Sheida Shahnazar, Samira Bagheri*, Amin TermehYousefi, Javad Mehrmashhadi, Mohd Sayuti Abd Karim and Nahrizul Adib Kadri

Structure, mechanism, and performance evaluation of natural gas hydrate kinetic inhibitors

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Abstract: Ice-like crystal compounds, which are formed in low-temperature and high-pressure thermodynamic conditions and composed of a combination of water molecules and guest gas molecules, are called gas hydrates. Since its discovery and recognition as the responsible component for blockage of oil and gas transformation line, hydrate has been under extensive review by scientists. In particular, the inhibition techniques of hydrate crystals have been updated in order to reach the more economically and practically feasible methods. So far, kinetic hydrate inhibition has been considered as one of the most effective techniques over the past decade. This review is intended to classify the recent studies regarding kinetic hydrate inhibitors, their structure, mechanism, and techniques for their performance evaluation. In addition, this communication further analyzes the areas that are more in demand to be considered in future research.

Keywords: flow assurance; hydrate inhibitor; KHI; low dosage; THI.

Introduction

“Clathrate hydrate” is a term defining solid crystalline compounds formed by gas and water molecules (Sloan 1998, Sloan Jr and Koh 2007). The cage-like structure of water molecules can embrace guest gas molecules such as methane, ethane, propane, isobutene, n-butane, nitrogen, carbon dioxide, hydrogen sulfide, etc. and form clathrate hydrate (Makogon and Cieslewicz 1981, Sloan Jr and Koh 2007). Based on the number and type of cavities and sizes of guest gas molecules, three various structures of hydrate are known as structure I (sI), structure II (sII), and structure H (sH). These structures’ detailed description and differences could be found elsewhere (Ripmeester et al. 1987, Sum et al. 1997, Mao et al. 2002, Sloan Jr and Koh 2007).

Gas hydrate has attracted the attention of scientists in many fields of studies (Kvenvolden 2003). Although initially it was just a matter of concern due to the problems it caused in the oil and gas industry (Carson and Katz 1942), today, it is becoming more favorable, thanks to its emerging applications (Shahnazar and Hasan 2014, Ansari et al. 2015) such as alternative energy resource (Englezos and Lee 2005, Klauda and Sandler 2005, Makogon et al. 2007), novel gas transportation (Sun et al. 2003, Ansari et al. 2016c), gas storage technique (Gudmundsson et al. 1994, Masoudi and Tohidi 2005, Strobel et al. 2007, Ogata et al. 2008, Talyzin 2008, Veluswamy and Linga 2013), separation technology (Shiojiri et al. 2004, Arjmandi et al. 2007, Nagata et al. 2009, Eslemianes et al. 2012, Tang et al. 2013), and carbon dioxide sequestration (Rajnauth and Barrufet 2009, Rajnauth et al. 2010, Gholinezhad et al. 2011, Li et al. 2011, Eslemianes et al. 2012, Ida et al. 2012, Rajnauth 2012, Kang et al. 2013). In addition to the abovementioned applications, the recent increase in deep-water oil and gas production has enlarged the number of studies on hydrate formation. It is according to this fact that deep-water temperature and pressure condition favor the formation of hydrate crystals (Mehta et al. 2000, 2002).

In high-pressure and low-temperature condition and in the presence of water molecules in gas and oil systems, there is a high probability of hydrate formation. The oil
and gas systems are usually under high pressure because of hydrostatic head or operating pressure of the pipeline. In addition, they usually operate at low temperature because of the external environment or Joule-Thomson cooling effect due to the expansion of gas (Giavarini and Hester 2011, Ansari et al. 2016d). In order to save these systems from hydrate formation, three various methods are common: (1) removal of water from the mixture, (2) controlling temperature and depressurization (Yousif et al. 1990, Tang et al. 2007), and (3) inhibitor addition via various chemicals.

Hydrate formation, similar to any other phase transition phenomena, happens based on system's Gibbs free energy. Therefore, to prevent hydrate formation, we should try to enlarge the free energy of the system via adding inhibitors to the system. Two main classes of inhibitors are being used, which are known as follows:

i. Thermodynamic hydrate inhibitors (THIs): Methanol and glycol are common chemicals that are categorized in this group. These components can shift the thermodynamic equilibrium condition to a lower pressure and higher temperature by decreasing the chemical potential of aqueous water while diluting water molecules (Yasuda et al. 2009, Ansari et al. 2016b). Figure 1 illustrates how some THIs and their combination with some electrolytes take action on hydrate formation (Shahnazar and Hasan 2014, Ansari et al. 2016a). THIs form hydrogen-bonded network with water molecules through their hydroxyl groups (Sloan Jr and Koh 2007, Yousefi et al. 2015b) and, as a result, make the hydrate formation conditions more inaccessible (Tavasoli et al. 2011, Yousefi et al. 2015a). However, the amount of THF that should be added to the system to be effective is around 10–50 wt%, which is quite high and therefore very expensive. In Figure 2 (Sohn and Seo 2017), it is shown how monoethylene glycol (MEG) presence, which is one very common THI, limits the hydrate particle agglomeration.

ii. Low-dosage hydrate inhibitors (LDHIs): In the beginning of 1990s, scientists shifted their attention to the inhibitors that delayed hydrate nucleation and crystal growth, instead of changing the thermodynamic condition of hydrate formation. Because of the fact that this type of inhibitor is more effective at a much smaller dosage than THIs, they are often called LDHI. Based on the preventive mechanism of LDHIs, they are classified into two main groups: (a) kinetic hydrate inhibitors (KHI) and (b) anti-agglomerates (AA) (Huo et al. 2001, Amir et al. 2015). Both groups are added to the system at small quantities (around 0.1–1.0 wt%). KHIs are usually water-soluble polymers, and they take part by being adsorbed on the hydrate surface (Figure 3B) or perturbation of local water structure (Figure 3C) and delaying hydrate nuclei formation (Sa et al. 2013). While the cost per weight of KHIs is commonly more than that of THIs, aqueous concentrations of KHIs need to be generally less than 1 wt% versus 10–60 wt% for methanol. This can help up to 50% savings when using KHIs. In spite of the initial interest on KHIs, their application has been limited and work continues on finding these inhibitors with a large effective sub-cooling range and longer residence time capabilities. In most real cases, such as sub-water operation conditions, sub-cooling can be over 294 K. AAs are usually surfactants that permit hydrate nucleation while they stop them from agglomerating and accumulating into large masses. AA allows the hydrate particles to form as transportable non-sticky slurry dispersed in the liquid hydrocarbon phase while flowing smoothly through oil-gas or condensate pipeline. All current commercial AAs are quaternary ammonium (“quat”) surfactants (Klomp et al. 1995, Kelland et al. 2012).

In this review paper, we have categorized studies based on their objectives and the parameters being investigated. Therefore, in section “Hydrate formation and inhibitive mechanisms”, articles have been reviewed encountering the effective mechanisms of KHI. Section “Kinetic hydrate inhibitor components” overviews papers aiming to test new chemicals and structures as KHIs. In sections “Experiments in realistic conditions”, published materials presenting experiments in more realistic conditions are surveyed, and eventually, section “Novel techniques and devices” reviews new techniques and devices for KHI performance evaluation.
In order to discuss the mechanism of KHI inhibition, initially, it is of importance to overview the hydrate formation mechanism. Although thermodynamic knowledge of hydrate formation is essential for any hydrate-related studies, it is not enough per se and cannot meet all requirements. Hydrate crystal formation rate is also the vital knowledge that grabbed scientists’ attention over the past two decades. Hydrate formation is known to have

**Figure 2:** Conceptual image of how MEG prevents the interaction between hydrate particles leading to agglomeration (Sohn and Seo 2017).

**Figure 3:** KHI mode of action on hydrate crystal growth inhibition: (A) system without inhibitor; (B) KHI adsorption on hydrate surface; (C) local water molecule perturbation, preventing hydrate nuclei to form (Sa et al. 2013).

**Hydrate formation and inhibitive mechanisms**

In order to discuss the mechanism of KHI inhibition, initially, it is of importance to overview the hydrate formation mechanism.
the same mechanism as crystal nucleation and growth. Crystal nucleation happens spontaneously or artificially after super-saturation of solute. If the thermodynamic condition of the system favors crystallization, the primary nuclei grow up to a critical size when no further energy barrier stops nucleation.

Fandiño and Ruffine (2014) investigated the nucleation and growth of hydrate where some of the previous theories were proven to be reliable and some were not. They observed two mechanisms for hydrate crystallization. The first one was characterized by a rapid formation of a hydrate layer at the gas-liquid interface (Figure 4), as reported by previous workers (Takeya et al. 2000, Sloan Jr and Koh 2007). This theory has also been proven recently by Zylyftari et al. (2014), and the oil-aqueous phase interface gives us the proper site of hydrate heterogeneous nucleation. The second one was defined by the occurrence of multiple nucleation points within the bulk phase. The former mechanism was observed at the lower investigated pressure and quickly limits the hydrate growth process, whereas the latter was encountered at the higher investigated pressure. Another widely cited theory is the “labile cluster model,” in which water molecules already form structures such as labile rings of pentamers and hexamers in the pure water phase without dissolved gas molecules cavities (Christiansen and Sloan 1994, Chong et al. 2016).

In another investigation, Schicks and Luiz-Helbing (2015) assume that the solid phase that formed at the very first state is not a hydrate phase in terms of crystalline structure but some kind of an amorphous hydrate, which transforms subsequently into crystalline hydrate phase. Furthermore, the results suggest that the formation process and the properties of the resulting hydrate phase strongly depend on the properties of guest molecules.

In recent years researchers have been actively studying hydrate local structuring nucleation through molecular simulation tools (Radhakrishnan and Trout 2002, Moon et al. 2003b, Jacobson et al. 2010, Barnes and Sum 2013, Yi et al. 2014). Figure 5 is an example of the molecular modeling result that shows the hydrate nuclei growth in 100 ns at $T=240$ K. In 2015, English and MacElroy (2015) overviewed the available molecular simulation studies for hydrate crystallization, also on its thermodynamics, equilibrium properties, and thermal conductivity.

Knowing the formation mechanism of hydrate ignited this question in scientists’ minds: the possibility of blocking the progress of hydrate formation reaction. Therefore, a series of studies began to investigate the effect of surfactant and polymer additions to the hydrate prone

![Figure 4](image_url) **Figure 4:** Hydrate growth in gas-liquid interface: (A) before cooling, (B) 28 min, (C) 30 min, (D) 5 h, (E) 23 h, and (F) 72 h after formation (Moon et al. 2003b).
Although the exact KHI mechanism is not fully discerned, it is believed that when KHI is in contact with clathrate hydrate crystal, the polar functional groups interact with molecular cages on the hydrate surface. KHIs are effective in small sub-cooling and residence time. For example, polyvinyl pyrrolidone (PVP) is effective for sub-cooling of less than 278–279 K and less than 20 min of residence time. Nonetheless, additives that are more complex, such as poly-N-vinylcaprolactam (PVCap), can allow up to 283 K sub-cooling and up to several days of residence time. KHIs’ performance is closely related to operating temperature, pressure, and salinity. In addition to these factors, the clathrate hydrate molecular structure can affect KHI performance. For instance, KHI developed for sII hydrates may not behave effectively for sI hydrates.

By utilizing a high-pressure pendant drop tensiometer, the surface activity of different KHIs and their effects on the rheological properties of the gas-water interface were studied inside and outside the hydrate stability zone by Duchateau et al. (2012). Although all the tested KHIs showed substantial interfacial properties, neither their surface activity nor the interfacial dilatational elasticity of the KHI layer adsorbed at the water/gas interface measured outside the hydrate stability zone correlates with their performance as hydrate inhibitors. In the experiments conducted inside the hydrate stability zone, the variation rate of the dilatational elastic modulus of the water/gas interface measured in the initial moments of hydrate film growth appeared to be directly related to the KHIs’ performance. This experimental observation offers a new way of evaluating KHIs in the laboratory.

The main focus in previous studies is mainly on hydrate nuclei growth on the guest gas molecule and water interface or water droplet surface. Nevertheless, Lee et al. (2014) studied hydrate crystal growth at the surface of the gas bubble. The results proved that sodium dodecyl sulfate (SDS) or PVCap affects the morphological characteristics of methane-propane hydrate crystal on the surface of the gas bubble. In this work, by using an optical microscope, methane-propane crystal’s growth on the surface of a bubble in pure water was investigated and compared with those in aqueous solutions of SDS or PVCap. Initially, smooth hydrate film was formed and the surface became rough on the bubble as the experiment continued with the presence of only pure water. In addition, it was discovered that the crystals of hydrate formed as the dendritic shape of the surface of hydrate film. In the case of SDS presence, extreme variations in morphology were noticed in that smoke-like crystals appeared from the top of the gas bubble. Moreover, the gas bubble was not fully covered by hydrate film when the SDS concentration increased. In the PVCap solution, a seed-like or small spot of hydrate crystals occurred sparsely on the bubble surface and spread out on the whole surface as the experiment progressed.

In the field of hydrate inhibition mechanism, molecular dynamic simulation (MD) has become helpful in recent years as well (Kvamme et al. 2005, English and MacElroy 2015). Molecular simulation has much to offer especially considering the fact that the underlying principles of gas-hydrate inhibition are not particularly well understood. Therefore, simulation tools can help in increasing the level of understanding and targeting the design of environmentally friendly and effective inhibitors. Freer and Sloan carried out preliminary MD simulations of earlier inhibitors, assessing their potential as agents (Freer and Sloan 2013).

**Figure 5**: Nucleus of sI hydrate at the beginning of simulation (left) and after 100 ns growth (right) (Johnston et al. 2010).
Sloan 2000, Li et al. 2016). Moon et al. (2003a, 2007) discussed in a clear way how molecular simulation could address these questions of limiting hydrate formation. Storr et al. (2004) and Anderson et al. (2005) have reported impressive and insightful results from MD simulation of direct inhibition of hydrate formation by tailored KHI-type compounds, including the effect of various functional groups and hydrogen bonding interactions on influencing hydrophobic interactions as the template for hydrate cage formation.

In one recent work by Li et al. in 2017, the hydrate growth process in the presence and absence of PVP is studied. The binding interaction between the water molecules and KHI proved to play a key role in preventing hydrate growth. Some MD simulation in this work showed that suitable KHI could prevent hydrate nuclei reaching the critical nucleus size for subsequent spontaneous growth through perturbing the assembly of free water molecules on their surface.

**Kinetic hydrate inhibitor components**

In hydrate formation concept, induction time is defined as the time that elapsed from experiment start point to the hydrate formation onset (Talaghat 2014). KHIs play an important role in hydrate formation inhibition by affecting induction time and decreasing the pace of crystal formation by binding to hydrate surface and preventing the hydrate crystal nuclei growth. Usually, KHIs are water-soluble polymers with low molecular weight, for example, a polyethylene (or polyvinyl) backbone chain with attached polar groups (typically amides with carbon numbers of 5–7) (Ziao et al. 2002). Up to now, KHI polymers that have been discovered are mostly vinylic polymers containing amide or imide groups (Ajiro et al. 2010, Xu et al. 2010, Lou et al. 2011, Chua and Kelland 2012a). In addition, in order to improve the KHI polymer performance, a variety of synergist molecules has been designed, which are mainly blends of N-vinyl caprolactam polymers. These synergists include tetraalkylammonium salts, trialkylamine oxides, and small ionic or non-ionic amphiphilic molecules (Nakarit et al. 2013).

Nature delivers some evidence into some special molecular structures that can prevent the crystallization of ice and ice-like materials in the form of natural antifreeze proteins (AFPs). There are some fishes (e.g. Winter Flounder) living in or near the polar regions that have an interesting mixture of proteins to stop them from freezing in the cold temperature. These proteins have two categories: (i) antifreeze glycoproteins (AFGP) and (ii) AFP. They can bind to embryonic ice crystals and prevent their growth within a certain temperature range and, consequently, depress the freezing point of body fluid in a non-colligative manner (Yeh and Feeney 1996). In 1977, inhibition activity has been proposed by Raymond et al. derived from the Kelvin effect induced by the adsorption of AFPs on the ice surface and is referred to as the adsorption-inhibition hypothesis (Raymond and DeVries 1977). AFPs can reduce the water freezing point. For example, Gordienko et al. (2010) introduced AFPs as tetrahydrofuran (THF) hydrate crystal inhibitor. The fluorescently tagged AFPs were visualized to study their effect on THF hydrate crystals and were compared to PVP. The results indicated that AFPs could be considered as an effective hydrate inhibitor agent.

AFPs’ capability to stop the arctic fish from freezing by inhibiting ice crystallization provoked the question as to whether it is possible to artificially synthesize similar chemicals of such proteins (Zeng et al. 2006). Early studies on KHIs were started in the late 1980s at the Colorado School of Mines (Sloan Jr and Koh 2007). They first introduced the new KHIs such as PVP and polyvinyl caprolactam (PVCap). In addition, a number of other inhibitors were suggested, frequently used in combination with synergistic materials (Kelland 2006).

Ajiro et al. (Kelland et al. 2013) in 2010 started a systematic study on the performance of poly(N-alkyl-N-vinylamide)s versus their structure. This group has synthesized five different polymers and checked their performance as KHI in a high-pressure autoclave. Those KHIs having the largest alkyl groups on the side-chain nitrogen atoms proved to be a better inhibitor.

In 2012, Kelland et al. (2012) studied the inhibitive effect of some components on THF. The tested components were trialkylamine oxides, tri-n-butylamine oxide (TBAO), tri-iso-pentylamine oxide (TiPAO), and tri-n-pentylamine oxide (TPAO). TBAO showed the best inhibition of hydrate crystal growth among all of them. However, the longest crystal growth phase recognized obtained by the addition of TPAO and not of TBAO is the superior THF hydrate inhibitor. The effectiveness of trialkylamine oxides was shown by examining their ability as a synergist to enhance the performance of PVCap. Their test experiments were conducted in high-pressure rocking cell utilizing structure II hydrate former natural gas. TPAO proved to be a better synergist than TBAO, the best THF hydrate crystal growth inhibitor, or TiPAO. The authors further concluded that adsorption onto hydrate crystal surfaces may not be the only synergistic kinetic inhibition mechanism operating and that the more hydrophobic TPAO is perturbing bulk.
water phase and the nucleation of hydrate was more than the less hydrophobic TBAO.

Hu et al. in 2012 investigated a new copolymer, poly(N-vinyl-2-pyrrolidone-co-2-vinyl pyridine)s (HGs), having good biodegradability character because of having 2-vinyl pyridine, considering that pyridine can be degraded to carbon dioxide and ammonia by some bacteria. The performance of this copolymer was investigated while being used in addition to TBAB for prevention of THF hydrate crystals. The results show that this novel hydrate inhibitor is superior and performs better than commercial inhibitor N-vinyl caprolactam-N-vinyl pyrrolidone 1:1 copolymer, In-hibex501. The mechanism of HGs inhibiting THF hydrate formation is discussed. It is proposed that HGs function as KHI in hydrate nucleation and hydrate crystal growth stage.

Chua and Kelland (2012b) synthesized homo-polymers poly(N-vinyl azacyclooctanone) (PVACO) and studied its behavior as KHI for the first time. Their test experiments were carried out in a high-pressure rocking cell utilizing structure II hydrate former natural gas. PVACO proved to be a more powerful kinetic hydrate inhibitor than the other 5–7-ring poly(N-vinyl lactam)s of analogous molecular weight made in an otherwise identical method to PVACO. Mono-n-butyl glycol ether (BGE) has a robust synergistic effect with PVACO. The team was able to optimize powerful synergistic blends of PVACO and BGE by optimizing the polymerization procedure and the polymer molecular weight, which could prevent rapid hydrate plugging at about 291 K sub-cooling and 68 bar in non-saline water for over 200 h.

In 2013, Reyes and Kelland (2013b) checked the inhibitive behavior of water-soluble 1-alkyl-VP polymer for the first time. In this work, a series of 1-alkyl-N-vinyl pyrrolidone monomers (1-alkyl-VPs) from VP with different alkyl groups (methyl, ethyl, isopropyl, and n-propyl) was synthesized in order to adjust lipophilicity. KHI performance tests were conducted in five high-pressure 40-ml steel rocking cells containing a steel ball. The analysis in this study proves that a more lipophilic ring than PVP gives better structure II gas hydrate kinetic inhibition than PVP itself. Alkylation of PVP gives a better KHI than expansion of the PVP lactam ring with the same number of carbon atoms as used in the alkylation. The 1-lactam protons in PVP are not acidic enough to alkylate this vinyl monomer with a milder base than LDA or equivalent. Therefore, at this stage, the scale-up of 1-alkylated PVPs to an industrial level for use as KHI is not viable.

In one study by Reyes and Kelland (2013a) in 2013, a series of new polymers has been synthesized and their performance as KHI has been investigated. The high-pressure rocking cell was used as test experiment apparatus. The copolymers being synthesized are of N-vinylazacyclooctanone (VACO) with more hydrophilic monomers, including the 5–7-ring N-vinyl lactams, N-vinyl-N-methyl acetamide (VIMA), and N-vinyl acetamide (NVA). The performance of these novel copolymers has been compared to some known KHI, which is poly (N-vinylazacyclooctanone) (VACO). VACO 1:1 copolymers with the smaller 5–7-ring N-vinyl lactam monomers showed increasing performance as the ring size decreased from 7 to 5 when tested at 5000 ppm but had negligible performance difference at 2500 ppm. In addition, the copolymer performance of VACO/VP probably exceeds PVACO homopolymer of similar molecular weight. Various copolymers of VACO/VIMA with different monomer mole ratios were investigated. It was shown that the 1:1 copolymer gave the best KHI performance. The 1:1 copolymers of VACO with VIMA monomer also exceeded the performance of PVACO homopolymer. VIMA copolymers with the four different ring-sized N-vinyl lactams performed better than equivalent NVA copolymers except for the copolymers with VP monomer. Finally, BGE was shown to be a good solvent and synergist for VACO/VIMA copolymers. VACO is not commercially available and currently would be too expensive to make for use in KHI polymers.

Naeiji et al. (2016) in 2014 tested a series of natural amino acids, L-leucine, and glycine, which are biodegradable and environmentally friendly as KHI. The KHI performance was checked for THF hydrate crystal formation. The results showed that the inhibition effect of glycine is not as high as that of PVC and PVCcap; however, as it is biodegradable, it was worth being considered as KHI. In addition, L-leucine shows the acceptable inhibition behavior in the presence of acetone and is proven to be better than glycine, which is thanks to its nonpolar side chain. Glycine is shown to be a better KHI when it is having lower hydrophobicity.

In 2013, Perrin et al. (2013) conducted an extensive review on chemistry of LDHIs being synthesized. Table 1 summarizes their overview on chemical structures.

In some oil and gas operation units, especially those producing hydrogen sulfide (H₂S), considering the hydrate formation probability of this gas has also become so important. In 2013, Salamat et al. (2013) investigated the induction time of hydrogen sulfide hydrate in the presence of PVP and L-tyrosine. The apparatus has been used is a 25-L, temperature-controlled reactor with a magnetic stirrer. The materials used were H₂S as a hydrate former gas with 99.60 mol% purity and PVP and L-tyrosine as KHI with 99.50 mol% purity, respectively. This group has developed a new experimental procedure...
Table 1: Low-dosage clathrate hydrate inhibitors.

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<tr>
<th>Kinetic hydrate inhibitors</th>
<th>Structure</th>
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<tr>
<td>Poly(N-vinyl pyrrolidone) (PVP)</td>
<td><img src="image1" alt="Structure" /></td>
<td>Park et al. 2013, Reyes and Kelland 2013b, Sharifi et al. 2014, Xu et al. 2015, Posteraro et al. 2015a,b</td>
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<tr>
<td>Polyvinilcaprolactam (PVCap)</td>
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<td>Kelland et al. 2013, Lee et al. 2014, Sharifi et al. 2014, Sohn et al. 2015, Zhao et al. 2015</td>
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<td>Terpolymer of vinyl pyrrolidone (VP), vinyl caprolactam (VCap), and dimethylaminoethyl methacrylate</td>
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<td>Tetra(iso-hexyl) ammonium bromide (TiHexAB)</td>
<td><img src="image4" alt="Structure" /></td>
<td>Chua and Kelland 2012a</td>
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<td>Polyvinyl piperidone (PV Pip)</td>
<td><img src="image5" alt="Structure" /></td>
<td>O'Reilly et al. 2011a,b</td>
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<td>N-methyl-N-vinylacetamide (VIMA)</td>
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<td>Polycryloloylpyrrolidino (polyAP)</td>
<td><img src="image7" alt="Structure" /></td>
<td>Kelland 2006</td>
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<td>Polyisopropylacrylamide (polyIP)</td>
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<td>Polyalkylacrylamides</td>
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<td>Hyperbranched poly(esteramide)</td>
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<td>Klomp 2007</td>
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<td>Polyvinyl alcohol (VOH)</td>
<td><img src="image6" alt="Structure" /></td>
<td>Du et al. 2011</td>
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and named it as “sudden cooling”. KHIs included PVP and L-tyrosine with different concentrations (100, 500, and 1000 ppm) were investigated, and the results indicated PVP having the best performance when being used in a concentration of 1000 ppm, increasing induction time to about 58 min compared with gas hydrate formation in the presence of distilled water at nearly the same experimental conditions. However, it is also clear that L-tyrosine may not have considerable effects, or even in some case, contradictory effects, on the hydrate formation time of the hydrogen sulfide.

A recent review by Kamal et al. (2016) highlighted the structures and factors affecting the performances of various categories of water-soluble polymers (vinyl lactam homopolymers and copolymers, amide-based homopolymers and copolymers, dendrimeric polymers, fluorinated polymers, and novel green polymers) when being used as KHI.

Almost all of currently commercially used KHIs are amide/imide-containing polymers, in which the amide/imide keeps the polymers water-soluble via hydrogen bonding in addition to being effective in the inhibition process of hydrate nucleation and crystal growth. Recently, the work by Lin et al. (2017) investigated the possibility of using non-amide polymers as KHIs. This study was the first foray into poly (phosphonate)s as KHIs. Some mediocre performance as a KHI in high-pressure rocking cells using a structure-II-forming gas mixture was found. The proven biodegradation of these poly(phosphonate)s renders them interesting for their use in the marine environment because they will ultimately fully degrade, by either biodegradation or additional hydrolysis.

### Experiments in realistic conditions

Quite recently, many scientists narrowed their attention into investigations considering more realistic condition (Tomson et al. 2006, Mokhtari and Pourabdollah 2011). In order to simulate the real condition of multiphase reservoir, typical brine solutions are used in addition to crude oil to evaluate their impact on the formation of gas hydrate. In addition, in some cases, even drilling mud is added to the system in order to mimic the condition of deep-water drilling (Kelland et al. 2008, Zhao et al. 2015). As previously mentioned, salinity is one of the factors that can affect phase equilibrium condition by lowering the water activity in the liquid phase. In 2014, Daraboina et al. (Talaghat 2014) measured the inhibitor strength in the presence of 5 wt% NaCl and also 30% volume of the Middle East crude oil. They showed that the presence of NaCl may not affect the strength of KHIs, although the combined use of salts and inhibitor has a cumulative effect on inhibition of hydrate formation. However, in case studies where crude oil was available, hydrate nucleation temperature was reduced by approximately 277 K. These results indicate that the presence of crude decreases the natural gas hydrate stability compared to the control pure water system. It has been reported that if the hydrate former is natural gas, the hydrate stability temperature slightly decreases in the presence of crude oil. However, the presence of crude oil is not always beneficial for hydrate formation. Daraboina et al. (2015b) showed that performance of KHIs could be considerably decreased by the presence of crude oil. Therefore, it could be concluded that for each crude oil and water cuts, different hydrate formation kinetics may appear.

In another effort trying to test in more realistic conditions and more relevant to oil and gas reserves, especially in deep waters, Sharifi et al. in 2014 tested the effect of salinity and hydrocarbon liquid phase presence on hydrate formation. In order to more precisely simulate the off-shore reservoir condition, high driving forces are applied in the form of sub-cooling and over pressure mixture of gas, hydrate formers are used. In addition, a mixture of hydrate former gases is used (93% CH₄, 5% C₂H₆, 2% C₃H₈). In this work, PVP and PVPCap are used as KHI. (A) In order to simulate pipeline conditions, a constant cooling rate method (Ajiro et al. 2010, O’Reilly et al. 2011a) using constant pressure was applied. In this procedure, the temperatures of the crystallizers were reduced from outside of the hydrate stability zone to a stable region under constant pressure. Gas hydrate formation is an exothermic process. Hydrate formation was considered complete when stirring was no longer possible and thus simulated blocked pipeline conditions. Dissociation of the hydrate crystals was achieved by increasing the water bath temperature from 274.15 K to 301.15 K with similar heating profiles for all the experiments.

Another study that investigated the performance of KHI in realistic condition was conducted by Del Villano and Kelland (2010). In this work, the inhibition behavior of ionic liquids in typical subsea temperature and subcoolings was examined. In addition, the synthetic gas, which forms structure II hydrate, was used according to the fact that this is the commonest structure in pipeline production. The imidazolium-based ionic liquids EMIM-BF₄ and BMIM-BF₄ performed very poorly as KHIs on SII gas hydrates at 85–90 bar and about 283 K subcooling compared to the commercial KHIs, Luvicap 55W and RE5131 HIO. Thus, there still appear to be no official
reports of non-polymeric organic compounds with significant KHI activity on SII (or SI) hydrate. BMIM-BF₄ proved to act as a synergist for vinyl caprolactam:v vinyl pyrrolidone copolymer. However, this effect was not as significant as TBAB. The results clearly revealed that neither of the ionic liquids had a significant effect in inhibiting the crystal growth of hydrate at 272 K.

In one study by Yang et al. (2016) the dissociation kinetic of carbon dioxide hydrate in porous media was investigated in the presence of salt. Two different temperature driving forces of 4 and 10 K were investigated. The results proved the thermodynamic inhibition of NaCl salt; however, no significant kinetic inhibition has been observed. Compared to pure water, the presence of salt slightly increased the pace of hydrate dissociation at lower driving force (4 K).

In 2015, Daraboina et al. (2015a) studied the hydrate crystal kinetic with the Middle East crude oil and salt. The results show the reduction of hydrate nucleation temperature in their presence, compared to pure water. It has been proven in this study that salt does not alter the inhibition behavior of polymer-based KHIs. However, the significant effect of crude oil is reported.

Just like transportation lines, hydrate particle formation is highly probable in deep-water drilling where low temperature and high pressure cause the drilling fluid to be at risk of hydrate formation (Barker and Gomez 1989, Ouar et al. 1992, Ebeltoft et al. 1997). In one study by Kelland et al. (2008), KHI performance in highly saline water-based drilling fluid has been checked. The studied KHs were three neutral and anionic KHI polymers. In addition, Kelland et al. examined the compatibility of KHIs with water-based drilling fluid with and without the presence of clays. The performance of KHI was significantly reduced in the presence of very active clays (having a high adsorption surface area and containing a significant amount of sodium montmorillonite), which is attributed to polymer adsorption onto the clay. They also proved that in KHI performance in drilling mud, not only that sub-cooling temperature plays an important role but also pressure could have a significant effect. Kelland and Iversen (2010) further continued this investigation by studying the KHI performance at a very high pressure of up to 760 bar. Compatibility of several commercial KHIs with various brine solutions has also been checked, which showed that N-vinyl caprolactam copolymers with 50 wt% and preferentially 67 wt% N-vinyl pyrrolidone had high cloud points in high-salinity brines. This property is highly desirable for deep-water-based drilling fluid applications. The hydrate equilibrium results indicated that even in very high pressure conditions, KHIs still can delay the hydrate crystal formation.

Jensen et al. (2010) conducted some experiments in a high-pressure stirred cell in order to check the SⅠ and SⅡ hydrate formation rate in the presence of salt and heptane as light crude when using AFPs as an inhibitor and compared to PVCap. It was found that the formation of SⅡ hydrate was slower than in SⅠ hydrate and that the induction time of hydrate formation can be significantly improved by adding small amounts of impurities to the hydrate-forming system. The presence of salt and heptane in the system increases the hydrate formation rate.

In this work, an experimental crystal growth inhibition (CGI) method (Anderson et al. 2011, Glénot et al. 2011) was used for the performance evaluation of a commercial KHI (in the absence and presence of CI) for a real field multicomponent gas system (Luna-Ortiz et al. 2014). Finally, a methodology to recreate real pipeline flowing, shut-in, and restart conditions was developed, with results agreeing closely with CGI and induction time data in demonstrating that KHI could offer better protection for long periods of shut-in (e.g. >168 h at up to 288 K absolute subcooling) followed by restarting. As previously mentioned, KHs are usually high-molecular-weight, water-soluble polymers that require polar carrier solvents such as methanol and ethylene glycol. In some cases where the carrier may evaporate in pipelines, hotspots are created and solid polymer will be phased out of the system. Therefore, the interaction among KHI and carrier is of great importance as well. Heidaryan et al. in 2010 (Raymond and DeVries 1977) investigated the synergistic effects between methanol and poly vinyl methyl ether as LDHIs. Results indicated higher efficiency of this mixture rather than using only methanol in terms of injected volume, toxicity, flash point, etc.

In 2013, Daraboina et al. (Hu et al. 2012) investigated the effect of Luvicap on hydrate nucleation time. The results showed that it considerably decreases the time. Also, the effect of poly ethylene oxide (PEO) and NaCl was investigated on the efficiency of Luvicap. However, they also have proven that hydrate solid that is formed in the presence of KHs is more difficult to decompose later, which could be a considerable fact while using KHs in the system (Obanijesu et al. 2014, Xu et al. 2015).

Another challenge hardwired with using KHs in the industry is their recycling, as their application contaminates the water. Some conventional KHI separation techniques are chemical coagulation, solvent extraction, adsorption, etc. However, most of these methods are not only complex and expensive but also just able to remove a slight amount of used KHI. For example, in a work by...
Talley and Colle (2011), heating the aqueous phase to temperature above the boiling point of the water is not beneficial for the cases having polymers with cloud point below the boiling temperature. Detailed analysis of recycling techniques is beyond the scope of this article. Latest technique, in addition to an overview of previous works, could be found in a recent publication by Golpour and Pakizeh (2017).

KHIs are not only tested in laboratories but also being examined in real field cases. For example, in a work by Fu et al. (2001), a copolymer of vinylcaprolactam and vinylmethylacetamide has been successfully deployed in a number of fields, including both in-land and off-shore applications. In another early and first-of-its-kind study, N-vinyl, N-methyl acetamide-co-vinyl caprolactam (VIMA-VCap) was first in Exxon’s 4-in diameter, 275-foot-long hydrate flowloop at pressures up to 1800 psi. It was then field-tested in a 2-in diameter, 1.5-mi-long buried gas flowline in Alberta, Canada, in 1996–1997. KHI proved to be more cost-effective compared to methanol (Talley and Mitchell 1999). Detailed description of other studies concerning KHI real field application is out of the scope of this work and could be found elsewhere (Bloys and Lacey 1995, Leporcher et al. 1998, Mitchell and Talley 1999).

**Novel techniques and devices**

As previously mentioned, KHIs are expensive chemicals. Therefore, it is of great significance to figure out the minimum effective concentration for oilfield scale. Various test devices have been used by researchers such as autoclaves, rocker rigs, differential scanning calorimeter, a batch stirred tank, flow loops, and pipewheels (Kelland 2006, Luo et al. 2007). There has been series of works reported on the KHI evaluation with this apparatus. However, there are two issues that encourage scientists to be constantly on a lookout for new techniques and devices: (1) inconsistency of hydrate formation and inhibition behavior due to the stochastic nature of crystallization, which makes the experiments unrepeatable (Duchateau et al. 2009b), and (2) not being suitable for scale-up in order to be used in industrial applications.

In this section, some of the recent attempts to overcome these difficulties are being surveyed.

Stirred reactors – initially designed by Vysniauskas and Bishnoi (1983) and further modified (Cohen et al. 1998, McCallum et al. 2007, Al-Adel et al. 2008) – are generally used by oil and gas companies in order to simulate the pipeline condition. However, this device is not suitable for testing the biological inhibitors because they are available only in small quantities. Therefore, in 2011, Daraboina et al. (2011a) modified the stirred tank reactor and reduced the equipment size and successfully compared the performance of commercial inhibitors and AFPS.

Kelland research team has been using the five high-pressure steel rocking cells (Figure 6) for a number of their investigations on effectiveness of various KHIs (Chua and Kelland 2012b, Ree et al. 2016). After filling half of each cell volume with water, including dissolved polymer, they are cooled down, vacuumed, and pressurized and the hydrate formation is judged by fast pressure drops.

In 2014, Kelland et al. (2015b) established a new wheel loop device (Figure 7) for testing LDHIs. The results
acquired with this device were compared to those from high-pressure rocking cell. Rocking cell application in LDHI testing has surpassed autoclave. However, compared to a real pipeline, fluid motion in rocking cells is clearly not ideal. In addition, rocking cells are generally small in size. Kelland et al. (2015b) reached the conclusion that the two equipment almost performed the same; however, more inhibitor was required in the wheel tests in order to acquire the same result. It was hoped that the wheel loop would give a more accurate representation of the flow of fluids in pipelines.

Visual observation has been considered as one of the most common techniques for evaluation of hydrate formation kinetics. However, in many cases, this method is insufficient and not reliable enough, which in turn causes a significant amount of error. In one study by Yang and Tohidi (2011), the ultrasonic test technique was used to experimentally examine whether the polymers delay hydrate formation by controlling hydrate nucleation or growth or both. An ultrasonic test technique was developed for detecting nucleation and growth of hydrates (Tohidi and Yang 2005). It is based on attenuation analysis (in the time domain) and fast Fourier transform (FFT) analysis (in the frequency domain) of the received ultrasonic signal, which propagates through the fluid system under examination. The combination of attenuation analysis and FFT analysis of ultrasonic signal creates a novel method, which is more reliable and sensitive than visual observation and turbidimetry. Using the above-mentioned ultrasound technique, three sequential phases of hydrate crystal formation could be identified.

Some researchers applied in situ Raman spectroscopy in order to better understand the kinetics of hydrate formation and inhibition (Sum et al. 1997, Tlili et al. 2002, Yoon et al. 2004, Ohno et al. 2009, Wang et al. 2009). This technique helps scientists to analyze time-dependent behavior of molecules instead of static ones. In a more recent study, Hong et al. (2012) conducted some experiments comparing the microscopic (Raman spectroscopy) and macroscopic measurement (gas uptake measurement) for performance evaluation of PVCap. Raman spectroscopy analyses capture the molecular behavior of hydrate such as cage variation and reveal valuable information on the microscopic performance of KHIs.

Magnetic resonance imaging (MRI) is also another method being used for monitoring kinetics of hydrate crystallization (Baldwin et al. 2009, Bagherzadeh et al. 2011, Xue et al. 2012). Daraboina et al. (2013) examined the performance of both chemical and biological kinetic inhibitors by MRI. In addition, the results have been compared to the common device, which was stirred autoclave. Both MRI (1 l) and gas uptake (batch, 10 ml) experiments showed the same trend in that hydrate nucleation time. Microscopic (MRI) and macroscopic (gas uptake) experiments were in good agreement for hydrate growth assessments as well. Different chromatography techniques (Daraboina et al. 2011b, Nakarit et al. 2013, Kelland et al. 2015a), differential scanning calorimeter (Varma-Nair et al. 2007), pendant drop tensiometer (Duchateau et al. 2012), and photodetector (May et al. 2014) are among the other techniques being used for KHI studies.

Various methods are common for performance evaluation of KHIs, such as the isothermal method (Arjmandi et al. 2005, Lee and Englezos 2006, Del Villano et al. 2008), constant cooling method (Buffett and Zatsepina 2000, Villano et al. 2009, Ajiro et al. 2010), and ramping method (Buffett and Zatsepina 2000, Stern et al. 2001). The detailed description of them could be found elsewhere (Del Villano and Kelland 2011). In order to overcome the inconsistency of data acquired from hydrate formation, a new technique has been introduced by Duchateau et al. (2008, 2009a,b). This method, which is called superheated hydrate method by Del Villano and Kelland, includes forming and re-melting of hydrate crystals. This technique is claimed to be more reliable for KHI ranking in small equipment, giving less scattering in the hold time data due to avoiding the stochastic nature of the first hydrate formation.

Del Villano and Kelland investigated this claim by comparing superheated and non-superheated hydrate. Results indicate that hold times are shorter than when using non-superheated hydrate test methods, but they are more reproducible with less scattering. The reduced scattering occurs in isothermal or slow ramping experiments even when the hydrates are melted at more than 10°C above the equilibrium temperature. However, if a rapid cooling method is used, the improved reproducibility is retained when melting hydrate at 275 K but lost when warming at 281 K. Using the ramping test method, most but not all the KHIs tested agreed with the same performance ranking obtained using traditional non-superheated hydrate test methods. This may be related to the variation in the dissociation temperature of gas hydrates with different KHIs and different KHI inhibition mechanisms. Results also varied between different size autoclave equipment.

A broad and recent review was conducted by Ke and Kelland (2016). This article with a very comprehensive literature survey has overviewed the most commonly used experimental apparatus, detection tools, monitoring and characterization techniques, and experimental methods for conducting KHI-related gas hydrate studies.
Conclusion and further remarks

Traditionally, hydrate management measures included expensive techniques for altering operating temperature and pressure of the system, such as insulating pipeline, reducing pressure, or injecting hydrate thermodynamic inhibitors. Quite recently, novel techniques are being developed such as injection of KHIs. The complexity of natural gas hydrate formation motivated scientists to do extensive studies on various aspects of KHIs application. The most recent research in this area is being reviewed in the current communication. Most of the studies proved the stochastic and often unpredictable behavior of hydrate formation and its kinetic inhibition. Current experimental data are not sufficient to fully explain the inhibition mechanism of inhibitors, given the various natural gas compositions depending on production sites. The reported results show that numerous aspects have to be taken into account to understand the hydrate formation process. Particularly in the formation of mixed hydrates, both thermodynamic and kinetic aspects have to be considered. New chemicals are being presented to the industry to be used as KHIs. However, they are proving to have disadvantages that make their application infeasible in the industry. For example is their low cloud point, which makes them precipitate in real field applications. Therefore, more polymers should be studied as KHIs having better inhibitive performance while being more thermally and physically stable.

Considering the fact that the precise mechanism of KHIs is not established yet and the system parameters affecting their inhibition effect are not fully known, therefore, screening process should be performed for each pipeline/field in order to select the most effective KHI that also is compatible with other chemicals such as scale and corrosion inhibitors. This screening process is often very expensive, time-consuming, and unreliable.

In several articles, the performance of KHIs is being examined in realistic conditions as well. However, due to lack of sufficient experimental apparatus, their performance in downhole dynamic conditions during deep- or ultra-deep-water drilling is still not clear. Therefore, more experiments are needed on real downhole conditions during drilling and deep-water production. Hydrate inhibition testing techniques are also another area that still needs more focus. Over the past few years, various new techniques have been developed for investigating hydrate formation conditions. Among them, ultrasonic, FTIR, Raman spectroscopy, and MRI proved to be suitable for this application. As the nucleation step is stochastic, the results of experiments can often exhibit scatter, making single measurements unreliable. Therefore, a large number of repetitions are usually required in order to eliminate the randomness of the measurements. However, this potentially entails a time-consuming experimental campaign with the potential consequence of delaying project schedules. The newly presented method, superheated hydrate test method, is considered as a promising technique for ranking some KHIs but only for chemicals from same structural class to have same nucleation and growth properties. Therefore, more research with a focus on test condition/procedure and wider range of KHIs is required. In addition, to increase the number of field applications, more research is crucial for developing better or greener KHIs, understanding their optimizing test methods, and developing commercial KHI recycling technology.

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