, longer chain hydrocarbons such as ethane and propane also present in thermogenic natural gases ($C_1/C_{2+} < 100$) [21,23]. The occurrence of natural gas hydrates requires sufficient quantity of natural gas, water availability and natural conditions within the hydrate phase boundary [18,24–27].

By comparing the geothermal gradients of permafrost and marine environments with the equilibrium curve of natural gas hydrates, hydrate stability zone illustrating a rough estimate of regions in which gas hydrate could form is shown in Fig. 2. Several factors affecting the accuracy of this analysis are:

1. *Gas composition and hydrate structures.* Methane, ethane and propane form different hydrate structures and are stable at different conditions. Due to the difference in molecular size, propane forms sII hydrate whereas methane and ethane form the sI hydrate. It has been reported that at different compositions, these hydrocarbon mixtures can form a combination of structures, depending on the in situ conditions [28]. Mixture of methane and ethane or propane forms sII hydrate, which is stable at higher temperatures and lower pressures than pure methane hydrate, as illustrated in Fig. 2. Owing to the higher stability, mixed hydrates can exist at deeper depths than the predicted stability zone for pure methane hydrate. While sI and sII hydrates are most commonly found, sH have been also been recovered in certain locations, such as the coast of Vancouver Island in Canada [29];
2. *In situ properties.* Hydrate stability is affected by the local sediment properties, such as pore sediment type, sediment permeability, pore size and water salinity [30–34];
3. *Geotherms and hydrotherms.* The geothermal gradient and hydrothermal gradient of the natural environment vary with their location and seasonality [35,36].

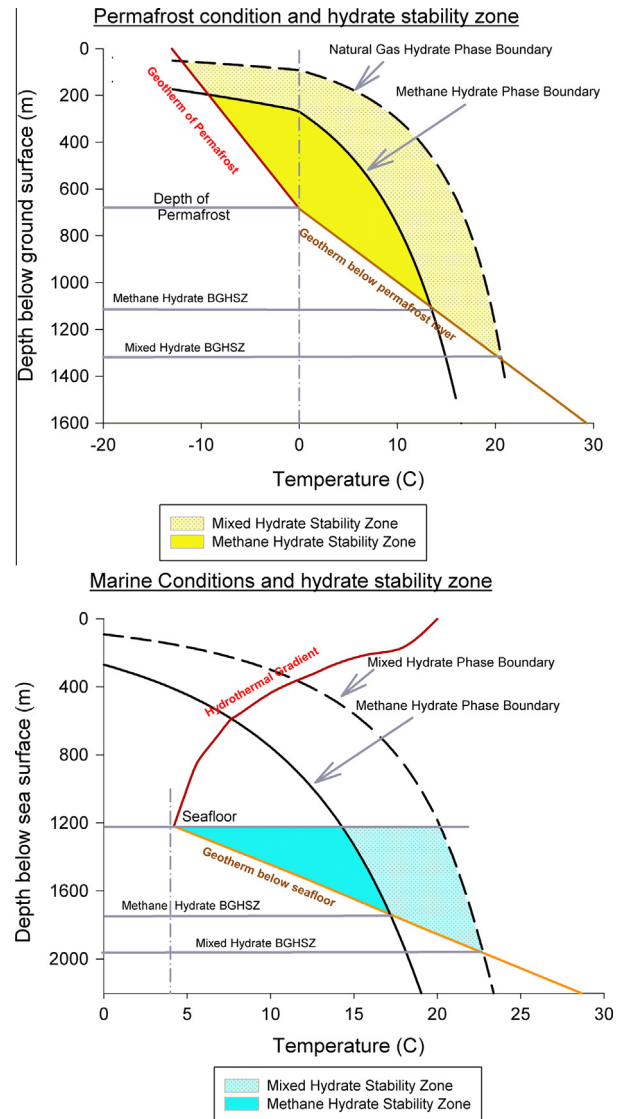


Fig. 2. Hydrate stability zone in Nature. Mixed hydrate and methane hydrate equilibrium data are computed via CSMGem [18], with a model natural gas mixture consisting of 93% methane, 5% ethane and 2% propane. Geothermal gradients applied in permafrost region were 1.9 °C/100 m and 3.2 °C/100 m [248], whereas hydrothermal and geothermal gradients for marine setting were retrieved from Birchwood et al. [249].

The occurrence of gas hydrate is observed through direct sampling or inferred from observing a reflection named “Bottom Simulating Reflector” (BSR) by seismic data acquisition. In BSR acquisition, the presence of gas hydrate in sub-seafloor zone is inferred from a sharp decrease in seismic velocity along the interface between overlying hydrate bearing sediment of anomalously high seismic velocity and underlying free gas containing sediment with low seismic velocity [37]. As the basis of BSR is dependent on the sharp discontinuity in the seismic velocity at interface, it is expected that sediments with lower hydrate saturation or without free gas zone will not be detecting BSR.

Most natural gas hydrates are of the sI structure. They have been observed in the Gulf of Mexico [35,38], Ulleung Basin [39], the Nankai Trough [40] and South China Sea [41] and in several other locations. On the contrary, thermogenic natural gas hydrate deposits form sII or sH hydrate structure and exist at milder conditions where pure methane does not form hydrate. They have been found in several locations including the Gulf of Mexico [35,42],

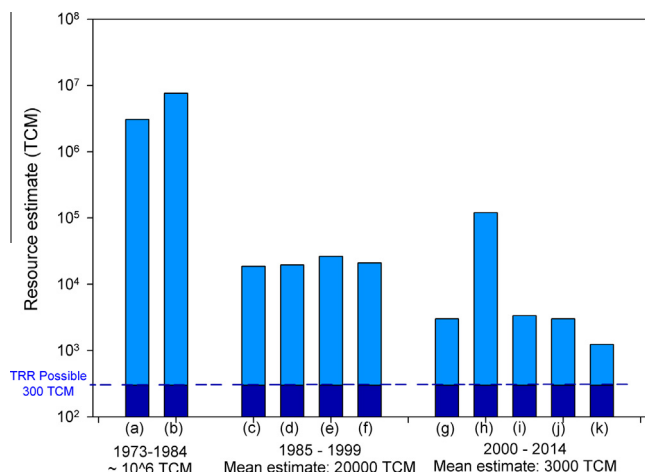


Fig. 3. Resource estimation of hydrates. Modified from Boswell and Collett [11] and Milkov [48]. (a) Trofimuk et al. [47], (b) Dobrynin et al. in [48], (c) Kvenvolden [49], (d) MacDonald [50], (e) Gronitz and Fung [51], (f) Kvenvolden [52], (g) Milkov [48], (h) Klauda and Sandler [53], (i) Archer et al. [55], (j) Boswell and Collett [11], (k) Johnson [54].

Caspian Sea [43,44] and the Northern Cascadia Margin [45]. A recent report also revealed the occurrence of sII hydrate in the permafrost zone of Qilian Mountain [41].

2.3. Estimations of hydrate resources

Since the occurrence of hydrate resource was discovered in 1967 [46], many have attempted to assess the total amount of natural gas hydrate on earth. These estimations typically focus on three key points: (1) how and how much methane originates in the natural environment; (2) how thick the Gas Hydrate Stability Zone (GHSZ) is and how does methane reach this zone; (3) how saturated the natural sediments in the GHSZ are with methane hydrate [41]. Fig. 3 summarizes resource estimates from literature [11,47–56].

The earlier estimations varied significantly – from Trofimuk et al. [47] who assumed that hydrates could occur wherever satisfactory conditions exist and coined the maximum amount at $3053 \times 10^{15} \text{ m}^3$ methane (STP) to Soloviev [57] who gave a minimum value of $0.2 \times 10^{15} \text{ m}^3$ methane (STP) due to considerations of limiting factors such as availability of methane, limited porosity, and percentages of organic matter. Early studies often report the resource estimation of permafrost environment and marine environment separately, with the marine hydrate estimates outnumber that in the permafrost environment by more than 2 orders of magnitude [47,49,53].

As illustrated in Fig. 3, the resource estimations have been decreasing over time due to improved understanding from the field trials, with the notable exception of Klauda & Sandler [53] which estimated a total amount of oceanic hydrate to be approximately $120 \times 10^{15} \text{ m}^3$ methane (STP). The fugacity based model revised several key assumptions such as the global average value of pore space filled (from *a priori* 5% to 3.4%) and demonstrated a good prediction of 68 out of the 71 occurrences of natural gas hydrates with explanations provided for the 3 exceptions. It should be noted that this appreciably high resource estimate included very deep and dispersed hydrate, which is usually unaccounted for in other resource estimates, and the study estimated a quantity of $44 \times 10^{15} \text{ m}^3$ methane (STP) for continental hydrate.

However, it must be noted that there exists a fundamental difference between the estimates of total amount of methane hydrates exist on earth and those technically recoverable and

economically feasible hydrate resources [11]. Generally, the large range of estimates presented by various groups over the past 40 years have focused on the total amount of methane found in hydrate form – without the consideration on resource recoverability. In order to be considered as a potential resource, the geological methane hydrate accumulation has to possess a minimum amount of gas concentration, frequently measured with gas yield (in $\text{m}^3\text{-gas}/\text{m}^3\text{-sediment}$), and a significant total amount of gas. These properties have to be comparable with existing medium or large gas reserves (conventional or unconventional) [48]. Apart from that, in terms of the types of reservoir, hydrates from sand reservoir is more recoverable as compared to other types of reservoir owing to its higher permeability and similarity with the conventional production technology [55,58].

The prevailing consensus is that majority of marine hydrate sediments are diffuse and exist in low-saturation [11,48,59]. An example is the hydrate formations in the Blake Ridge which are too dispersed to be considered for methane recovery [60]. However, it has been suggested that local, anomalous accumulations of gas hydrates of high concentration could exist in amounts greater than what were previously thought [11,61]. Recent field drilling programs for gas hydrate have discovered concentrated gas hydrate accumulations with examples being the marine sands in the Nankai Trough [40,62], Cascadia Margin [63,64] and Gulf of Mexico [65,66] and other types in offshore India [67], Malaysia [68] and Korea [39,69]. These concentrated hydrate deposits present a great potential for energy resource in the future. Nonetheless, greater efforts are needed in locating and quantifying such deposits.

To sum up, vast amount of natural gas hydrate resources has been identified in various location around the world. The consensus value of gas hydrate resource estimation has decreased from 20,000 trillion cubic meters (TCM) in 1990s [52] to 3000 TCM in recent years [11,48,55] from additional understanding towards limiting factors for hydrate formation obtained during the field trials. Nonetheless, the estimate of hydrate resource is still enormous as compared to the conventional gas resources (~404 TCM) and shale gas (204–456 TCM). Techniques to recover this vast amount of energy resource are reviewed in the following sections.

3. Recovery techniques

The conventional and most of the other unconventional natural gas are trapped in the earth due to geological properties – impermeable ‘cap’ sealing conventional NG reservoir and ultra-low permeability reservoir condition for unconventional NG. Techniques for gas recovery from these resources focus on creating conduit for these gases to flow out of the geological formation. An example is hydraulic fracturing – a technique which has unlocked methane from unconventional shale formations, work by generating artificial fractures in the reservoir rock around the wellbore, thereby providing rooms for the adsorbed natural gas to flow to the surface.

Gas hydrates, in contrary, are fundamentally different from the other unconventional natural gas sources. Gas molecules in the hydrate reservoir are trapped within cages formed by water molecules by van der Waals forces in molecular level [70]. Therefore, in addition to creating conduits for gas flow, techniques to recover methane from gas hydrates involve dissociating the natural gas hydrates in situ. Three most commonly proposed and studied techniques in dissociating methane hydrate are thermal stimulation, depressurization and inhibitor injection, as illustrated in Fig. 4. Thermal stimulation and depressurization techniques alter the local P–T conditions such that methane hydrate is no longer stable and dissociates into water and gas; whereas chemical inhibitor injection method involves introduction of chemical that can alter the phase boundary of hydrate system such that the hydrate

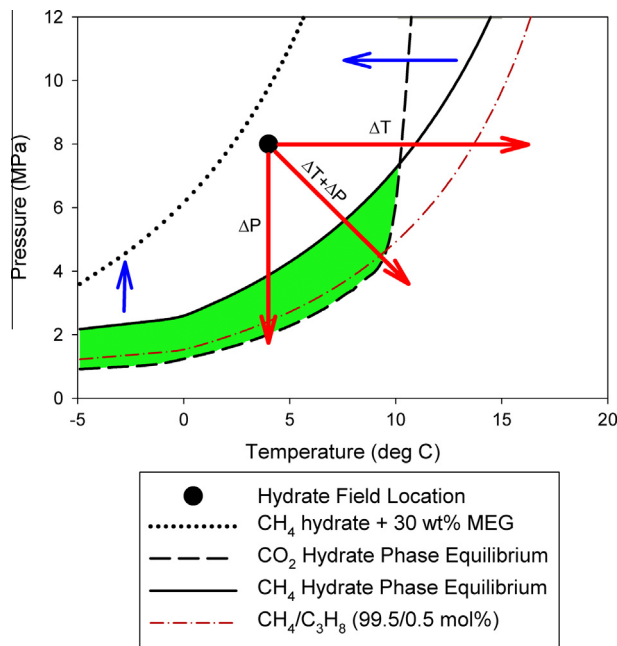


Fig. 4. Schematic diagram of commonly proposed natural gas recovery methods. (Red: Thermal stimulation, depressurization and combination; blue: inhibitor injection; and green zone: CH_4 - CO_2 exchange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dissociates at the in situ conditions. An illustrative example is shown in Fig. 4 for an arbitrary methane hydrate sediment at sea-floor temperature (4°C , 8 MPa). In order to recover methane from this sediment, a minimum temperature perturbation of 7 K or a minimum depressurization of 4.2 MPa is required. If the resource is to be recovered from one of the widely known inhibitor, ethylene glycol (EG), the required concentration of EG will be approximately $30\text{ wt.}\%$.

In this section, we will look into the research progress on each of the three recovery methods and some important findings. Before we proceed, it should be noted that the hydrate dissociation process is endothermic in nature [71]. Hence, a source of energy will be required for hydrate dissociation [72].

3.1. Thermal stimulation

The concept of thermal stimulation is straightforward – natural gas hydrates are heated in situ till the local temperature is away from the hydrate stability region. When hydrate decomposes, the entrapped gas is released from water cages and flows through the wellbore to be recovered. External heat is supplied through wellbore or point sources. In this section, we first look into the thermal properties of hydrate bearing sediment and the self-preservation phenomena observed in hydrates. Briefly, the results from numerical simulation are discussed and subsequently, various laboratory activities investigating methane production by thermal stimulation are reviewed, and some specific techniques for heat delivery will also be looked into.

3.1.1. Thermal properties

As hydrates are solid substances, thermal conductivity is the main property that characterizes the heat transfer. A comprehensive study by Waite et al. [73] reported the thermal conductivity and other thermal properties of pure methane hydrate at conditions encompassing hydrates in the natural environment (-20°C to 17°C , 31.5 – 102 MPa) using a needle probe. It was found that

while thermal conductivity of methane hydrate was similar to that of water [74], the thermal diffusivity was more than twice of water and the specific heat was half that of water [27]. The thermal conductivity of methane hydrate lies within the range of 0.5 – 0.65 W/m K [75–78], comparable with water (0.56 W/m K at 0°C) rather than with ice (2.14 W/m K) [79,80].

However, naturally occurring gas hydrates do not exist in the bulk form [73]. Typical hydrate bearing sediments consist mainly of clay or sand, with hydrates and water filling up the pore spaces. The in situ thermal conductivity of hydrate sediments in permafrost [81,82] and marine environments [83] has been estimated in the literature. On a whole, the presence of minerals increases the overall conductivity of the specimens, since mineral grains typically have a thermal conductivity an order of magnitude higher than that of water. However, these field studies highlighted the importance of laboratory scale research in obtaining higher precision data due to limited understanding to the in situ conditions (hydrate saturation, composition and wide distribution in sediment properties [81,84]). As every single hydrate bearing reservoir is unique in its characteristics, a combination of field studies with laboratory measurements is needed to adequately quantify and understand the thermal properties of hydrate deposits.

3.1.2. Self-preservation phenomena

When hydrate dissociates at temperatures below the freezing point of ice ($<273.2\text{ K}$) yet outside the hydrate region of stability, unexpectedly slow rate of hydrate dissociation is observed, which is a phenomenon termed as “self-preservation” or “anomalous preservation” in the literature [85–87]. The most popular explanation for the phenomenon is that the endothermic heat of dissociation causes the dissociated water to form ice, preventing further dissociation within the hydrate region. Self-preservation phenomenon has been observed for sl methane hydrates as well as sll natural gas hydrates at 1 atm and temperatures between 242 and 271 K [88,89]. A study reported that less than 0.5% of the originally stored gas was released in 24 h due to this phenomenon. The self-preservation concept was also found in electrolyte systems. At 1 atm , the phenomenon was observed at temperature region below the eutectic point of the system and dissociation rates increased greatly once the eutectic temperature was exceeded [90]. This phenomenon could potentially hinder thermal stimulation or depressurization recovery method if inappropriate conditions are applied. This is more so true in permafrost locations where the temperature may be below the freezing point of water. For the case of marine locations whereby the average temperature is about 277.2 K , depressurization may cause localized zones near the down hole where the temperature can decrease below the freezing point of water thereby restricting the release of gas. From the scope of this review, it is noted that the self-preservation effect has not been reported when hydrates are dissociated above the freezing point of water. On the other hand, the self-preservation effect could be useful when considering hydrates as a potential transport and long term storage medium for natural gas [91,92].

3.1.3. Numerical simulation

Numerical simulation has also been conducted to model the behaviour of energy recovery through thermal stimulation [93–100]. Mathematical models coupling heat and mass transfer, hydrate dissociation kinetics and phase transition have been developed to understand the recovery behaviour and possible challenges. In an early study, a physical model describing hydrate dissociation under thermal stimulation in porous media described the ‘moving boundary’ between two zones – a dissociated zone of gas and water and the un-dissociated hydrate zone [93]. The study highlighted the possible scenario where an impermeable layer was

formed during the initial hydrate dissociation, preventing further dissociation if pressure and temperature conditions were below a certain limit. The same conclusion was drawn by a latter study which looked into geological characteristics such as media permeability [94]. A comprehensive comparison of kinetic and equilibrium reaction models revealed that kinetic limitations are important and neglecting them can lead to a significant under-prediction of gas recovery from hydrates [96]. Equilibrium reaction models are often used for simulating recovery from gas hydrates due to the ease of applying them and to avoid the computational effort required to solve the complex kinetic models. Further studies in numerical simulation could investigate the impact of interfacial forces between rock minerals, hydrates, water and gases as well as the impact of chemicals (e.g. salt, impurities, and additives) on the thermal behaviour during recovery process.

3.1.4. Laboratory studies

Apart from theoretical studies on the thermal behaviour of gas hydrates, research works applying thermal methods in recovering gas from hydrate have been conducted in laboratory settings. In general, thermal stimulation in laboratory scale was achieved by hot water injection or water bath immersion to temperatures above hydrate equilibrium point, thereby dissociating the hydrate sample.

3.1.4.1. Thermal stimulation by water injection. In one study, methane hydrate formed in a sand bed of 30% porosity saturated with 2.0 wt.% NaCl solution was thermally stimulated by injection of steam/hot water at different temperature in the middle of the reactor [101]. The dynamic variables, such as temperature distribution, gas and water production rate, and thermal efficiency during thermal stimulation was studied. Gas production rate was observed to increase initially, followed by a decrease; whereas water production rate was constant during the course of thermal stimulation. The study identified several factors which affect overall energy efficiency (ratio of energy extractable from gas produced against energy spent to recover gas), including temperature, rate of water injection, and hydrate saturation. It was concluded that a higher hydrate saturation, lower water injection rate and lower temperature resulted in better energy efficiency but slower gas production rate.

The recovery of methane hydrate by water injection (298 K) at different injection rate and pressure in a 10 L reactor was also investigated [102]. It was reported that the higher injection rate and lower pressure returned a higher recovery of methane. The authors also observed a temperature “buffer” zone during injection due to the endothermic nature of hydrate dissociation. It was determined that the rate determining factors of hydrate dissociation in that study were the thermodynamic driving force and the rate of heat transfer.

3.1.4.2. Thermal stimulation by immersion. Other than hot water injection, thermal stimulation studies in laboratory setting have also been done by water/air bath. In one study, the dissociation behaviour of methane hydrate in pure water and silica sand was conducted under a constant pressure of 4.6 MPa [103]. This approach maintained a constant temperature driving force, which was defined as the difference between the temperature of the crystallizer and the equilibrium temperature of methane hydrate at 4.6 MPa. Two different stages in the dissociation process was observed, with an initial stage having a faster rate than the latter stage. The same study which experimented different bed size also observed that the gas release behaviour is dependent on size of hydrate bed, which highlighted the importance of sampling size during the data transfer to numerical simulation and testing of naturally occurring hydrate samples.

The dissociation kinetics of methane hydrate in seawater/pure water and porous media have also been studied [104]. The methane hydrate samples were thermally stimulated by changing the water bath temperature to 10 °C and 20 °C above equilibrium temperature under a constant pressure of 4.8 MPa. While the relationship between dissociation rate and temperature driving force is consistent with that reported in literature, it was observed that temperature profiles differed between samples in pure water and seawater, with the dissociation rate of seawater hydrate noticeably lower than pure water hydrate. The authors reasoned this observation to the inhibitory nature of salts in seawater and suggested that further work could be performed to study the role of salt during hydrate dissociation.

The heat transfer aspect of thermal stimulation was investigated in one study by measuring the temperature difference between two points at different radial position, ΔT_{oi} [105]. Heat was supplied and controlled by water bath within a range of temperatures from 10 °C to 40 °C. The study observed that increasing the temperature of water bath caused an increase in ΔT_{oi} until 35 °C, and dropped at 40 °C. From this observation, the author proposed the possibility of adopting an optimal temperature which enhances the efficiency of heat transfer.

Apart from hot water injection and water bath methods, methane hydrate dissociation kinetics have also been investigated under a range of heat fluxes from 255 to 13,700 W/m² [106]. While experimental methodology differed significantly from previous investigations into the thermal method, a general conclusion was that increasing heat flux leads to an increase in dissociation rate and at high heat fluxes, the phenomenon of “self-preservation” could be avoided.

Reviewing several works on thermal stimulation using different approach, several key issues are observed:

1. *Definition of driving force for thermal stimulation.* In order to have a fair comparison between the works of different groups, the definition of driving force for thermal stimulation has to be consistent and quantified accurately. As gas are released from thermal stimulation which in turn increases the system pressure, the system equilibrium will shift towards a higher temperature. Works performing dissociation at constant pressure have been able to quantify this driving force by considering the temperature difference between the reactor environment and the hydrate equilibrium point [103,104]; alternatively, using heat flux to quantify thermal driving force may be appropriate, as it can shed the light on the exact amount of energy provided via thermal stimulation to the hydrate sample as well as the effectiveness of thermal stimulation as a dissociation method for methane hydrate.
2. *Other factors such as reactor dimensions and nature of porous media* should be considered and isolated in order to measure the contributions of thermal stimulation to the dissociation process. For example, the effect of hydrate bed volume and size on the dissociation process was observed [103].
3. *Linkage between laboratory and field scale thermal stimulation.* The method of heat delivery to the system can have an effect on the measured dissociation rates. The techniques of heat delivery include the changing of environment temperature (water/air bath heating) [102–105], injection of hot fluid into the hydrate sample [101], supplying heat via point sources [107] and combustion of in situ methane [106,108]. While water/air bath heating is a technique that work in the laboratory setting, it will not be feasible for use in the field. Thus, the question of how thermal stimulation can be achieved efficiently when exploiting methane hydrates in the natural

environment is raised. The following section will discuss two plausible techniques of delivering heat to in situ methane hydrates found in the natural environment.

3.1.5. Alternate heat transfer approaches

The most direct method of thermal stimulation is the injection of hot water or brine into the hydrate formation. However, this method has numerous drawbacks, such as significant heat loss during delivery of hot fluid from the ground/ocean surface to the hydrate formation, which is ineffective to be used as the main strategy of thermal stimulation [109]. This limitation has led interest in developing alternative methods of thermal stimulation.

3.1.5.1. Electromagnetic heating. The idea of electromagnetic heating of in situ methane hydrates was proposed by Islam in 1994 [110]. By introducing an electromagnetic heating source downhole, heat losses due to transmission through the well tubing can be avoided. This technique has already been applied in heavy oil extraction and could possibly be used for hydrate dissociation. Early numerical simulations concluded that energy efficiency could be increased greatly as compared to hot water injection [101,111]. Hydrate dissociation through microwave heating was studied in the laboratory setting and reported an increase in dissociation rate [111].

3.1.5.2. In situ combustion. Another method of thermal stimulation involves the in situ combustion of methane from the hydrate formation itself. Early simulations by Castaldi et al. [112] reported high energy efficiency up to 90% and also discussed the possibility of CO₂ sequestration coupled with this method. A more detailed description of the technique to deploy this approach in the field was suggested by Cranganu [113]. Fitzgerald et al. [114] have performed in situ combustion study on a laboratory scale, which achieved a lower energy efficiency as predicted by the previous simulations. Moreover, the feasibility of in situ combustion in hydrate deposits should be validated from a process safety point of view as an un-controlled combustion may lead to the release of large amount of methane.

3.2. Depressurization

The method of depressurization achieves gas production by lowering the pressure of the hydrate deposit below the hydrate equilibrium pressure at the local temperature conditions. In terms of energy requirement, depressurization technique consumes lesser energy as compared to thermal stimulation. In this section, we first review various models depicting the dynamic behaviour during depressurization, followed by laboratory studies applying depressurization to recover natural gas from hydrate reservoir.

3.2.1. Numerical simulation

Many literature works have focussed in gas recovery via depressurization by developing numerical models to simulate natural gas hydrate recovery [115–125]. Sung et al. [116] simulated a three-dimensional, multiphase (gas–water–hydrate) numerical model to estimate recovery performances implementing a kinetic model proposed earlier [115]. The study identified that flow factors such as *in situ* permeability or free gas fraction have a greater effect than the extent of depressurization on the gas production. The significant impact of *in situ* conditions on gas production rate from hydrate reservoirs were further confirmed by research findings from other groups [124–126]. For instance, a recent numerical simulation on gas production using single vertical well depressurization method from Qilian Mountain permafrost deposits reported

a 2.3% recovery from the total gas hydrate in the simulated reservoir of low permeability [125].

Nonetheless, it is important to gain a good understanding on how well pressure as a parameter can be optimized to maximise gas production from a hydrate reservoir given its unalterable intrinsic properties. A two-dimensional simulation study investigated the distribution of pressure, temperature, gas saturation and hydrate saturation during depressurization [127]. The gas recovery from a porous hydrate reservoir at 4.5 °C and 4.0 MPa (with corresponding equilibrium pressure at 3.875 MPa) was simulated by lowering wellbore pressures to 1.0, 2.0 and 3.0 MPa. It was shown that lower wellbore pressures led to faster recovery. However, the authors also highlighted that using higher wellbore pressure can enhance the stability and security of the reservoir. Thus, a balance between gas production rate and reservoir stability has to be considered in selecting the optimal operating pressure.

A molecular dynamic simulation study was also conducted to investigate the microscopic mechanism of sl methane hydrate dissociation via depressurization [128]. A “vacuum removal” mechanism, of which methane at the layer near the hydrate surface is continually removed to maintain near vacuum conditions, was applied to simulate depressurization. From the molecular simulation study, it was deduced that hydrate decomposition via depressurization occurs layer by layer and recovery by depressurization was found to be slower as compared to thermal stimulation and chemical inhibitor injection techniques.

3.2.2. Laboratory experiments

The dissociation of methane hydrate through rapid depressurization to 0.1 MPa at a range of temperatures between 272 K and 289 K was investigated [129]. Significant thermal buffering was observed, where the temperature in the middle section of the hydrate samples decreased to and maintained at temperature below 272.7 K until the dissociation process was almost complete (above 95%). It was postulated that the thermal buffering was due to the endothermicity of hydrate dissociation. However, the methane hydrate phase boundary at 0.1 MPa does not correspond to the temperature conditions in the experiments. The authors also identified that even though depressurization was supposed to provide the driving force for dissociation, the main factor controlling hydrate dissociation was the heat flow into the system, highlighting that heat is required for depressurization technique.

Another work was done on methane hydrates formed at 273.5 K, 6.8–13.6 MPa in porous media consisting different combinations of glass beads of 100 µm, 5000 µm and synthetic ceramic at different levels of water saturation [130]. Hydrate decomposition was accomplished by controlled depressurization starting at a pressure of 2.72 MPa when the temperature was maintained at 273.5 K. The decomposition rates were found to be of zero order and first order on methane concentration, depending on the type of porous media. The experimental data was fitted with a lumped dissociation rate constant (k_d), which was a function of pressure, temperature and bed voidage.

Comparison of methane hydrate dissociation at 3 different pressures (0.1 MPa, 0.93 MPa and 1.93 MPa) has also been conducted at temperature of 273–275 K [131]. It was shown that depressurization to the lowest pressure (0.1 MPa) resulted in the fastest dissociation. The experimental data was also fitted into ‘TOUGH-Fx/Hydrate’ simulator and obtained dissociation constant of the order of $10^4 \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$, which is a good agreement with the estimation from the another group [132]. However, from numerical simulation, the group highlighted that the hydrate dissociation kinetics, though plays an important role in laboratory scale production, will not have significant influence over production rates on a field-scale production, as flow property will be the limiting mechanism. These conclusions are in a good agreement with those

proposed by the numerical simulations reviewed earlier in the paper [116, 133].

A model for laboratory scale depressurization experiments which expressed gas recovery rate as a function of heat and mass transfer has been proposed and fitted with experimental data [134]. Experiments were performed at higher temperature (285–286 K) and a large range of production pressures from 0.2 MPa to 8.4 MPa. The experimental results showed good agreement with the model predictions. This study reported that on a laboratory scale, heat transfer was the dominant factor of gas production. Extrapolating these observations to the field, the authors deduced that sensible heat of surrounding sediments may provide the heat of dissociation required.

In another study which studied the depressurization of methane hydrate in silica sand bed, enhanced gas recovery rate was observed when the temperature falls below freezing point of water [135]. During depressurization to 2.3 MPa, a stage of which the temperature of hydrate sample falls below freezing point was identified, and gas recovery was observed to increase during that stage. The increased gas recovery at low temperature was consistent with previous theoretical [136] and experimental studies [137], which is explained by a simultaneous dissociation of hydrate into water, ice and gas.

Li et al. [138] investigated the gas production behaviour from methane hydrate in porous sediment by depressurization at 281.15 K and a production pressure range of 4.5–5.6 MPa. Methane hydrate was formed in quartz sand saturated with water at 281.15 K, 20 MPa in a 5.8 L reactor. Gas production started when the pressure in the reactor reached 11.8 MPa to mimic hydrate reservoir in the Shenhu Area of the South China Sea, and 3 production pressures of 4.5, 5.0 and 5.6 MPa were experimented. The gas production was categorized into three phases: free gas production (the gas production from non-hydrate phase), mixed gas production and finally, hydrate-gas production. It was concluded that the gas production process was mainly controlled by the rate of the pressure reduction in the system and the heat supplied from the ambient environment. A subsequent study performed on a 117.8 L vessel also demonstrated that dissociation via depressurization is limited by heat and mass transfer, and identified free gas saturation as a key factor in determining the production feasibility from marine hydrate deposits [139].

Through a review on depressurization technique, we observe that most of the laboratory experiments have raised the importance of heat transfer to enhance the recovery process. This is not unexpected as it has been established that hydrate dissociation is an endothermic process. Hence, it is generally agreed that depressurization will have to be combined with other methods, e.g. thermal stimulation, for economical gas production [125,139]. However, one recent work reported a temperature increase of 0.26–0.35 K during depressurization from a high pressure (14.5 MPa) [140]. The authors reasoned that the presence of free gas resulted in reformation of methane hydrate during gas production.

It has also been noted that in most numerical simulations on a large reservoir scale, flow factors were identified as the main controlling factors; whereas in laboratory scale experiments, heat transfer was agreed as the main rate controlling factor for gas production. One point not well understood is the gas and liquid flow through porous hydrate sediments at different pressure conditions as well as different hydrate conditions (levels of saturation, sediment porosity etc.). The works by Li et al. [138,141] have made some progress in measuring flow resistance during gas production and revealed that in general, flow resistance decreases as production progresses due to hydrate dissociation.

Since simulations have stressed upon the importance of flow factors in large reservoirs, it is important to produce representative hydrate sample in laboratory scale by increasing the scale of

laboratory experiment and mimic sediment property, especially the permeability. To investigate the effect of limiting flow factor, laboratory experiment can be done using a high hydrate sample size to well size ratio, or locally depressurize a small region of a hydrate sample with minimal direct depressurization on the rest of the sample.

It should also be noted that theoretical models have assumed that hydrate does not re-form after it has dissociated [116,127]. However, this is highly probable in the natural environment given the fact that ambient conditions in nature will not be as easily manipulated as in a laboratory reactor and chances for hydrate re-formation always exist should the appropriate conditions exist at a different location during recovery [140].

3.3. Chemical inhibitor injection

As compared to thermal stimulation and depressurization, chemical inhibition as a recovery method has been relatively less studied. Chemical inhibitor injection works by shifting the equilibrium curve towards higher pressures and lower temperatures, thereby destabilizing hydrate at natural conditions. There are two main types of inhibitors, namely thermodynamic inhibitors which alter the hydrate equilibrium conditions and kinetic inhibitors which slow down the rate of hydrate formation. Thermodynamic inhibitors are of particular interest to the applications for gas production. Two of the most common thermodynamic inhibitors used are methanol and ethylene glycol (EG) [142]. EG is more commonly studied due to its higher availability in the market, lower toxicity and better performance in inducing hydrate dissociation owing to its higher density compared to methanol [143]. Several factors have been identified to control the rate of dissociation, including the concentration and temperature of inhibitor solution, inhibitor injection rate [144], pressure, and hydrate-inhibitor interfacial (contact) area [145].

A comparison between methanol injection and depressurization to recover methane hydrate formed in Berea sandstone has been conducted [133]. 30 wt.% methanol solution was injected within the hydrate stability zone (273.7 K and 4.0 MPa), and hydrate dissociation was observed by an increase in pressure to 5.5 MPa. The step was followed by opening of outlet valves to reduce the pressure back to 4.0 MPa. Upon opening the outlet valve, a rapid drop in pressure was observed in both inlet and outlet, which is in contrast to the response from depressurization method of which initial dissociation was only observable at region closer to the outlet. This inferred that dissociation via inhibitor injection was spontaneous and occurred throughout the entire hydrate sample, as compared to localized dissociation for the case of depressurization.

The 'gas production ratio', defined as the ratio of gas recovered from hydrate dissociation to the initial amount of gas in the hydrate phase, was a commonly used metric to compare inhibitor efficiency. Increasing EG concentration generally results in an increased gas production ratio [146,147]. These studies also reported the existence of an optimal 'production efficiency', defined as volumetric rate of gas recovered per unit mass of EG injected. This optimum amount of inhibitor was later found to be related to the pore volume below the well inlet [147]. It has also been reported that the presence of inhibitor lowers the heat of dissociation which improves heat efficiency by approximately 3.5 times according to the concentration of inhibitor [144].

Apart of EG and methanol, NaCl also possesses inhibitory properties and it is widely found in nature [148]. A molecular dynamic study has provided an insight into the possible roles of Na⁺ and Cl⁻ on methane hydrate recovery [149]. The possibility of using brine injection to recover gas from methane hydrate in pure water and Berea sandstone was also explored [150]. From the study, a low brine concentration (3.45 wt.%) was able to bring about

dissociation and significantly increase gas production. Excessively high brine concentration (20 wt.%), on the other hands, was observed to reduce the rate of hydrate dissociation due to the formation of impermeable NaCl layer within the sandstone pores which reduced the sample permeability.

Comparing the research on EG against NaCl, we observe a difference in the effect of increasing inhibitor concentration. An optimum concentration exists when NaCl was used as an inhibitor and it was postulated that excess brine concentration caused the clogging of pores, thus reducing the permeability of the hydrate. Such issues do not exist with EG where we observe a monotonic increase in gas production ratio with an increasing inhibitor concentration.

The use of NaCl as an inhibitor is of particular interest particularly in a marine setting. While it has been well established that NaCl is a thermodynamic inhibitor, recent research found that the salt also inhibits hydrate formation and dissociation kinetically [104]. It is worth investigating in-depth how NaCl at various concentrations affect not only the equilibrium but also the formation and dissociation behaviour of CH₄ hydrate to evaluate its usefulness as an inhibitor or agent to promote dissociation during gas production, since hot brine injection has also been proposed as a means of thermal stimulation.

Nonetheless, the feasibility of chemical inhibitor injection for gas recovery is questioned from several perspectives. Most significantly, it is noted that in all laboratory studies thus far, the ratio of chemical inhibitor to hydrate has been significantly high. Achieving such a high level of inhibitor in a natural formation may not be feasible and economical. One direction should be the investigation on how EG is transported through a hydrate bed when injected in small amounts relative to hydrate volume and how the actual dissociation takes place.

The fact that hydrate dissociation is an endothermic process is seen as a main challenge in the development of effective recovery techniques. As chemical injection lowers the heat of dissociation [144], this technique can be effective accompanying depressurization, which suffers from the drawback of requiring heat transfer. It also possesses the potential to enhance the effectiveness of thermal stimulation since it lowers the amount of heat required for hydrate dissociation. On the other hand, another chemical that has been proposed to be injected into hydrate sediment to recover methane is the notorious greenhouse gas, CO₂, which will be discussed in detail in the latter chapter.

3.4. Combination of approaches

Since each of the recovery techniques discussed above has their own limitation, it is widely agreed that a combination of the techniques can enhance the effectiveness of gas production. The huff and puff method is one of such technique that combines thermal stimulation and depressurization in a single vertical well. Some groups have investigated this technique in enhancing the effectiveness of hot fluid injection [141,151,152]. The huff and puff method involves numerous cycles of hot fluid injection, soaking and gas production. A large scale gas production study was carried out in a Pilot-Scale Hydrate Simulator (PHS) of a volume 117.8 L using huff and puff method [141]. The gas production was stimulated by cyclic hot water injection (160 °C, 0.2 L/min). Three phases, namely injection phase (10–30 min), soaking phase (30 min) and production phase (10 min) were identified in the study, with each cycle began with a pressure of 4.7 MPa. This pilot scale study justified the economic feasibility of huff-and-puff method from a high gas-to-water ratio, $R_{GW} > 55 \text{ m}^3 \text{ CH}_4 \text{ (STP)/m}^3 \text{ of water}$. While comparing the efficiency of gas production under different injection duration, it was reported that a longer duration of injection period increases the efficiency of gas production, subjected to limitation

in the rate of depressurization. Though improvements in efficiency have been achieved, a main drawback of this method is the soaking phase which occurred without depressurization resulted in an increased system pressure, decreasing the driving force for hydrate decomposition [141,151].

The methane production from samples of 40% hydrate saturation in Toyoura sand by depressurization with a heated wellbore was compared with depressurization technique alone [153]. For the same well pressure of 6 MPa, it was found that gas production increased by 3.6 times on average using a heated wellbore over a period of 90 min. For depressurization alone, it was also observed that using a lower well pressure of 4 MPa as compared to 6 MPa resulted in a greater initial production rate, but the overall recovery in 90 min was the same in both cases.

Investigations have also moved beyond single well configuration into multiple well schemes to mimic the real production scenario [154–156]. Wang et al. [154] compared the gas production behaviour and energy efficiency of three methods, namely single well depressurization, five-spot thermal stimulation method, and the combination of the two, under a similar hydrate saturations and environment conditions. As expected, single well depressurization yielded the highest energy efficiency, but the production rate was deemed too slow. The combination method returned the shortest production time and its energy efficiency was 15 times higher than thermal stimulation alone. The authors deduced that depressurization stage in combination technique enhanced the heat transfer by decreasing the local temperature, thereby promoting decomposition across the entire hydrate reservoir.

Various schemes for the combination production techniques, ranging from single well to multiple well schemes, have been outlined in one study [155]. According to the authors, most of the complex production techniques were inspired from existing oil production technologies and had yet to be tested out on hydrate systems except for the Steam Assisted Gravity/Anti-Gravity Drainage (SAGD/SAAD) methods which combined thermal stimulation, depressurization and brine injection in two horizontal wells [157,158]. SAGD and SAAD methods have been applied to recover gases in laboratory settings, where experiments were carried out in a 117.8 L pressure vessel. The Anti-Gravity Drainage method, of which the production well is above the injection well, was reported to produce more gas and less water and have a higher long term energy efficiency as compared to the gravity assisted method. A recent work investigated the inverted five-spot flooding method in detail, where one centre well was used as an injection well while the four well at the corners were production wells [155]. The study reported an improvement in energy efficiency ratio of about 33% from the huff and puff method.

In summary, each of the recovery method has their own advantage and disadvantage. Depressurization, although been reported as the most energy efficient method, suffers from a low production rate. Thermal stimulation and chemical injection, on the other hand, have high energy requirements in order to heat the injection fluid and pump inhibitors down to the hydrate sediment. Although a combination of these methods may be feasible in improving the overall efficiency and production rate, these methods involve dissociating in situ hydrate, which may cause weakening of seafloor and potential release of methane. In the following section, we will look into the concept of CH₄–CO₂ swapping, its potential benefits and research progress.

4. CO₂ Injection and CH₄/CO₂ exchange process

4.1. Principle and motivations

Carbon dioxide is another gas species that forms gas hydrates at appropriate conditions. CO₂ has a molecular diameter of 5.12 Å,

which is larger than methane (4.36 Å), and both of the molecules typically form sl hydrate [18]. The idea of utilizing CO₂ in the natural gas hydrate production process has been proposed and investigated since 1980s – CO₂ assists in recovering methane from hydrate reservoir and at the same time be sequestered in the natural formation as CO₂ hydrate [159,160]. In an ideal scenario where the same amount of, if not more, CO₂ is captured in the formation than natural gas produced, the energy generation process can become carbon neutral, as shown in Fig. 5. Apart from the potential carbon neutral methane production, in terms of heat requirement, the process may be self-sustainable, as the heat released from exothermic CO₂ hydrate formation (−57.98 kJ/mol) is larger in amount than the heat required for endothermic CH₄ hydrate dissociation (54.49 kJ/mol) [161]. Other benefits associate with the exchange techniques include the significant reduction in water production and maintenance of seafloor integrity, since water released during dissociation is taken up for CO₂ hydrate formation, and CO₂ hydrate can substitute CH₄ hydrate in the sediment to maintain sediment strength.

The basis of this approach is the difference in the phase equilibria between CH₄ and CO₂ hydrates, as shown in Fig. 4. At lower temperatures (<10 °C), CO₂ hydrate is more stable than CH₄ hydrate, as shown in the green zone of Fig. 4. The experimental evidence of CO₂ being the preferred guest species of hydrates was demonstrated for a CH₄–CO₂ mixed hydrate system at 280 K [162]. In the study, the average ratio of distribution coefficient (defined as the ratio of mole fractions in gaseous phase to hydrate phase, y/z) between CH₄ and CO₂ was 2.5, indicating higher tendency of CH₄ to be in the gaseous phase and CO₂ in hydrate phase.

The thermodynamic feasibility of the replacement reaction of CH₄ hydrate by CO₂ was justified in a molecular dynamic study which reported a Gibbs free energy of −12 kJ/mol for the exchange reaction [163]. However, latter critiques pointed out that the study assumed ideal conditions of pure water, pure gas and fully saturated hydrates; while in reality most hydrates are found in heterogeneous conditions that include porous environments, impurities like salts and hydrates in nature are frequently not completely saturated.

While considering the hydrate phase equilibrium, it is recalled that the stability of NGHs change significantly with composition. As the proportion of larger hydrocarbons (e.g. propane) increases, the stability of the corresponding hydrate increases. The phase equilibrium curves for CO₂ hydrates and mixed hydrates of 99.5 mol% methane and 0.5 mol% propane was also shown in Fig. 4. In the presence of propane, even at low concentrations of

0.5 mol%, slI hydrate with a greater stability than pure methane hydrate is formed (CSMGEM, [18]). From Fig. 4, we observe that CO₂ hydrate is only slightly more stable than the mixed hydrate at temperature below 10 °C. In such cases, the difference in phase equilibria will not be a strong argument to drive the exchange process. The guest exchange process of slI CH₄–C₃H₈ and CH₄–C₂H₆ hydrate with gaseous CO₂ was studied using Raman and Powdered X-ray diffraction (PXRD) [164]. From the results in structural transition, the authors found that the exchange process occurred within 10 h. The same work also studied the reverse direction reaction (exchange of CO₂ hydrate with hydrocarbon gas) and observed that the direction of reaction is dependent on the composition of the surrounding gas phase. This observation indicated that the driving force for guest exchange is not only the difference in thermodynamic stabilities but also due to a chemical disequilibrium between gas phase and hydrate phase composition. This implies an increased feasibility for natural gas recovery from NGHs through CO₂ fixation as it is possible to recover hydrocarbons from hydrates more stable than CO₂ hydrate by creating a CO₂ rich environment.

Upon appreciating the principles of the gaseous exchange, its benefit and potential to displace higher stability hydrate, we will look into the research progress of various laboratory studies on the guest-exchange process for natural gas production.

4.2. Laboratory studies on the exchange process

4.2.1. Exchange process in bulk, crystalline hydrate

The initial studies on the exchange process have been conducted on bulk phase hydrates with pure water without considering the effects of porous media and saline water. Recovery of CH₄ hydrate in the bulk phase using liquid CO₂ was experimented at conditions within the hydrate stability region (274–277 K, 4–5 MPa) of both CO₂ and CH₄ hydrate in an early study [165]. In two runs lasting over 800 h, an approximately 12.5% of CH₄ was recovered. As the study was conducted within hydrate stability zone of both hydrates and the hydration number of CO₂ hydrate is higher than that of CH₄ hydrate, it was reported that all free water was consumed during the liquid CO₂ soaking stage. Since the final conversion remained low, it was suggested that the conversion of CH₄ hydrate into CO₂ hydrate at the hydrate–liquid CO₂ interface inhibited the mass transfer of CH₄, CO₂ and H₂O.

In a microscopic level, the occupancy of large and small cages of the slI hydrate at various CH₄–CO₂ compositions, ranging from 100% to 1.5% CH₄, were examined through nuclear magnetic

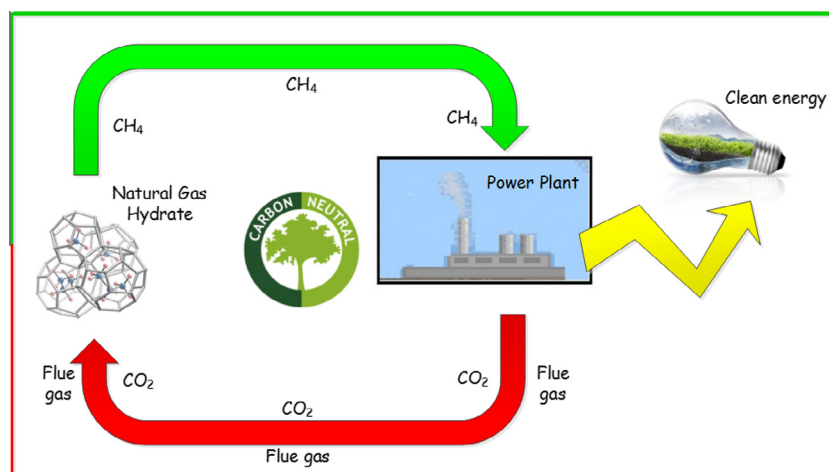


Fig. 5. A sustainable approach to sequester CO₂ and produce methane from natural gas hydrates.

resonance (NMR) [166–168]. With the assumption that the large cage is fully occupied ($\theta_L = 1$), and the equilibrium occupancy ratio (θ_L/θ_S) for CH₄ is 0.23 at highly diluted CH₄ conditions, the study proposed a theoretical minimum methane recovery of 64% with a CO₂/CH₄ ratio of 1.8 in the hydrate phase. The same publication also reported the kinetics of exchange reaction using CH₄ hydrate formed from finely powdered ice (particle size 5–50 μm). In less than 5 h, about half of the total methane in the hydrate was recovered by CO₂ gas injection, resulting in a CO₂/CH₄ ratio of 1 in the hydrate phase, which was less than the theoretical estimation. The study concluded that the replacement of CH₄ by CO₂ in hydrate is favourable from both thermodynamics and kinetics consideration. The particle size of hydrates were found to have significant effect on the overall conversion, again posing mass transfer limitation as a main obstacle during the exchange process.

The CH₄–CO₂ replacement reaction was also investigated in a small cell using in situ laser Raman spectroscopy [169]. The experimental data was correlated with a fugacity based model assuming a constant hydrate surface area. The reaction was modelled as a two-step process – a CH₄ hydrate dissociation step followed by a CO₂ hydrates formation step. Fugacities were calculated from the van der Waals–Platteeuw theory and the Soave–Redlich–Kwong equation of state (SRK–EOS). Good fitting was only observed at the later stages of the experiment (>10 h) and it was reasoned that during the initial stages of the reaction, the surface area available to the bulk gas changed quickly, which was unaccounted for by the model. Through numerical modelling, the research reported activation energies for CH₄ hydrate decomposition and CO₂ hydrate formation to be 14.5 kJ/mol and 73.3 kJ/mol respectively and inferred that the exchange process is limited by solid phase transport of CO₂. Further work performed by the same group observed that the occupancy of CH₄ in both L and S cages decreased during the exchange process but the rate of decrease of CH₄ in the S cages was slower [170]. This was attributed to the fact that it is more difficult for the larger CO₂ molecules to occupy the small cages and hence CH₄ molecules could reoccupy the small cages. The study estimated that the amount reoccupied by CH₄ was approximately one third of CO₂ hydrate formed during the exchange process.

4.2.2. Exchange process in dispersed hydrates

The effect of porous media and saline environment in the exchange reaction has been examined in more recent research. In one study, the gas production behaviour from guest exchange process was investigated from a hydrate sample formed in pure water and unconsolidated sand [171]. The initial water saturation of the hydrate bed was 30% and a 36% CH₄ recovery from hydrate through the swapping process was achieved. Mass transfer limitations were cited as the leading cause hindering the swapping process as it was postulated that the hydrates in the centre of the core remained rich in CH₄ and replacement only took place near the interface. It is noted that the replacement procedure in this study did not remove excess CH₄ in the hydrate sample before CO₂ injection.

As the diffusion of CO₂ across hydrate layer is widely identified the main limiting factor, one study experimented the exchange reaction using liquid CO₂ and a carbon dioxide-in-water (C/W) emulsion at conditions of 281.2 K, 5 MPa [172]. Methane hydrate samples in this study were prepared in a quartz sand medium with sodium dodecyl sulfate solution (SDS). It was found that the C/W emulsion increased the rate of reaction as compared to liquid CO₂ injection due to a more favourable heat and mass transport in the multiphase flow system. In a separate publication by the same group [173], the hydrate equilibrium curves were plotted with the geotherms in both marine environments and permafrost to determine the most suitable conditions to replace CH₄ with CO₂ hydrate, alongside with experimental results on the respective

conditions. It was found that the optimal condition for the replacement lies within the area between 3 curves: ($L_{\text{CO}_2} - V_{\text{CO}_2}$), ($H - L_w - L_{\text{CO}_2}$) and ($H - L_w - V - \text{CH}_4$), of which CH₄ hydrate is unstable whereas CO₂ hydrate is stable. It was proposed that the most effective method to recover CH₄ was to depressurize the hydrate reservoir, followed by CO₂ emulsion injection. However, technical challenges have to be overcome in producing the C/W emulsion.

The naturally occurring hydrate reservoirs can be categorized into 3 classes according to their physical characteristics: Class I (with an underlying two-phase fluid zone of free gas and mobile water); Class II (with an underlying mobile water zone, e.g. aquifer), and Class III (no underlying mobile zone) [174–176]. To identify how suitable each classes of hydrate reservoir is for the replacement process, the replacement efficiencies of three different types of hydrate samples: high gas saturation, high water saturation and high methane hydrate saturation were investigated in a 7 L reactor [177]. The methane hydrate sample was prepared with 3.35 wt.% of Na₂SO₄ and 20–40 mesh quartz sands with a porosity of 38.7%. CO₂ was in the gaseous phase at the experimental pressure and temperature conditions. It was concluded that Class I reservoir with underlying free gas, high gas saturation and low water saturation was most suitable for recovering CH₄ with CO₂. Good agreement between the experimental results and a fugacity based mechanism was shown in the study. In a separate work using the same reactor [178], similar hydrate samples were formed, but temperature and pressure conditions were altered to investigate the effect of applying liquid phase CO₂. At conditions where pure CH₄ hydrate was unstable whereas CO₂ hydrate was stable, a maximum methane recovery of 35% was achieved. By comparing results from both studies, it was demonstrated that the use of liquid CO₂ resulted in higher recovery from all three types of hydrate reservoirs as compared to gaseous CO₂, of which recovery was only significant for class I reservoirs. The authors explained the improved efficiency from liquid CO₂ system by a smaller decrease in fugacity of liquid CO₂ during the exchange process as compared to the significant fugacity change of CO₂ in gaseous system.

The methane recovery from methane hydrates in quartz sand with pure ice particles by step-wise injection of supercritical CO₂ at 95 °C in a flow-through apparatus was also investigated [179]. The supercritical CO₂ was injected into methane hydrate samples at 2 °C, 8 °C and 10 °C and pressure of 8–13 MPa to achieve a comparison between the conditions where both hydrates were stable and that with only CO₂ hydrate was stable. This unique method reported a high recovery of 40.7% in a relatively short duration of 44 h, but similar to the previous studies, mass transfer limitations was identified to prevent further recovery. It was also observed that production at conditions where both CO₂ and CH₄ hydrate were stable resulted in rapid formation of CO₂ hydrate, which reduced the transport pathway for CH₄ to be produced; whereas at conditions that favoured CH₄ hydrate decomposition, the hot CO₂ was channelled through certain pathways and not accessing the entire CH₄ hydrate medium. However, this pioneering work of supercritical CO₂ injection did not include any temperature measurement during the exchange process, which is an important parameter in reservoir exploitation.

The replacement in Bentheim sandstone cores with mildly saline water (0.1 wt.% NaCl) was also investigated using Magnetic Resonance Imaging (MRI) which detects hydrogen atoms outside the hydrate cages (water or free CH₄) [180,181]. The study highlighted the ability of MRI to image the spatial distribution around hydrate sample, thereby providing a way to study the exchange reaction in microscopic level. The MRI results did not show any noticeable free water production during the exchange process, inferring that the replacement reaction did not occur with bulk CH₄ hydrate dissociation into free water and gas before the CO₂ hydrates formation. This result is potentially beneficial as it shows that water

production, which is one of the hassle in gas production through hydrate, may be prevented through guest-exchange process.

As quantitative assessment of gas recovered is essential, a recent study developed a systematic approach for quantitative analysis during gas exchange via liquid CO₂ injection [182]. The study established mole balance by measuring the initial amount of CH₄ in hydrate phase, the amount produced during the liquid CO₂ soaking stage and the amount dissociated, and reported errors less than 5.3% for 8 runs. The study also considered the scenarios of 'gas exchange' and 'no exchange' case where CO₂ hydrate did not form. By fitting experimental data into the two models, the authors concluded that exchange reaction occurred in the first 48 h, followed by a low exchange ratio. The recovery efficiencies achieved from this study lie between the range of 9–40%.

The hydrate guest molecule exchange phenomenon has also been studied on molecules apart from CO₂ and CH₄. For instance, the replacement of C₂H₆ hydrate with CH₄ gas has been investigated to look into the possible scenario that might occur in marine sediment [183]. Using in situ neutron diffraction and Raman spectroscopy, the transformation from sl C₂H₆ hydrate into slI mixed hydrate of CH₄ and C₂H₆ was observed. From the experimental observation, the authors proposed a mechanism for the exchange reaction: a layer of mixed hydrate was firstly formed on the surface of C₂H₆ hydrate, and it continued to grow inwards, causing the initial sl C₂H₆ hydrate "core" to shrink.

While recovery ratios between the different works carried out should not be compared directly with one another since the conditions such as temperature, pressure, sample morphology and size differ, it is worth noting that the experimental works thus far, either from the bulk hydrate or in unconsolidated porous media, have not been able to achieve high recovery of CH₄. Reviewing various experimental work on gas exchange process, typical CH₄ recoveries have been below 40% with the exception of Deusner et al. [179] who used hot supercritical CO₂ at 90 °C for the exchange reaction. This observation leads to a need to investigate the exchange mechanism in detail, including determination of optimal injection condition and the nature of CH₄ and CO₂ hydrates in different media and salinity condition.

4.3. Factors influencing the exchange process

Reviewing various works done on the exchange process, the following is a summary of significant factors identified to influence the exchange process:

1. *The particle size of the hydrate sample.* The factor of particle size is commonly cited as one of the reasons for the higher recovery of CH₄. In one study, the methane recovery dropped by more than 3 times when the particle size of hydrate sample increased from 5–50 µm to 1 mm [166].
2. *Diffusion barrier from CO₂ hydrate formation.* The presence of an outer layer of mixed hydrate during the replacement process hinders mass transfer of guest species and water for further replacement [171,184]. To compute the diffusivity of CO₂ in hydrates and ice, a molecular dynamic study was conducted [185]. It was found that the diffusion coefficients of CO₂ and H₂O molecules in hydrate were $1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $1 \times 10^{-23} \text{ m}^2 \text{ s}^{-1}$ at 273 K and 200 K respectively and that of H₂O in ice was $1.3 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ at 200 K, highlighting the greater mass transfer resistance in hydrates as compared to ice. In another study, the diffusivity of CH₄ in CH₄ hydrate was found to be within the range of $3.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ to $7.6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ under experimental conditions between 3–15 MPa and 263–268 K [186].
3. *Excess fugacity of the guest species.* As the driving force for the exchange reaction comes from fugacity difference, the effect

of guest species fugacity was identified as one of the factor affecting recovery efficiency [183]. For example, the use of liquid CO₂ has been proven to achieve a higher production as compared to gaseous CO₂ injection [178].

4. *The nature and properties of medium.* In most of the reviewed studies, the production was experimented from unconsolidated sands to mimic marine sandstone. It might be of interest to understand the difference in morphology when methane hydrate is formed in consolidated, rigid sandstone cores as compared to unconsolidated sands. In studies which experimented the replacement of methane hydrate formed in Bentheim sandstone core, high methane recovery efficiencies were reported from the analysis of MRI results (50% [181]–60% [180]).
5. *Conditions in which guest exchange takes place.* As shown in Fig. 4, there exist a region where CH₄ hydrate was unstable and CO₂ hydrate is stable, and the region has been shown to achieve a better production rate [173]. Apart from that study, the replacement reaction with high temperature supercritical CO₂ injection achieved a higher recovery [179], affirming the importance of the exchange process condition.

4.4. Key challenges

Although various studies have shown possible gas production from CO₂ replacement, the theories behind this process is complex and some key challenges need to be elucidated. These challenges are mostly pertaining to the kinetics of hydrate formation and dissociation for this process, and are summarized as follow.

1. *In-depth understanding on how the replacement is taking place.* Though microscopic measurements and molecular dynamic studies provide insight into the process to certain extent, a holistic understanding towards the exchange process – how water is transported or rearranged during replacement reaction, whether parent hydrate dissociates before the exchange process, is not well elucidated and needs to be further investigated;
2. *Kinetics of methane production from CO₂ injection.* Although various studies reported the rate of methane production, it is not well resolved whether the production is caused by local condition which drives dissociation or CO₂ replacement. Therefore, a key challenge would be on determining how fast would methane dissociate in porous sediments in the presence of CO₂ without additional stimulation by depressurization or heat supply;
3. *Kinetics of CO₂ hydrate formation.* More information on the kinetics of CO₂ hydrate formation in porous sediments, the role of permeability and sediment properties that influence the kinetics are required to affirm the viability of CO₂ sequestration via guest exchange process;
4. *Understanding on heat and mass transfer during the exchange process.* As the exchange process involves an interplay of endothermic hydrate dissociation and exothermic formation as well as mass transfer of water and guest molecules, the transport mechanism of heat and mass has to be elucidated;
5. *Development of reservoir simulation models.* Upon obtaining sufficient inputs from various research activity, reservoir simulation models are required to develop optimal well placement and production strategies.

5. Field trials

After reviewing various recovery techniques in laboratory settings, this section provides an overview on several significant field trials on gas production from hydrate reservoir. For a more

comprehensive review on the hydrate expeditions and projects around the world, readers are referred to a report compiled in 2013 by Consortium for Ocean Leadership [187]. The locations of the fields outlined in this section are mapped in Fig. 6.

5.1. Messoyakha Gas Field

The Messoyakha Gas Field in the Arctic on the border of West Siberia has been producing gas since 1969. The geology of the field has been identified to consist of unseparated gas hydrate and free gas layers [188,189]. It has been claimed that the field has a cumulative gas production of $12.9 \times 10^9 \text{ m}^3$ thus far, with $5.4 \times 10^9 \text{ m}^3$ obtained via hydrate decomposition using the method of depressurization [46]. However, the reported amount of water produced from this reservoir is at least 3 orders of magnitude lower than what is expected to be produced during hydrate decomposition. Collett and Ginsburg [190] have questioned whether the gas production from this gas field was originated from the hydrate layer. Nonetheless, the proven existence of significant amounts of gas hydrates in this gas field makes it a very useful test site to study the potential hydrate production techniques and geological research.

5.2. Mount Elbert Well – Alaska

The Alaska North Slope is one of the regions where significant hydrate deposits exist in the permafrost setting. It is estimated that 2.4 TCM of undiscovered, technically recoverable gas hydrate resources exist in the region [191]. In collaboration with BP Exploration (Alaska) and the U.S. Department of Energy (DOE), the U.S. Geological Survey (USGS) drilled a stratigraphic test well in 2007 to assess the potential of hydrates on the North Slope to become technically and commercially viable gas resource. Results were positive as the core data obtained from wireline Modular Dynamic Testing (MDT) analysis conformed well to pre-drill predictions and modelling techniques were validated and improved [192,193].

5.3. Malik gas hydrate site – Canada

The Mackenzie Delta in Canada is another region where active hydrate testing has been performed. Most significantly from 2007 to 2008, researchers from the Japan Oil, Gas and Metals National Corporation (JOGMEC), Natural Resources Canada and Aurora conducted production tests using depressurization

technique [194]. Using a staggered depressurization to 4.5 MPa, gas and water were successfully produced and delivered to the surface for 6 days at a gas production rate of 2000–3000 m^3/d and water production rate of 10–20 m^3/d . It was postulated that during the initial phase of depressurization, conduits of high permeability were formed, resulting in an initial rapid increase in production rates, followed by a decrease. Hydrates near these high permeability regions then started to dissociate, releasing gas stably during the production period. However after some time, these conduits were postulated to have collapsed or deformed as the hydrates dissociated, causing the subsequent decline in production rate.

5.4. Ignik Sikumi field trials

ConocoPhillips and researchers from the University of Bergen have collaborated on laboratory studies on hydrate production through $\text{CH}_4\text{--CO}_2$ exchange [180,195–199]. Notably, a patent has been awarded to the group on developing MRI method to monitor the $\text{CH}_4\text{--CO}_2$ exchange process in hydrates, as discussed in Section 4 [200]. Further conclusions have been similar to those outlined previously: fugacity/chemical potential provides the driving force for the reaction although mass transfer limitations dominate the overall conversion [201]. The first field trial of methane hydrate production using CO_2 has been completed successfully in the Ignik Sikumi Gas Hydrate Field in Alaska North Slope in 2012. Researchers from ConocoPhillips, with partnership from the Japan Oil, Gas & Metals National Corp. (JOGMEC), injected approximately 210,000 standard cubic feet of flue gas (23% CO_2 – 77% N_2 mixture) into the targeted hydrate bearing formation. Of the total injected volume of gas (167.3 MSCF of N_2 and 48.6 MSCF of CO_2), approximately 70% of the injected nitrogen was recovered. In contrast, only 40% of the injected carbon dioxide was recovered during the production period, inferring the occurrence of replacement reaction which leave CO_2 sequestered in the formation. A total of 855 MSCF of methane was produced over the total production period, including a six weeks sustained flow back of gas. The analysis of field test data has shown that $\text{CH}_4\text{--CO}_2$ exchange did take place in solid phase [202].

5.5. MH-21 Japan Nankai Trough

Onshore field tests have proceeded at a faster pace than offshore trials due to the greater engineering challenges involved in offshore hydrate resource recovery. Driven by high natural gas



Fig. 6. The location of field tests performed on gas hydrates resources. (Adapted from US Geological Survey (USGS), Map courtesy of USGS (updated December, 2013)).

Table 1
Summary of resource estimates and production costs.

Source	Resource estimate (TCM)	Cost (USD \$/Mbtu)	Refs.
Conventional	404	2.00–9.00 0.53–6.02	[6] [250]
Tight gas	84–210	3.00–8.00 2.75–8.03	[6] [250]
Shale gas	204–456	3.00–7.00 4.01–9.08	[6] [250]
Coal bed methane (CBM)	118–256	3.00–8.00 4.01–8.03	[6] [250]
Natural gas hydrates (NGH)	1000–5000	4.65–9.08	[250]

TCM: trillion cubic meters.

Mbtu: Million British thermal units.

price in Japan, the JOGMEC has been actively investigating the methane hydrate deposits in the marine sediments in the Nankai Trough off the Pacific coast of central Japan. After some work on sediment and resource characterization [203–205], the world's first offshore production test was accomplished in 2013 employing depressurization technique [58,206]. Provisional results thus far indicate that the offshore gas production lasted for 6 days, with a total gas production of 120,000 m³ [207]. Compared to the Mallik onshore production test which also applied depressurization as the recovery technique, the average daily gas production rate from Nankai Trough is almost one order of magnitude larger.

5.6. Summary of field tests and future road map

The data from the field tests is summarized in Table 2. As can be seen in the table, so far one field test has been conducted employing thermal stimulation and the other field tests were done by employing depressurization. It is also noted that progressively over the tests, there has been an increase in the production volumes while the tests have not lasted more than 6 days except the CO₂–CH₄ tests done in Alaska. Sand and water management, the low permeability within the deposits are challenges that hinder production at longer time scales. It is expected that in order to achieve a commercial scale for production, it is needed to sustain a prolonged production over a longer period of time and higher production volumes need to be established in the future field trials.

A recent review outlined the global progress in gas hydrate research and development, highlighting the hydrate exploration technology and research status in various countries [15]. On the other hand, a roadmap for hydrate research and development was prepared by a team of the U.S. National Methane Hydrate R&D program, projecting the possible research prospects from 2015 to 2030 [208]. According to the report, 4 key research focus were highlighted: the characterization of gas hydrate system, development of in situ sampling technologies, development of production technology and the investigation on linkages of gas hydrate to global climate change.

Fig. 7 is a roadmap adapted from USGS to show the 25-year-projection towards the future of gas hydrate. As shown in the

figure, it is projected that more and more field trials for longer term production will happen in the next two decades, enabling the commercial production from hydrate to be realized in thirty years' time. From experiences accumulated from onshore production test, the first commercial small-scaled gas production is projected to occur in an onshore hydrate reservoir in US or Canada around 2025–2030 [209]. The first commercial production from offshore hydrate reservoir is expected to occur in Asia, most possibly Japan, China or Korea. It is noted that there is a need for successful long-duration field tests with a production of 20,000–30,000 cubic meters of gas per day for a longer duration of time (about 2 months or so) in order to continue to the path of commercializing production from natural gas hydrates. From Fig. 7, it can be summarized that production of gas from NGH is expected to reach a significant level only after 2030 and above. However, it is necessary to follow the developments of NGH research as this could have a disruptive effect on the international gas markets similar to the impact of shale gas development.

6. Prospects and challenges in NGH research

6.1. Evaluation of environmental impact

Aside from developing techniques for economical gas production from methane hydrates, it is of utmost importance to evaluate the possible environmental impact of hydrate recovery given the unique nature of these resources. CH₄ is a greenhouse gas about 21 times more potent than CO₂ according to the assigned global warming potential (GWP) over 100 years [210]. Given the large amounts of CH₄ found in the form of hydrates in nature, the “clathrate gun” hypothesis has been suggested by several researchers [52,211–215]. It was postulated that the warming of oceans could cause a widespread dissociation of methane hydrate deposits leading to the release of a large amount of methane into the atmosphere, further increasing the amount of greenhouse gases in the atmosphere. While this issue in itself is important, it should be highlighted that naturally occurring hydrates, according to their in situ condition, has different vulnerabilities to destabilization [11]. The impact of global warming on methane hydrate dissociation was investigated using a mathematical model based on heat conduction in single and composite media [216]. The critical time required to dissociate was reported to be dependent on the global warming scenario, the thermo-physical properties of the earth and the driving force required for hydrate dissociation [216]. Based on the current understanding, hydrate formations likely to become energy resources are least vulnerable to the changes in oceanic and atmospheric conditions, whereas those that may contribute to climate change are shallow hydrates which are not suitable for energy recovery.

The main environmental concerns from gas hydrate exploitation are the uncontrolled leakage of gas from the seafloor upon dissociation, the discharge of produced water into the ocean, seafloor subsidence and submarine landslides [217]. To address these potential environmental problems during hydrate reservoir exploitation, 4 research directions have been proposed by JOGMEC [218]:

Table 2
Summary of NGH field production test results.

Field name	Location	Year	Method	Production period	Cumulative gas volume (m ³)	References
Mt. Elbert Well Mallik site	Alaska North Slope Mackenzie River Delta, Canada	2007	Depressurization	11 h	–	[193]
		2002	Thermal	5 days	516	[251]
		2007	Depressurization	12.5 h	830	[187]
		2007–2008	Depressurization	139 h	13,000	[194]
Ignik Sikumi	Alaska North Slope	2012	CO ₂ /CH ₄ exchange	~6 weeks	24,085	[202]
Nankai Trough	Margin of the Daini Atsumi Knoll	2013	Depressurization	6 days	120,000	[207]

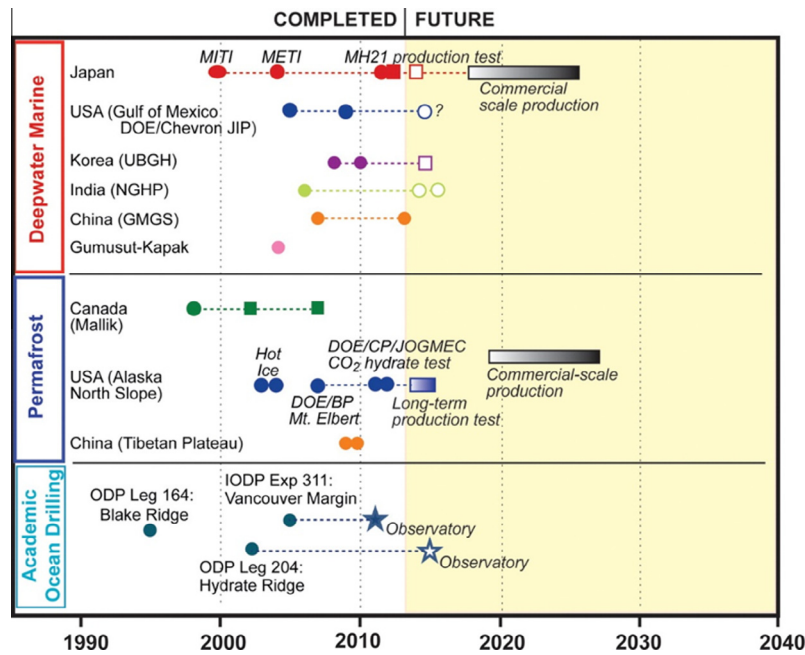


Fig. 7. The proposed road map for natural gas hydrates (map courtesy of the US Geological Survey).

1. To enhance the understanding of the geological formations and marine environment.
2. To develop numerical models in postulating the impact of possible methane and water discharge into the ocean.
3. To develop technologies and capabilities in monitoring these hazards in the offshore environment.
4. To improve understanding on environmental impact assessment and management systems.

In summary, a better and in-depth understanding towards gas hydrate would not only enable a better assessment to the resource potential for energy production, but also essential in evaluating the role of natural gas hydrate in global carbon cycle. Therefore, an improved framework for environmental impact assessment will be important for every development of gas hydrate resources [206].

6.2. Mechanical strength of hydrates in nature

Another challenge to be overcome for hydrate exploitation is the possible seafloor subsidence or landslides brought about by a loss of strength as hydrates dissociate from the sediments [214,219,220]. In a geophysics research investigating the strength and rheology of pure methane hydrate, it was reported that methane hydrates is over 20 times stronger than ice at the same conditions and strain rate [221], highlighting the importance of understanding the mechanical properties of hydrate in nature.

The bulk properties of hydrate reservoir is largely dependent on how hydrates distribute within the pore space. Three hydrate distribution patterns within pore space have been identified: hydrate floating within pore fluids; hydrate becoming load-bearing member of the sediment matrix; and hydrates that cements sediment grains [219,222]. From a laboratory study which investigated the hydrate distribution in unconsolidated Ottawa sand [222], it was observed that methane hydrate surrounds and cements sediment grains in excess gas environment. The authors also highlighted that the physical and mechanical properties for methane hydrates formed in a gas-rich setting (e.g. laboratory setting) will be different from hydrates formed in water-rich environment.

Recent works have looked into the morphology and changes in mechanical strengths of methane hydrate under different gas and water saturation and different types of porous media [223,224]. In a series of studies, Li et al. [225–228] studied the effect of temperature, confining pressure, strain rate, and porosity on the mechanical properties of methane hydrate under simulated offshore deepwater conditions. In general, several conclusions were made from these studies:

1. The strength of hydrate reservoir decreases with increasing temperature.
2. Gas-saturated hydrates tend to have greater stiffness and higher failure strength as compared to water-saturated hydrates [223,229].
3. The higher hydrate saturation results in larger failure strength and more apparent shear dilation [230].
4. Confining pressures within hydrate samples have an effect on the failure strengths of the hydrate samples. It was reported that the failure strength increased with confining pressure till 5 MPa and decreased with further pressure increment as a result of particle crushing and high pressure melting of ice [226,228].

Further investigations have looked into the changes in mechanical properties during dissociation by thermal stimulation or depressurization [224,231]. It was found that failure strength of sediments after dissociation was lower as compared to pure Toyoura sand. Both thermal stimulation and depressurization resulted in sediment failure when axial load exceeded the strength of the sediment after dissociation. As the hydrate bearing sediment sample was small (30 mm in diameter, 60 mm in height), future work conducted on a larger scale can be done to better represent the in situ natural conditions.

As the CH_4 – CO_2 exchange process involves the formation of CO_2 hydrate during the exploitation, a recent work compared the difference in mechanical strength between CO_2 and CH_4 hydrate bearing sediments [232]. The preliminary study reported that the synthetic CO_2 hydrate could maintain the mechanical stability of reservoir during CH_4 – CO_2 gas exchange provided that they are well

distributed in the pore space. Further works injecting CO₂ into CH₄ hydrate are needed to elucidate the mechanical properties of the mixed-hydrate bearing sediment during the gas replacement.

From a series of review, it is found that the characteristics of hydrate bearing sediments vary over a wide range of conditions. Hence, there is a need to develop more understanding on the mechanical properties of gas hydrates in nature. It is also important to develop novel techniques to ensure that the hydrate samples formed in laboratory setting are reasonably similar to that in nature, following which deeper understanding on CH₄ hydrate dissociation and CO₂ hydrate formation can be obtained.

6.3. Use of geological hydrate formations for CO₂ storage

While the utilization of CO₂ in CH₄ recovery from hydrates is still under development, the storage of CO₂ in geological formations has been proposed for greenhouse gas mitigation. The earlier proposal for CO₂ sequestration typically involve storage of CO₂ in gaseous or liquid form within geological formations such as depleted oil and gas field, deep ocean, saline aquifers and salt caverns [233–236]. However, storage of CO₂ in fluid form has the disadvantage of possible leakage from fluid flow depending on the sealing capacity of the caprock [235]. Storing CO₂ in hydrate form could resolve the problem of fluid flow as CO₂ is stored in solid hydrate phase of significantly lower mobility [237,238].

Numerical simulation studies of CO₂ sequestration in a depleted reservoir consisting methane as residual gas have shown that after 1000 days from initial injection, the amount of CO₂ stored in hydrate form could be more than 9 times the original CH₄ gas-in-place [239]. In laboratory setting, the storage of CO₂ under hydrate formation conditions using two typical gas injection methods: gas cap mode and spiral tube mode has been investigated [240]. The authors observed that spiral tube mode injection could achieve a higher water conversion and reported that the storage capacity increased by 100% as compared to CO₂ injection without hydrate formation at the same P–T condition (3.2 MPa, 277.15 K).

Although the importance of carbon capture has been emphasized for decades, commercial scale CO₂ capture and sequestration (CCS) activity has not been seen. One of the major drawback that hinders the application of CCS technology is the cost consideration. The costs of CO₂ capture for pulverized coal plant and integrated gas combined cycle (IGCC) plant are estimated to be between US\$ 50–75 and US\$ 35–46 per tonnes of CO₂ avoided respectively [241]. For the cost of sequestration, US EPA has published a technical report to evaluate various cost components including the geological characteristics, well operation, structural integrity and maintenance [242]. The cost of carbon capture and sequestration will be added up to the overall cost for energy production, which increase the total cost of energy.

On the other hand, if natural gas production is achieved during CO₂ sequestration, the value of methane produced may offset the sequestration cost. The feasibility of injecting flue gas has been tested and affirmed in laboratory scale as well as field scale as highlighted in previous chapters [243,244]. The direct injection of flue gas eliminates the steps to concentrate CO₂, thereby increasing the economic feasibility of the guest-exchange process.

To sum up, it is essential to further understand the stability of CO₂ hydrate in different geological setting. Furthermore, various issues arising from the test production (e.g. limited injectivity of liquid CO₂, limited understanding towards multicomponent equilibrium system) highlight the importance of more research at large scale laboratory setting to further understand and evaluate the feasibility of the utilization of hydrate reservoirs as stable CO₂ sinks [245].

6.4. Economic analysis

Aside from technical studies, the viability of exploiting natural gas from hydrate is dependent on the economic feasibility. The economic feasibility of methane production from hydrate is highly dependent on the price of natural gas extracted from other resources (conventional reserves, shale gas). A comparison of production cost and estimated amount of reserve is summarized in Table 1.

The cost related information has not been widely available due to limited data released from hydrate exploitation trials. However, some preliminary studies have performed economic analysis with educated assumptions to investigate the economic feasibility of exploiting gas hydrates as an energy resource [246,247]. An estimate of \$CDN₂₀₀₅ 7.50/Mscf was presented to be the lowest gas price that would allow economically viable production from onshore gas hydrates with an overlying gas room; whereas for onshore hydrate reservoir in the absence of free gas room, the viable gas price is estimated to increase to \$CDN₂₀₀₅ 12.00/Mscf [246]. These estimated figures were based on the assumption that the hydrate deposits are large and concentrated. For offshore resources, it was estimated that production from marine hydrates would cost \$USD₂₀₀₈ 3.50–4.00/Mscf more than conventional marine gas resource [246].

On the other hand, Döpke and Requate [247] studied the economics of exploiting gas hydrates as an energy resource and proposed an economic model based on two main tenets: firstly the natural decay of the resource at a certain rate, and secondly the geological risk resulting from sea-floor mining. Externalities resulting from these two tenets include the increase in greenhouse emissions due to carbon fuel consumption as well as any possible submarine landslides that might occur. The authors concluded that the optimal exploitation path for methane hydrate is dependent on the assessment of environmental risk, and policy instruments can be applied to manage the optimal path.

7. Conclusion

It is undisputed that natural gas hydrates are one of the largest sources of carbon on earth and a potential source of clean carbon-based energy for humanity in the near future. Given the unique geographical distribution and vast resource quantity of natural gas hydrates, the production of methane from natural gas hydrates is expected to have a far higher impact on global economy than the impact of shale gas. Further, the transition of the economy from oil based to natural gas based will accelerate greatly with the inclusion of natural gas hydrates as reserves and this is like to happen within the next decade or so. Therefore, this paper reviews the current state of the art techniques in hydrate exploitation, research progress in relevant studies around the world and proposes possible direction for NGH-related studies. Apart from extraction of methane from the vast hydrate resource, this review also looks into the huge potential of sequestering CO₂ as hydrates in the porous sediments in the existing natural gas hydrates locations as a safe CO₂ mitigation method. There is a need for further field tests and also for a gas production rate of about 20,000–30,000 m³ per day over a sustained longer duration of time to continue to the path of commercialization of technology for gas production from natural gas hydrates. Whilst there are no technology stoppers to exploit or produce methane from hydrates, specific technological breakthroughs will depend on the effective management of the sand and water during production, as well as the appropriate mitigation of environmental risks.

Acknowledgements

The financial support from the Singapore MOE AcRF Tier 1 (R-279-000-386-112) and the National University of Singapore (R-279-000-420-750) is greatly appreciated. Xiao-Sen Li would like to appreciate the financial support from the National Science Fund for Distinguished Young Scholars of China (51225603).

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