Periodica Polytechnica Chemical Engineering, 70(1), pp. 124–140, 2026

Integrative Approaches to Gas Hydrate Mitigation: From Molecular Inhibitors to Machine Learning Based Flow Assurance

Irfan Akram[1], Bhajan Lal[2], Shailendra Kumar Singh[3], Khor Siak Foo[4], Raj Tiwari[5],
Bharvee Srivastava[6], Prashant Kumar[1*]

[1] School of Chemical Engineering and Physical Science, Lovely Professional University, G.T. Road, 144411 Phagwara, Punjab, India
[2] Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi Petronas, 32610 Seri Iskandar, Perak, Malaysia
[3] Department of Biochemistry, Sadanlal Savaldas Khanna Girls' Degree College Khatri Vidhyalay, Near Gol Park Chauraha, Tilak Rd., 21100 Atteusuiya, Prayagraj, Uttar Pradesh, India
[4] Centre of Carbon Capture, Utilization and Storage (CCCUS), Universiti Teknologi Petronas, 32610 Seri Iskandar, Perak, Malaysia
[5] Petronas Research Sdn Bhd, Kawasan Institusi Bangi, Jalan Ayer Itam, 43000 Bandar Baru Bangi, Selangor, Malaysia
[6] Department of Biochemical Engineering, Sam Higginbottom University of Agriculture, Technology and Sciences, Rewa Road, 211007 Naini, Prayagraj, India
[*] Corresponding author, e-mail: prashant.25338@lpu.co.in

Received: 13 September 2025, Accepted: 12 January 2026, Published online: 19 February 2026

Abstract

Gas hydrate formation in oil and gas pipelines, particularly under deepwater and high-pressure conditions, presents severe operational and safety risks. These ice-like crystalline compounds, composed of water and gas molecules, can block flow channels and disrupt production, posing significant threats to infrastructure reliability, flow assurance, and economic efficiency. This review offers a comprehensive analysis of hydrate formation mechanisms, including phase behavior, thermodynamic properties, and structural classifications across varied pipeline systems. It highlights conventional mitigation strategies such as thermodynamic inhibitors, kinetic hydrate inhibitors, and anti-agglomerants, while emphasizing recent advances in eco-friendly and dual-function inhibitors, including ionic liquids, amino acids, and nanoparticles, which promise improved efficiency with lower environmental impact.

In addition, the review critically evaluates predictive modelling techniques ranging from classical statistical and thermodynamic models to modern machine learning approaches such as Artificial Neural Networks and decision trees, which enable faster and more accurate hydrate risk assessments. By integrating core scientific principles with cutting-edge chemical and computational innovations, this study identifies sustainable, cost-effective, and scalable strategies for gas hydrate control. The paper further underscores the need for interdisciplinary collaboration between academia and industry to develop next-generation inhibitors and robust predictive frameworks tailored to evolving operational demands in flow assurance.

Keywords

oil industry, gas industry, flow assurance, machine learning, gas hydrate inhibitors

1 Introduction

The global population has quadrupled over the last century, reaching approximately eight billion people [1]. This rapid growth has led to a substantial rise in energy demand. In parallel, the increasing severity of climate change has emphasized the urgent need for cleaner and more environmentally sustainable energy sources [2]. Among fossil fuels, natural gas is considered relatively clean due to its lower emissions of CO_2, nitrogen oxides (NO_x), and minimal sulfur oxide release during combustion compared to coal and oil [3]. According to projections, the global demand for natural gas is anticipated to grow at an average annual rate of 1.7% through 2040, outpacing the growth of other fossil fuels such as coal (1.3%) and liquid fuels (0.9%) [4]. While conventional fossil fuel reserves are depleting and may be exhausted within the next five decades, gas hydrates have emerged as a potential alternative. Gas hydrates-solid crystalline compounds where gas molecules are trapped within water lattices-contain a vast quantity of methane. It is estimated that hydrate-bearing sediments may hold more than 150% of the global

Cite this article as: Akram, I., Lal, B., Singh, S. K., Foo, K. S., Tiwari, R., Srivastava, B., Kumar, P. "Integrative Approaches to Gas Hydrate Mitigation: From Molecular Inhibitors to Machine Learning Based Flow Assurance", Periodica Polytechnica Chemical Engineering, 70(1), pp. 124–140, 2026. https://doi.org/10.3311/PPch.42216

conventional natural gas reserves, potentially providing a clean energy source for the next 200 years [5]. However, in oil and gas transportation systems, gas hydrates are also known for their undesirable formation within subsea pipelines, posing serious flow assurance challenges. Their formation can lead to blockages, increased operational risks, and even catastrophic failures, causing significant safety hazards and economic losses [6, 7].

The basic knowledge of clathrate hydrate science has been greatly influenced by hydrate of natural gases as nitrogen, chlorine, oxygen and ethylene oxide. The field began with sir Humphary Davys by discovery of chlorine hydrate in 1811, which offered the first proof that water may physically include gas molecules rather than chemically link them within an ice-like lattice [8]. Later in the 19th century scientist like Faraday, de la Rive and Villard confirmed that small diatomic gases, including O_2 and N_2 are also capable of forming hydrates under extreme pressure and low temperature. Due to weak host-guest interactions and poor cage stability these hydrate commonly adopt Structure II and in some cases Structure I [8, 9]. Pauling and March originally described and thoroughly examined ethylene oxide hydrate forming capacity and structural properties in the middle of 20th century [10]. This hydrate is usually crystalline in structure and form easier under relatively modest pressure and temperature [11]. These early findings offered fundamental concept for subsequent advancement in gas hydrate thermodynamics, inhibitions and flow assurance [12]. They also set the groundwork for the current understanding of clathrate structures (sI, sII and sH) [13].

2 Gas hydrates: structure, composition, and hazards

Gas hydrates are non-stoichiometric crystalline solids formed by the inclusion of gas molecules (guest) within a three-dimensional hydrogen-bonded network of water molecules (host), under high-pressure and low-temperature conditions [14]. These structures closely resemble ice but differ in that the guest molecules reside within the voids or cavities (cages) of the host lattice without forming chemical bonds, stabilized purely by van der Waals interactions [15].

The cavity diameters within hydrate structures typically accommodate gas molecules ranging in size from 3.8 to 6.95 Å [15]. Common hydrate-forming gases include methane, ethane, propane, carbon dioxide, nitrogen, and hydrogen sulfide [16]. Depending on the size and type of guest molecule, hydrates typically crystallize into Structure I (sI), Structure II (sII), or Structure H (sH). Methane and ethane generally form sI hydrates, while larger hydrocarbons like propane stabilize sII structures.

Hydrate formation is favored in environments with pressures above 4–5 MPa and temperatures below 25 °C, conditions frequently encountered in subsea oil and gas pipelines. Under such conditions, the sudden formation of gas hydrates can result in plugging of pipelines, leading to severe flow assurance problems, increased operational costs, and potential safety hazards [17].

The phenomenon of gas hydrate formation in industrial settings was first systematically investigated by Hammerschmidt in 1934, who recognized the formation of methane hydrates as a serious issue in natural gas transport systems [18]. Since then, hydrate-related flow blockages have been acknowledged as one of the most critical challenges in offshore petroleum engineering, prompting extensive multidisciplinary research over the last several decades [19].

2.1 Structure of gas hydrate

Gas hydrates crystallize into three primary structures depending on the size and type of guest molecules: Structure I (sI), Structure II (sII), and Structure H (sH) [20]. These structures differ in terms of unit cell geometry, cavity size, and the type of gas molecules they can encapsulate. Structure I (sI) has a cubic crystal symmetry and consists of 46 water molecules per unit cell, forming two types of cavities: 6 small pentagonal dodecahedra (5^{12}) and 2 larger tetrakaidecahedra ($5^{12}6^{2}$). It is typically stabilized by small guest molecules with effective diameters between 4.2 and 6.0 Å, such as methane, ethane, carbon dioxide, and hydrogen sulfide [21]. Structure II (sII) also has cubic symmetry but contains 136 water molecules per unit cell, forming 16 small 5^{12} and 8 large $5^{12}6^{4}$ cages. It is stabilized by slightly larger guest molecules (typically above 6 Å), such as propane, isobutane, and nitrogen [22]. Mixtures of smaller and larger molecules can also stabilize sII. Structure H (sH), which exhibits hexagonal symmetry, contains 34 water molecules per unit cell and includes 3 small 5^{12}, 2 mediums $4^{3}5^{6}6^{3}$, and 1 large $5^{12}6^{8}$ cages. This structure is stabilized by a combination of large guest molecules such as neohexane (C_5H_{12}) or methylcyclohexane, along with smaller help gases like methane or nitrous oxide (N_2O) [23]. Although sH has been synthesized in laboratory settings, it is rare in natural systems due to the specific molecular size requirements and coexistence of large–small gas mixtures.

An overview of hydrate types, cavity configurations, and typical guest molecules is illustrated in Table 1, while Fig. 1 provides a schematic of the cage structures and

Table 1 Comparative table of hydrate structures

Structure	Symmetry	Water molecules/unit cell	Cavity types	Typical guest molecules
sI	Cubic	46	6×5^{12}, $2 \times 5^{12}6^2$	CH_4, CO_2, H_2S, C_2H_6
sII	Cubic	136	16×5^{12}, $8 \times 5^{12}6^4$	N_2, C_3H_8, C_4H_{10}
sH	Hexagonal	34	3×5^{12}, $2 \times 4^35^66^3$, $1 \times 5^{12}6^8$	$C_5H_{12} + CH_4$ or N_2O

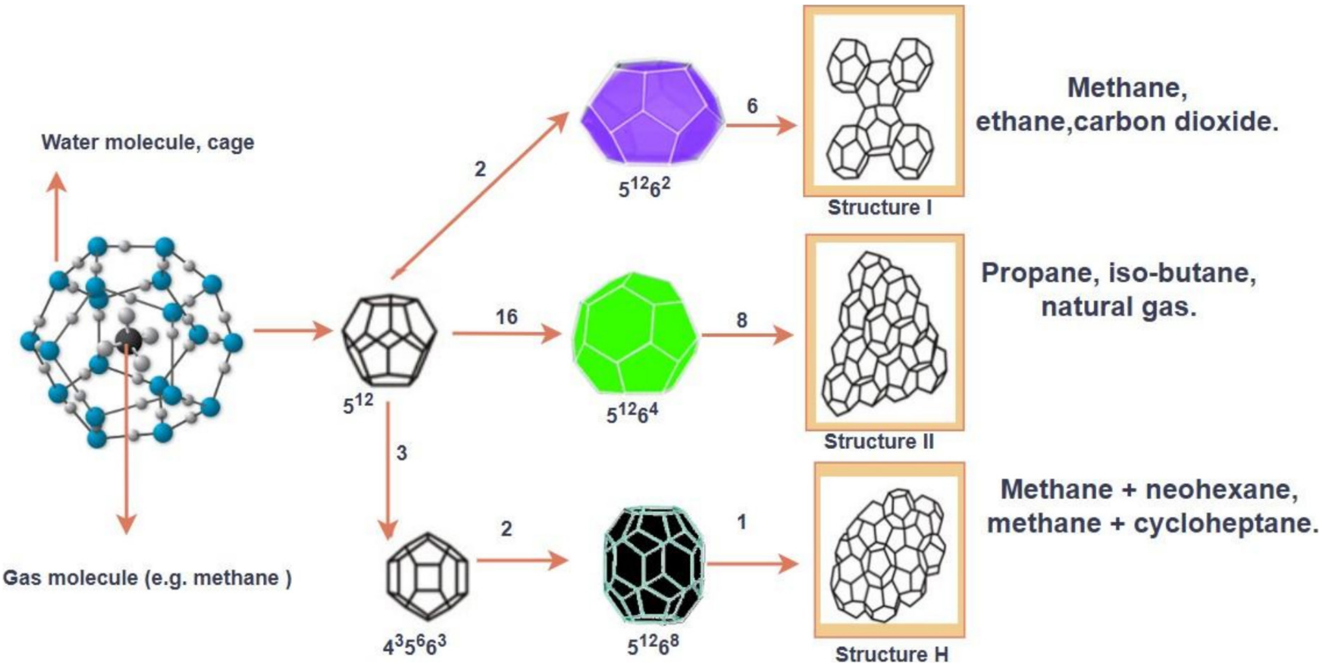


Fig. 1 Schematic of the cage structures and their respective diameters

their respective diameters. The structural configurations of the three primary gas hydrate Types-Structure I (sI), Structure II (sII), and Structure H (sH) – along with their characteristic cavity types and typical guest molecules. The hydrate structures are formed by water molecules (blue) creating cages stabilized by guest gas molecules (e.g., CH_4, CO_2, C_3H_8). sI contains two large $5^{12}6^2$ and six small 5^{12} cages, sII includes eight $5^{12}6^4$ and sixteen 5^{12} cages, while sH comprises one $5^{12}6^8$, two $4^35^66^3$, and three 5^{12} cages. Guest molecule size and type determine the stable hydrate structure formed (Table 2) [24].

2.2 Classification of gas hydrate

Based on phase composition and geological setting, natural gas hydrates are broadly classified into four categories [21]:

1. Class 1 hydrates are typically found between impermeable geological layers and consist of two distinct strata: an upper hydrate-bearing layer and an underlying zone containing a mixture of gas and water. A representative example is the North Slope of Alaska.
2. Class 2 hydrates also occur between impermeable layers but are characterized by the presence of a mobile water layer beneath the hydrate layer, as observed in the Nankai Trough, Japan.
3. Class 3 hydrates form as a single, continuous hydrate-bearing layer within impermeable boundaries, with no underlying free gas or water zones. An example includes the Qilian Mountains, China.
4. Class 4 hydrates are dispersed deposits with low hydrate saturation and are not confined by impermeable layers. These are typically found in unconsolidated sediments, such as in the Krishna-Godavari Basin, India [25].

This classification aids in understanding hydrate stability, extraction feasibility, and the associated risks in different geological environments (Table 3) [26].

2.3 Formation mechanism of gas hydrates in pipelines

Pipelines that transport oil and gas typically carry a multiphase mixture of gas, water, and hydrocarbons. These exist in three main physical phases: gas, liquid hydrocarbon, and aqueous liquid. Based on the dominant fluid characteristics, the thermal and flow behavior in pipelines can be categorized into four main hydrate formation flow models: oil-dominated systems, gas-dominated systems, condensate systems, and high water cut systems [9]. In oil-dominated systems, water exists in the form of small dispersed

Table 2 Structural classification of hydrates formed by Cl_2, SO_2, CO_2, N_2 [24]

Gas	Hydrate type	Structure	Findings
Cl_2	$Cl_2 \cdot 6H_2O$	sI or sII	Chlorine molecules are trapped in water cage, forming a crystalline solid. Hydrate is unstable at room temperature and pressure.
SO_2	$SO_2 \cdot H_2O$	Hydrogen-bonded network	Forms a molecular complex rather than a typical gas hydrate and form a crystalline solid at room temperature. Water molecules hydrogen-bonded with SO_2.
CO_2	$CO_2 \cdot xH_2O$	sI or sII	Forms cage like clathrate hydrate. In sI, CO_2 occupies the small and large cages of a cubic lattice. Stable at low temperature and high pressure (−0.15 °C–9.85 °C, >30 bar).
N_2	$N_2 \cdot xH_2O$	sII	Forms clathrate hydrates with N_2 trapped in the cage. N_2 hydrate is stable at high pressure and low temperature.

Table 3 Classification of gas hydrates [26]

Type of classification	Category	Examples/notes
Unit cells	Structure I (sI)	Small gas molecules (e.g., methane, ethane)
	Structure II (sII)	Larger molecules (e.g., propane, iso-butane)
	Structure H (sH)	Mixed large and small guests (e.g., neohexane + methane)
Geological formation and phase composition	Class 1	Hydrate above gas–water zone (e.g., North Slope, Alaska)
	Class 2	Hydrate above mobile water layer (e.g., Nankai Trough, Japan)
	Class 3	Isolated hydrate layer (e.g., Qilian Mountains, China)
	Class 4	Dispersed hydrates with no cap rock (e.g., KG Basin, India)
Origin	Natural	Formed in marine/permafrost sediments
	Synthetic	Produced in controlled conditions (lab/industry)

droplets within the continuous oil phase. Hydrate formation in such systems is generally limited due to the encapsulation of water by oil, which restricts water-gas contact.

In gas-dominated systems, a small amount of liquid hydrocarbon may be present, which facilitates gas transport. However, when gas and water coexist and interact under favorable pressure and temperature conditions, hydrate particles can form rapidly, resulting in the generation of a hydrate slurry within the pipeline [27]. As hydrate formation progresses, the solid-to-liquid ratio in the flow increases, leading to a decrease in the liquid content. Eventually, hydrate particles begin to adhere to the inner walls of the pipeline, forming a solid layer that reduces flow diameter and may ultimately cause a complete blockage [28, 29].

This hydrate build-up is gradual but dangerous. As illustrated in Fig. 2 [30], methane hydrate formation over time leads to the narrowing of the pipeline, which can severely restrict or even stop the flow. Once hydrates begin forming, preventing blockage becomes extremely challenging, making hydrate inhibition especially critical in gas-dominated systems. In contrast, condensate systems exhibit high shear forces, which may either dissolve the water in the condensate or suspend it as fine droplets, thereby influencing hydrate formation dynamics [31]. In high water cut systems, water can comprise up to 70% of the total fluid volume. Under such conditions, water and oil tend to exist as separate continuous phases, increasing the likelihood of hydrate formation due to significant water–gas contact and minimal protective dispersion.

3 Gas hydrates and their impact on flow assurance

The emergence of flow assurance engineering has become a critical discipline in the oil and gas industry, particularly as exploration and field development have expanded

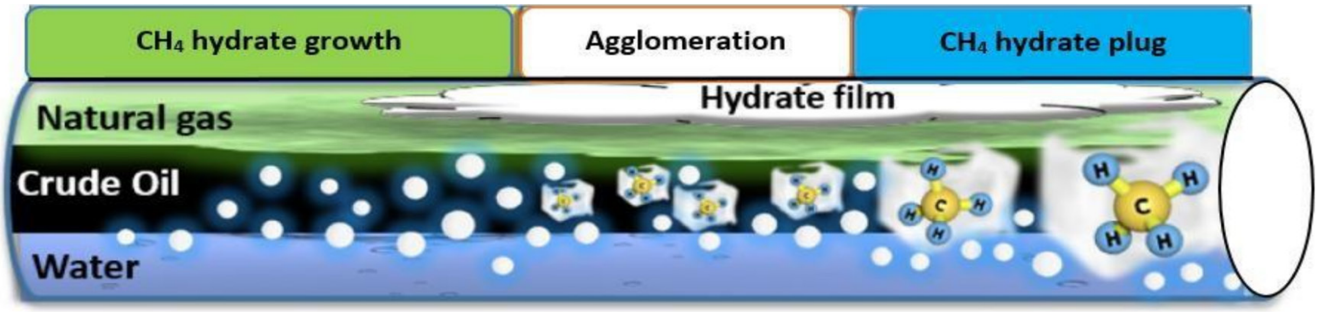


Fig. 2 The movement of methane hydrates in a pipeline carrying crude oil [30]

into deepwater regions exceeding depths of 500 m. In such environments, the use of longer subsea pipelines under harsh pressure and temperature conditions significantly increases the risk of gas hydrate formation [6]. One of the key challenges in deepwater production is the presence of non-uniform production profiles, characterized by fluctuations in gas composition, pressure, temperature, and fluid content (oil and water) throughout the lifecycle of the field. These variations complicate the prediction and control of hydrate formation dynamics [32].

The low temperatures commonly encountered in deepwater systems often fall within the hydrate stability zone, making these regions highly susceptible to hydrate formation. Compounding this issue are operational events such as cold start-ups, shutdowns, and restarts, which can cause drastic temperature and pressure shifts-further increasing the likelihood of hydrate blockages. Flow assurance engineers continue to face significant technical hurdles in accurately predicting and managing the effects of transient flow regimes. Failure to effectively mitigate hydrate risks can lead to catastrophic pipeline blockages, resulting in severe financial losses, operational downtime, and potential environmental hazards [33]. Despite extensive research and mitigation strategies, including thermal insulation, chemical injection (e.g., thermodynamic inhibitors, kinetic inhibitors, and anti-agglomerants), and active heating, a permanent and universally applicable solution to gas hydrate formation remains elusive.

4 Gas hydrate inhibition strategies

The challenge of gas hydrate formation in pipelines was first documented by Hammerschmidt in 1934, marking the beginning of systematic efforts to develop effective hydrate mitigation strategies [18]. Since then, extensive global research has been conducted to explore and refine various methods for inhibiting gas hydrate formation, as illustrated by the increasing number of scientific publications on the subject over time (Fig. 3) [34]. Gas hydrate inhibition techniques are broadly categorized into chemical and physical methods (Fig. 4).

Physical inhibition involves altering the environmental conditions to prevent hydrate stability. This includes:

- Depressurization, which reduces the pressure below the hydrate formation threshold.
- Thermal heating, which increases the temperature to move the system outside the hydrate stability zone.

Chemical inhibition focuses on preventing hydrate nucleation and growth using specific compounds. These are subdivided into:

- Thermodynamic hydrate inhibitors (THIs): such as methanol and monoethylene glycol (MEG), which shift the hydrate stability zone.
- Kinetic hydrate inhibitors (KHIs): which delay hydrate nucleation and slow the growth rate.
- Anti-agglomerants (AAs): which allow small hydrate particles to form but prevent them from clumping together and forming plugs.

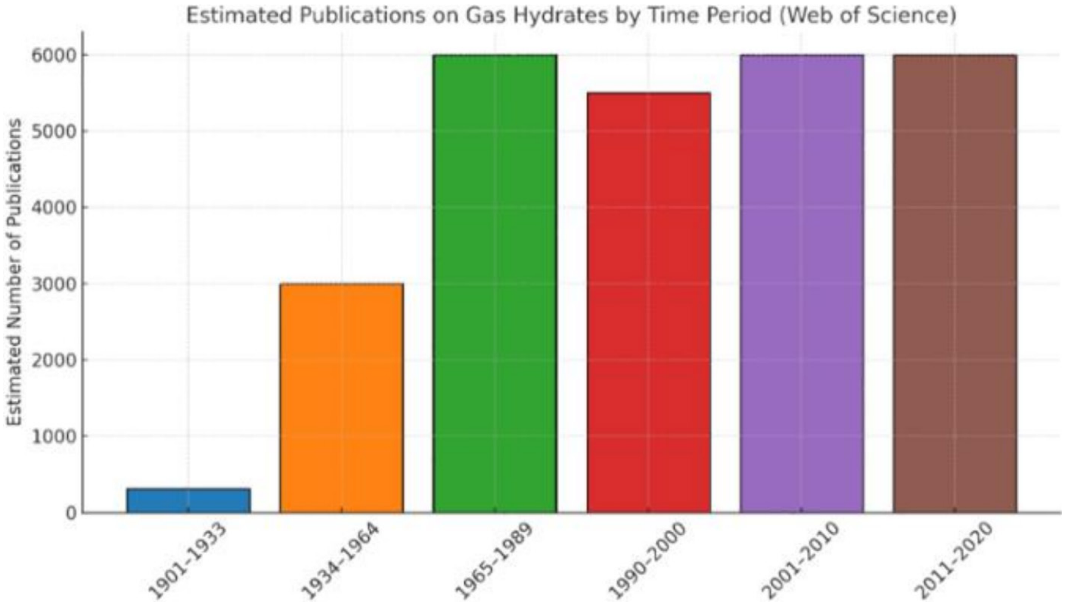


Fig. 3 A concise chronology illustrating the rise in the quantity of gas hydrate inhibition methods suggested in scholarly works [34]

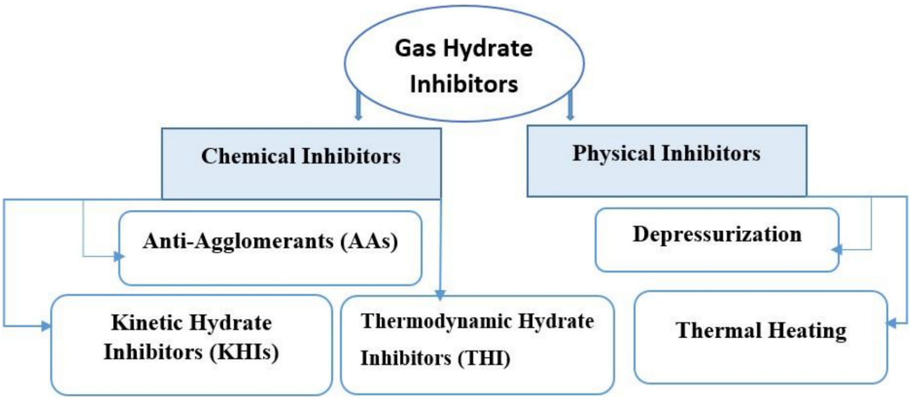


Fig. 4 Types of gas hydrate inhibitor

These methods are often applied in combination, depending on the operating conditions, economic feasibility, and environmental considerations. The continuous rise in research output reflects the ongoing complexity and importance of effective gas hydrate management in modern oil and gas operations.

4.1 Methods to avoid or reduce the formation of gas hydrates

The oil and gas industry employs a range of strategies to prevent or manage gas hydrate formation, which can disrupt flow assurance and pose safety risks. These approaches can be broadly categorized into thermodynamic, non-thermodynamic, and advanced or hybrid methods.

4.1.1 Thermodynamic methods (shifting the hydrate stability zone)

These methods aim to alter the pressure-temperature conditions to move the system outside the hydrate formation region.

Temperature control

Hydrate formation is unlikely above 21 °C. Maintaining system temperatures above this threshold is a primary method to prevent hydrate nucleation [35].

Pressure control

Reducing the system pressure below the hydrate equilibrium line effectively prevents hydrate formation [36].

Dehydration

Since water is essential for hydrate formation, removing free water or reducing its concentration below saturation levels is a direct and reliable strategy [37].

Thermodynamic hydrate inhibitors

Chemicals like methanol and MEG lower the hydrate formation temperature by disrupting water's hydrogen bonding. However, they are typically required in high concentrations, making them costly and potentially environmentally detrimental [21].

4.1.2 Non-thermodynamic methods (targeting kinetics and agglomeration)

These techniques do not shift the thermodynamic boundary but instead interfere with the hydrate formation process itself.

Kinetic hydrate inhibitors

These are low-dosage polymers (typically <2 wt%) that delay the nucleation and growth of hydrate crystals, allowing short-term operation within the hydrate formation zone [38].

Anti-agglomerants

AAs are surfactants that prevent hydrate particles from clumping together, keeping them suspended as a flowable slurry. Quaternary ammonium salts are common AAs used in flowlines and subsea operations [39].

4.1.3 Advanced and hybrid techniques

These innovative approaches combine the benefits of both thermodynamic and non-thermodynamic strategies or introduce novel mechanisms for hydrate mitigation.

Dual-function inhibitors

These multifunctional agents exhibit properties of both THIs and KHIs, offering a more holistic solution for hydrate management in dynamic environments [40].

Gas exchange techniques
In methane hydrate reservoirs, injection of CO_2 or CO_2/N_2 mixtures can displace methane and simultaneously sequester CO_2 in the hydrate structure, serving both production and environmental objectives [41].

Downhole pressure regulation
Installing pressure regulators in deeper, warmer sections of gas wells helps maintain pressure below hydrate formation limits in the upper wellbore, reducing risk in high-capacity gas production systems [42].

5 Dual-function gas hydrate inhibitors

A significant focus in recent gas hydrate research has been the development of dual-function inhibitors, a novel class of chemical agents capable of simultaneously exhibiting the properties of both thermodynamic hydrate inhibitors and kinetic hydrate inhibitors [43]. These multifunctional compounds are designed to address the limitations of conventional single-mode inhibitors by offering enhanced hydrate control with reduced chemical dosage requirements. Notable examples of dual-function inhibitors include nanoparticles, amino acids, and ionic liquids, each of which demonstrates the ability to interfere with both the thermodynamic stability and kinetic growth of hydrate structures [44, 45]. Qasim et al. [46] investigated the application of these multifunctional agents for mitigating not only gas hydrate formation but also pipeline corrosion, presenting an integrated solution for flow assurance in subsea environments. Mechanistically, dual-function inhibitors reduce the hydrate formation potential by shifting equilibrium conditions-similar to the action of THIs-while concurrently delaying nucleation and crystal growth, akin to KHIs [46, 47]. This combined effect leads to superior inhibition performance under a wider range of temperature and pressure conditions. Furthermore, the dual-action strategy allows for lower chemical dosages, thereby minimizing operational costs and reducing the environmental footprint compared to high-dosage traditional inhibitors [48]. As a result, dual-function inhibitors present a promising avenue for sustainable and efficient flow assurance in oil and gas production and transportation systems (Table 4) [49–56].

5.1 Ionic liquids

Ionic liquids (ILs) have emerged as highly promising materials in the field of gas hydrate inhibition due to their unique physicochemical properties. The pioneering work by Shin et al. [57] demonstrated the effectiveness of five imidazolium based ionic liquids in controlling hydrate formation. Their study systematically evaluated the influence of these ILs on both the hydrate equilibrium curve and the induction time for hydrate nucleation. The findings revealed that ionic liquids exhibit clear dual-functionality as hydrate inhibitors. As thermodynamic hydrate inhibitors, they shift the hydrate equilibrium curve to lower temperatures, thereby reducing the window for hydrate stability. Concurrently, they act as kinetic hydrate

Table 4 Dual function gas hydrate inhibitors

S. No	Inhibitor type	Example(s)	Functions	References
1	Ammonium-based ionic liquids (AILs)	Tetraethylammonium bromide (TEABr), Tetra-n-butylammonium bromide (TBAB)	Shift hydrate equilibrium (THI) and delay nucleation/growth (KHI)	[49]
2	Quaternary ammonium salts	Tetrabutylammonium fluoride, chloride, iodide	Thermodynamic suppression and kinetic inhibition	[50]
3	Deep eutectic solvents (DESs)	Choline chloride + urea or glycerol	Lower hydrate formation temperature and extend induction time	[51]
4	Hydrophobically modified polymers	Modified poly(N-vinylpyrrolidone)	Kinetic inhibition and minor thermodynamic effect	[52]
5	THI-KHI synergistic blends	Methanol + KHI (e.g., polyvinylpyrrolidone or poly-caprolactam	Combined suppression of hydrate formation and crystal growth	[53]
6	Imidazolium-based ionic liquids	1-Butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium chloride	Dual inhibition depending on gas type and conditions	[54]
7	Quaternary phosphonium salts	Tetrabutylphosphonium bromide (TBPB)	Act as inhibitors under specific hydrate structures (e.g., CO_2)	[55]
8	Alcohol-ether hybrid molecules	Diethylene glycol monoethyl ether	Moderate thermodynamic and kinetic inhibition	[56]

inhibitors by prolonging the induction time before hydrate formation commences. This combined effect significantly enhances their performance in hydrate mitigation strategies. The dual-action mechanism is largely attributed to the strong hydrogen bonding and electrostatic interactions between ionic liquid constituents and water molecules. These interactions disrupt the water lattice structure essential for hydrate formation, thereby enhancing both thermodynamic and kinetic inhibition characteristics. Consequently, ionic liquids have outperformed many conventional inhibitors, offering higher efficiency and the potential for reduced environmental impact. Their tunable molecular structure further allows for optimization toward specific operational conditions in oil and gas flow systems, making them a valuable class of next-generation hydrate inhibitors (Table 5) [57–64].

5.1.1 Thermodynamics and kinetic performance of quaternary ammonium salt inhibitors

Quaternary ammonium salts act primarily as thermodynamic hydrate inhibitors by shifting hydrate equilibrium to lower temperatures and high pressure, while some salts also exhibit kinetic inhibition effects by delaying nucleation and crystal growth [65]. Their dual functionality, reduced volatility, and lower dosage compared to conventional alcohols have attracted increasing attention in natural gas hydrate mitigation [66]. The comparative performance and data can be seen in Table 6 [67].

Table 5 Dual function ionic liquids as gas hydrate inhibitors

S. No	Ionic liquid (IL)	Cation type	Anion type	Inhibition type	Mechanism	Reference
1	1-Butyl-3-methylimidazolium tetrafluoroborate	Imidazolium	BF_4^-	THI + KHI	Shifts equilibrium temp, increases induction time	[57]
2	1-Hexyl-3-methylimidazolium chloride	Imidazolium	Cl^-	THI + KHI	Electrostatic interaction, hydrogen bonding	[58]
3	Tetra-n-butylammonium bromide	Ammonium	Br^-	THI + KHI	Forms semi-clathrate structures; stabilizes water structure	[59]
4	Tetraethylammonium bromide	Ammonium	Br^-	THI + KHI	Alters hydrate phase boundary, delays growth	[60]
5	1-Butyl-3-methylimidazolium acetate	Imidazolium	CH_3COO^-	THI + KHI	Disrupts water network, delays nucleation	[61]
6	Choline-based ILs (e.g., choline chloride)	Choline	Cl^-	THI + KHI	Strong hydrogen bonding with water, eco-friendly	[62]
7	1-Ethyl-3-methylimidazolium dicyanamide	Imidazolium	$N(CN)_2^-$	THI + KHI	Lowers hydrate stability and growth rate	[63]
8	Tetrabutylphosphonium bromide	Phosphonium	Br^-	THI + KHI (system-specific)	Alters CO_2 hydrate systems, delays plug formation	[64]

Table 6 Comparative performance and evaluation [67]

Inhibitors	Thermodynamic performance (THI)	Kinetic performance (KHI)	Advantage	Limitations
Tetraethylammoniumbromide	Moderate to strong equilibrium shift, effective for CO_2-rich and mix gas hydrate	Moderate delay in nucleation and growth	Lover dosage than methanol, dual THI and KHI, good solubility in water	Limited industrial field data, bromide related corrosion concerns
Tetrabutylammoniumbromide	Strong THI effect, form semi clathrate hydrate that suppress gas hydrate formation	Limited kinetic inhibitions	High inhibition efficiency, stable under high pressure	High molecular mass, viscosity increase, potential plugging due to semi-clathrates
Tetrapropylammonium bromide (TPABr)	Intermediate THI performance between TEABr and TBAB	Moderate kinetic inhibitions	Balanced thermodynamic and kinetic behavior, lower viscosity than TBAB	Less experimental data than TBAB, cost considerations
Other quaternary ammonium salts (tetrabutylammonium chloride (TBACl), tetraethylammonium chloride (TEACl))	Variable THI performance depending on alkyl chain length and counter-ion	Generally weak to moderate KHI behavior	Tunable structure, potential for synergistic blends	Counter-ion effects on corrosion, environmental impact not fully assessed

5.2 Amino acids

With increasing environmental concerns surrounding the use of conventional chemical inhibitors, the oil and gas industry is progressively shifting toward green and sustainable alternatives. Among these, amino acids have gained significant attention as eco-friendly and biodegradable gas hydrate inhibitors [68]. Their non-toxic nature, water solubility, and low environmental footprint make them particularly attractive for offshore and environmentally sensitive applications.

Several experimental investigations have demonstrated the efficacy of various amino acids in inhibiting hydrate formation. These biomolecules exhibit dual-inhibition capabilities-similar to conventional thermodynamic and kinetic hydrate inhibitors-by interfering with both the nucleation and growth phases of hydrate formation. Their ability to form hydrogen bonds with water molecules disrupts the ordered water structure needed for hydrate crystal formation, thereby lowering the thermodynamic driving force and delaying the onset of hydrate nucleation. In addition to their environmental benefits, amino acids offer advantages such as low dosage requirements, compatibility with existing flow assurance chemicals, and cost-effectiveness due to their availability from natural sources or biosynthesis. Table 7 summarizes the most commonly studied amino acids and their relative performance as gas hydrate inhibitors based on recent literature [53, 54, 69–74].

5.3 Nanoparticles

Nanoparticles have emerged as a promising class of dual-function gas hydrate inhibitors due to their unique physicochemical characteristics, including a high surface area-to-volume ratio, tunable surface functionality, and strong interfacial interactions with water molecules [75]. These properties enable nanoparticles to interfere with both the thermodynamic stability and the kinetic pathways of hydrate formation (see in Table 8 [76–83]).

By altering the local water structure and disrupting the hydrogen-bonding network necessary for hydrate cage formation, nanoparticles can act as thermodynamic inhibitors. Simultaneously, they hinder crystal nucleation and growth, thereby functioning as kinetic inhibitors. This dual-action mechanism enhances the overall efficiency of hydrate prevention and allows for lower dosage levels, which contributes to cost-effectiveness and environmental compatibility. Recent studies have explored various types of nanoparticles, such as silica, carbon nanotubes, graphene oxide, and metal-organic frameworks (MOFs)-demonstrating their effectiveness in delaying hydrate onset and shifting equilibrium conditions. Moreover, surface modification of nanoparticles (e.g., with hydrophilic or amphiphilic functional groups) can further optimize their performance by enhancing dispersibility and interaction with water molecules. As research continues, nanoparticle based inhibitors are anticipated to play a vital role in developing next-generation flow assurance strategies for oil and gas pipelines.

6 Fundamentals of modeling techniques for gas hydrate formation

The foundational principles for modeling gas hydrate formation can be traced back to the pioneering work of Ng et al. [84], who introduced the concept of phase equilibrium over a century ago. His thermodynamic criteria

Table 7 Dual function amino acids as gas hydrate inhibitors

S. No	Amino acid	Structure type	Function	Mechanism	Remarks	References
1	Glycine	Simple aliphatic	THI + KHI	Forms hydrogen bonds with water; interferes with hydrate nucleation	Biodegradable, low toxicity	[69]
2	L-Glutamic acid	Acidic	THI + KHI	Lowers hydrate equilibrium temperature; delays formation	Highly effective at low concentrations	[54]
3	L-Serine	Polar, uncharged	THI + KHI	Disrupts hydrate cage formation *via* hydrogen bonding	Shows good kinetic inhibition	[53]
4	L-Leucine	Nonpolar, aliphatic	THI + KHI	Alters structure of water and interferes with hydrate growth	High thermal stability	[70]
5	L-Lysine	Basic	THI + KHI	Electrostatic interaction with water; delays hydrate nucleation	Effective at mild concentrations	[71]
6	L-Tyrosine	Aromatic	THI + KHI	π-p interactions and hydrogen bonding hinder hydrate cage stability	Less soluble, used in blends	[72]
7	L-Arginine	Basic	THI + KHI	Strong hydrogen bonding; shifts hydrate equilibrium	High water solubility	[73]
8	L-Aspartic acid	Acidic	THI + KHI	Alters hydrogen-bonding network in water phase	Environmentally friendly option	[74]

Table 8 Dual function nanoparticles as gas hydrate inhibitors

S. No	Nanoparticle type	Chemical composition	Function	Mechanism	Remarks	References
1	Silica nanoparticles (SiO_2)	Silicon dioxide	THI + KHI	Disrupt water structure, hinder hydrate cage formation	Can be surface-modified for enhanced effect	[76]
2	Carbon nanotubes (CNTs)	Cylindrical carbon structures	THI + KHI	Adsorb water/gas molecules, alter local thermodynamics	High surface area and thermal conductivity	[77]
3	Graphene oxide (GO)	Oxidized graphene	THI + KHI	Hydrogen bonding with water, delays hydrate nucleation	Eco-friendly and thermally stable	[78]
4	Metal oxide nanoparticles	ZnO, Al_2O_3, TiO_2, CuO	THI + KHI	Interact with water molecules, interfere with hydrate lattice formation	Effective at low concentrations	[79]
5	Silver nanoparticles (AgNPs)	Nanoscale silver	THI + KHI	Electrostatic and van der Waals interactions with hydrate-forming species	Antimicrobial and inhibitory dual role	[80]
6	Magnetite nanoparticles	Fe_3O_4	THI + KHI	Disrupt hydrogen bonding, magnetic field enhances dispersion	Can be recovered magnetically	[81]
7	Copper oxide nanoparticles	CuO	THI + KHI	Interfere with gas diffusion and water structuring	Stable in harsh environments	[82]
8	Cellulose nanocrystals (CNCs)	Natural polymer-based	THI + KHI	Modify hydrogen bonding network of water	Renewable and biodegradable	[83]

for equilibrium laid the groundwork for the development of advanced modeling tools used in predicting gas hydrate behavior. According to Gibbs' conditions for phase equilibrium:

- the chemical potential of each component must be equal in all coexisting phases;
- the temperature and pressure must be uniform across all phases;
- the global Gibbs free energy of the system must be minimized.

These principles are fundamental to accurately describing the phase behavior of complex gas hydrate systems. They enable the formulation of models capable of predicting hydrate formation and dissociation conditions under varying temperature, pressure, and compositional regimes.

Over time, three major modeling approaches have evolved to estimate hydrate formation conditions:

- statistical model;
- equilibrium model;
- multi-component statistical model.

6.1 Statistical model

These models are primarily based on the van der Waals–Platteeuw theory [6], which employs statistical thermodynamics to describe the occupancy of guest molecules in hydrate cages. This pioneering framework was the earliest theoretical approach designed to quantify the thermodynamic behavior of gas hydrate systems, specifically focusing on the occupancy of guest molecules within the hydrate lattice. The key assumption is that hydrate formation is a non-stoichiometric process, and the model uses Langmuir adsorption isotherms to compute the probability of cage occupancy. The model drew inspiration from adsorption theory, treating the incorporation of guest molecules into hydrate cages similarly, to how gases adsorb onto a solid surface. It laid the theoretical foundation for modern hydrate thermodynamic modeling, particularly for systems involving a single guest molecule occupying a specific cavity type in the hydrate structure.

6.1.1 Thermodynamic framework

At the core of the statistical model lies the expression for the chemical potential difference between water in the hydrate phase (μ_H) and in the reference empty lattice phase (μ_β), given as:

$$\mu_H - \mu_\beta = RT \sum\nolimits_i V_i \ln\left(1 - Y_i\right), \tag{1}$$

where:

- μ_H: chemical potential of water in hydrate phase;
- μ_β: chemical potential of water in the empty hydrate lattice;
- R: universal gas constant;
- T: absolute temperature;
- V_i: number of cavities of type i per water molecule;
- Y_i: probability that a cavity of type i is occupied by a guest molecule.

6.1.2 Probability function

The occupancy probability Y_i, which represents the likelihood of a cavity of type *i* being occupied by a guest molecule, is given by the Langmuir-type expression:

$$Y_i = \frac{C_i P}{1 + C_i P}, \tag{2}$$

where:

- C_i: Langmuir constant for cavity type i, a function of guest-host interaction;
- P: partial pressure of the guest gas.

This model assumes that:

- hydrate formation is a non-stoichiometric process;
- guest molecules do not distort the hydrate cage;
- there is no interaction between guest molecules in adjacent cavities.

The van der Waals–Platteeuw model remains the cornerstone of hydrate thermodynamic modeling and has been extended over the years to handle multi-component systems, varying pressure-temperature conditions, and structural variations in hydrate cages.

6.2 Equilibrium model

These models use thermodynamic equilibrium criteria, incorporating equations of state (e.g., Peng-Robinson, Soave-Redlich-Kwong) and activity coefficient models to describe fluid phases. Hydrate phase is typically modeled using empirical or semi-empirical formulations derived from experimental data. The model proposed by Ng et al. [84] marked a significant advancement in gas hydrate modeling. This approach enabled the prediction of gas hydrate formation under equilibrium conditions in systems where hydrocarbons coexist with an aqueous phase [6]. Before applying this model, it is essential to assess volumetric changes and enthalpy variations during hydrate formation. Additionally, an equivalent expression for permeability (perms) can be utilized to enhance model accuracy [85]. To calculate component fugacity, the model employs the Peng–Robinson equation of state (EoS), which was originally introduced in 1976 [86]. This equation provides a versatile framework for simulating hydrates in both gas and non-aqueous liquid phases, making it suitable for complex multiphase systems. To better match the specific systems modeled by Ng and Robinson, modifications to the EoS parameters were later proposed [84]. Alternatively, the Soave equation of state, introduced in 1972, or other dual-purpose EoS formulations that perform effectively in both gas and liquid phases, can also be employed. Over time, the Peng-Robinson and Soave EoS-along with their modified forms-have become essential tools for thermodynamic modeling in the oil and gas industry, particularly in the domains of flow assurance and hydrate prediction [87].

6.3 Multi-component statistical model

While the original statistical model provided a foundational framework for calculating gas hydrate formation, it was eventually found to lack the precision needed for reliable predictions. To address these limitations, Parrish and Prausnitz [88] introduced a modified statistical model that significantly improved the accuracy of hydrate formation estimates. This enhanced model incorporated two major advancements over its predecessor:

1. it accounted for multi-component gas mixtures participating in hydrate formation;
2. it considered the overall composition of all components within the system [89].

The model is expressed as:

$$\mu_H - \mu_\beta = RT \sum\nolimits_i V_i \ln\left(1 - \sum\nolimits_k Y_{ki}\right). \tag{3}$$

In Eq. (3):

- The first equation represents the chemical potential difference between the hydrate phase (μ_H) and the empty lattice or reference phase (μ_β).
- The second equation defines the occupancy probability Y_{ki} of guest molecule *k* in cavity type *i*, which depends on the Langmuir constant c_i, the partial pressure P_k, and contributions from all competing gases. This model captures the competitive occupancy of hydrate cavities by multiple gas species, reflecting the non-ideal behavior of the gas phase-especially at high pressures, where such competition becomes significant. Importantly, even non-occupying gases are considered, as their presence influences cavity occupancy probabilities by reducing the likelihood of guest molecule encapsulation. To further enhance predictive capability and improve agreement with experimental data, minor modifications were later made to better capture pressure-induced effects and to fine-tune curve fitting.

7 Models for machine learning and scientific inquiry

7.1 Artificial neural networks

An artificial neural network (ANN) is a type of machine learning (ML) model that draws inspiration from the composition and operations of the human brain. They are very good at capturing complicated nonlinear correlations between input and output variables, which makes them ideal for modeling complex processes that frequently involve multivariate, nonlinear, and dynamic interactions, such as gas hydrate formation and inhibition [90]. In gas hydrate systems, where temperature, pressure, composition, inhibitors, and flow dynamics interact in a nonlinear way, artificial neural networks are effective stand-in models for classic physical or empirical models that are either computationally or analytically unfeasible [91].

7.1.1 Architecture and working mechanism

ANNs typically consist of multiple layers of interconnected computational units or "neurons", organized as follows:

- input layer: receives the feature vector, which may include variables such as pressure, temperature, gas composition, and inhibitor concentration;
- hidden layers: perform nonlinear transformations using weighted summation and activation functions. These layers enable the network to capture and learn complex patterns;
- output layer: produces the final prediction, such as the probability of hydrate formation, induction time, or inhibition efficiency.

The artificial neural network in gas modeling can be seen in Fig. 5 [92]. The descriptions of the symbols of Fig. 5 can be seen in Table 9.

7.2 Decision tree

Decision trees are a widely used supervised machine learning ML algorithm applicable to both classification and regression tasks. They operate by recursively partitioning the dataset based on feature values, creating a tree-like structure where each internal node represents a decision rule, and each leaf node corresponds to an outcome. Due to their transparency and simplicity, decision trees are particularly favored in applications where model interpretability is essential, as they closely emulate human reasoning.

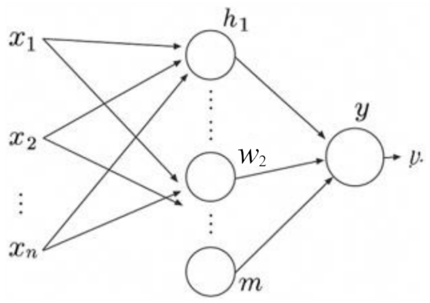
7.2.1 Working mechanism

The construction of a decision tree follows these key steps:

1. Initialization: begin with the entire training dataset at the root node.
2. Feature selection: at each node, select the feature and corresponding threshold that best splits the data. This is typically based on criteria such as *Gini impurity*, *information gain*, or *variance reduction* (for regression).
3. Data partitioning: split the dataset into subsets according to the chosen feature and threshold.
4. Recursive splitting: apply the same procedure recursively to each subset (branch), building the tree layer by layer.
5. Stopping criteria: Terminate the splitting process when a predefined condition is met (e.g., maximum tree depth, minimum number of samples per node, or minimal gain from further splits).
6. Prediction assignment: Assign a final output (class label or regression value) to each terminal node

$$y = f\left(\sum_{i=1}^{2} {}^{w_j b} + b\right)$$

$$h = f\left(w_{i,j}^{(n)} x_i + b_j^{(1)}\right)$$



$$y = g\left(w_j^{(2)} h_j + b_j^{(2)}\right)$$

Fig. 5 Artificial neural network in gas hydrate modeling [92]

Table 9 Symbols and descriptions of artificial neural network in gas modeling

Symbol	Description
y	Output of the neuron
x_i	x_i is the i^{th} input or activation from previous layer
w_i	Weight assigned to each input
n	Number of input features
$\sum$	Summation symbol, indicating that we add up the products of all inputs nad weight from 1 to n
$v.$	Producing a final output value
h_1	The first neuron in the hidden layer
b	Bias term
$w_j^{(2)}$	Weight associated with the input h_j for the second layer
f	Activation functions (e.g., ReLU, Sigmoid)
$w_{i,j}^{(n)}$	Weight associated with the connection between the i^{th} input and j^{th} neuron in the n^{th} layer
h_j	Output from the j^{th} hidden neuron
$b_j^{(1)}$	Bias term for the j^{th} neuron in the first layer
$b_j^{(2)}$	Bias term for the j^{th} neuron in the second layer
m	Represent the total number of nodes in the hidden layer
g	Activation functions (e.g., ReLU, Sigmoid)

(leaf) based on the majority class or average value of data points within the leaf.

Decision trees offer intuitive insights into feature importance and decision pathways, making them a foundational model in explainable ML. The data of field scale and Pilot scale experiences with inhibitors and predictive modeling can be seen in Table 10 [93].

When sophisticated corrosion inhibitors and predictive modelling methods are used together in industrial settings, there are obvious operational, environmental, and economic benefits [94]. High performance, environmentally safe inhibitors minimize toxic waste and guarantee long lasting protection in challenging oil and gas environments [95]. In the mean-time data driven optimization of inhibitor dosing and asset management is made possible by ML, probabilistic, and life cycle models. This reduces chemical usage and maintenance cost and supports well-informed, long term infrastructure and sustainability decisions.

8 Conclusion

In the oil and gas industry, gas hydrates continue to provide serious and complex problems, particularly in subsea and deepwater pipeline environments. They can seriously impair flow assurance when they form in high-pressure, low-temperature environments, resulting in operational delays and significant financial losses. The mechanisms of hydrate formation, structural classifications, and their effects on pipeline systems have all been thoroughly examined in this review. Conventional mitigation strategies, such kinetic and thermodynamic inhibitors, have been crucial, but they are frequently limited by issues like low efficiency, high cost, and environmental problems. By improving inhibition performance while reducing ecological effect, recent developments, such as the creation of dual-function inhibitors including ionic liquids, amino acids, and nanoparticles, provide intriguing substitutes. Additionally, predictive capabilities and operational planning have been greatly enhanced by the use of sophisticated modelling techniques, which range from statistical and thermodynamic models to ML tools like artificial neural networks and decision trees. A comprehensive strategy combining cutting-edge chemical solutions, ongoing monitoring, and sophisticated predictive modelling is necessary for the oil and gas industry to maintain safe, effective, and economical energy transfer. The development of next-generation inhibitors and strong modelling frameworks to successfully address hydrate-related problems in an operational environment that is becoming more and more demanding will require ongoing multidisciplinary research and cooperation between industry and academia.

Acknowledgement

The authors express their heartfelt gratitude to the University Grants Commission (UGC), India, for funding this study through the National Eligibility Test (NET) Junior Research Fellowship (JRF) program and also extend their thankful to Universiti Teknology Petronas, Malaysia and Lovely Professional University, Punjab, India. The preparation of this review paper, including the required research and analysis, was made possible through this support. The assistance from UGC's has been crucial in accomplishing the goals of this work.

Table 10 Field scale and pilot scale experiences with inhibitors and predictive modeling [93]

Category	Approach/system	Key findings	Practical benefit
Green inhibitors	Organic inhibitor, eggshell-drives extraction	Achieved inhibition efficiency exceeding 80–90% in acidic pickling environments	Reduce environmental toxicity, safe waste disposal, and compliance with green regulations
Hybrid inhibitors	Organic-inorganic combinations	Demonstrate superior durability under high- stress industrial conditions	Extended service life and reduce maintenance frequency
Oil and gas inhibitors	Water dispersible inhibitors	Continue to serve as industry standards for CO_2/H_2S corrosion control	Proven reliability and long term pipeline integrity
ML-based models	ANN, Adaptive neuro-fuzzy inference system	Accurately predict full corrosion-rate time profiles	Shift from reactive maintenance to predictive corrosion management
Real–time optimization	Data driven plant scale models	Utilize daily operational data to dynamically adjust inhibitor dosage	Reduce over dosing, low operating costs, and real time process control
Molecular modeling	Density functional theory, simulation modeling	Provide detailed adsorption and interaction insights, through limited in real world complexity	Improved inhibitors design when integrated with experimental validation

References

[1] Cohen, J. E. "Human Population: The Next Half Century", Science, 302(5648), pp. 1172–1175, 2003. https://doi.org/10.1126/science.1088665

[2] Omer, A. M. "Energy, environment and sustainable development", Renewable and Sustainable Energy Reviews, 12(9), pp. 2265–2300, 2008. https://doi.org/10.1016/j.rser.2007.05.001

[3] Economides, M. J., Wood, D. A. "The state of natural gas", Journal of Natural Gas Science and Engineering, 1(1–2), pp. 1–13, 2009. https://doi.org/10.1016/j.jngse.2009.03.005

[4] Holuszko, M. E., de Klerk, A. "Chapter 3 - Coal Processing and Use for Power Generation", In: Future Energy: Improved, Sustainable and Clean Options for our Planet, Elsevier Science, 2014, pp. 53–73. ISBN 978-0-08-099424-6 https://doi.org/10.1016/B978-0-08-099424-6.00003-X

[5] Makogon, Y. F., Holditch, S. A., Makogon, T. Y. "Natural gas-hydrates — A potential energy source for the 21st century", Journal of Petroleum Science and Engineering, 56(1–3), pp. 14–31, 2007. https://doi.org/10.1016/j.petrol.2005.10.009

[6] Sloan, E. D., Koh, C. A., Sum, A. (eds.) "Natural Gas Hydrates in Flow Assurance", Gulf Professional Publishing, 2010. ISBN 9781856179454

[7] Zhang, S., Shang, L., Zhou, L., Lv, Z. "Hydrate Deposition Model and Flow Assurance Technology in Gas-Dominant Pipeline Transportation Systems: A Review", Energy & Fuels, 36(4), pp. 1747–1775, 2022. https://doi.org/10.1021/acs.energyfuels.1c03812

[8] Kótai, L., Gács, I., Bálint, S., Lakatos, G., Angyal, A., Mehrotra, R. N. "A review on the oldest known gas-hydrate - The chemistry of chlorine hydrate", Trends in Inorganic Chemistry, 13, pp. 33–92, 2012. [online] Available at: https://www.researchgate.net/publication/257922152_A_review_on_the_oldest_known_gas-hydrate_-_the_chemistry_of_chlorine_hydrate [Accessed: 11 January 2026]

[9] Lal, B., Nashed, O. "Chemical Additives for Gas Hydrates", Springer Cham, 2020. ISBN 978-3-030-30750-9 https://doi.org/10.1007/978-3-030-30750-9

[10] Rehman, A. U., Lal, B. "Gas-Hydrate-Forming Reactors for Carbon Capture and Storage", In: Lal, B., Manjusha, A. (eds.) Gas Hydrate in Carbon Capture, Transportation and Storage: Technological, Economic, and Environmental Aspects, CRC Press, 2024, pp. 44–60. ISBN 9781032726366

[11] Lal, B., Nallakukkala, S. (eds.) "Gas Hydrate in Water Treatment: Technological, Economic, and Industrial Aspects", John Wiley & Sons, Inc., 2022. ISBN 9781119866145 https://doi.org/10.1002/9781119866145

[12] Atta, M. R., Lal, B., Abdulwahab, A., Manjusha, A., Shariff, A. M., Foo, K. S. "Regenerated Monoethylene Glycol: A comprehensive systematic review of contaminant profiles and hydrate inhibition efficacy", Journal of Industrial and Engineering Chemistry, 147, pp. 1–19, 2025. https://doi.org/10.1016/j.jiec.2024.12.007

[13] Lal, B., Manjusha, A. (eds.) "Gas Hydrate in Carbon Capture, Transportation and Storage: Technological, Economic, and Environmental Aspects", CRC Press, 2024. ISBN 9781032726366 https://doi.org/10.1201/9781032726366

[14] Liang, S., Hall, K. W., Laaksonen, A., Zhang, Z., Kusalik, P. G. “Characterizing key features in the formation of ice and gas hydrate systems”, Philosophical Transactions of the Royal Society A, 377(2146), 20180167, 2019. https://doi.org/10.1098/rsta.2018.0167

[15] Cai, W., Huang, X., Lu, H. "Instrumental Methods for Cage Occupancy Estimation of Gas Hydrate", Energies, 15(2), 485, 2022. https://doi.org/10.3390/en15020485

[16] Rezania, P., Ranjbar, V., Nasrifar, K. "High Pressure Solubility of Light Gases (CH_4, C_2H_6, C_3H_8, H_2S, CO_2, N_2, Xe, Ar and Kr) and Certain Gas Mixtures in Water from Cubic Equations of State", Journal of Solution Chemistry, 50(9), pp. 1169–1188, 2021. https://doi.org/10.1007/s10953-021-01110-6

[17] Chatti, I., Delahaye, A., Fournaison, L., Petitet, J.-P. "Benefits and drawbacks of clathrate hydrates: A review of their areas of interest", Energy Conversion and Management, 46(9–10), pp. 1333–1343, 2005. https://doi.org/10.1016/j.enconman.2004.06.032

[18] Hammerschmidt, E. G. "Formation of Gas Hydrates in Natural Gas Transmission Lines", Industrial & Engineering Chemistry, 26(8), pp. 851–855, 1934. https://doi.org/10.1021/ie50296a010

[19] Theyab, M. A. "Fluid Flow Assurance Issues: Literature Review", SciFed Journal of Petroleum, 2(1), 1000001, 2018. [online] Available at: https://www.researchgate.net/publication/323733946_Fluid_Flow_Assurance_Issues_Literature_Review [Accessed: 11 January 2026]

[20] Kirchner, M. T., Boese, R., Billups, W. E., Norman, L. R. "Gas Hydrate Single-Crystal Structure Analyses", Journal of the American Chemical Society, 126(30), pp. 9407–9412, 2004. https://doi.org/10.1021/ja049247c

[21] Hassanpouryouzband, A., Joonaki, E., Vasheghani Farahani, M., Takeya, S., Ruppel, C., …, Aman, Z. M. "Gas hydrates in sustainable chemistry", Chemical Society Reviews, 49(15), pp. 5225–5309, 2020. https://doi.org/10.1039/C8CS00989A

[22] Liu, Z., Liu, X., Yang, M., Pang, W., Dou, B., Song, Y. "Thermodynamic and kinetic properties of gas hydrate phase transition from formation to decomposition with applications: A review", Journal of Environmental Chemical Engineering, 12(6), 114614, 2024. https://doi.org/10.1016/j.jece.2024.114614

[23] Amouzad Khalili, A., Yeganegi, S. "Molecular simulations of the adsorption and separation of hydrogen sulfide, carbon dioxide, methane, and nitrogen and their binary mixtures (H_2S/CH_4), (CO_2/CH_4) on NUM-3a metal-organic frameworks", Journal of Molecular Modeling, 27(5), 133, 2021. https://doi.org/10.1007/s00894-021-04709-0

[24] Ripmeester, J. A., Alavi, S. (eds.) "Clathrate Hydrates: Molecular Science and Characterization", Wiley-VCH GmbH., 2022. ISBN 9783527695058 https://doi.org/10.1002/9783527695058

[25] Hunter, R. B., Collett, T.S., Boswell, R., Anderson, B. J., Digert, S. A., Pospisil, G., Baker, R., Weeks, M. “Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope: Overview of scientific and technical program”, Marine and Petroleum Geology, 28(2), pp. 295–310, 2011. https://doi.org/10.1016/j.marpetgeo.2010.02.015

[26] Wei, N., Pei, J., Li, H., Zhou, S., Zhao, J., Kvamme, B., Coffin, R. B., Zhang, L., Zhang, Y., Xue, J. "Classification of natural gas hydrate resources: Review, application and prospect", Gas Science and Engineering, 124, 205269, 2024. https://doi.org/10.1016/j.jgsce.2024.205269

[27] Chupin, G. "An Experimental Investigation of Multiphase Gas-Liquid Pipe Flow at Low Liquid Loading", PhD thesis, Norwegian University of Science and Technology, 2003. [online] Available at: https://hdl.handle.net/11250/2660938 [Accessed: 11 January 2026]

[28] Vijayamohan, P. "Experimental investigation of gas hydrate formation, plugging and transportability in partially dispersed and water continuous systems", PhD dissertation, Colorado School of Mines, 2016.

[29] Aman, Z. M., Koh, C. A. "Interfacial phenomena in gas hydrate systems", Chemical Society Reviews, 45(6), pp. 1678–1690, 2016. https://doi.org/10.1039/C5CS00791G

[30] Shao, Z., Sun, J., Wang, J., Lv, K., Liao, B., Wang, R., Jiang, H. "Effects of Modified Cellulose on Methane Hydrate Decomposition: Experiments and Molecular Dynamics Simulations", ACS Sustainable Chemistry & Engineering, 9(29), pp. 9689–9697, 2021. https://doi.org/10.1021/acssuschemeng.1c01495

[31] Al-Sharify, Z. T., Faisal, M. L., Hamad, L. B., Jabbar, H. A. "A Review of Hydrate Formation in Oil and Gas Transition Pipes", IOP Conference Series: Materials Science and Engineering, 870(1), 012039, 2020. https://doi.org/10.1088/1757-899X/870/1/012039

[32] Zerpa, L. E., Salager, J.-L., Koh, C. A., Sloan, E. D., Sum, A. K. "Surface Chemistry and Gas Hydrates in Flow Assurance", Industrial & Engineering Chemistry Research, 50(1), pp. 188–197, 2011. https://doi.org/10.1021/ie100873k

[33] Gbaruko, B. C., Igwe, J. C., Gbaruko, P. N., Nwokeoma, R. C. "Gas hydrates and clathrates: Flow assurance, environmental and economic perspectives and the Nigerian liquified natural gas project", Journal of Petroleum Science and Engineering, 56(1–3), pp. 192–198, 2007. https://doi.org/10.1016/j.petrol.2005.12.011

[34] Ke, W., Kelland, M. A. "Kinetic Hydrate Inhibitor Studies for Gas Hydrate Systems: A Review of Experimental Equipment and Test Methods", Energy & Fuels, 30(12), pp. 10015–10028, 2016. https://doi.org/10.1021/acs.energyfuels.6b02739

[35] Salmin, D. C., Estanga, D., Koh, C. A. "Review of gas hydrate anti-agglomerant screening techniques", Fuel, 319, 122862, 2022. https://doi.org/10.1016/j.fuel.2021.122862

[36] Yu, Y.-S., Zhang, X., Liu, J.-W., Lee, Y., Li, X.-S. "Natural gas hydrate resources and hydrate technologies: A review and analysis of the associated energy and global warming challenges", Energy & Environmental Science, 14(11), pp. 5611–5668, 2021. https://doi.org/10.1039/D1EE02093E

[37] You, K., Flemings, P. B., Malinverno, A., Collett, T. S., Darnell, K. "Mechanisms of Methane Hydrate Formation in Geological Systems", Reviews of Geophysics, 57(4), pp. 1146–1196, 2019. https://doi.org/10.1029/2018RG000638

[38] Bozorgian, A., Samimi, A. "A review of Kinetics of Hydrate Formation and the Mechanism of the Effect of the inhibitors on it", International Journal of New Chemistry, 8(1), pp. 41–58, 2021. https://doi.org/10.22034/ijnc.2020.120906.1093

[39] Erfani, A., Varaminian, F., Muhammadi, M. "Gas hydrate formation inhibition using low dosage hydrate inhibitors", presented at 2nd National Iranian Conference on Gas Hydrate (NICGH), Semnan, Iran, May 15., 2013. [online] Available at: https://www.researchgate.net/publication/324606867_Gas_hydrate_formation_inhibition_using_low_dosage_hydrate_inhibitors [Accessed: 11 January 2026]

[40] Delroisse, H., Torré, J.-P., Dicharry, C. "Effects of a Quaternary Ammonium Salt on the Growth, Wettability, and Agglomeration of Structure II Hydrate Crystals", Energy & Fuels, 32(12), pp. 12277–12288, 2018. https://doi.org/10.1021/acs.energyfuels.8b02980

[41] Shahnazar, S., Bagheri, S., TermehYousefi, A., Mehrmashhadi, J., Abd Karim, M. S., Kadri, N. A. "Structure, mechanism, and performance evaluation of natural gas hydrate kinetic inhibitors", Reviews in Inorganic Chemistry, 38(1), pp. 1–19, 2018. https://doi.org/10.1515/revic-2017-0013

[42] Király, M., Sántha, K., Kállai-Szabó, B., Pencz, K. M., Ludányi, K., Kállai-Szabó, N., Antal, I. "Development and Dissolution Study of a β-Galactosidase Containing Drinking Straw", Pharmaceutics, 14(4), 769, 2022. https://doi.org/10.3390/pharmaceutics14040769

[43] Jha, N. K., Ali, M., Sarmadivaleh, M., Iglauer, S., Barifcani, A., Lebedev, M., Sangwai, J. "Low Salinity Surfactant Nanofluids For Enhanced CO2 Storage Application At High Pressure And Temperature", In: Fifth CO2 Geological Storage Workshop, Utrecht, Netherlands, 2018, pp. 1–4. ISBN 9781510876675 https://doi.org/10.3997/2214-4609.201802975

[44] Abbasian Rad, S., Rostami Khodaverdiloo, K., Karamoddin, M., Varaminian, F., Peyvandi, K. "Kinetic study of amino acids inhibition potential of Glycine and l-leucine on the ethane hydrate formation", Journal of Natural Gas Science and Engineering, 26, pp. 819–826, 2015. https://doi.org/10.1016/j.jngse.2015.06.053

[45] Amanullah, M., Al-Tahini, A. M. "Nano-Technology - Its Significance in Smart Fluid Development for Oil and Gas Field Application", In: SPE Saudi Arabia Section Technical Symposium, Al-Khobar, Saudi Arabia, 2009, SPE-126102-MS. ISBN 978-1-61399-021-6 https://doi.org/10.2118/126102-MS

[46] Qasim, A., Lal, B., Shariff, A. M., Ismail, M. C. "Role of Ionic Liquid-Based Multipurpose Gas Hydrate and Corrosion Inhibitors in Gas Transmission Pipeline", In: Inamuddin, Asirir, A. M. (eds.) Nanotechnology-Based Industrial Applications of Ionic Liquids, Springer, Cham, 2020, pp. 221–244. ISBN 978-3-030-44995-7 https://doi.org/10.1007/978-3-030-44995-7_11

[47] Herri, J.-M., Bouchemoua, A., Kwaterski, M., Fezoua, A., Ouabbas, Y., Cameirao, A. "Gas hydrate equilibria for CO_2–N_2 and CO_2–CH_4 gas mixtures—Experimental studies and thermodynamic modelling", Fluid Phase Equilibria, 301(2), pp. 171–190, 2011.
https://doi.org/10.1016/j.fluid.2010.09.041

[48] Both, A. K., Gao, Y., Zeng, X. C., Cheung, C. L. "Gas hydrates in confined space of nanoporous materials: new frontier in gas storage technology", Nanoscale, 13(16), pp. 7447–7470, 2021.
https://doi.org/10.1039/D1NR00751C

[49] Lee, S., Lee, Y., Park, S., Seo, Y. "Phase Equilibria of Semiclathrate Hydrate for Nitrogen in the Presence of Tetra-n-butylammonium Bromide and Fluoride", Journal of Chemical & Engineering Data, 55(12), pp. 5883–5886, 2010.
https://doi.org/10.1021/je100886b

[50] Kashish, Yusuf, M., Beg, M., Kamyab, H., Muzammil, K., Ahmad, M., Gupta, M., Kumar, S., Rezania, S., Ibrahim, H. "Natural gas hydrates: A review of various inhibitors and respective mechanisms", Journal of Molecular Liquids, 403, 124809, 2024.
https://doi.org/10.1016/j.molliq.2024.124809

[51] Zhang, T., Yu, Y., Lu, Y., Tang, H., Chen, K., Shi, J., Ren, Z., Wu, S., Xia, D., Zheng, Y. "Bridging biodegradable metals and biodegradable polymers: A comprehensive review of biodegradable metal–organic frameworks for biomedical application", Progress in Materials Science, 155, 101526, 2026.
https://doi.org/10.1016/j.pmatsci.2025.101526

[52] Tutova, T. N., Ivanova, T. E., Sokolova, E. V., Nesmelova, L. A. "Influence of seed onion planting time on productivity and quality of bulb onion varieties", IOP Conference Series: Earth and Environmental Science, 949(1), 012082, 2022.
https://doi.org/10.1088/1755-1315/949/1/012082

[53] Kang, S.-P., Lee, J.-W. "Kinetic behaviors of CO_2 hydrates in porous media and effect of kinetic promoter on the formation kinetics", Chemical Engineering Science, 65(5), pp. 1840–1845, 2010.
https://doi.org/10.1016/j.ces.2009.11.027

[54] Kelland, M. A. "History of the Development of Low Dosage Hydrate Inhibitors", Energy & Fuels, 20(3), pp. 825–847, 2006.
https://doi.org/10.1021/ef050427x

[55] Qureshi, M. F., Atilhan, M., Altamash, T., Tariq, M., Khraisheh, M., Aparicio, S., Tohidi, B. "Gas Hydrate Prevention and Flow Assurance by Using Mixtures of Ionic Liquids and Synergent Compounds: Combined Kinetics and Thermodynamic Approach", Energy & Fuels, 30(4), pp. 3541–3548, 2016.
https://doi.org/10.1021/acs.energyfuels.5b03001

[56] Elhenawy, S., Khraisheh, M., Almomani, F., Al-Ghouti, M. A., Hassan, M. K., Al-Muhtaseb, A. "Towards Gas Hydrate-Free Pipelines: A Comprehensive Review of Gas Hydrate Inhibition Techniques", Energies, 15(22), 8551, 2022.
https://doi.org/10.3390/en15228551

[57] Shin, B. S., Kim, E. S., Kwak, S. K., Lim, J. S., Kim, K.-S., Kang, J. W. "Thermodynamic inhibition effects of ionic liquids on the formation of condensed carbon dioxide hydrate", Fluid Phase Equilibria, 382, pp. 270–278, 2014.
https://doi.org/10.1016/j.fluid.2014.09.019

[58] Li, B., Lu, Y.-Y., Li, Y.-L. "A Review of Natural Gas Hydrate Formation with Amino Acids", Journal of Marine Science and Engineering, 10(8), 1134, 2022.
https://doi.org/10.3390/jmse10081134

[59] Li, H., Li, S., Hou, R., Rao, Y., Guo, S., Chang, Z., Zhou, H. "Recent advances in zinc-ion dehydration strategies for optimized Zn–metal batteries", Chemical Society Review, 53(15), pp. 7742–7783, 2024.
https://doi.org/10.1039/D4CS00343H

[60] Qin, Y., Shang, L., Song, R., Zhou, L., Lv, Z. "Progress in research on dispersants in gas hydrate control technology", Journal of Dispersion Science and Technology, 44(8), pp. 1500–1515, 2023.
https://doi.org/10.1080/01932691.2021.2022492

[61] Li, Y., Xiao, S., Yuan, B., Wang, P., Zhang, B., Su, Q., Wang, X., Han, S., Zhu, J., Zhao, Y. "Ability of ionic liquids to inhibit the formation of methane hydrate: Insights from molecular dynamics simulations", Gas Science and Engineering, 110, 204878, 2023.
https://doi.org/10.1016/j.jgsce.2023.204878

[62] Kelland, M. A. "Production Chemicals for the Oil and Gas Industry", CRC Press, 2009. ISBN 9780429195921
https://doi.org/10.1201/9781420092974

[63] Kelland, M. A. "Production Chemicals for the Oil and Gas Industry", CRC Press, 2014. ISBN 9780429195945
https://doi.org/10.1201/b16648

[64] Qasim, A., Khan, M. S., Lal, B., Ismail, M. C., Rostani, K. "Quaternary ammonium salts as thermodynamic hydrate inhibitors in the presence and absence of monoethylene glycol for methane hydrates", Fuel, 259, 116219, 2020.
https://doi.org/10.1016/j.fuel.2019.116219

[65] Haq, I. U., Qasim, A., Lal, B., Zaini, D. B. "Mini review on environmental issues concerning conventional gas hydrate inhibitors", Process Safety Progress, 41(S1), pp. S129–S134, 2022.
https://doi.org/10.1002/prs.12325

[66] Sayani, J. K. S., Lal, B., Pedapati, S. R. "Comprehensive Review on Various Gas Hydrate Modelling Techniques: Prospects and Challenges", Archives of Computational Methods in Engineering, 29(4), pp. 2171–2207, 2022.
https://doi.org/10.1007/s11831-021-09651-1

[67] Kelland, M. A. "Gas Hydrate Control", In: Production Chemicals for the Oil and Gas Industry, CRC Press, pp. 225–250. ISBN 9780429195945

[68] Sloan, E. D., Koh, C. A. "Clathrate Hydrates of Natural Gases", CRC Press, 2007. ISBN 9780429129148
https://doi.org/10.1201/9781420008494

[69] Carroll, J. "Natural Gas Hydrates: A Guide for Engineers", Gulf Professional Publishing, 2014. ISBN 9780128005750

[70] Shin, S.-H., Lee, W., Kim, S.-M., Lee, M., Koo, J. M., Hwang, S. Y., Oh, D. X., Park, J. "Ion-conductive self-healing hydrogels based on an interpenetrating polymer network for a multimodal sensor", Chemical Engineering Journal, 371, pp. 452–460, 2019.
https://doi.org/10.1016/j.cej.2019.04.077

[71] Sloan, E. D. "Gas Hydrates: Review of Physical/Chemical Properties", Energy & Fuels, 12(2), pp. 191–196, 1998.
https://doi.org/10.1021/ef970164+

[72] Sun, R., Duan, Z. "Prediction of CH_4 and CO_2 hydrate phase equilibrium and cage occupancy from ab initio intermolecular potentials", Geochimica et Cosmochimica Acta, 69(18), pp. 4411–4424, 2005.
https://doi.org/10.1016/j.gca.2005.05.012

[73] Park, S., Lee, S., Lee, Y., Seo, Y. "CO_2 Capture from Simulated Fuel Gas Mixtures Using Semiclathrate Hydrates Formed by Quaternary Ammonium Salts", Environmental Science & Technology, 47(13), pp. 7571–7577, 2013.
https://doi.org/10.1021/es400966x

[74] Xu, C.-G., Li, X.-S. "Research progress on methane production from natural gas hydrates", RSC Advances, 5(67), pp. 54672–54699, 2015.
https://doi.org/10.1039/C4RA10248G

[75] Gudmundsson, J.-S., Parlaktuna, M., Khokhar, A. A. "Storage of Natural Gas as Frozen Hydrate", SPE Production & Facilities, 9(01), pp. 69–73, 1994.
https://doi.org/10.2118/24924-PA

[76] Sloan, E. D. "Fundamental principles and applications of natural gas hydrates", Nature, 426(6964), pp. 353–359, 2003.
https://doi.org/10.1038/nature02135

[77] Englezos, P. "Clathrate hydrates", Industrial & Engineering Chemistry Research, 32(7), pp. 1251–1274, 1993.
https://doi.org/10.1021/ie00019a001

[78] Makogon, Y. F. "Hydrates of Hydrocarbons", PennWell Publishing Company, 1997. ISBN 0-87814-718-7

[79] Sloan, E. D. "Clathrate hydrates of natural gases", CRC Press, 1998. ISBN 0824799372

[80] Sloan, E. D. "A changing hydrate paradigm—from apprehension to avoidance to risk management", Fluid Phase Equilibria, 228–229, pp. 67–74, 2005.
https://doi.org/10.1016/j.fluid.2004.08.009

[81] Licence, P. "Clathrate Hydrates of Natural Gases, third ed., E. Dendy Sloan, A. Koh Carolyn. Chemical Industries Series. CRC Press (2007). 752 p., £130, Hardcover.", Fuel, 87(13–14), p. 3158, 2008.
https://doi.org/10.1016/j.fuel.2008.03.028

[82] Ripmeester, J. A., Ratcliffe, C. I. "Low-temperature cross-polarization/magic angle spinning carbon-13 NMR of solid methane hydrates: structure, cage occupancy, and hydration number", The Journal of Physical Chemistry, 92(2), pp. 337–339, 1988.
https://doi.org/10.1021/j100313a018

[83] Ripmeester, J. A., Alavi, S. "An Introduction to Clathrate Hydrates", In: Clathrate Hydrates: Molecular Science and Characterization Wiley-VCH GmbH., 2022, pp. 27–63. ISBN 9783527695058
https://doi.org/10.1002/9783527695058.ch2

[84] Ng, H.-J., Petrunia, J. P., Robinson, D. B. "Experimental measurement and prediction of hydrate forming conditions in the nitrogen-propane-water system", Fluid Phase Equilibria, 1(4), pp. 283–291, 1977.
https://doi.org/10.1016/0378-3812(77)80011-3

[85] Koh, C. A., Sloan, E. D. "Natural gas hydrates: Recent advances and challenges in energy and environmental applications", AIChE Journal, 53(7), pp. 1636–1643, 2007.
https://doi.org/10.1002/aic.11219

[86] Wei, Y., Chen, Z., Satyro, M., Dong, C., Deng, H. "Compositional Simulation Using the Advanced Peng-Robinson Equation of State", In: SPE Reservoir Simulation Symposium, The Woodlands, TX, USA, 2011, SPE-141898-MS. ISBN 978-1-55563-324-0
https://doi.org/10.2118/141898-MS

[87] Koh, C. A. "Towards a fundamental understanding of natural gas hydrates", Chemical Society Reviews, 31(3), pp. 157–167, 2002.
https://doi.org/10.1039/B008672J

[88] Parrish, W. R., Prausnitz, J. M. "Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures", Industrial & Engineering Chemistry Process Design and Development, 11(1), pp. 26–35, 1972.
https://doi.org/10.1021/i260041a006

[89] Koh, C. A., Sum, A. K., Sloan, E. D. "Gas hydrates: Unlocking the energy from icy cages", Journal of Applied Physics, 106(6), 061101, 2009.
https://doi.org/10.1063/1.3216463

[90] Sahu, C., Kumar, R., Sangwai, J. S. "Comprehensive Review on Exploration and Drilling Techniques for Natural Gas Hydrate Reservoirs", Energy & Fuels, 34(10), pp. 11813–11839, 2020.
https://doi.org/10.1021/acs.energyfuels.0c02202

[91] Sloan, E. D. "Clathrate hydrates of natural gases", Marcel Dekker Inc., 1989. ISBN 0824782968

[92] Patroni Zavala, J. A., Mackay, E. J., Vazquez, O., Boak, L. S., Singleton, M., Ross, G. "The Cost and Value of Field, Laboratory, and Simulation Data for Validating Scale Inhibitor Treatment Models", In: SPE International Oilfield Scale Conference, Aberdeen, UK, 2008, SPE-114106-MS. ISBN 978-1-55563-169-7
https://doi.org/10.2118/114106-MS

[93] Aydinsoy, E. A., Aghamaliyev, Z. Z., Aghamaliyeva, D. B., Abbasov, V. B. "A systematic review of corrosion inhibitors in marine environments: insights from the last 5 years", Processes of Petrochemistry and Oil Refining, 25(3), pp. 793–843, 2024.
https://doi.org/10.62972/1726-4685.2024.3.793

[94] Rana, A., Arfaj, M. K., Saleh, T. A. "Advanced developments in shale inhibitors for oil production with low environmental footprints – A review", Fuel, 247, pp. 237–249, 2019.
https://doi.org/10.1016/j.fuel.2019.03.006

[95] Al-Hajri, N. M., Al-Ghamdi, A., Tariq, Z., Mahmoud, M. "Scale-Prediction/Inhibition Design Using Machine-Learning Techniques and Probabilistic Approach", SPE Production & Operations, 35(04), pp. 0987–1009, 2020.
https://doi.org/10.2118/198646-PA