Review

Towards Gas Hydrate-Free Pipelines: A Comprehensive Review of Gas Hydrate Inhibition Techniques

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Abstract: Gas hydrate blockage is a major issue that the production and transportation processes in the oil/gas industry faces. The formation of gas hydrates in pipelines results in significant financial losses and serious safety risks. To tackle the flow assurance issues caused by gas hydrate formation in the pipelines, some physical methods and chemical inhibitors are applied by the oil/gas industry. The physical techniques involve subjecting the gas hydrates to thermal heating and depressurization. The alternative method, on the other hand, relies on injecting chemical inhibitors into the pipelines, which affects gas hydrate formation. Chemical inhibitors are classified into high dosage hydrate inhibitors (thermodynamic hydrate inhibitors (THI)) and low dosage hydrate inhibitors (kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs)). Each chemical inhibitor affects the gas hydrate from a different perspective. The use of physical techniques (thermal heating and depressurization) to inhibit hydrate formation is studied briefly in this review paper. Furthermore, the application of various THIs (alcohols and electrolytes), KHIs (polymeric compounds), and dual function hydrate inhibitors (amino acids, ionic liquids, and nanoparticles) are discussed thoroughly in this study. This review paper aims to provide a complete and comprehensive outlook on the fundamental principles of gas hydrates, and the recent mitigation techniques used by the oil/gas industry to tackle the gas hydrate formation issue. It hopes to provide the chemical engineering platform with ultimate and effective techniques for gas hydrate inhibition.

Keywords: hydrate inhibition; gas hydrates; thermodynamic inhibitors; oil and gas industry

1. Introduction

Millions of dollars ($) are spent annually in the oil and gas industry to inhibit the production of gas hydrates in the pipelines to assure an uninterrupted flow of natural gas in the pipelines [1,2]. Gas hydrates are considered among the most catastrophic problems that face the flow of natural gas in the pipelines. Significant economic losses and severe safety threats are caused by gas hydrate formation in the pipelines. The formation of gas hydrates in the pipelines may occur during the production, processing, or transportation of hydrocarbons, depending on the thermodynamics of the surrounding environment [3,4]. Thus, their production inhibition is a necessity for a more efficient natural gas production process.

Gas hydrates are ice crystalline-like structures consisting of gas and water molecules. The water molecules form a cage-like crystal lattice structure via hydrogen bonding, and the gas molecules occupy the interstitial vacancies (cages) in the lattice without possessing a lattice position [5]. The average size of a guest gas molecule that can occupy the hydrate cages ranges from 3.8 to 6.95 Å [3,4]. These guest molecules include the small-sized hydrocarbon molecules by nature (e.g., CH_4, C_2H_6, C_3H_8, etc.), as well as H_2S, N_2, and CO_2.

There are three fundamental gas hydrate structures that have been identified so far, based on the structure and the number of hydrate cavities and the size of the guest molecule, and include cubic structure I (sI), cubic structure II (sII), and hexagonal structure H [6–8]. Gas hydrates are stable at low temperatures and high-pressure environment. Gas hydrates can efficiently contain gas molecules, since they are non-flowing crystalline solids [9]. Consequently, since their discovery, they have spawned a slew of new applications [10–12]. Gas hydrates are continually evolving in the field of the oil and gas industry. They are efficiently used in energy storage [13,14], gas separation [15–17], desalination of water [18,19], CO_2 sequestration [20,21], and many other environmental fields [22–24]. Despite their numerous applications, their formation in some fields causes disastrous issues. Hence, their removal is a must.

The mitigation solutions for gas hydrate formation took place initially when Hammer Schmidt (1934) first reported the formation of hydrates in gas pipelines [25]. As time passed, extensive research on gas hydrate inhibition techniques have been performed by several scientists and researchers around the world, as seen in Figure 1.
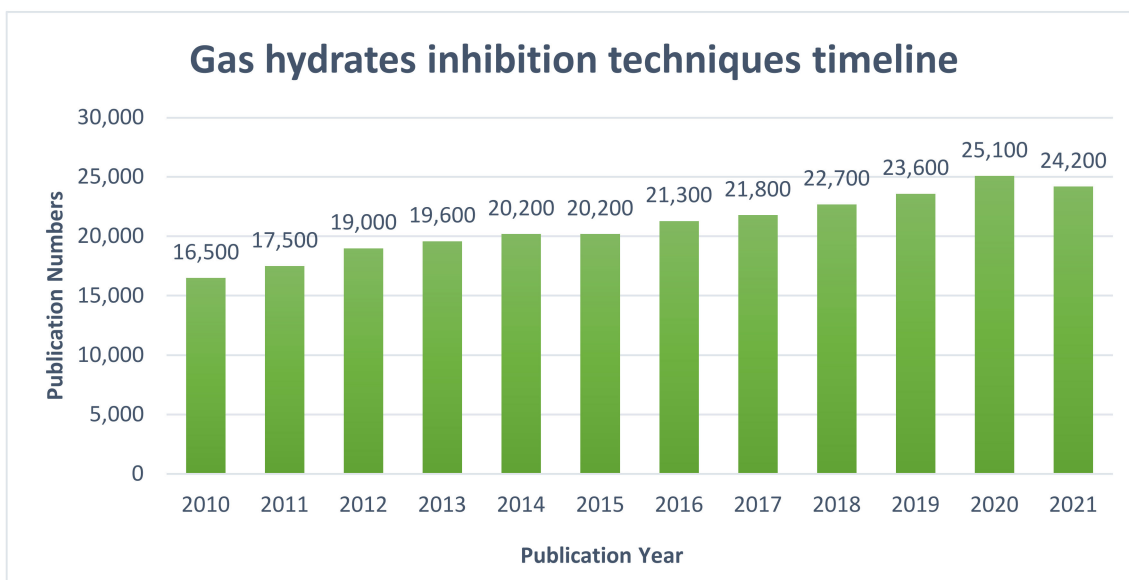

Figure 1. A short post-2010 gas hydrate inhibition techniques timeline representing the number of techniques proposed in hydrate inhibition-related academic publications (Source: Google Scholar).

By looking at Figure 1 above, it is clearly seen that the number of publications about the techniques used for inhibiting gas hydrate formation have increased over time. The gas hydrate inhibition techniques are primarily classified into two categories: physical techniques and chemical inhibitors. The physical techniques include thermal heating and depressurization. On the other hand, the chemical inhibitor techniques involve the usage of thermodynamic hydrate inhibitors (THI), kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs).

This review paper provides a comprehensive study on gas hydrate inhibition techniques. It hopes to propose numerous numbers of methods to solve the gas hydrate issue in the oil/gas industry.

2. Essential Concepts of Gas Hydrate Formation

2.1. Gas Hydrate Formation

The flow process of oil and gas in the pipeline is usually accompanied by water. Therefore, there are three main phases present in the pipeline: an aqueous liquid phase, a liquid hydrocarbon phase, and a gas phase. The hydrate formation flow model is classified into four categories: oil-dominated system, gas-dominated system, condensate system, and

high-water-cut system [26]. In the oil-dominated system, the presence of oil dominates the system, in which all of the water is mixed as droplets in the oil phase. Furthermore, in the gas-dominated system, liquid hydrocarbon is present in a small quantity. Thus, more gas occupies the pipelines. As the water and gas flow in the pipeline of a gas-dominated system, they combine to form hydrate particles and hydrate slurry. The hydrate formation in the pipelines requires the consumption of the water present. The more the hydrates are formed, the higher the solid–liquid ratio of hydrate slurry [27]. As the solid–liquid ratio increases, the solid content increases, and liquid content decreases. This leads to a sudden blockage in the pipeline and the formation of a hydrate film on the pipe wall. The hydrate film thickens gradually over time, causing a reduction in the pipe diameter which eventually leads to clogging (Figure 2). Figure 2 below shows a schematic diagram of the methane gas hydrate flow process in a crude oil pipeline. It is clear from Figure 2 below that the methane hydrate develops over time, causing a clog in the pipeline. Thus, the inhibition of hydrate formation in the gas-dominant system is more important than in the oil-dominant system, since it is very hard to protect the pipelines from clogging up once the hydrates are formed. Moreover, in the condensate system, a high shear is present that causes the water to dissolve in the condensate or to suspend as droplets in the condensate. Lastly, in the high-water-cut system, the quantity of water is very high, and reaches up to 70% by volume. Thus, the water cannot be combined with the oil phase.
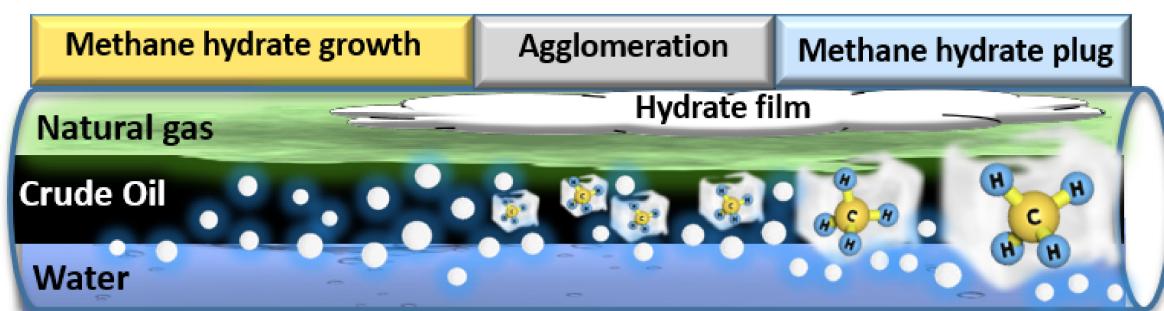

Figure 2. Methane hydrate flow process in a crude oil pipeline.

Gas hydrates are mainly formed when water and non-polar or slightly polar low molecular mass gases or volatile liquids are exposed to low temperatures and high pressures. The formation temperature of gas hydrates ranges from 275 to 285 K, while the formation pressure ranges from 3–10 MPa [28]. Gas hydrates are nonstoichiometric crystalline ice-like compounds that are formed by water molecules connected via hydrogen bonds, which form polyhedral structures. The water molecules form cage-like structures that entrap a guest gas inside them using van der Waals forces [29].

2.2. Gas Hydrate Structures

Gas hydrates are formed in one of the following crystal structures: structure I (sI), structure II (sII), and structure H, (sH). Natural gas hydrates (NGH) are classified into three types, based on their crystal structures: cubic structure I (sI), cubic structure II (sII), and hexagonal structure (sH), as shown in Figure 3 below. NGH is designated as structure I if the guest molecules have diameters ranging from 4.2 to 6 Å, as is the case for CH_4, C_2H_6, CO_2, and H_2S. Furthermore, a structure II hydrate has a diameter of less than 4.2 Å [30]. The single guest gases that can occupy a structure II include N_2, H_2, C_3H_8, and C_4H_{10}. In addition, structure H is formed when larger molecules, usually between 7 and 9 Å (C_5H_{12} and $HC(CH_3)_3$), combine with smaller ones (CH_4, H_2S, and N_2O). Despite the fact that sH is rarely present in nature [31], it has a distinguishable structure in comparison to the others (Figure 3). Figure 3 below shows the cavity types and hydrate structures, along with the guest gas molecules that can occupy each hydrate type.
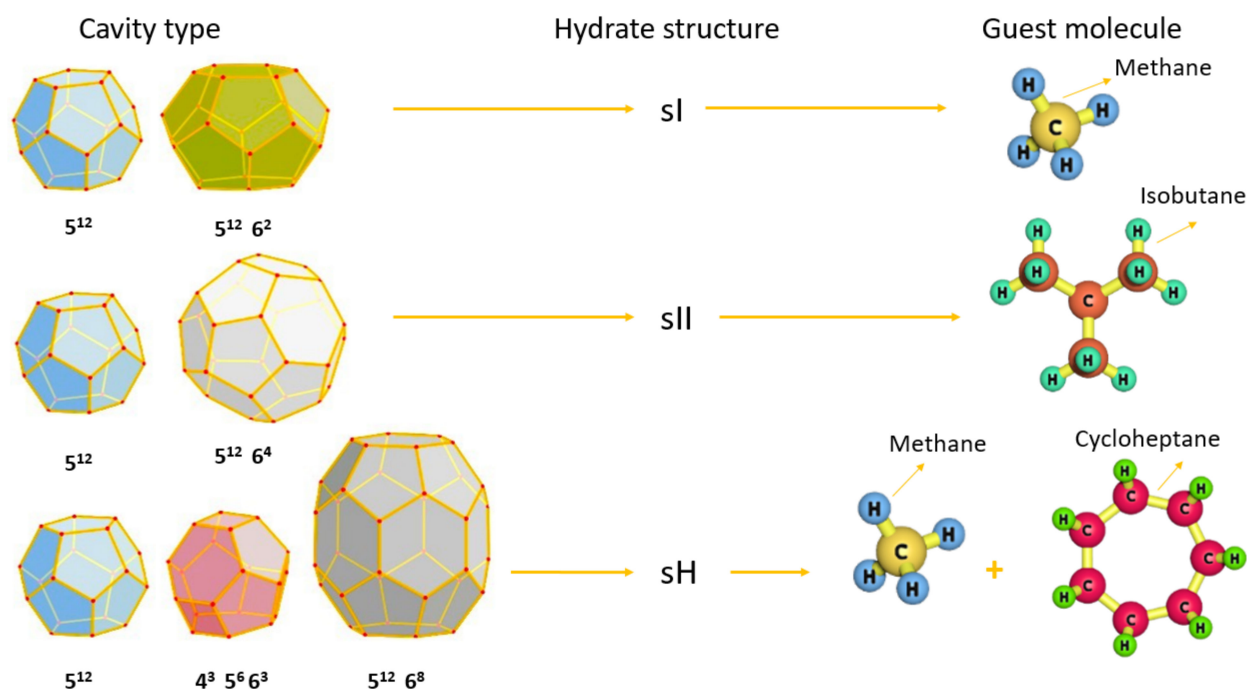
Figure 3. Gas hydrates cavity types and structures, along with the guest gas molecules that can occupy each hydrate type.

3. Gas Hydrate Inhibition

Several techniques have been proposed to inhibit and mitigate the production of gas hydrates in pipelines. These techniques are grouped in two major categories: physical methods and chemical methods. The physical methods include depressurization, heating, and dehydration. On the other side, the chemical methods include the addition of additives, such as thermodynamic inhibitors (THI), kinetic inhibitors (KHI), and anti-agglomerates (AA). Each technique has its own advantages and disadvantages.

Generally, depressurization is applied as a remediation technique, in which pressure is decreased on one side of the gas transport line to form a pressure difference. This pressure difference allows the hydrates to move to the lower pressure end. This approach is usually applied after the hydrate has been formed. Hence, it does not inhibit the formation of the gas hydrate. In long and high-pressure gas transport pipe lines, the line-depressurization technique is impractical. Depressurization causes the hydrate plug's velocity to rise, which can damage the whole pipeline structure. Kavianpour, et al. [32] has successfully proposed a new mechanism for gas hydrate inhibition using depressurization. The authors have used the Peng-Robinson EOS, along with depressurization, in their study. The flow rates of several hydrocarbon gas mixtures were compared in thirteen experimental cases to validate the results. The results of the authors' study showed that depressurization can effectively inhibit the gas hydrates. Chen, et al. [33] studied the effect of three depressurization modes on methane hydrate dissociation by using in situ magnetic resonance imaging. The results of the authors' study showed that the three depressurization modes successfully inhibited the generation of ice during the production process of methane hydrate.

Thermal heating is another common hydrate inhibition method, in which steam is used in the gas pipeline to ensure that its temperature is outside the hydrate formation temperature zone. Unfortunately, the major drawback for this technique is the extremely high cost. The preventive measures cost approximately over $1 million per kilometer of pipeline length. Therefore, thermal heating is rarely used in the gas hydrate inhibition processes. Dehydration is a very effective permanent gas hydrate inhibition solution that has been suggested in several studies. If all the water in the gas stream is dehydrated

(removed), then gas hydrates will not form. However, this technique is unviable, since it is very hard to keep all of the water out of the gas stream.

The most effective and widely applied approach for gas hydrate inhibition is using chemical inhibitors. Chemical inhibitors are chemical compounds that are inserted in gas pipelines to keep the pipeline's operating temperature and pressure outside of the gas hydrate formation temperature and pressure to maintain a hydrate-free region. These inhibitors either slow down or alter the phase behavior of the gas hydrate. Chemical inhibitors are not obtrusive and do not adversely affect pipeline flow, which guarantees a smooth, continuous flow. A further classification of chemical hydrate inhibitors is shown in Figure 4 below. Figure 4 demonstrates that hydrate inhibitors are classified into high dosage hydrate inhibitors (thermodynamic hydrate inhibitors (THI)) and low dosage hydrate inhibitors (kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs)).
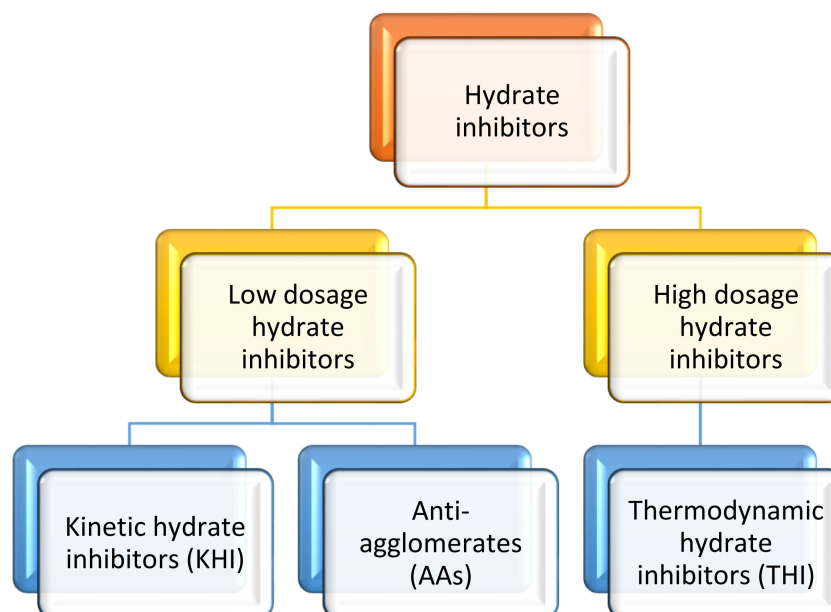
Figure 4. Hydrate inhibitors classification.

THIs inhibit the development of hydrates by lowering the hydrate formation temperature below the operating temperature of the pipeline and/or by shifting the hydrate formation to higher pressure zones. KHIs, on the other hand, postpone the hydrate nucleation time beyond the pipeline residence time. Furthermore, AAs do not stop the gas hydrates from forming, but they stop the plugging of the pipeline. Yang, et al. [34] studied the effect of KHIs on the kinetics of the methane—propane hydrate formation process. The study was evaluated under a wide range of sub-cooling temperatures and concentration conditions. The results of the authors' study revealed that the KHIs successfully inhibited the formation of the methane–propane hydrate [34]. Liu, et al. [35] studied the effect of kinetic inhibitors (three ionic liquids, PVCap, and apple pectin) on gas hydrate nucleation, growth, and blockage. The results of the study showed that kinetic inhibitors successfully inhibited the nucleation and growth of gas hydrates [35].

The most frequently used KHI inhibitors in natural gas pipelines are Polyvinylpyrrolidone (PVP) and Polyvinylcaprolactum (PVCap). In addition, methanol and monoethylene glycol (MEG) are the most regularly utilized THIs in natural gas pipelines. These commercial inhibitors, on the other hand, are only used for one purpose—hydrate inhibition. Hence, both KHI and THI can be used as hydrate inhibitors in natural gas pipelines. A new emerging class of compounds that can act as dual-purpose inhibitors are currently the main focus of much research. This class of inhibitors can simultaneously act as THIs and KHIs. Dual-function inhibitors include ionic liquids, amino acids and nanoparticles [36]. Farhadian, et al. [37] studied the effect of dual-purpose gas hydrates and corrosion inhibitors to

overcome gas hydrate formation issues in pipelines. The authors have synthesized and applied waterborne polyurethanes (WPUs) as an effective dual-purpose gas hydrate and corrosion inhibitor via experimental and computational techniques. The results of the study showed that WPUs can be successfully employed as effective dual-function inhibitors for limiting the formation of gas hydrates in an oil/gas pipeline [37].

3.1. Heating

Gas hydrates are considered one of the main energy sources on the planet right now. They originate at high pressures and low temperatures, and are primarily made up of water and methane. When water molecules are dissociated, a tremendous amount of water is created [38]. However, their formation in pipelines causes huge issues to the oil and gas industry.

Cranganu [39] proposed a new mechanism using in situ thermal stimulation to dissociate gas hydrates. The authors incorporated a newly designed hydrate heating device into a horizontal borehole that was drilled into a gas hydrate zone (GHZ). The mixture of air/gas was introduced from the surface into a combustion vessel using a fuel injection tubing string, and directed to the GHZ. The resultant heat from fuel burning was used by the authors to dissociate the gas hydrate. The results of the authors' study demonstrated that the heat produced from the burning of the fuel successfully dissociated the gas hydrate. Thus, thermal heating can be effectively applied in the inhibition of gas hydrates [39]. Nowadays, natural gas hydrates are gaining great attention as an unconventional natural gas resource, and permafrost hydrate recovery has received a lot of interest in the last decade. The investigation of various growth and dissociation procedures in the laboratory is an essential phase in the inhibition process of gas hydrates. Fitzgerald and Castaldi [40] used a large laboratory size reactor, with a sample volume of 59.3 L, to investigate the formation and dissociation process of gas hydrates in quartz sand sediment. The authors used a point source thermal stimulation technique to thermally dissociate the gas hydrate at a high heating rate of 100 W and a low heating rate of 20 W. The results of the authors' study showed that the gas hydrates were successfully dissociated via thermal heating [40]. Natural gas hydrates are highly unstable and readily breakdown when heated or depressurized. Kou, et al. [41] proposed a new technique for the decomposition of gas hydrates using a thermal stimulation method, along with X-CT scans in real time and depressurization. The findings of the study revealed that the proposed technique incorporating thermal stimulation efficiently decomposed the gas hydrate [41].

Natural gas hydrate is a promising and environmentally friendly energy source with substantial reserves in marine and permafrost environments. The efficient recovery of methane gas from gas hydrates has piqued interest around the world. Wan, et al. [42] studied gas hydrate dissociation and gas recovery processes using several techniques, including electrical heating, depressurization, and several injection modalities, in a high pressure reactor employing two vertical wells. The results of the study showed that direct electrical heating, along with depressurization, can have dramatic effects on the dissociation process of the gas hydrates. Hence, heating is a very promising technique in the dissociation of gas hydrates [42].

Natural gas hydrate is a promising methane supply that must be collected from underneath the seabed. Production methods such as depressurization, thermal stimulation, and inhibitor injection are being researched for the economic recovery of methane from natural gas hydrates. Nair, et al. [43] researched the efficacy of gas hydrate dissociation methods, such as thermal stimulation, depressurizations, and a combination of the two, for energy recovery from hydrate-bearing clayey sediments beneath a free gas zone. For methane hydrate formation and decomposition investigations, pure water and two distinct mud samples containing 3 and 5 wt percent bentonite were used by the authors. The thermal stimulation investigation was performed at a rate of 7.5 K/h for $\Delta T = 15$ K, and the findings on methane recovery were noted. The results of the authors' study highlighted that the combination of thermal stimulation and depressurization techniques had the highest

dissociation efficiency. Thus, the highest production rate of methane gas was produced via the two methods combined together [43]. Roostaie and Leonenko [44] used thermal heating technique to dissociate methane hydrate. The results of the authors' study showed that thermal heating can be successfully applied in gas hydrate dissociation [44].

3.2. Depressurization

As energy scarcity grows, natural gas hydrate can be seen as a future energy resource with tremendous potential for exploitation, and it accounts for roughly twice the quantity of typical fossil fuel energy. Its utilization research and development has attracted unparalleled attention throughout the world. One of the primary means of hydrate production is depressurization, and its availability has been demonstrated in a number of field production tests from real hydrate reservoirs. Due to its practical implementation and economic advantages, depressurization is regarded as the most successful approach for hydrate extraction [45]. Recent attention has been focused on stepwise depressurization, due to its effectiveness in preventing ice formation and hydrate reformation during gas recovery [32].

The fundamental premise of hydrate exploitation is to disrupt the thermodynamic equilibrium state of hydrates, and the depressurization approach lowers the system pressure below the hydrate phase equilibrium condition by removing fluid from the system. In the depressurization process, the temperature of the reservoir eventually drops, due to the loss of gas and hydrate dissociation, which influences both the gas production and dissociation fronts. Researchers have found that the depressurization rate has a substantial effect on the gas generation of hydrate dissociation; however, the thermodynamic properties of the depressurization process at a constant rate have not been thoroughly investigated. Consequently, further research on hydrate depressurization methods is urgently required for the safe and efficient extraction of hydrates. Wang, et al. [46] studied the effect of changing the pressure, temperature, and hydrate saturation on the hydrate decomposition process using a stepwise depressurization technique. The results of the authors' study showed that depressurization techniques can effectively decompose hydrates [46]. Shao, et al. [47] investigated the dissociation process of a methane hydrate reservoir, via depressurization, to produce methane gas. Using TOUGH + HYDRATE v1.5, the physical model of a cylindrical reactor was created and numerically simulated by the authors. The dissociation behavior of methane hydrate was investigated by the authors at various experimental conditions, including pressure, temperature, and thermal conductivities, particularly those involving ice formation. The simulation findings revealed that as the wellhead pressures increased, the dissociation rate increased. Furthermore, the gas production rate reached its maximum level when the inhibition of ice formation and the driving force were balanced at an optimal pressure [47].

Being one of the most promising exotic fossil fuels, the production of natural gas hydrates (NGHs) in a safe and efficient manner has become a global research priority. Depressurization is considered one of the most effective methods for the dissociation of gas hydrates to produce natural gas. Yang, et al. [48] investigated the dissociation of methane hydrate using three depressurization modes, along with water flow erosion and in situ magnetic resonance imaging. The results of the authors' study demonstrated that the three modes of depressurization successfully eliminated ice formation during the methane hydrate production process. Furthermore, the results demonstrated that, as the water flow rate increased, the effect of depressurization on hydrate dissociation rate also increased. Consequently, depressurization is a promising technique in gas hydrate dissociation [49].

In the near future, marine methane hydrate will be a significant energy resource. Numerous studies are focusing on the decomposition of gas hydrates and the obstacles that the dissociation process faces. Yang, Zheng, Gao, Ma, Lv and Song [48] have used the depressurization method to examine the behavior of the methane hydrate production process in South China Sea sediments. The results of the authors' study showed that an increase by 8% in hydrate saturation could extend the dissociation time interval under

the same backpressure. This study highlights that the depressurization technique can be applied effectively for the dissociation of marine gas hydrates [48]. Zhang, et al. [50] used the depressurization technique to investigate the hydrate dissociation process to form methane in a cubic hydrate simulator (CHS). The study was conducted across the range of 16.0%–40.7% hydrate saturation. The process of hydrate dissociation consists of two phases: depressurization and constant pressure. The results of the authors' study showed that as the pressure increased, the dissociation rate increased, thus increasing the gas production rate [50].

3.3. Thermodynamic Inhibitors (THIs)

Thermodynamic hydrate inhibitors (THIs) are a type of chemical compound that can modify the thermodynamic conditions of hydration by transferring the zone of hydrate formation to a lower temperature and greater pressure. The purpose of a thermodynamic hydrate inhibitor is to reduce the formation of gas hydrates by disrupting the hydrogen bonds between water molecules [51]. This disturbance of hydrogen bonds, which are crucial for the development of hydrate structures, causes the hydrate–liquid–vapor equilibrium curve to move to a lower temperature and greater pressure. Thus, thermodynamic hydrate inhibitors cause a change in the thermodynamic parameters of hydrate formation under the particular operating conditions that encourage gas hydrate formation [36].

In the oil and gas industry, the most common types of THIs are methanol (MeOH), monoethylene glycols (MEG), and electrolytes. In addition, ionic liquids are also considered as very promising THI candidates that effectively dissociate gas hydrates. These THIs can create hydrogen bonds with water molecules to prevent the creation of cage-like structures. THIs are extremely volatile substances. To successfully dissociate a gas hydrate in a gas- or oil-dominated stream, a significant concentration of THIs is necessary [52].

3.3.1. Alcohols as THIs

Alcohols, including methanol, glycol, and diethylene glycol are commonly employed in the prevention of gas hydrate formation in the oil and gas industry [53]. Figure 5 below shows the three-dimensional structures of the primary alcohols applied as THIs (methanol, monoethylene glycol, and diethylene glycol). High alcohol concentration is required to thermodynamically inhibit a gas hydrate and to shift the hydrate thermodynamic equilibrium curve to a lower temperature and higher pressure region [53]. As an example, 10–20 percent methanol is often used in deep water operations to prevent hydrate development in the pipelines [54,55]. The rate of methanol injection depends on the water cuts and inhibitor dosage. In brief, the inhibitory injection rate is obtained by multiplying the methanol dosage by the water generation rate. It is worth mentioning that a rise in methanol concentration could drive up the cost of oil and gas production by $500 million per year [56]. Because methanol disposal can create serious environmental issues, ranging from corrosion to toxicity, strong federal regulations are now in action. In high concentrations, both methanol and mono-ethylene glycol (MEG) can suppress gas hydrate formation, with 0.7 to 1 barrel of methanol per barrel of water being usually advised for commercial use. Methanol provides better inhibition than MEG; nonetheless, large losses in both the liquid and gas phases of hydrocarbons raise concerns, due to their high volatility. Table 1 below shows a comparison between methanol and MEG based on hydrate inhibition performance.
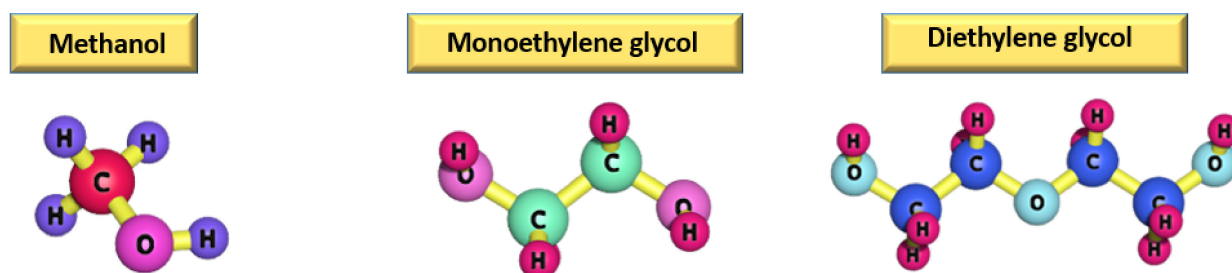
Figure 5. Three-dimensional structures of the main alcohols used as THIs (methanol, monoethylene glycol, and diethylene glycol).

Table 1. Comparison between methanol and MEG based on hydrate inhibition.

Hydrate Inhibitor	Pros		Cons	
Methanol	✓	Results in a greater decrease in temperature, at the same MEG weight%	✓	High loss
	✓	Low viscosity	✓	Low percentage recovery <80%
	✓	Less salt precipitate	✓	High contamination level
	✓	Low regeneration cost	✓	Low flash point
			✓	High fugitive discharge
			✓	Rigorous environmental protection regulations.
MEG	✓	High percentage recovery up to 99%	✓	High viscosity
	✓	Low gaseous and condensate solubility.	✓	High pumping costs
			✓	High salt precipitate

A lot of studies nowadays are focusing on the application of alcohols as THIs in the oil and gas industry. Lu, et al. [57] studied the molecular interaction during the thermodynamic inhibition of methanol and ethylene glycol with gas hydrates. The authors discovered that the hydrophobic groups from glycols were capable of approaching the hydrate cages to limit the spatial distribution of neighboring water molecules, and therefore act similarly to the guest molecules that spontaneously served to maintain the water framework. These glycols have the ability to raise the size of the critical nucleus, which is regarded to be the intrinsic mechanism of thermodynamic inhibition [57].

One of the oil and gas industry's top priorities nowadays is to find new, more powerful hydrate inhibitors. Dimethyl sulfoxide (DMSO) has shown to be an effective new thermodynamic hydrate inhibitor. Semenov, et al. [58] investigated the application of Dimethyl sulfoxide (DMSO) as a new thermodynamic hydrate inhibitor. The authors applied several physicochemical methods to characterize DMSO and its aqueous solutions. For a wide range of DMSO concentrations (0–55 mass percent), temperatures (242–289 K), and pressures (3–13 MPa), the methane hydrate phase equilibria in the system were determined. Over the whole concentration range, X-ray observations demonstrated that DMSO does not generate a double hydrate with methane. Furthermore, the authors discovered that DMSO was a more effective THI than monoethylene glycol and methanol at concentrations above 33 and 53 mass percent, respectively. In addition, a comparison of the kinematic viscosity and density of DMSO and methanol aqueous solutions was carried out by the authors. DMSO was discovered to be a potential hydrate inhibitor with low volatility and satisfactory aqueous viscosity properties [58]. For years, methanol has been employed in the industrial management of hydrate-forming, water-containing mixtures as an inhibitor. In nations where low-cost alcohols are readily available, ethanol can also be employed as a hydrate inhibitor. These alcohols contain surfactant capabilities that encourage hydrate formation, but when added to water in large enough concentrations, the hydrate inhibition properties will take precedence. Kvamme, et al. [59] studied the effect of the addition of alcohols, including methanol, ethanol, and glycols, on gas hydrates. The results of the

authors' investigation revealed that these alcohols can successfully inhibit the formation of gas hydrates in water-containing industrial mixtures [59].

Increasing the thermodynamic inhibitory effect of alcohols on hydrate formation has been the focus of a number of recent investigations. Semenov, et al. [60] studied the thermodynamic inhibitory effect of methanol and salts mixtures (NaCl, $CaCl_2$, KCl, and $MgCl_2$) on sII gas hydrates using a high-pressure cell. The investigations were carried out by the authors at a constant concentration of salts in 18 wt% aqueous solutions, where the pressure ranged from 1 to 4.7 MPa, and methanol mass fraction ranged from 0 to 50 wt%. The results of the authors' study revealed that the addition of salts to methanol caused a greater s shift in the thermodynamic curve of the sII gas hydrates. Furthermore, as the concentration of methanol increased, the sII gas hydrates curve shifted more notably. Thus, the addition of salts to methanol is a new potential technique for better thermodynamic inhibition of gas hydrates [60]. Mohammadi, et al. [61] studied hydrogen sulfide hydrate dissociation using the aqueous solutions of thermodynamic inhibitors (methanol, ethylene glycol, ethanol, NaCl, $CaCl_2$ and KCl). The results of the authors' study demonstrated that the addition of salts to the alcohol resulted in better thermodynamic inhibition of hydrogen sulfide hydrates [61].

3.3.2. Electrolytes as THIs

The use of electrolyte salts to prevent the formation of gas hydrates is based on the contact between the electrolyte molecules and the dipole of the water molecules, as well as solution ionization. The coulombic bond, which prevents the formation of hydrate, is responsible for this strong contact. The attraction between the water molecules and ions is more favorable than the attraction between the hydrate structures. Moreover, the presence of ions decreases the guest molecule's solubility in water. This phenomena is known as salting out. This delays the formation of hydrates by slowing down the structural change. Quaternary ammonium salts (QASs), such as tetraethylammonium iodide (TEAI), tetramethylammonium bromide (TMAB), and tetraethylammonium bromide (TEAB), are the most commonly applied electrolytes for use as THIs. Figures 6–8 below show the three-dimensional structures of TEAB, TMAB, and TEAI respectively. Numerous studies are based on the use of QASs as THIs. Qasim, et al. [62] studied the thermodynamic inhibitory effect of three distinct quaternary ammonium salts (QASs) on the growth of methane gas hydrates, namely, tetraethylammonium iodide (TEAI), tetramethylammonium bromide (TMAB), and tetraethylammonium bromide (TEAB). For TMAB and TEAB, the THI effect was also tested in the presence of monethylene glycol (MEG). The authors used the average suppression temperature to measure the inhibition capacity. The study was carried out by the authors at pressures ranging from 3.45 to 8.3 MPa, with concentrations of 1, 5, and 10 wt%. In comparison to TEAB and TEAI, TMAB had a greater influence on the hydrate growth when used alone or in combination with MEG. As a result, these salts can be effectively used as a thermodynamic hydrate inhibitors to ensure smoothly flowing gas streams in pipelines [62]. The application of electrolytes as a thermodynamic hydrate inhibitors is growing by time. Liu, et al. [63] investigated the effect of using electrolyte thermodynamic hydrate inhibitors, including NaCl and KCl, on the growth of hydrates. The results of the authors' study revealed that the use of NaCl and KCl thermodynamic hydrate inhibitors successfully slowed down the growth of the hydrates. In addition, during the hydrate growth phase, Cl^- were observed as a guest molecules in the hydrate cages more frequently than Na+ ions. Thus, electrolytes are potential thermodynamic hydrate inhibitors that can successfully delay the growth of hydrates [63].
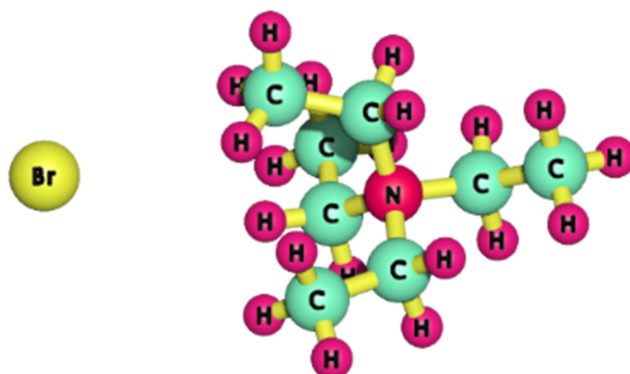
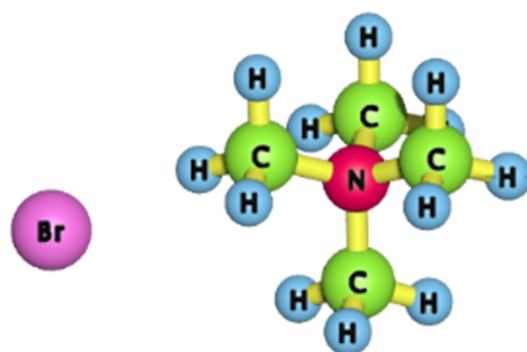**Figure 6.** Three-dimensional structure of tetraethylammonium bromide (TEAB).

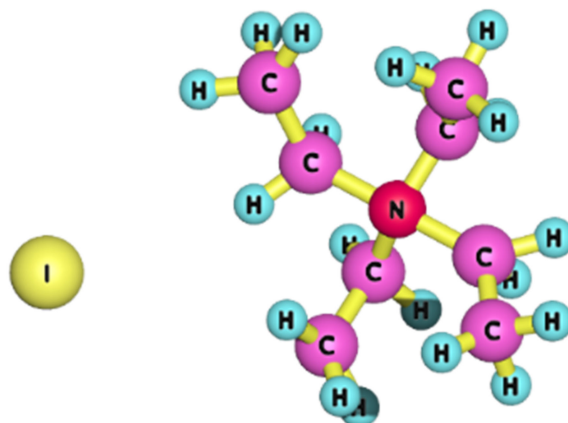**Figure 7.** Three-dimensional structure of tetramethylammonium bromide (TMAB).

Figure 8. Three-dimensional structure of tetraethylammonium iodide (TEAI).

Acknowledging the phase equilibrium of hydrogen sulfide (H_2S) hydrates is critical for sour gas production, storage, and transportation processes. Sun, et al. [64] investigated the hydrogen sulfide gas (H_2S) hydrate dissociation rate in several aqueous solutions including NaCl, $MgCl_2$, KCl, Na_2SO_4, NH_4Cl, and K_2SO_4, at various experimental conditions. The results of the authors' study showed that the inhibition impact of the salt electrolytes on the gas hydrate were in the following decreasing order $MgCl_2$ > NH_4Cl > NaCl > KCl > Na_2SO_4 > K_2SO_4. To anticipate the dissociation conditions of H_2S gas hydrate in electrolyte solutions, a thermodynamic model was created by the authors. This study revealed that electrolytes are very effective in inhibiting the formation of gas hydrates [64]. Deep investigations on gas production from marine sediments requires acknowledgment of the phase equilibria of hydrates. Li, et al. [65] studied the inhibitory effect of chloride salt solutions (NaCl, KCl, $CaCl_2$ and $MgCl_2$) on the development of methane hydrates at various temperatures and pressures. The results of the authors' study showed that

MgCl$_2$ had the greatest inhibitory effect on the development of methane hydrate. Thus, electrolytes can successfully act as a thermodynamic inhibitors for gas hydrates [65].

3.4. Low Dosage Hydrate Inhibitors (LDHIs)

In recent years, both the industry and academics have conducted substantial research on LDHIs. LDHIs are divided into two main forms: Kinetic hydrate inhibitors (KHIs) and anti-agglomerates (AAs).

3.4.1. Early History of KHIs

The first KHIs studies were conducted in the 1990s. Kelland, et al. [66] used an apparatus called the tetrahydrofuran (THF) to rapidly screen a new category of KHIs [66]. Polyvinylpyrrolidone (PVP, was the first potential KHI discovered [67]. The second generations of KHIs included Polyvinylcaprolactam (PVCAP), N-vinyl pyrrolidone/N-vinyl caprolactam (VP/VC), N-vinyl pyrrolidone/N-vinyl caprolactam/N, and N-dimethyl aminoethyl methacrylate, which share the same lactam-ring polymers group with PVP, while being more efficient [56]. The inhibitory effect of these polymers increases as the molecular weight of their lactam rings increases. More recently, acrylamide-based KHIs have been synthesized. Several more KHIs were developed over time and are now utilized as efficient hydrate inhibitors.
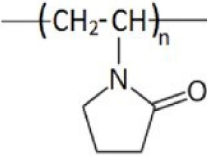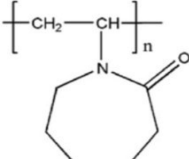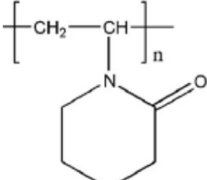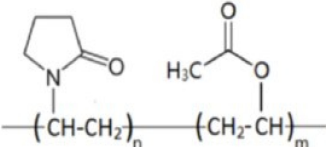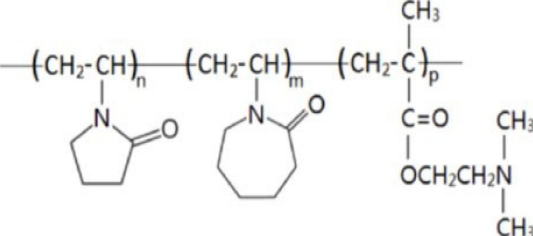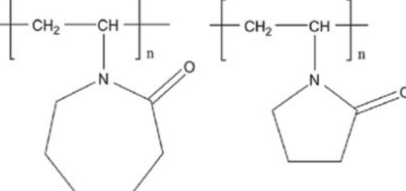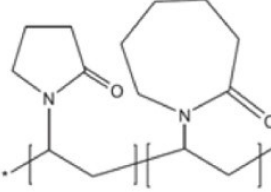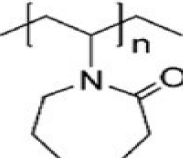
3.4.2. Kinetic Hydrate Inhibitors (KHIs)

Another often used hydrate inhibition approach is the use of low dosage hydrate inhibitors (LDHIs). Kinetic hydrate inhibitors (KHIs) are one of the LDHI categories that are characterized by having low molecular weight polymers that are dispersed in a solvent. In the gas-transporting pipelines, KHIs introduce an aqueous phase. As a result, KHIs do not prohibit hydrate formation or alter thermodynamics, but rather postpone them by decreasing the rate of hydrate formation [68]. A KHI concentration as low as 1% can successfully stop the growth of crystals or nucleation. Hence, the use of KHIs reduces the overall cost of the oil/gas production process, since low concentrations of KHIs are required to inhibit the hydrates. Fu, et al. [69] mentioned in their study that when compared to methanol, which is a traditional THI, KHIs can effectively decrease the overall cost of hydrate inhibition by up to 16 percent and as high as 50 percent. KHIs that are commonly used in the oil/gas industry are either copolymer derivatives or synthetic polymers. These KHIs are found in either liquid or solid form in nature, and are subsequently diluted to an appropriate concentration for usage. The molecular mechanism by which these KHIs function is not well understood.

I.   Polymeric compounds as KHIs

Polymeric compounds containing Poly-N-vinyllactam are classified based on the number of lactam rings contained within the polymer. For example, there is five-ring poly-vinyl-pyrolidone (PVP) [70], six-ring poly-vinyl-piperidone (PVP) [71], seven-ring poly-vinyl-caprolactam (PVCap) [72], and eight-ring poly-vinyl-azacycl-octanone (PVACO) [73]. In the oil/gas industry, the most commonly used KHIs are PVP and PVCap [74]. The lactam ring size, as well as the process parameters, have an impact on their hydrate inhibition activity [75]. Zhou, et al. [76] studied the inhibition performance of PVP-K90 and PVCap on methane hydrates at very low temperatures below the ice point. According to the study findings, the dissociation of methane hydrate at 268 K could be separated into 4 phases. Furthermore, a slight increase in PVP and PVCap concentrations from 0.5 to 2.0 wt% resulted in a dramatic increase in methane hydrate dissociation. The SEM images of the study showed that PVP-K90 was found embedded in the crystal hydrate surface structures, thus deforming the hydrate shape, whereas PVCap was found to stimulate the dendritic growth of methane hydrates, resulting in an increase in their specific surface area. Consequently, PVP and PVCap are both considered to be very promising kinetic hydrate inhibitors that can efficiently dissociate hydrates and inhibit their formation [76]. Table 2 below shows the most commonly utilized polymeric KHIs in the oil/gas industry.

Table 2. The most commonly applied polymeric KHIs in the oil/gas industry.

Polymer	Chemical Structure	Molecular Weight (Da)	Ref
PVP		5000–16,000	[77]
PVCap		20,000	[78]
PVPip		4000–85,000	[79]
PVP-VA73		38,000–40,000	[80]
VC-713		82,700	[81]
VCap/VP		1000–6,000,000	[82]
Inhibex 501		5000–8000	[83]
Luvicap EG		2000	[84]

II.   Poly(vinyl pyrrolidone) (PVP) as KHI

The first polymeric compound used as a KHI in the oil/gas industry is poly (vinyl pyrrolidone) (PVP). PVP is made up of five lactam rings, and is one of the most widely utilized KHIs, due to its inexpensive cost and widespread availability [85], Figure 9 below shows the three-dimensional structure of poly(vinyl pyrrolidone) (PVP). With molecular weights ranging from 10,000 to 350,000 g/mol, as shown in Table 2 below, this class of chemicals is water soluble. Poly (vinyl pyrrolidone) can endure temperatures up to 12 degrees Celsius, but if the temperature drops below 4 degrees Celsius, it loses its inhibitory function [86]. In addition, PVP serves as a benchmark against which the inhibition efficiency of other polymer KHIs is measured. Table 3 below shows several PVP types with distinct monomers that are efficiently applied as hydrate inhibitors.
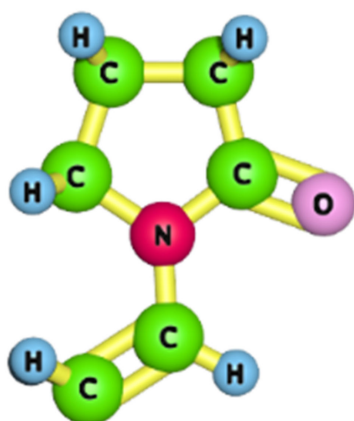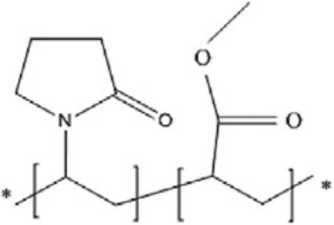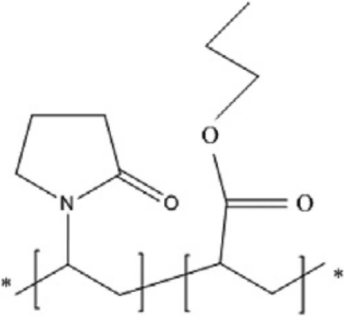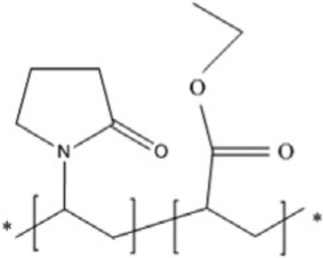

Figure 9. Three-dimensional structure of poly(vinyl pyrrolidone) (PVP).

Table 3. Molecular structures of several types of PVP with different monomers.

PVP Type	Monomer	Monomer	Molecular Structure	Reference
PVP	Vinylpyrrolidone			[87]
PVP-A	Vinylpyrrolidone	Butyl acrylate		[88]

Table 3. *Cont.*

PVP Type	Monomer	Monomer	Molecular Structure	Reference
PVP-ME	Vinylpyrrolidone	Methyl acrylate		[89]
PVP-PE	Vinylpyrrolidone	Propyl acrylate		[89]
PVP-EE	Vinylpyrrolidone	Ethyl acrylate		[89]

The PVP hydrate inhibition mechanism relies on the adsorption of the penta-lactam group at the hydrate surface, which causes hydrate structural deformation and efficiently limits further hydrate crystal formation. Furthermore, very small concentrations of PVP are required to efficiently inhibit hydrates. Aghajanloo, et al. [90] investigated the inhibition effect of varying concentrations (<2 wt%) of Poly N-vinyl pyrrolidone (PVP) and L-Tyrosine on the induction time of methane + hydrogen sulfide hydrate. The results of the study showed that, at low concentrations of Poly N-vinyl pyrrolidone (PVP) and L-Tyrosine, the induction time increased and a significant dissociation rate of the hydrate occurred. Thus, Poly N-vinyl pyrrolidone (PVP) and L-Tyrosine are promising KHIs that can effectively dissociate hydrates [90]. Zhao, et al. [91] studied the inhibition effect of PVP and NaCl on hydrates using molecular dynamics techniques. The authors' findings suggested that combining PVP with NaCl gave the optimum hydrate dissociation performance. The findings also demonstrated that NaCl stimulates methane molecule buildup, while PVP attracts methane molecules. This study proved that PVP is a very effective KHI that can successfully decompose hydrates [91]. Table 4 below demonstrates the inhibition effects of several PVP inhibitors on distinct types of hydrates, relying on several studies.

Table 4. The inhibition effect of several PVP inhibitors on distinct types of hydrates.

Hydrate Inhibitor	Hydrate Type	Function	Inhibition Effect	Reference
PVP	Methane–propane hydrate	KHI	The methane–propane hydrate was successfully inhibited by increasing the induction time of the hydrate formation.	[92]
PVP ramification (PVP-BP)	Methane hydrate	KHI	Hindered the formation of methane gas hydrate.	[93]
PVP	Methane hydrate	KHI	The hydrate was successfully inhibited.	[94]
PVP	Methane hydrate	KHI	The formation of methane hydrate was prohibited successfully.	[95]
PVP-K90	Methane hydrate	KHI	The hydrate nucleation time was prolonged. Thus, the methane hydrate growth was hindered.	[96]
PVP	Structure II (SII) gas hydrate	KHI	Prolonged the development of gas hydrate crystals	[79]
PVP	Tetrahydrofuran (THF) clathrate hydrate	KHI	The formation of tetrahydrofuran (THF) was prohibited successfully	[97]
PVP	Natural gas hydrate	KHI	Prolonged the development of natural gas hydrate	[98]
PVP	Structure II methane–propane hydrate	KHI	Prevented the methane–propane hydrate growth	[99]
PVP	Natural gas hydrate	KHI	Successfully inhibited the formation of hydrate	[100]

III.   Poly (vinyl caprolactam) (PVCap) as a KHI.

The second generation of KHIs consists of the Poly (vinyl caprolactam) (PVCap) polymeric compounds. Various research show that the negative charge of the carbonyl group makes it an effective hydrogen bond acceptor [101] which inhibits crystal formation by adsorbing on the surface of hydrate crystals [102]. PVCap has an ideal concentration value for inhibitory efficiency, and its effectiveness deteriorates when employed at lower or higher concentrations. Lederhos, Long, Sum, Christiansen and Sloan [56] mentioned that the best inhibitory efficiency of PVCap was obtained at a 0.5 wt % PVCap concentration. PVCap's performance as a KHI is mostly determined by its molecular weight. The lower the molecular weight of the PVCap, the greater the brine capability, the higher the cloud point, and the faster the polymer re-dissolution time at room temperature. Greater molecular weight, on the other hand, has a lower cloud point and precipitates [101]. PVCap hydrate inhibition efficiency for sII hydrate is substantially better than for sI hydrate at the same concentration [72]. When comparing the performance of PVP and PVCap, it is evident that PVCap is a superior KHI for successfully dissociating hydrates. Sharifi, et al. [103] used a high-pressure cell, along with a rotational rheometer, to study the performance of PVP and PVCap as KHIs in the presence of NaCl and n-heptane. The hydrate inhibition performance of the PVP and PVCap were compared by the authors based on several parameters. The overall result showed that the use of both PVP and PVCap as KHIs increased the hydrate induction time and delayed the hydrate formation. However, the hydrate agglomeration process was rapid. PVP was more successful than PVCap at prolonging the hydrate nucleation time, but PVCap was more effective at controlling growth and postponing hydrate agglomeration. These results confirmed that both PVP and PVCap are promising KHIs that can effectively inhibit hydrate growth [103].

Numerous research are focusing on the use of PVCap as a KHI. Wan, et al. [104] synthesized a hydroxy-terminated poly(N-vinylcaprolactam) (PVCap-OH) with a very small molecular weight to inhibit methane gas hydrates. The authors used microscopy (cryo-SEM) to investigate the hydrate structure after the addition of KHI. According to the authors' findings, PVCap-OH had a better KHI functionality than PVCap under the

same conditions, with a longer hydrate induction time, as well as a lower hydrate formation rate. Based on the results, both PVCap and PVCap-OH were superior KHIs that can effectively inhibit hydrates [104]. Liu, et al. [105] used first-principle calculations and simulations to study the hydrate inhibition mechanism and performance of four common KHIs: poly(N-vinyl pyrrolidone) (PVP), poly(N-vinyl piperidone) (PVPip), poly(N-vinyl caprolactam) (PVCap), and poly(N-vinyl azacyclooctanone) (PVAco). According to the authors' observations, the KHI inhibition efficacy improved as the lactam ring size increased, i.e., PVP < PVPip < PVCap < PVAco. In addition, all the KHIs used could efficiently inhibit the growth of hydrates [105]. Table 5 below shows the inhibition effect of several PVCap inhibitors on distinct types of hydrates, based on several studies.

Table 5. Summary of PVCap hydrate inhibitors used in several studies.

Inhibitor Type	Hydrate Type	Function	Inhibition Effect	Reference
PVCap	Methane hydrate	KHI	Increased the dissociation rate of methane hydrate.	[78]
PVCap	Cyclopentane Hydrate	KHI	Hydrate film growth was significantly slowed, requiring over 2 h for complete conversion.	[106]
PVCap	Methane hydrate	KHI	Sped up the methane hydrate dissociation	[107]
PVCap	Methane hydrate	KHI	Increased the methane hydrate dissociation temperature.	[108]
PVCap	Methane hydrate	KHI	Increased dissociation temperature	[109]
PVCap	Methane hydrate	KHI	Increased the induction time of methane hydrate formation by approximately 1400 min.	[110]
PVCap	Natural gas hydrate	KHI	Hindered the formation of the hydrate	[111]
PVCap	Methane hydrate	KHI	Suppressed the methane hydrate formation by hindering the nucleation of methane hydrate crystals	[112]
PVCap	Methane hydrate	KHI	Hindered the formation of methane gas hydrate.	[100]
PVCap	Natural gas hydrate	KHI	Stopped the formation of the gas hydrate	[113]
PVCap	Tetrahydrofuran hydrate	KHI	Inhibited the formation of tetrahydrofuran hydrate.	[114]
PVCap	Tetrahydrofuran hydrate	KHI	Inhibited the formation of THF hydrate by delaying the nucleation process of the hydrate.	[115]
PVCap	Natural gas hydrate	KHI	Hindered the formation of gas hydrate by delaying the onset time of the hydrate significantly.	[116]
PVCap	Tetrahydrofuran hydrate	KHI	Inhibited the formation of THF hydrate.	[117]
PVCap	Natural gas hydrate	KHI	Successfully inhibited the natural gas hydrate formation, by delaying the hydrate onset time.	[118]
PVCap	Tetrahydrofuran hydrate	KHI	Inhibited the formation of THF hydrate.	[119]
PVCap	Methane hydrate	KHI	Hindered the formation of methane gas hydrate.	[120]
PVCap	Natural gas hydrate	KHI	Successfully inhibited the development of natural gas hydrate.	[121]
PVCap	Methane hydrate	KHI	Hindered the formation of methane gas hydrate.	[122]

IV.　Vinyl pyrrolidone/vinyl caprolactam copolymer as a KHI

Polymers containing amide groups are widely used in a number of commercial KHIs, with poly(N-vinylcaprolactam) P(Vcap) and similar copolymers being the most frequently used. Vinyl pyrrolidone/vinyl caprolactam copolymer are efficient KHIs that can successfully inhibit hydrates, depending on the VP/VCap ratio. At a VP/VCap ratio lower than 0.333 [56], the functionality of this copolymer becomes similar to PVCap. A lot of studies have been conducted that used this copolymer as a KHI. Imran, et al. [123] studied the inhibition capability of *N*-vinylcaprolactam (Vcap) copolymers having *N*-acryloyl

type comonomers on structure I-type gas hydrates under sour environments. The authors effectively copolymerized Vcap with N-acryloylmorpholine, N-acryloylpyrrolidine, N-Isopropylacrylamide, and N-acryloylpiperidine to produce a range of low molecular weight copolymers. The inhibitory effect of all copolymers as KHIs on structure I-type gas hydrates was assessed by the authors, via high-pressure rocking cells at a pressure range of 130 to 140 bar. The results of the authors' study showed that the performances of all the synthesized copolymers as KHIs were superior to the performance of the P(Vcap) homopolymer with the same molecular weight. In addition, when the ratio of acryloyl monomer to Vcap was increased, the KHI performance of the copolymers improved tremendously. The results of this study proved that the VP/VCap copolymers are efficient KHIs that can be successfully used in inhibiting hydrates [123]. The copolymers of Poly(N-vinylcaprolactam) PVCap are commonly employed as kinetic hydrate inhibitors in the oil/gas industry. Yang, et al. [124] synthesized copolymers of (PVCap-b-PCL) that contained a range of biodegradable poly(ε-caprolactone) (PCL) ratios. The authors' findings revealed that the copolymers utilized as KHIs outperformed the PVCap in terms of methane hydrate inhibition, and had significantly longer induction times [124].

V.   Poly (N-vinyl piperidone) as a KHI

The use of N-vinyl piperidone (PVPip) polymers as kinetic hydrate inhibitors is rarely investigated, due to their commercial lack of availability. Figure 10 below shows the structure of a PVPip. There is only one study about Poly (N-vinyl piperidone) as a KHI. O'Reilly, et al. [125] investigated the performance of N-vinyl piperidone (PVPip) in inhibiting the formation of tetrahydrofuran sII hydrate crystals. According to the authors, the results showed that N-vinyl piperidone (PVPip) had successfully inhibited the growth of tetrahydrofuran sII hydrate crystals [125].
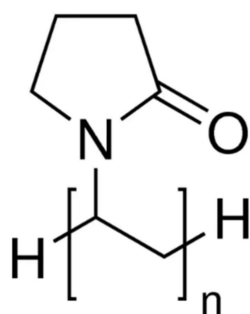

Figure 10. Two-dimensional structure of N-vinyl piperidone (PVPip).

VI.   VP/VCap/dimethylaminoethyl methacrylate terpolymer as a KHI

Another type of kinetic hydrate inhibitor are terpolymers. This polymer is referred to as a terpolymer because it is made up of three distinct monomers. Five and seven lactam rings, as well as a pentane group, make up the terpolymer of VP, VCap, and dimethylaminoethyl methacrylate. VP/VCap/dimethylaminoethyl methacrylate terpolymers are referred to as Gaffix® VC-713, with compositions of 17–32 wt% for VP, 65–80 wt% for VCap, and 3–6 wt% for dimethylaminoethyl methacrylate [126]. VC-713 is a promising hydrate inhibitor that can prevent the growth of the hydrate by increasing the induction time by up to 1200 min at moderate pressure conditions. However, at pressures above 10.3 MPa, the inhibitory efficiency of VC-713 deteriorates [56]. In contrast, the concentration has an inversely proportional relationship with the inhibitory effectiveness of VC-713. This means that, as the concentration of VC-713 decreases, the inhibitory efficiency of VC-713 increases.

3.4.3. Anti-Agglomerates (AAs)

Anti-agglomerates (AAs), unlike thermodynamic and kinetic hydrate inhibitors, are surface active compounds that do not hinder the formation of hydrate crystals. Rather, they divide the hydrates into precisely separated fine particulate matter to keep the fluid

viscosity low and allow the hydrates to be carried safely in the slurry state [127]. Anti-agglomerates (AAs) adsorb on the surface of a hydrate, which instantly converts all existing water into hydrate [27]. AAs work by allowing the chemical's head group to connect to the hydrate, while the prolonged hydrocarbon tail keeps the hydrate particle distributed in the fluid phase [128]. In extreme situations, such as very high pressure under water, AAs outperform KHIs as a hydrate inhibitor, and are more cost effective [129]. Quaternary ammonium salts (QAS) and surfactants are the mostly used anti-agglomerates in the oil/gas industry. These AAs are composed of long-chain compounds with hydrophilic and hydrophobic ends. In a gas/oil pipeline, a dipole–dipole interaction is formed between the hydrophilic head of the AA and the hydrogen ion of the water molecule, while the hydrophobic end gets dissolved in the oil or gas phase.

A potential mechanism for lowering the risk of gas hydrate clogging in oil/gas operations is the inclusion of anti-agglomerates (AAs). In reality, it is unclear whether AAs trigger or hinder hydrate nucleation and development. The use of AAs as hydrate inhibitors in oil and gas operations is the subject of numerous studies nowadays. Ning, et al. [130] investigated the inhibition effect of several AAs, including dodecyl benzene sulfonic acid, tetramethyl ammonium bromide, 1-naphthylacetic acid, Span80, rhamnolipid, and co-camidopropyl dimethylamine, at various concentrations on methane hydrate formation kinetics. According to the authors' various water cut systems, different AA concentrations were pressurized with CH_4 at a temperature of 3.0 °C and a pressure of 6.0 MPa. The authors' findings demonstrated that AAs could induce hydrate growth in systems with 100% pure water and 95% water cuts. On the other hand, in systems with low water cuts, such as 20% and 60%, AAs have the capability of delaying or even entirely prohibiting the hydrate nucleation and development. Thus, AAs are very promising candidates in the inhibition of hydrates [130]. Song, et al. [131] utilized a high-pressure cell to conduct a number of hydrate formation investigations from natural gas + diesel oil + water systems at various water cuts and anti-agglomerate concentrations in order to examine the properties of hydrate formation in oil–water systems. According to the authors' study results, the anti-agglomerates successfully inhibited the hydrate growth by increasing the induction formation time of the hydrates at the various concentration ranges of AAs [131].

In practice, gas hydrates are easily generated. They have a tendency to aggregate during the generation of marine natural gas hydrates, deposit on the pipe walls, and finally block the pipe. Zhao, et al. [132] investigated the effect of using anti-agglomerates on hydrate formation in an anti-oil-free gas–water system. The results of the authors' study indicated that anti-agglomerates can effectively inhibit hydrate formation [132]. Chen, et al. [133] investigated the inhibitory effect of the anti-agglomerates sorbitan mono-laurate (Span 20), rhamnolipid, and (Span 20 + esters polymer) at various water cut and anti-agglomerate concentrations on hydrate formation. Water cut percentages varied from 5 vol% to 30 vol%, and anti-agglomerate concentrations varied from 0.5% to 3.0%. According to the authors' study results, all the anti-agglomerates used at different concentration ranges aided in inhibiting the formation of hydrates. Thus, anti-agglomerates are promising candidates that can successfully inhibit hydrate formation [133]. Sa, et al. [134] studied the inhibitory impact of AAs on gas hydrate and ice formation under the flow of water and oil. The authors noticed that, without the addition of AAs, solid hydrates formed a layer on the pipe's bottom, thus decreasing the overall flow efficiency. After the addition of AAs, the solid hydrates were distributed into flowing slurries, thus ensuring an efficient fluid flow. Although the AAs did not prevent the ice chunks from forming, they ensured that the ice chunks are dispersed so that the fluid flowed freely without interruption. Thus, AAs are promising hydrate inhibitors [134]. Table 6 below shows a summary of several anti-agglomerates used as hydrate inhibitors in oil/gas industry, based on several studies.

Table 6. Summary of several anti-agglomerates used as hydrate inhibitors in oil/gas industry.

Inhibitor Type	Hydrate Type	Function	Inhibition Effect	References
Quaternary ammonium salt	Cyclopentane hydrates	AAs	Decreased the hydrate slurry.	[135]
Fluorinated Quaternary Ammonium Bromides	Tetrahydrofuran hydrate	AAs	Successfully reduced tetrahydrofuran hydrate slurry.	[114]
Quaternary ammonium salt	Methane–propane sII hydrate	AAs	Decreased the slurry of methane–propane sII hydrate.	[136]
Quaternary ammonium surfactants	Natural gas sII hydrate	AAs	Inhibited the hydrate successfully.	[137]
Quaternary ammonium salts	Natural gas hydrate	AAs	Decreased the hydrate slurry and inter-particle interactions.	[138]

3.5. Dual Function Gas Hydrate Inhibitors

3.5.1. Ionic Liquids

Ionic liquids are promising materials that are used extensively as dual-function inhibitors for hydrate formation. The performance of this class of materials as hydrate inhibitors was first reported by Xiao and Adidharma [55]. The authors investigated the inhibitory effect of five imidazolium-based ionic liquids on hydrate formation. The authors have also studied the impact of ionic liquids on the hydrate equilibrium curve and the hydrate formation induction time. According to the study's findings, these ionic liquids can act as both thermodynamic and kinetic inhibitors by shifting the equilibrium hydrate curve to a lower temperature, and by increasing the induction time by which hydrates form. The dual functionalities of the ionic liquids are based on their strong electrostatic charges and hydrogen bonds that they form with water. Thus, ionic liquids' dual functionality makes them a superior hydrate inhibitor that outperforms all other inhibitors [55]. Several studies have focused on the use of ionic liquids as dual-function hydrate inhibitors. Table 7 below shows a summary of ionic liquids used as dual-function hydrate inhibitors in the oil/gas industry.

Table 7. Summary of ionic liquids used as a dual function hydrate inhibitors in oil/gas industry.

Ionic Liquid	Hydrate Type	Function	Concentration	References
$[C_4C_1im][BF_4]$ $[C_4C_1im][BF_4]$ $[C_2C_1im][N(CN)_2]$ $[C_2C_1][CF_3SO_3]$ $[C_2C_1im][C_2SO_4]$	CH_4	KHI/THI	0.1–10 10 10 10 10	[55]
$[C_4C_1im][BF_4]$ $[C_4C_1im][C_1SO_4]$ $[OHC_2C_1Pyrr]Cl$ $[OHC_2C_1Pyrr][BF_4]$ $[C_4C_1Pyrr]Br$ $[C_4C_1Pyrr][BF_4]$ $[2\text{-}(OHC_2)C_1Mor]Br$ $[2\text{-}(OHC_2)C_1Mor][BF_4]$	CH_4	THI/KHI	0.6–7 wt% & 0.1–10 wt%	[139]
$[C_2C_1im]Cl$ $[C_4C_1im]Cl$ $[C_2C_1im]Br$ $[C_4C_1im]Br$ $[C_3C_1im]I$ $[C_4C_1im]I$	CH_4	KHI/THI	10	[140]

Table 7. *Cont.*

Ionic Liquid	Hydrate Type	Function	Concentration	References
$[C_4C_1im][BF_4]$	CO_2	KHI/THI	0.0008–0.1 mol%	[141]
$[2-(OHC_2)C_1Mor][BF_4]$ $[C_2C_1im][NO_3]$ $[C_2C_1im][BF_4]$ $[C_2C_1im]\,[CF_3SO_3]$	CO_2	THI/KHI	0.10–1.04 mol%	[142]
TMACl TEAOH TPrAOH	CO_2	THI	1 wt% 5 wt% 10 wt%	[143–145]
$[C_2C_1im][BF_4]$ $[2-(OHC_2)C_1Pyrr][BF_4]$ $[C_4C_1Pyrr][BF_4]$	CH_4	THI/KHI	0.1–10 wt%	[146,147]
$[BMIM][BF_4]$ $BMIM][MeSO_4]$ $[BMIM][HSO_4]$	CH_4	THI/KHI	0.6 wt%	[148]
$[BMIM][Cl]$, $[BMIM][Br]$	CH_4	THI/KHI	1 wt%, 5 wt%, 10 wt%, 15 wt%	[149]
$[2,3-(OHC_3)_2C_1im][f_2N]$ $[2-(OHC_2)C_1im][f_2N]$ $[C_2C_1im][BF_4]$ $[C_4C_1im]\,[BF_4]$ $[C_4C_1im][OAc]$ $[C_2C_1im][C_2SO_4]$	CH_4	THI/KHI	0.5–1.0 wt%	[150]
$[BMIM][BF_4]$, $[BMIM][I]$	CH_4	THI/KHI	3 mol%	[151]
TEAOH, TPrAOH, TBAOH	CO_2/CH_4	THI/KHI	40 wt%	[152]
TMAOH,	CO_2/CH_4	THI/KHI	25 wt%	[152]

I. Ionic liquids as THIs

Ionic liquids are frequently employed nowadays as THIs to inhibit the formation of hydrates. Hydrogen bonding has a significant impact on the thermodynamic nature of inhibitors. Hydrogen bonds can easily develop between water molecules and ionic liquids. Therefore, when ionic liquids come into contact with hydrates, the water molecules in the hydrates create hydrogen bonds with the ionic liquid, resulting in the deformation of the hydrate. External variables, such as ion type and concentration, have an impact on the thermodynamic behavior of ionic liquids. These factors have a significant impact on slowing the nucleation process and lowering the temperature at which hydrates form.

Various studies have focused on the thermodynamic hydrate inhibition capacities of ionic liquid. Nevertheless, due to the high concentrations of cations and anions, experimental studies alone have been inadequate to analyze all possible ionic liquid combinations. Thus, Khan, et al. [153] predicted the ILs' thermodynamic inhibitory abilities by relying on their primary characteristics, particularly their hydrogen bonding energy. The authors have simulated and researched the fundamental properties of the IL-hydrate system using the software Conductor-Like Screening Model for Real Solvent (COSMO-RS). The results of the authors' studies revealed that ILs can successfully act as thermodynamic hydrate inhibitors [153]. Sulaimon and Tajuddin [154] used the software Conductor-Like Screening Model for Real Solvents (COSMO-RS) to investigate the thermodynamic inhibitory effect of [EMIM][Cl][HSO$_4$], [OH-EMIM] [Cl] and [OH-EMIM][HSO$_4$] ionic liquids on hydrates. The results of the authors' study demonstrated that the hydrogen bonding energy (E$_{HB}$) was identified as the primary energy that influenced the ability of ionic liquids to inhibit hydrates. The results also demonstrated that, whilst increasing cation E$_{HB}$ lowered inhibitory ability, increasing anion E$_{HB}$ enhanced it. In addition, a high hydrogen bonding energy resulted from combining chloride [Cl$^-$] and hydrogen sulphate [HSO$_4$].Thus, this

study proves the efficacy of ILs as hydrate inhibitors [154]. Menezes, Pessôa Filho and Robustillo Fuentes [149] investigated the inhibitory effect of the ionic liquids 1-Butyl-3-methylimidazolium chloride ([BMIM][Cl]) and 1-Butyl-3-methylimidazolium bromide ([BMIM][Br]) on methane hydrates at high pressures, ranging from 9.6 to 100 MPa, and several mole fractions (1.0%, 5.0%, 10.0%, and 15.0%). The authors' study findings demonstrated that these ionic liquids behaved like KHIs and THIs, but they also stimulated hydrate formation at mole fractions of 1% and 5% in the pressure range investigated. The authors also compared the hydrate inhibitory performance of these ionic liquids with and without methanol. The findings reveal that, at equimolar solutions, [BMIM][Cl] was more effective than [BMIM][Br] at inhibiting methane hydrates. Thus, ionic liquids are very promising hydrate inhibitors that can be used efficiently in the oil/gas industry [149]. Nashed, et al. [155] investigated the thermodynamic inhibition performance of four distinct ionic liquids—1-methyl-3-octylimidazolium chloride [MOIM-Cl], 1-methylimidazolium hydrogen sulfate [H-MIM-HSO$_4$], tetraethylammonium iodide [TEA-I], and 1-hexyl-3-methylimidazolium iodide [HMIM-I]—on the development of methane hydrates. The results indicated that, of the four ionic liquids investigated in this study, 1-methylimidazolium hydrogen sulfate [H-MIM-HSO$_4$] had the greatest methane hydrate inhibitory performance [155]. Zare, et al. [156] studied the inhibition of methane hydrate using imidazolium-based aqueous ionic liquid solutions, including 1-buthyl-3-methylimidazolium methyl sulfate ([BMIM][MeSO$_4$]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO$_4$]), 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO$_4$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]), and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([OH-EMIM][BF$_4$]), at a temperature range of 281.9–287.4 K and a pressure range of 7.08–12.16 MPa. The results of the authors' study showed that the studied ionic liquids acted as THIs to cause the hydrate equilibrium dissociation curve to shift to a higher pressure and lower temperature region. Furthermore, the THI with the highest inhibition performance was [OH-EMIM][BF$_4$], and, among ionic liquids containing alkylsulfates, [EMIM][HSO$_4$] and [BMIM][MeSO$_4$] had greater thermodynamic inhibition effects than [EMIM][EtSO$_4$]. Consequently, ionic liquids are superb materials that can be applied effectively as THIs [156]. Bavoh, et al. [157] have extensively studied the use of ionic liquids as THIs in the oil/gas industry. The results of the authors study revealed that ionic liquids are very promising candidates that can be used as thermodynamic hydrate inhibitors in the oil/gas industry. In addition, the authors mentioned that ionic liquids are going through continuous growing experimental study and development over time [157]. Table 8 below shows a summary of ionic liquids used as thermodynamic hydrate inhibitors in the oil/gas industry.

Table 8. Summary of ionic liquids used as THIs in oil/gas industry.

Ionic Liquid	Hydrate Type	Function	Concentration	References
TMACl TEAOH TPrAOH	CO$_2$	THI	1 wt% 5 wt% 10 wt%	[143–145]
[C$_4$C$_1$im]Cl [C$_6$C$_1$im]Cl [C$_8$C$_1$im]Cl [C$_4$C$_1$im][BF$_4$] [C$_6$C$_1$im][BF$_4$] [C$_4$C$_1$im][TFA] [C$_4$C$_1$im][PF$_6$]	CO$_2$	THI	-	[158]
[C$_1$C$_1$im]I [C$_2$C$_1$im]I [OHC$_2$C$_1$im]Cl [N$_{1111}$]Cl [N$_{111}$C$_2$OH]Cl	CH$_4$	THI	0.1 MF	[159]

Table 8. *Cont.*

Ionic Liquid	Hydrate Type	Function	Concentration	References
$[C_4C_1im][C_1SO_4]$ $[C_2C_1im][HSO_4]$ $[C_2C_1im][C_2SO_4]$ $[C_4C_1im][BF_4]$ $[2\text{-}(OHC_2)C_1im][BF_4]$	CH_4	THI	10 wt% 10 wt% 8–10 wt% 10 wt% 10–20 wt%	[156]
$[P4441][C_1SO_4]$	CH_4, CO_2	THI	0.2611–0.5007 MF	[160]
$[C_2C_1im]Cl$ $[C_2C_1im]Br$ $[C_2C_1im]Br + [C_2C_1im]Cl$ (1:1) $[C_2C_1im]Cl + MEG$ (1:1 $[C_2C_1im]Cl + NaCl$ (1:1)	CH_4	THI	5–40 wt% 20 wt% 20 wt% 10–30 wt% 10 wt%	[161]
$[C_2C_1im]Cl$ $[(OHC_2)C_1im]Cl$	CH_4	THI	wt%	[162]
$[C_4C_1im][BF_4]$ $[C_4C_1im][N(CN)_2]$ $[N_{2222}]Cl$	CH_4	THI	0.10–0.20 MF 0.1 MF 0.1 MF	[163]
[OH-EMIM][Cl] [OH-EMIM][Br] [BMIM][Br] [BMIM][Cl] [BMIM][ClO$_4$] [BMIM][N(CN)$_2$] [BMIM][HSO$_4$] [BMIM][CF$_3$SO$_3$] [BMIM] [CH$_3$SO$_4$]	CH_4	THI	0.1 MF	[164]
TMAOH	CH_4/CO_2	THI	10 wt%	[165]
[EA][Of], [DMEA][Of], [DMA][Of]	CH_4	THI	5 wt%, 10 wt%	[166]
[BMIM][Cl] [OMIM][Cl] [BMIM][Br] [HMIM][Br] [BMIM][HSO$_4$] [ET$_2$NH$_2$][HSO$_4$] [Pr$_3$NH][HSO$_4$] [Bu$_3$NH][HSO$_4$]	CH_4	THI	0.01 MF	[167]
TMAOH	CO_2 (70%) + CH_4 (30%)	THI	25 wt%	[168]
TEAOH, TPrAOH, TBAOH	CO_2 (70%) + CH_4 (30%)	THI	40 wt%	[168]
TEACl + BMIM-BF$_4$	CH_4	THI	4.55 + 4.85 wt%	[169]

II.   Ionic liquids as KHIs

The usage of kinetic hydrate inhibitors in oil/gas operations is increasing over time, and the enhancement of their hydrate inhibition performance is a critical concern. All KHIs reported so far are polymers that can dissolve in water. However, some non-polymeric organic compounds can improve their performance. Several studies have focused on the application of imidazolium-based ionic liquids as kinetic hydrate inhibitors with higher performance, compared to the basic commercial KHIs. Del Villano and Kelland [170] investigated the ionic liquids' kinetic hydrate inhibitory effects, and their effectiveness was compared with that of commercial KHIs. The results of the authors' study revealed that the performance of ionic liquids as KHIs was better than the performance of commercial KHIs based on vinyl lactam polymers and hyperbranched poly(ester amide)s [170].

Lee, et al. [171] studied the kinetic inhibitory effects of several ionic liquids on CH_4 hydrate, with/without polymeric hydrate inhibitor (PVCap). The findings of the authors' investigation showed that ILs had a better CH_4 hydrate inhibition performance compared to PVCap. Additionally, a mixture of ILs and PVCap showed improved kinetic inhibitory effects for the development of CH_4 hydrates [171]. Therefore, the application of ionic liquids enhanced the overall KHI performance. Altamash, Khraisheh, Qureshi, Saad, Aparicio and Atilhan [166] studied the kinetic inhibitory effects of the alkylammonium-based protic ionic liquids (PIL) ethylammonium formate ([EA][Of]), dimethylammonium formate ([DMA][Of]), and dimethylethylammonium formate ([DMEA][Of]) on methane gas hydrates. The results of the authors' study demonstrated that the investigated ionic liquids were successfully capable of kinetically inhibiting the methane gas hydrate [166]. Xiao, Wibisono and Adidharma [140] studied the application of six dialkylimidazolium halide ionic liquids as novel kinetic gas hydrate inhibitors. The results of the authors' study demonstrated that the six dialkylimidazolium halide ionic liquids increased the induction time of the gas hydrates, thus slowing down the gas hydrate rate of formation. Therefore, ionic liquids can be used successfully as KHIs [140].

Table 9 below shows a summary of ionic liquids used as kinetic hydrate inhibitors in the oil/gas industry.

Table 9. Summary of ionic liquids used as KHIs in oil/gas industry.

Ionic Liquid	Hydrate Type	Function	Concentration	References
$[C_2C_1im][BF_4]$ $[C_4C_1im][BF_4]$	SNG	KHI	5000–10,000 ppm 10,000 ppm	[170]
$[C_4C_1im][PF_6]$	CH_4	KHI	0–1000 ppm	[172]
$[BMIM][BF_4]$	CH_4	KHI	1 wt%, 10 wt%, 15 wt%, 20 wt%	[173]
BMIM-DCA, TEACL	CH_4	KHI	10 wt%	[173]
EMIM-BF_4 EMP-BF_4 EMP-Br EMP-Cl BMP-BF_4 BMP-Br BMP-ClHEMP-BF_4 HEMP-Cl	CH_4	KHI	0.5 wt%, 1.0 wt%, 2.0 wt%, 3.0 wt%	[171,174]
[OH-EMIM][Br], [BMIM][Br] [OH-EMIM][Cl] [BMIM][Cl], $[BMIM][CF_3SO_3]$ $[BMIM][CiO_4]$ $[BMIM][N(CN)_2]$, $[BMIM][HSO_4]$	CH_4	KHI	0.97 MF 0.09 MF 0.95 MF 0.93 MF 0.94 MF	[154]
$[BMIM][BF_4]$ [BMIM][DCA] TEACl	CH_4	KHI	1–20 wt%	[175]

3.5.2. Amino Acids

The negative impact of chemical inhibitors on the environment urges the use of green and environmentally friendly hydrate inhibitors in the oil and gas industries. Amino acids are superb green hydrate inhibitors that can be used effectively instead of the commercial chemical inhibitors. Numerous studies have focused on the use of amino acids in oil/gas operations as hydrate inhibitors. Table 10 below shows a summary of the most widely used amino acids in the oil/gas industry.

Table 10. Summary of the most widely used amino acids as hydrate inhibitors in the oil/gas industry.
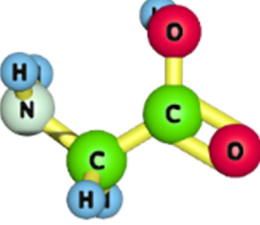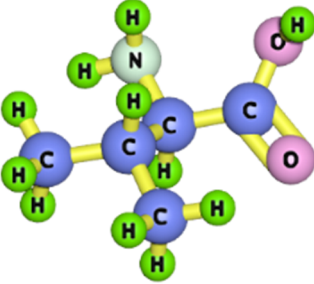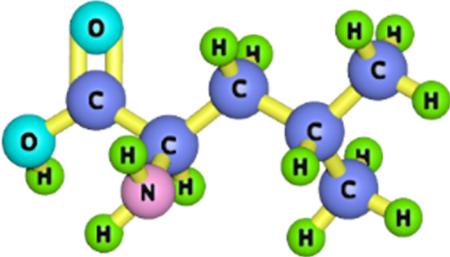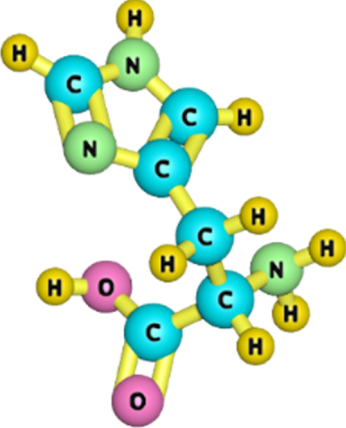
Amino Acid	Structure	Weight (g/mol)	References
Alanine		89.09	[176]
Glycine		75.07	[177]
Valine		117.151	[178,179]
Leucine		131.17	[180]
Histidine		155.1546	[181]

Table 10. *Cont.*
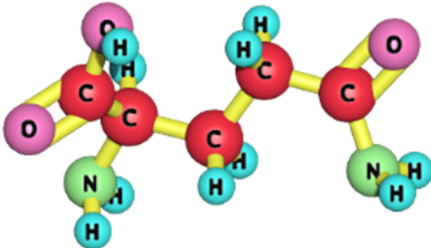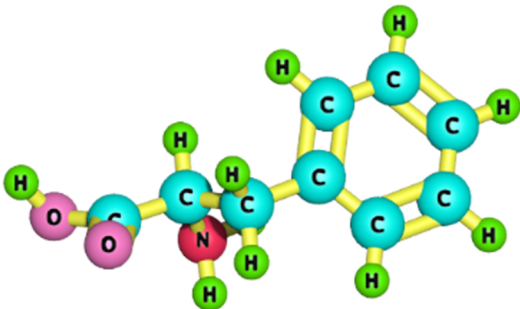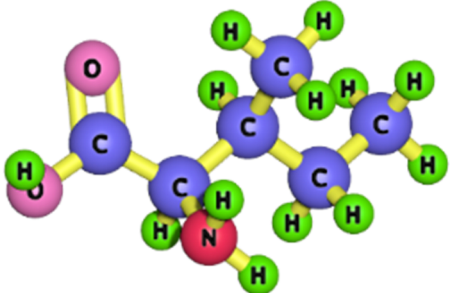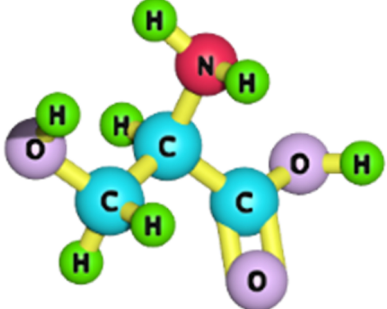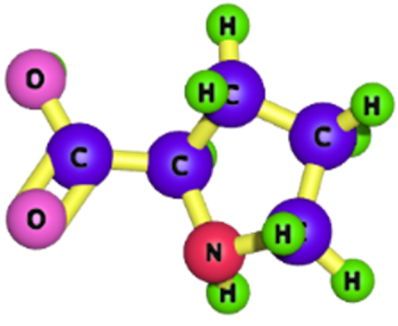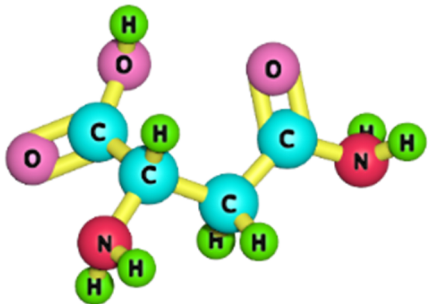
Amino Acid	Structure	Weight (g/mol)	References
Glutamine		146.14	[182]
Phenylalanine		165.19	[183]
Isoleucine		131.17	[184,185]
Threonine		119.1192	[186]
Serine		105.09	[187]

Table 10. *Cont.*

Amino Acid	Structure	Weight (g/mol)	References
Proline		115.13	[188,189]
Asparagine		132.12	[190]

I.   Amino acids as THIs

Nowadays, numerous research have focused on the use of amino acids as thermodynamic hydrate inhibitors. Masri and Sulaimon [191] developed three amino acid-based ionic liquids (AAILs), 1-ethyl-3-methyl-imidazolium-glutamate (EMIMGlu), 1-(3-cyanopropyl)-3-methyl-imidazolium-glutamate (CPMIMGlu), and 1-butyl-3-methyl-imidazolium-glutamate (BMIMGlu), to study their thermodynamic inhibition performance on methane hydrate. The results of the authors' study showed that all of the AAILs investigated successfully behaved as thermodynamic hydrate inhibitors. The AAILs shifted the methane hydrate dissociation curve to a region with lower temperature, and also increased the induction time of methane hydrate formation. With an average temperature shift of 1.14 K, EMIMGlu exhibited the best THI performance, followed by CPMIMGlu (0.91 K) and BMIMGlu (0.87 K). In addition, the AAIL thermodynamic inhibition characteristics were observed to be affected by the polarity of the AAILs [191]. This study proved that amino acids are very effective thermodynamic hydrate inhibitors. Mehrabi, et al. [192] studied the dissociation of methane and CO_2 hydrates using the aqueous solutions of the following amino acids: Glycine, Alanine, Serine, Valine, Proline, Arginine, Threonine, Asparagine, Phenylalanine and Histidine. The results of the authors' study showed that all of the amino acids acted as thermodynamic hydrate inhibitors to affect the formation of methane and CO_2 hydrates [192]. Bavoh, et al. [193] used an isochoric pressure search technique in a high-pressure stirring reactor to investigate the thermodynamic hydrate inhibitory effect of the following amino acids: valine, threonine, asparagine, and phenylalanine. Their study was conducted at amino acid weight percents of 1 wt% and 5 wt%, a temperature range of 275.71 to 286.10 K, and a pressure range of 3.5 to 10.25 MPa. According to the authors' study results, the development of methane gas hydrate was thermodynamically inhibited by all the investigated amino acids, with valine showing the strongest inhibitory effect at an average depression temperature of 0.529 K at 5 wt%. The differences in their inhibitory impacts were discovered to be caused by the amino acid side chain characteristics. Thus, this study indicates the efficiency of amino acids as thermodynamic gas hydrates inhibitors [193]. Sa, Kwak, Han, Ahn, Cho, Lee and Lee [187] studied the thermodynamic effects of amino acids on methane and natural gas hydrate formation in the presence of water. The authors

claim that the presence of amino acids in water caused structural changes that hindered the production of natural gas hydrates and methane. Thus, amino acids are very promising hydrate inhibitors that can be successfully used as thermodynamic hydrate inhibitors [187].

Long, et al. [194] studied the effect of combining thermodynamic methane hydrate inhibitors with amino acids. The authors used various concentrations of the following amino acids: ethylene glycol and glycine. The results of the authors study showed that the addition of glycine and ethylene glycol considerably increased the thermodynamic methane hydrate inhibition, proving the ability of amino acids in acting as THIs that ensure a smooth flow of oil/gas in pipelines [194]. Mannar, et al. [195] studied the thermodynamic inhibition impact of lysine amino acid on methane and carbon dioxide hydrates, at a temperature range of 276.45–285.15 K and a pressure range of 1.87–10.45 MPa. The findings of the authors' study showed that lysine thermodynamically inhibited the formation of methane and carbon dioxide gas hydrates by shifting the methane and carbon dioxide gas hydrate equilibrium curves to regions with higher pressures and lower temperatures. In addition, as the concentration of lysine increased, its hydrate inhibition effect also increased. Furthermore, for methane and carbon dioxide hydrate, average depression temperatures of 1.44 K and 1.49 K, respectively, were noted at 10 wt%. Thus, amino acids are promising thermodynamic hydrate inhibitors that can be successfully used to hinder the formation of gas hydrates [195]. Qureshi, Khraisheh and AlMomani [188] investigated the thermodynamic inhibitory hydrate effects of the amino acids glycine and alanine, and their inhibitory performance was compared to that of choline-based ionic liquids in the presence of water. The findings of the authors' investigation show that the amino acids glycine and L-alanine were substantially more efficient thermodynamic hydrate inhibitors at low concentrations [5 wt%] than the designated choline-based ionic liquids. Therefore, amino acids are very efficient thermodynamic hydrate inhibitors [188]. Lee, Go, Ko and Seo [177] studied the thermodynamic methane hydrate inhibitory effects of the amino acid glycine and the ionic liquid [BMIM][BF$_4$]. According to the findings, methane hydrate formation was significantly hindered by the combination of glycine and [BMIM][BF4] at 1.5 mol% for each. Consequently, amino acids can be used as thermodynamic hydrate inhibitors in oil/gas pipelines to ensure their proper flow [177]. Maddah, et al. [196] investigated the formation kinetics of methane hydrate using various amino acids as inhibitors. Glycine, alanine, proline, and serine were the designated amino acids, and they were present in varying dosages (<1.5%). According to the authors' findings, all the specified amino acids were capable of inhibiting the methane hydrates. Furthermore, serine was the most inhibiting amino acid, followed by glycine, alanine, and proline. Consequently, amino acids are highly effective hydrate inhibitors [196]. Bavoh, et al. [197] reported the thermodynamic inhibitory effect of five amino acids on the formation of methane hydrate. The amino acids investigated by the authors were glycine, alanine, proline, serine and arginine. According to the results, all of the designated amino acids thermodynamically inhibited the formation of methane hydrate. The greatest inhibitory effect was demonstrated by glycine, which had an average depression temperature of 1.78 K at 10 wt%. The amino acid's inhibitory behavior is based on their hydrogen bonding energies, which was predicted by the COSMO-RS. Hence, amino acids are effective thermodynamic hydrate inhibitors [197]. Bavoh, et al. [198] reported the inhibitory effect of the amino acids glycine, alanine, proline, serine and arginine on carbon dioxide gas hydrate, at a pressure range of 2.53 to 4.0 MPa and a concentration range of 5 to 20 wt%. The carbon dioxide gas hydrate equilibrium curve was notably shifted to a region with higher pressures and lower temperatures when all of the examined amino acids were present, indicating an inhibitory effect. The most effective inhibitor was reported to be glycine, with an average depression temperature of 1.83 K at 10 wt%. Therefore, amino acids are promising thermodynamic hydrate inhibitors that can effectively hinder the formation of hydrates [198]. Table 11 below shows a summary of amino acids used as thermodynamic hydrate inhibitors based on several studies.

Table 11. Summary of amino acids used as thermodynamic hydrate inhibitors relying on several studies.

Amino Acid	Hydrate Type	Function	Concentration	References
Glycine L-Alanine L-Valine	CO_2	THI	0.1–3.0 mol% 0.1–2.2 mol% 0.1–0.5 mol%	[176]
Glycine Alanine Serine Proline	CH_4	THI	0.5–3 wt% 0.5–2.2 wt% 1.3–3 wt% 1.3–9 wt%	[187]
Glycine Alanine Serine Proline Arginine	CH_4	THI	5–20 wt% 10 wt% 10 wt% 10 wt% 10 wt%	[197,198]
Glycine Alanine Serine Proline Arginine	CO_2	THI	5–20 wt% 10 wt% 10 wt% 10 wt% 10 wt%	[197,198]
Lysine	CH_4	THI	5–10 wt%	[195]
Lysine	CO_2	THI	5–10 wt%	[195]

II.   Amino acids as KHIs

A potential advantage of the amino acid kinetic hydrate inhibitors is their ability to hinder the formation of gas hydrates. As a result, multiple research have examined the kinetic inhibitory effects of various amino acids on the formation of hydrates. Hu, et al. [199] studied the hydrate inhibitory effects of glycine, serine, and valine amino acids on methane hydrate, using molecular dynamics (MD) simulations. The results of the authors' simulation revealed that all of the specified amino acids acted as a kinetic hydrate inhibitors to hinder the formation of hydrates [199]. Wang, et al. [200] investigated the effect of combining the hydrophilic amino acids L-arginine and glycine with the kinetic hydrate inhibitors PVP K90 and VC-713 on the formation of tetrahydrofuran (THF) hydrate. The results of the authors' study showed that L-arginine and glycine were capable of acting as KHIs by disturbing water molecules and lowering their activity. The best tetrahydrofuran (THF) hydrate inhibition effect was observed by the combination of 4.0 wt% glycine with 1.0 wt% VC-713 [200]. Thus, the addition of amino acids has increased the kinetic inhibitory effect on hydrates, and shows that they can be used as KHIs. Wang, et al. [201] studied the kinetic inhibitory effect of combining the hydrophilic amino acids glycine and l-arginine with the standard KHI polyvinylpyrrolidone (PVP) on the formation of tetrahydrofuran (THF) hydrate. According to the authors' research findings, glycine had a significant effect on water molecules. Therefore, glycine showed a high kinetic inhibitory effect on the THF hydrate. The best hydrate inhibitory performance of glycine was at a concentration of 1.0%, and it was found that, as the concentration of glycine increased, its hydrate inhibitory effect also increased. Furthermore, combining the hydrophilic amino acid with PVP significantly increased the kinetic hydrate inhibitory effect. In addition, the highest hydrate inhibitory effect was observed when glycine was combined with PVP K90 at a total inhibitor concentration of 1.0%. Thus, this study proves the ability of amino acids to behave like KHIs [201]. To minimize the negative consequences of chemical inhibitors, there is a growing need for environmentally friendly and green inhibitors. A large number of studies have reported the use of green hydrate inhibitors for to ensure flow in oil/gas pipelines. Naeiji, et al. [202] studied the kinetic inhibitory effect on THF (tetrahydrofuran) hydrate formation, using environmentally friendly amino acids. The specified amino acids were

glycine and l-leucine, which were used at a concentration range of 0.05 to 1.5 wt%, under atmospheric pressure, and in the presence and absence of acetone. According to the authors' research, amino acids with less hydrophobicity were better KHIs for delaying nucleation and stifling the hydrate equilibrium curve. As a result of its reduced hydrophobicity, glycine exhibited greater inhibitory effectiveness than l-leucine. In addition, the presence of acetone increased the overall kinetic hydrate inhibitory effect of the designated amino acids. Thus, amino acids can be successfully used as a kinetic hydrate inhibitors for hydrates, including THF hydrate [202]. Hu, et al. [203] studied the kinetic inhibitory effect of amino acids on the dissociation of methane hydrate. The specified amino acids were glycine, serine, and valine. According to the authors' findings, all of the specified amino acids successfully kinetically inhibited the methane hydrate. In addition, the best methane hydrate inhibitory performance was shown by serine. Thus, amino acids are capable of kinetically inhibiting hydrates [203]. Lee, et al. [204] investigated the use of a mixture of amino acids and ionic liquids as kinetic hydrate inhibitors on methane hydrate formation. The specified amino acid was glycine, and the ionic liquid was [BMIM][BF$_4$]. The results of the authors' study showed that glycine and [BMIM][BF$_4$] successfully behaved as KHIs by hindering the formation of methane gas hydrate. Thus, a mixture of amino acids and ionic liquids can be used as KHIs in oil/gas operations [204]. Zhu, et al. [205] investigated the kinetic inhibition effect of amino acids (glycine, valine, serine, alanine, and glutamic acid) on the dissociation of methane hydrates. The results of the authors' study showed that the kinetic inhibition methane hydrate performance of the amino acids was as followed: glycine > valine > serine > alanine > glutamic acid. Thus, glycine had the highest kinetic inhibitory performance at 5 mol%. Thus, amino acids are very promising candidates that can be used as KHIs in the oil/gas industry [205]. Abbasian Rad, Rostami Khodaverdiloo, Karamoddin, Varaminian and Peyvandi [180] investigated the kinetic inhibition effect of amino acid aqueous solutions containing glycine and l-leucine on ethane hydrate formation. The experiment was conducted by the authors at a temperature of 277 K and a concentration ranges from 0.05 to 3 wt% for the glycine and l-leucine. According to the authors' study results, low hydrophobic amino acids showed higher induction times and greater hinderance of ethane hydrate formation. Thus, glycine was a better KHI compared to l-leucine, as a result of its lower hydrophobicity. Consequently, amino acids can be used successfully as KHIs in oil/gas pipelines [180].

Bavoh, et al. [206] assessed the kinetic inhibition effects of two amino acids (arginine and valine) on the development of methane hydrate. The results of the authors' study showed that both of the amino acids kinetically inhibited the methane hydrate by hindering its formation rate. Thus, amino acids are very useful KHIs that can be effectively used to ensure a smooth oil/gas flow in pipelines [206]. Table 12 below shows a summary of amino acids used as kinetic hydrate inhibitors based on several studies.

Table 12. Summary of amino acids used as kinetic hydrate inhibitors relying on several studies.

Amino Acid	Hydrate Type	Function	Concentration	References
Glycine L-Alanine L-Valine Leucine Isoleucine	CO_2	KHI	0.01–1.0 mol% 0.1 mol% 0.1 mol% 0.1 mol% 0.1 mol%	[179]
L-Alanine Aspartic acid Asparagine Phenylalanine Histidine	CO_2	KHI	0.01–0.1 mol% 0.01 mol% 0.01 mol% 0.1 mol% 0.1 mol%	[207]
Glycine Leucine	C_2H_6	KHI	0.05–3 wt%	[180]

Table 12. *Cont.*

Amino Acid	Hydrate Type	Function	Concentration	References
Glycine Leucine	THF	KHI	0.05–1.5 wt%	[202]
L-threonine L-valine	CH_4	KHI	2770–1385 ppm	[208]
L-histidine	CH_4	KHI	0.1–1 wt%	[209]
PVP and L-Tyrosine	NG	KHI	1 wt%	[210,211]
PVP and L-Tyrosine	NG	KHI	100–275 ppm	[212]
Glycine Alanine Serine Proline	CH_4	KHI	0.1 wt%	[187]
Glycine Proline Serine Threonine Glutamine Histidine	CO_2	KHI	0.5–2 wt%	[182]

3.5.3. Nanoparticles (NPs)

Nanoparticles (NPs) have become the latest, next-generation materials for highly effective hydrate inhibition processes. Nanoparticles are typically described as tiny materials, with a particle size that ranges from 1 to 100 nm. Based on their characteristics, shapes, or sizes, they can be divided into many classifications. Fullerenes, metal NPs, ceramic NPs, and polymeric NPs are some of the various groupings. Due to their large surface area and nanoscale size, NPs have distinct physical and chemical characteristics. These properties make them ideal choices for a variety of industrial applications, including as hydrate inhibitors in the oil/gas industry. Heavy metal NPs of lead, mercury and tin are reported to be so rigid and stable that their degradation is not easily achievable, which can lead to many environmental toxicities.[143]. Nanoparticles are capable of facilitating dispersion and stabilizing emulsions. Consequently, they can create a protective barrier layer by being adsorbed at the water–gas interface to inhibit the formation of hydrates by prohibiting the agglomeration process. Hence, nanoparticles are widely used as hydrate inhibitors in the oil/gas industry. Table 13 below shows some of the nanoparticles commonly used as hydrate inhibitors.

Table 13. Some of the widely used nanoparticles in hydrate inhibition processes.
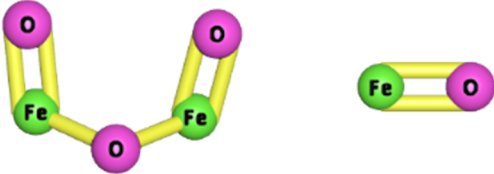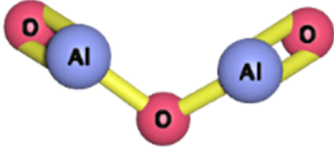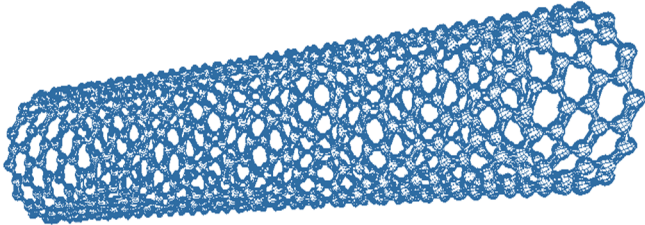
Nanoparticle	Three Dimensional Structure (3D)	Hydrate Inhibition Effect	Reference
Zinc oxide		Acts as a THI by shifting the hydrate equilibrium curve to a region with higher pressure and lower temperature	[213]
Magnetite		Functions as both kinetic inhibitor and anti-agglomerate.	[214]

Table 13. *Cont.*

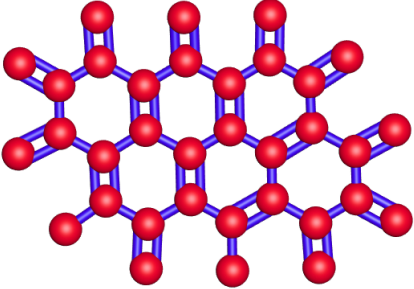| Nanoparticle	Three Dimensional Structure (3D)	Hydrate Inhibition Effect	Reference
Silica		Acts as KHI by increasing the induction time of the gas hydrate.	[215]
Graphene		Effectively inhibits hydrates formation.	[216]
TiO_2		Inhibits the hydrate formation by increasing the induction time.	[217]
Carbon nanotubes (CNTs)		Inhibits the hydrate formation by increasing the induction time.	[218]

I.   Nano particles as THIs

Due to the large concentration of inhibitors used in existing strategies to solve the hydrate clogging issues in gas pipelines, there is a major risk of ecological destruction. The creation of innovative recoverable green inhibitors is necessary to resolve these problems. Nanoparticles are promising hydrate inhibitors that can be used efficiently to inhibit hydrate formation. Several studies have focused on the application of nanoparticles as THIs in oil/gas operations. Li, et al. [219] studied the thermodynamic hydrate inhibitory effect of nano-copper particles on HFC134a (CH_2FCF_3) hydrate. The results of the authors' study showed that the addition of nano-copper shifted the HFC134a (CH_2FCF_3) hydrate dissociation curve to a region with higher pressure and lower temperature. This thermodynamic shift inhibited the formation of the gas hydrate. Thus, nano-copper particles can be successfully used as THIs in the oil/gas industry [219]. Yu, et al. [220] investigated the thermodynamic hydrate inhibitory effect of graphite nanoparticles on CO_2 hydrate. According to the authors' study results, the addition of graphite nanoparticles shifted the CO_2 hydrate equilibrium curve to a region with higher pressure and lower temperature. Thus, graphite nanoparticles behaved as THIs, inhibiting the formation of CO_2 hydrate [220]. Mohammadi, et al. [221] studied the thermodynamic hydrate inhibitory effect of synthesized zinc oxide (ZnO) nanoparticles on the development of CO_2 hydrate. The results of the authors' study indicated that the use of zinc oxide (ZnO) nanoparticles shifted the equilibrium curve of CO_2 hydrate to a region with higher pressure and lower temperature. Consequently, zinc oxide (ZnO) nanoparticles are efficient thermodynamic hydrate inhibitors that can be applied successfully in the inhibition of hydrates that develop in oil/gas pipelines [221].

II.   Nano particles as KHIs

The use of nanoparticles as KHIs is increasing over time, due their high efficiency in inhibiting hydrates. Numerous studies have reported the application of different types of nanoparticles as KHIs in oil/gas operations. Wang, et al. [222] studied the kinetic inhibitory effect of the hydrophilic silica nanoparticle on the development of gas hydrate in a methane/liquid-water system at various silica nanoparticle concentrations and grain sizes. According to the authors' study results, the highest kinetic inhibitory effect of the silica nanoparticles was achieved at a concentration of 4.0 wt% and a grain size of 50 nm. Furthermore, the addition of silica nanoparticles raised the hydrate induction time by 194% and reduced the amount and average rate of hydrate development by 10% and 17%, respectively. This superb kinetic inhibitory effect was owed to the hydrophilicity, concentration, and aggregation of silica nanoparticles. Thus, silica nanoparticles can be used efficiently in oil/gas operations as KHIs [222].

Mahmoodi, et al. [223] investigated the kinetic inhibitory effect of silver nanoparticles on the formation of CO_2 hydrate at various P–T conditions via the molecular dynamics (MD) approach. To investigate the impact of nanoparticle concentration on the gas hydrate system, the authors' used three nanofluid models with 2, 4, and 6 nanoparticles (NPs), as well as also a base model (without NPs). The results of the authors' study showed that silver nanoparticles at various concentration ranges behaved as KHIs [223]. Min, Kang, Ahn, Lee, Cha and Lee [214] studied the kinetic hydrate inhibitory effect of Span 20-adsorbed Fe_3O_4 nanoparticles and their reusability. The results of the authors' study showed that the Span 20-adsorbed Fe_3O_4 nanoparticles behaved as a KHI by inhibiting the formation of hydrate. In addition, the proposed inhibitor drastically prolonged the induction time by delaying the nucleation. Thus, Span 20-adsorbed Fe_3O_4 nanoparticles can be applied efficiently as a KHI, and they offers a new technique for inhibiting hydrate formation [214].

One of the most important concerns in the oil and gas sectors is the formation of gas hydrate inhibitors to avoid hydrate formation and ensure a smooth flow of oil/gas in pipelines. For environmental and economic benefits, low-dosage and recyclable hydrate inhibitors are a necessity. For the first time, Lee, et al. [224] developed an innovative category of kinetic hydrate inhibitors (KHIs) consisting of metal-organic frameworks (MOFs) coated with magnetic nanoparticles (NP), and investigated their kinetic inhibitory effects on methane hydrate. The proposed KHI is Fe_3O_4@UiO-66-NH_2. The results of the authors' study showed that Fe_3O_4@UiO-66-NH_2 successfully behaved as a KHI candidate by hindering CH_4 hydrate formation. In addition, this innovative inhibitor was successfully recovered and reused, and exhibited superior hydrate inhibition performance and characteristics. Thus, MOFs coated with nanoparticles provide a new platform for efficient kinetic hydrate inhibitors [224]. Xu, et al. [225] studied the kinetic inhibitory effect of adding hydrophilic silica nanoparticles to drilling fluid for the inhibition of natural gas hydrates. According to the authors' study results, the hydrophilic silica nanoparticles inhibited the formation of natural gas hydrates that develop in the drilling fluid system. Thus, hydrophilic silica nanoparticles can be used as a KHI to ensure a smooth flow of natural gas in the drilling system [225].

4. Drawbacks of Using THIs and KHIs, along with Ways to Minimize Their Negative Impacts

Salt precipitation is considered one of the main issues that oil/gas production plants face. When compared to all other salt scales, halite salt scales pose the most difficult scaling problem in the oil and gas industry. THI has a lot of advantages in the industry as a hydrate inhibitor, but it also causes an increase in salt scaling. A salt layer accumulates on the pipes during the scaling phase, which reduces the inhibitory impact of the THI. Thermodynamic inhibitors, which contain electrolyte salts such as KCL, NaCl, and $MgCl_2$, cause the highest scaling. As a result, the use of these inhibitors stimulates halite scaling and diminishes their function as hydrate inhibitors. Thus, for a better overall environmental health and gas

flow, alternative forms of environmentally friendly high efficiency inhibitors are desired. Table 14 below shows the potential drawbacks of using THIs in oil/gas operations.

Table 14. Drawbacks of using THIs in oil/gas operations.

THI Type	Drawback	Reason
THIs	High concentration is required to maintain high hydrate inhibition efficiency.	THIs have high water solubility and volatility.
THIs	High overall cost.	High volumes of THIs are required to efficiently inhibit hydrates.
Alcohols and glycols	Health hazard. Therefore, strict environmental regulations are required for their usage.	Alcohols and glycols are highly toxic.
Methanol	Health hazard. Hence, rigorous environmental laws are required for its application.	Highly flammable, due to its low flash point (11 °C).

The solubility of KHIs in water is considered the main drawback of using KHIs in the oil/gas field, since KHIs will have catastrophic and harmful effects on the water environment. Several KHIs precipitate in the water, leading to water pollution. Thus, filtering the KHIs after their use is considered an ultimate solution for preventing their negative impacts on the environment. A proposed technique, based on this concept, is to use nanofiltration membranes fabricated with nanomaterials to remove KHIs from water, as shown in Figure 11. Figure 11 below shows the removal of KHIs (PVP and leucine) via a graphene-based nanofiltration membrane. Golpour and Pakizeh [226] synthesized a novel thin film nanocomposite (TFN) nanofiltration (NF) membrane by incorporating graphene oxide (GO) into the membrane to remove KHIs from water. The authors investigated the performance of the NF membranes by measuring the KHI rejection and permeation flux under various feed concentrations and operating pressures. The results of the authors' study showed that the TFN membrane embedded with 0.1 wt% GO resulted in a KHI rejection of 99% and a permeation flux of 32.7 L/m^2 h, at a KHI feed concentration of 0.5 wt% and an operating pressure of 9 bar. Consequently, this study proved that TFN membranes are promising candidates for KHI removal from water, thus ensuring an environmentally friendly application of KHI in hydrate removal processes [226].
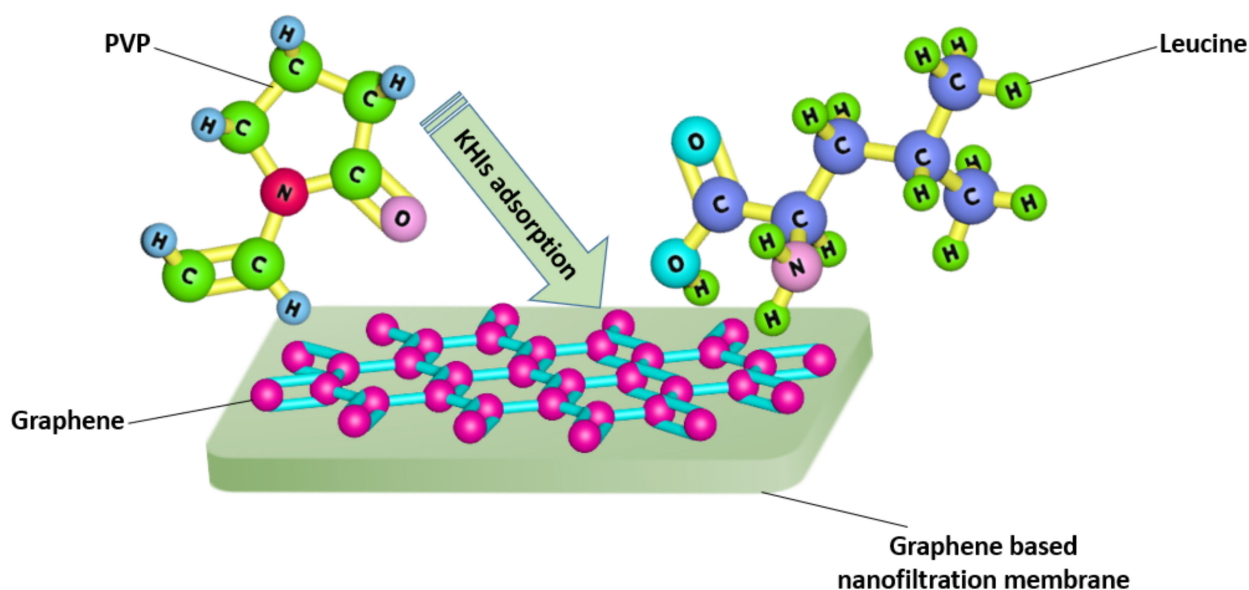

Figure 11. Removal of KHIs via graphene-based nanofiltration membrane.

5. Conclusions

The formation of gas hydrates in pipelines is of great concern to the oil/gas industry. Gas hydrates are primarily formed when water and non-polar or slightly polar low molecular mass gases, as well as volatile liquids are subjected to low temperatures and high pressures. Depending on the thermodynamics of the surrounding environment, this hydrate development may take place during the production, processing, or transportation of oil or gas. In-depth research was therefore performed to resolve techniques that inhibit the formation of gas hydrates. In the industries, some physical methods have been applied that involve subjecting the gas hydrates to thermal heating or depressurization. However, these techniques are costly and do not prevent the gas hydrates from forming. The best approach to inhibit the formation of gas hydrates is the use of chemical inhibitors. Chemical inhibitors are divided up into high dosage hydrate inhibitors (thermodynamic hydrate inhibitors (THI)) and low dosage hydrate inhibitors (kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs)).

Thermodynamic hydrate inhibitors (THIs) inhibit the formation of gas hydrates by shifting the hydrate equilibrium curve to a region with higher pressure and lower temperature. THIs include, alcohols (methanol, glycol, and diethylene glycol) and electrolytes. Several industrial processes use alcohols as hydrate inhibitors. However, their usage raises several environmental concerns and drawbacks. A high alcohol concentration is required to thermodynamically inhibit a gas hydrate, since alcohols are highly volatile. Therefore, using alcohols leads to a higher overall operational cost, and environmental hazards. To avoid these problems, alternative hydrate inhibitory techniques, including the use of KHIs and anti-agglomerates, are used by the industry.

Kinetic hydrate inhibitors (KHIs), such as polymeric compounds, are widely applied in oil/gas operations. KHIs function by delaying the hydrate formation time (induction time). Water pollution is the main drawback of using KHIs, since KHIs dissolve readily in water. Recent research suggest the use of nanofiltration membranes to remove KHIs from water. In addition, using dual-function hydrate inhibitors, such as amino acids, ionic liquids, and nanoparticles, is of a great interest nowadays. Dual-function hydrate inhibitors have the capability to act as THIs or KHIs, thus ensuring an effective hydrate inhibition process.

Anti-agglomerates (AAs), unlike THIs and KHIs, are surface-active compounds that do not prevent the formation of the hydrate. Rather, they divide the hydrates into precisely separated fine particulate matter by keeping the fluid viscosity low and allowing the hydrates to be carried safely in the slurry state. Quaternary ammonium salts (QAS) and surfactants are the most commonly used anti-agglomerates in the oil/gas industry.

The main focus of this review paper was to provide a comprehensive study on the fundamental principles of gas hydrates, as well the recent mitigation methods applied by the oil/gas industry to inhibit gas hydrate formation in pipelines.

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