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Perspective

Gas Hydrates: Applications and Advantages

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Abstract: Gas hydrates are promising components for a wide range of industries and the national economy. This paper outlines the gas hydrate application areas with the greatest potential. Gas hydrates of methane, ethane, propane, carbon dioxide and freon were investigated. Double gas hydrates were found to be coming into use. Natural and artificial hydrates are now being exploited. The main properties and component composition of hydrates, as well as their extraction methods are described. The key aspects of using hydrates in the energy industry, gas chemistry and petrochemistry, heat exchange systems and fire safety management are highlighted. These specific aspects were identified by analyzing the known experimental findings, results of mathematical modeling, bench and field tests, as well as trial runs of industrial systems. The recent advances in science and technology in this field were analyzed. The range of tasks that need to be tackled to improve the efficiency of using gas hydrates are defined.

Keywords: gas hydrates; potential uses; energy resources; conversion; fire safety; benefits

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1. Introduction

For a hundred years, the population increased four-fold and reached eight billion people [1]. The increase in population has led to an increase in energy consumption. Due to the deterioration of the climate, the need for environmentally friendly energy is increasing [2,3]. Burning natural gas is more environmentally friendly than burning coal or oil. The combustion of natural gas emits significantly less harmful gases NO_x and CO_2. When burning natural gas, there are practically no emissions of sulfur oxides. Today, natural gas is the largest source of energy growth. According to the Statistical Review of World Energy, the demand for natural gas is increasing every year [4].

By 2040, natural gas consumption is predicted to grow by 1.7% per annum compared to other fossil energy sources (0.9% per annum for liquid fuels and 1.3% per annum for coal) [5]. With the current world consumption of oil and natural gas produced by conventional methods, the reserves will last less than 50 years [1], which will lead to the search for new alternative energy sources. Production of only 15% of natural gas from open deposits of gas hydrates would provide mankind with clean energy for 200 years (at the current level of consumption) [1].

Gas hydrates are inclusion compounds in which the molecules of gas are located in the cavities of a polyhedral framework composed of water molecules. The guest–host interactions are of van der Waals type [6–8]. Huge reserves of natural gas hydrates occur in sub-oceanic sediments [9,10]. An increased interest in hydrates has given rise to production technologies for obtaining hydrates with certain properties and component composition [11]. Most often, methane hydrate is an object of study in the oil- [12] and energy industries [13,14]. In energy research, the methods of extracting natural gas from methane hydrate and its subsequent use as a fuel are most often investigated [15–19]. Despite the far-reaching prospects of gas hydrates, their application technologies still need elaboration [20–22]. Slow adoption of technologies for using gas hydrates is explained by a great number of unsolved scientific and technological problems that are reflected in this review. The motivation of this study stems from the need to summarize the latest advances in science and technologies of using hydrates in different applications and the importance of identifying a group of promising objectives for global science and leading engineering companies and centers. Known experimental findings, results of mathematical modeling, bench and field tests, as well as trial runs have been reviewed.

However, gas hydrate recovery technologies have not been widely accepted to date due to the high financial costs associated with extraction, storage and transportation compared to traditional methods for extracting natural gas [3,23]. For faster development of technologies associated with gas hydrates, further research is needed to reduce the cost of production, storage and transportation of this natural raw material.

The purpose of this research was to outline the most promising areas of gas hydrate application and relevant unaccomplished science and technology objectives in these areas by reviewing the new developments in science and technology.

2. Classification of Gas Hydrates

Gas hydrates can be formed of different gases [6,24]. The chief constituents are usually methane, propane, ethane, isopropanol and carbon dioxide [22,25–27]. The main gas hydrate structures are unit cells sI, sII and sH [8,24]. Pure methane hydrate forms the structure I (sI). It is almost impossible, though, to find pure methane hydrates, as they inevitably contain a certain amount of larger hydrocarbons such as ethane and propane. The properties of double gas hydrates are more complex than those of single gas hydrates. In addition to ethane, there is also propane in natural gas. It is a heavy hydrocarbon gas that also has a direct effect on the thermodynamics and kinetic properties of mixed gas hydrates. Even a small amount of propane mixed with methane was found to form a gas hydrate with the structure sII rather than sI. Including 3–5% propane in methane may improve the kinetics of a double gas hydrate formation [24].

Methane hydrate formation can be represented by the following exothermic reaction, where n is the hydration number that varies depending on the hydrate structure: 5.75 in gas hydrates of structure I (subject to change with partial cage occupancy and under thermobaric conditions): $CH_4 + nH_2O \rightarrow CH_4 \cdot nH_2O \Delta H = -54.49$ kJ/mol [28].

Depending on the geological formations and phase composition of clusters, natural gas hydrates can be divided into four main classes [29,30]. Class 1 is represented by hydrates between impermeable strata as two layers, where the upper layer is a hydrate layer underlaid by a gas–liquid two-phase layer (North Slope of Alaska). Class 2 consists of hydrates whose upper layer is underlaid by a mobile water layer. Both these layers are between impermeable layers (Nankai Trough, Japan). Class 3 is represented by hydrates forming a layer between impermeable layers (Qilian Mountain, China). Class 4 hydrates are deposits with a disperse and low hydrate saturation and absence of impermeable layers (Krishna Godavari Basin, India).

By origin, gas hydrates are usually divided into synthetic and natural ones [31]. Gas hydrates are often formed in natural gas production sites, such as well bores, pipelines and reservoirs [32]. This is a drawback for technological processes, because the formation of hydrates in this case may lead to flow line blockage and, consequently, accidents [33]. At the same time, gas hydrates can serve some practical needs such as sea water desalination, treatment and separation of gas, its storage in large volumes and others. Natural gas hydrates are formed far from production facilities in areas with low temperatures and high pressure: in permafrost zones, lakes, seas and oceans, at a depth of 300 to 1500 m [34,35].

Classification by several types is given in Table 1.

So far, little attention has been paid to double gas hydrates consisting of combustible gases (methane–ethane, methane–propane, methane–isopropanol, etc.). The study of double gas hydrate characteristics and specific aspects is a relevant issue to be addressed.

Table 1. Classification of gas hydrates.

Type of Classification	Types
Unit cells	sI sII sH
Geological formations and phase composition of clusters	Class 1 (North Slope of Alaska) Class 2 (Nankai Trough, Japan) Class 3 (Qilian Mountain, China) Class 4 (Krishna Godavari Basin, India)
Origin	Synthetic Natural

3. Improving Storage and Transportation Efficiency of Gas Hydrates

3.1. Prospects of Developing Technologies Based on Gas Hydrates

Liquefied natural gas transportation in tankers is associated with high energy costs, as it requires steady cryogenic temperatures. Moreover, there is a high gas explosion hazard during such transportation in case of improper storage conditions due to possible natural disasters. Large reserves of natural gas in gas hydrate deposits promote the search for new, safer ways of raw material transportation. The prospects of developing the technologies of extracting natural gas hydrates as a potential energy source were considered in [1,13,36–42]. Gas hydrate reserves are estimated to make up 1.5×10^{16} m^3 on the land and offshore. Programs of the study of natural gas hydrate properties and gas hydrate technology development are being developed in the USA, Japan, Russia, China, India, Korea and others [43–48]. The number of scientific papers focusing on gas hydrates is increasing every decade, which is driven by the need for reducing gas hydrate extraction, transportation and storage costs (Figure 1). Gas hydrate technology development has enormous potential not only due to the depletion of traditional energy sources such as oil and coal fuels, but also because of environmental issues. The reduction in hazardous emissions from hydrocarbon fuel combustion is a relevant issue nowadays. Different ways of cutting emissions from gas hydrate combustion were explored in [49–51].

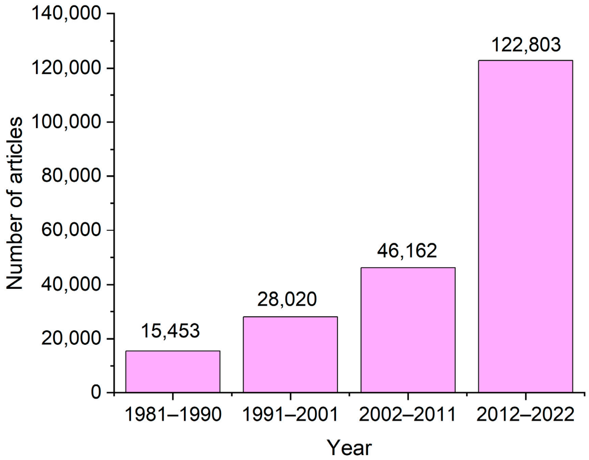


Figure 1. The number of published articles by years on the subject of gas hydrates according to the Web of Science.

The problem of studying natural gas hydrates is related to their occurrence at great depths in a porous medium containing silica, clays, zeolites and polymers. The properties of the environment and limited space have a strong influence on the kinetics of gas hydrate growth and decomposition [52]. The characteristic size of the cavity inside the pore can reach about 10 molecular diameters. A decrease in the number of neighboring molecules leads to a change in the interaction of molecules (the effect of confinement). The changed interaction of molecules leads to the appearance of new phase transitions in comparison with a bulk system without spatial restrictions [53].

The energy resource potential of natural gas hydrates was studied in [13,19]. The prospects of conducting laboratory and field studies were analyzed. Specific storage requirements of natural gas hydrates place some constrains on the efficiency of extracting this raw material. Problems associated with the mass production are also being addressed.

Within the German project SUGAR on the exploration and exploitation of natural gas hydrates, the prospects of transporting them as pellets were analyzed [54]. The economic estimates were provided. Methane hydrate production aspects were investigated with regard to assessing the main stages: hydrate formation, dewatering, pelletization and pellet cooling. A hydrate carrier was also considered. It includes a pivoted cargo system with the potential to mitigate sintering and an actively cooled containment.

Gas hydrate formations are very sensitive to changes in external conditions (temperature, pressure, salinity, etc.). A change in these conditions can lead to an imbalance in the gas hydrate, its dissociation with the release of a huge amount of gas. Therefore, the extraction of gas hydrates from the seabed can cause catastrophic consequences, such as underwater landslides, methane emissions during drilling, fires, accidents and also enhance the greenhouse effect [55–57]. Thus, it is necessary to pay special attention to studying the issue of safe, environmentally friendly and efficient production of natural gas from gas hydrate deposits.

One of the stages in the use of gas hydrates is their transportation and storage. It is important to pay special attention to the study of these stages. Self-preservation coupled with pelletization offers good prospects for the development of gas hydrate transportation and storage technologies. Since the gas hydrate dissociation kinetics is conditioned by temperature and pressure, it is necessary to control these parameters during transportation and storage. To create an efficient gas hydrate carrier, a number of new scientific and technological problems need to be tackled: active cooling of gas hydrates, measures to mitigate sintering and minimize the mechanical stress of hydrate pellets.

The most important criterion for the development of natural gas hydrate transportation technologies is safety in terms of reducing ignition and uncontrolled burning risks. Gas hydrate transportation costs remain quite high. This is because of high energy costs. To cut them down, it is necessary to increase the storage temperature by using the self-preservation phenomenon. The section below deals with the way two essential factors (self-preservation and pelletization) affect the dissociation kinetics.

3.2. Self-Preservation Phenomenon in Gas Hydrate Dissociation

The gas hydrate dissociation rate j should increase with a rise in the pressure and temperature deviation from equilibrium, which can be seen from the empirical Equation (1) [58]:

$$j = Sk_0 \exp[-\frac{E_a}{RT}](P_{\mathrm{d}}(T) - P_0), \tag{1}$$

where $P_{\mathrm{d}}(T)$ is the methane hydrate pressure at temperature T; P_0 is the gas pressure in the surrounding atmosphere, S is the surface area of the dissociation front, k_0 is the pre-exponential factor, E_a is activation energy at the phase transformation and R is the universal gas constant. Temperature variations change the equilibrium pressure, which is written in the form of the dependence (2) [59,60]:

$$Ln(P_{\mathrm{d}}(T)) = 15.517 - \frac{2105.16}{T}, \tag{2}$$

where $P_{\mathrm{d}}(T)$ is taken in kPa, the temperature corresponds to the range 148.8–262.3 K. For a higher temperature interval, dependence (3) was used [61]:

$$Ln(P_{\mathrm{d}}(T)) = 8.968 - \frac{2196.62}{T}, \tag{3}$$

where the temperature corresponds to 260–273 K. According to the dependences (2 and 3), minor temperature variations lead to significant equilibrium pressure changes. Equation (1) matches well with the above dependences for the temperatures above the ice melting point. At negative temperatures (below 273 K), the dissociation rate depends on the temperature interval. Gas hydrates dissociate into ice and gas. A porous ice crust forms on the particle surface. In the temperature range of 198–233 K, open pores through which methane is removed emerge inside the ice shell. In the temperature range from 233 K to 267 K, the dissociation rate decreases by 2–4 orders of magnitude and is non-linearly dependent on the temperature. This is due to closed pores and certain ice textures on the ice crust surface [62]. Anomalously low dissociation rates were named the self-preservation phenomenon. The impact of the key parameters on the gas hydrate dissociation rate at low temperatures was examined in [63,64].

The combined effect of self-preservation and heat exchange with the external environment at negative temperatures of a gas hydrate powder was studied in [65–67]. An increase in the external gas rate and a decrease in the powder layer thickness reduced the gas hydrate dissociation rate [65]. At low temperatures, the dissociation rate of natural gas hydrates is higher than that of synthetic ones, which is attributed to fewer faults in natural hydrates [66]. Misyura et al. [67] analyzed the methane hydrate dissociation of a powder layer in a wide range of heat fluxes and temperatures. An increase in the heat flux and heat transfer considerably accelerates the dissociation [26,68–70].

Extremely low dissociation rates of methane hydrates are possible at a sample temperature of approx. 268 K [63]. The dissociation of methane, methane–ethane and CO_2 hydrates at a temperature below the ice melting point occurs with ice texture changes [71]. Typical patterns of changes in the ice texture morphology on the ice shell surface during the low-temperature dissociation of gas hydrates are shown in [72–74].

The dissociation rate modeling at temperatures above the ice melting point is much easier due to the constant kinetic coefficient k_0 in Equation (1). As mentioned above, at low temperatures, the dissociation rate strongly depends on temperature. In this case, the diffusion coefficient of gas through the porous ice is not constant. It changes over time and depends on temperature [59]. Diffusion coefficients were derived by summarizing the experimental data on methane hydrate dissociation [59]. For low temperatures beyond the self-preservation region, with a temperature increase from 158 K to 189 K, the diffusion coefficient D rises almost tenfold (from 10^{-11} to 10^{-10} m^2/s) [59]. The diffusion coefficient of methane molecules through an ice layer (when generalizing the experimental curves) was 1.7×10^{-13} m^2/s (at 272.65 K) and 2.9×10^{-14} m^2/s (at 268.15 K) [75]. With a temperature rise from 189 K to 268.15 K, D decreases by three to four orders of magnitude. A similar dissociation rate reduction by four orders of magnitude was observed in the transition to the annealing temperature window (self-preservation region) [62]. Thus, a change in the dissociation rate at low temperatures is driven by methane diffusion through the porous ice shell. Such significant decrease in diffusion is attributed to greater strength of ice in the case of small ice grains [63,73]. Contrary to the grains of large polycrystalline ice (about 1–10 mm), the size of ice grains in gas hydrate dissociation is 10–50 μm. The relationship between the fracture tensile strength and the ice grain diameter (S, m) is given by Equation (4) [63,76],

$$\sigma_f = \sigma_i + kS^{-0.51}, \tag{4}$$

where σ_i and k are experimental constants (σ_i = 0.6 MPa, k = 0.02 MPa), σ_f is the fracture tensile strength (MPa).

In the dissociation of a spherical particle, the dissociation front radius decreases over time according to Equation (5) [77],

$$3(1 - R^2) + 2(R^3 - 1) = \frac{6D}{{r_{h0}}^2}\left(\frac{\rho_d(T) - \rho_a}{\rho_0 - \rho_a}\right)t, p_d(T) = \exp(a - \frac{b}{T}), \tag{5}$$

where $\rho_d(T)$ is the methane density under the dissociation pressure of the methane hydrate (at temperature T), a and b are constants, ρ_0 is the methane density in the gas hydrate, and

ρ_a is CH_4 density in the surrounding atmosphere, D is the methane diffusion coefficient through the ice layer, $R = r_h/r_{h0}$, r_{h0} is initial radius of the ice layer, r_h is the current radius of the ice crust and t is the dissociation time. The disadvantage of this equation is that the diffusion coefficient is unknown and is found experimentally. Gas hydrate dissociation was modeled using the diffusion coefficient in [78,79]. Using Equation (1) for dissociation, the Darcy and the Kozeny–Karman equations for diffusion through the porous shell made it possible to obtain a correlation between the dissociation rate (at a temperature below the ice melting point) and the ice porosity parameters [66,67,80].

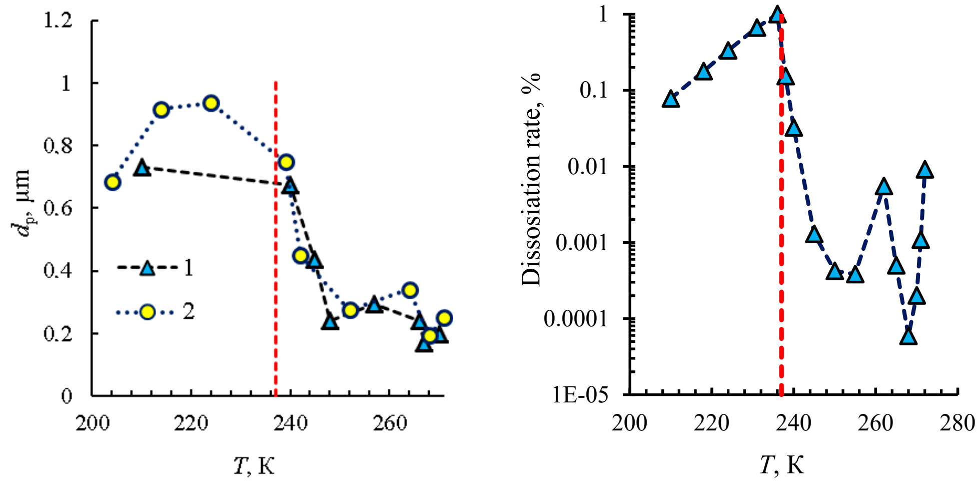
The conversion degree variation of a spherical particle over time Y ($Y = M_H/M_0$ (M_H is the mass of methane hydrate at the dissociation time (t), and M_0 is the initial methane hydrate mass) is connected with the particle pressure, geometry and porosity parameters by Equation (6):

$$\frac{dY}{d\tau} = -\frac{J^{G}}{bM_0} = -\frac{4\pi\left(R^{F}\right)^2 k^{R}}{bM_0}\left(p^{eq} + \frac{\gamma}{2} - \sqrt{\frac{\gamma^2}{4} + (p_0)^2 + \gamma p^{Eq}}\right), \tag{6}$$

$$\gamma = \frac{2R_0 k^{R} \mu R_g T}{k^{F} M_r}\left(Y^{\frac{1}{3}} - Y^{\frac{2}{3}}\right), \tag{7}$$

where R^F is the dissociation front radius, R_0 is the initial radius of a spherical particle, b is the initial mass concentration of methane, p^{Eq} is the equilibrium pressure, p_0 is the ambient gas pressure, k^F is the filtration coefficient that depends on porosity (pore radius and density), k^R is the kinetic coefficient and γ is given by Equation (7).

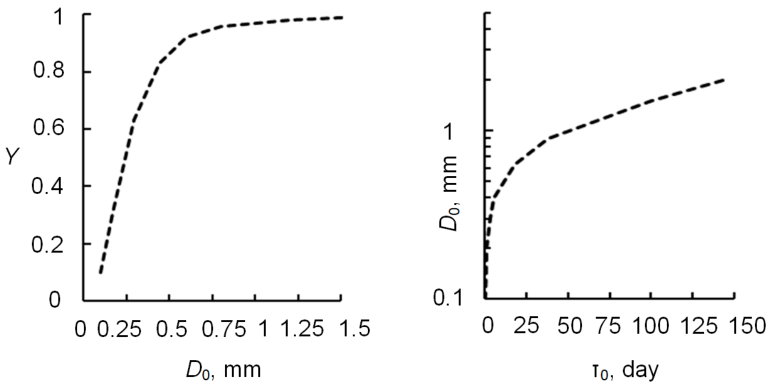
Equation (6) [67] was used to plot the curve of the average pore diameter variation d_p (Figure 2a) both for the self-preservation region (to the right of the vertical dashed line) and beyond it (to the left of the line). Figure 2b presents the calculated curve for the dissociation rate versus temperature. With a four- to five-fold decrease in the average pore diameter, the dissociation rate drops by four orders of magnitude.



(**a**) (**b**)

Figure 2. (**a**) The dependence of the pore diameter on the dissociation temperature (at negative temperatures) [67]; (**b**) The dependence of the integral dissociation rate of methane hydrate on the dissociation temperature.

The dissociation rate depends on the hydrate pellet diameter. The typical pellet diameters should be determined before industrial use. A powder layer, compressed tablet or sphere consist of fine particles (tentatively spheres). Gas hydrates break down to produce a porous ice crust 1 μm or less in diameter. The particles themselves are shaped into pellets with a porosity of 30 to 15%. Without compression, the powder layer porosity is 50–65%. The gas hydrate dissociation rates of a single particle and a compressed powder layer differ significantly. With lower porosity, the dissociation rate decreases. Falenty et al. [72] showed that the dissociation rate of a cylindrical CO_2 hydrate (a consolidated sample) is much lower than that of a powder layer. The effect of the methane hydrate particle size on the dissociation kinetics in a given heating temperature range was investigated in [81]. The particle diameter ranged from 20–45 µm to 1000–1400 µm. In the diameter range between 20 µm and 250 µm, self-preservation was not recorded. At larger diameters of particles, the dissociation rate was very low. Misyura et al. [67] obtained the calculated curves of the methane hydrate conversion degree Y versus the initial diameter of a single spherical particle D_0 (Figure 3a). There is strong correlation between the dissociation kinetics and size of gas hydrates with diameters up to 0.75–1 mm. Above this size, the conversion degree only slightly depends on the diameter. Thus, in terms of production costs, it is more reasonable to use particles about 1 mm in diameter. Particles of this diameter should be used to make tablets to improve methane hydrate storage and transportation efficiency. Figure 3b presents the calculated curve for the full dissociation time of methane hydrate versus the initial particle diameter.



(**a**) (**b**)

Figure 3. (**a**) The conversion rate dependence of the methane hydrate on the particle diameter D_0 (T = 268 K, pore diameter d_p = 0.2 µm, dissociation time for all the diameters is 14,400 s); (**b**) The dependence of the total dissociation time (τ_0) of the methane hydrate on diameter D_0 (T = 268 K, pore diameter d_p = 0.2 µm) [67].

The dissociation rate of a tableted gas hydrate sample is compared with that of an uncompressed powder layer in Figure 4. The experimental and modeling results for the effect of the key factors on the gas hydrate combustion were presented in [50,51]. The influence of the powder layer height on the dissociation kinetics was studied in [65].

The porosity of a compressed sample is 30%, while that of a powder layer is as much as 60%. Although the height of a tablet is three times as small, its dissociation rate is almost twice as low as that of a powder layer. Lower porosity of the tablet due to compression leads to additional filtration resistance of gas during the gas hydrate dissociation. The total filtration resistance of the gas flow in the tablet has two constituents: resistance of the porous ice in single particles and resistance of the compressed layer.

Compression reduces the sample length. After the hydrostatic compaction at 100 MPa (at a temperature of 280 K) of a cylindrical methane hydrate, the cylinder shortened in the direction of the maximum length by 19% without being fractured [82]. Due to self-preservation, the natural gas hydrate samples more than 0.5 mm in diameter broke down within two weeks [83]. Anomalously low dissociation rates of natural gas hydrate pellets at 253 K were obtained in [84]. The technical issues and economic feasibility of using gas hydrates as pellets for transportation and storage were considered in [85–88].

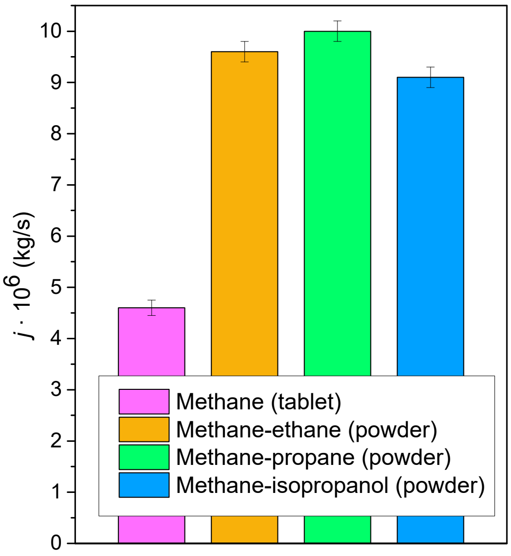


Figure 4. The dissociation rate *j* of gas hydrates burning in a high-temperature furnace (the initial thickness of the powder layer is 16 mm, the initial thickness of tablet is 5 mm, the furnace temperature is 1373 K) [50].

Thus, a high degree of compression of samples (pellets) should be applied for more efficient storage and transportation of gas hydrates. The diameter of single particles (used to produce a tablet) should not exceed 1 mm. The favorable storage and transportation temperature is about 268 K. It provides the maximum degree of self-preservation and reduces gas hydrate cooling costs. The following areas appear to be promising for research: increasing the rate of gas hydrate growth to obtain a particle diameter of 1 mm and above; increasing the ice shell strength (during gas hydrate dissociation) by reducing the ice grain diameter; reducing the average pore diameter in the ice shell to increase filtration resistance.

The issues of modernization and improvement of technologies that will simplify and reduce the cost of production of gas hydrates, extraction of natural gas from them, as well as storage are still relevant and unresolved.

4. Conversion and Composite Fuel Production

At present, there are four main mechanisms of gas hydrate conversion, all of which can be employed under proper conditions with rather low energy consumption [89]. These are thermal dissociation, depressurization, dissolution and gas exchange [89]. Each conversion type has both advantages and disadvantages associated with operating costs, formation water volumes and potential consumption. The optimal approach is chosen, keeping the specific formation conditions in mind. Three variables can be used to control gas hydrate conversion: temperature, pressure and concentration (usually of a hydrate-forming gas in the porous aqueous medium) [89].

To efficiently extract natural gas from gas hydrates, it is necessary to achieve high conversion rates [90]. In turn, high conversion rates may form an entrained flow and lead to hydrate pore plugging [91,92]. Moreover, the disintegration of sediments near a gas hydrate production well also limits the liquid and gas inflow with unwanted sand production, as in some common gas wells. Thus, gaining deep understanding of the specific characteristics of the exploited reservoir is essential [93]. It is necessary to know such parameters as porosity, permeability and hydrate-saturation [94].

A growing global concern about the environmental situation promotes the development of clean alternative energy sources [5]. Over 80% of the world's energy demand is satisfied by fossil fuels. With an ever-increasing population and a power-hungry lifestyle, the global energy consumption is expected to grow by another 28% by the end of 2040 [30]. Natural gas produces twice as little carbon dioxide as the other conventional energy sources [5]. Therefore, increased use of natural gas is unavoidable, if the same energy amount is to be generated.

Some countries with a high energy demand but limited traditional energy resources investigate the potential of using gas hydrate as the primary resource [95]. For countries such as the USA, relying on gas shale and traditional gas deposits to adequately meet their gas demand, gas hydrates are a backup resource in case the available production amounts are insufficient [30].

All the current energy technologies rely on feeding the fuel and oxidizer to the burner to be heated on-site, which means escalating storage and transportation costs, as well as injection energy consumption. The research findings of some scientists provide ways of solving this problem [96,97]. It was proposed to use gas hydrates as a fuel for direct combustion [96,97]. It was established, however, that methane hydrate combustion produces a large amount of water, which reduces the flame temperature [96,97]. The flame during combustion is unsteady and swaying. Thus, gas hydrate combustion characteristics need further optimization.

To date, there are few studies on the combustion of gas hydrates as a fuel composition. Experimental research has been carried out into the characteristics of flame spreading [98,99], flame changes [97,100–102], heat and mass transfer [103] and combustion behavior [21,25,104–106].

Flame characteristics are crucial for the evaluation of the energy efficiency of the combustion of gas hydrates as a fuel. Wang et al. [102] explored the flame characteristics in the combustion of spherical methane hydrates in a natural convective flow. The research findings revealed [102] that the changes in the flame characteristics during combustion can be divided into four stages. The flame height was found [102] to be affected by the rate of mass change and hydrate sphere diameter. There was a "dark region" near the methane hydrate sample surface, characterized by a dark flame and low temperatures (200 °C) [102]. An increase in the initial temperature in the center had a modest effect on the flame characteristics, only slightly increasing the flame height. The gas hydrate sphere diameter had a strong influence on the flame characteristics during combustion [102]. An increase in the sphere diameter was shown [102] to increase the flame height sharply and reduce the oscillation frequency, whereas the maximum flame temperature remained the same. The study by Cui et al. [25] confirmed that the typical size of a gas hydrate sample affects the combustion behavior. It was established that a change of a methane hydrate sample diameter during combustion followed the D^2 law, and the combustion rate decreased with an increase in the diameter or decrease in the initial temperature in the center. The water formed from the combustion of gas hydrate has a significant effect on this process. The water film accumulating on the sample surface facilitates the formation of methane bubbles and accelerates the water evaporation during the unstable combustion phase, thus leading to the flame instability [105]. The findings [105] indicate that adding water vapors significantly changes the proceeding of some elementary reactions, which leads to a lower flame temperature. On the other hand, the concentration of the intermediate element components decreases, which has an inhibitory effect on the combustion rate. Cui et al. [21] conducted experimental research into the effect of the gas content and the ambient temperature on methane hydrate combustion behavior. The combustion flame of methane hydrate spheres with high gas content (more than 6.5%) was found [21] to be bright yellow, whereas that of the methane hydrate spheres with low gas content (3.5%) was pale blue. It was established [21] that at low temperatures (293–303 K), a higher gas content provided increased combustion rates, flame height, flame oscillation frequency and brightness. When the ambient temperature increases, the combustion rate, flame height, flame oscillation frequency and brightness decrease slightly, which is due to self-preservation [21].

To assess the fire hazard during the storage, transportation and use of methane hydrates as fuel compositions, it is necessary to study the influence of external parameters. The influence of the air flow conditions on methane hydrate combustion behavior was investigated in [104]. An "eruption phenomenon" was recorded [104] under the conditions of natural convection and horizontal air flow. It consisted of the breaking of the ice layer and an instant release of a large amount of gaseous methane that created a high and bright flame. The vertical air flow reduced the methane mass transfer resistance, making combustion more stable and the flame height uniform [104]. With a horizontal airflow, the tilted flame increased the heat transfer to the gas hydrate surface [104].

The findings on the heat and mass transfer on the interface show [103] that the water layer in the transition region significantly prevents methane diffusion. Thus, the gas hydrate cannot burn steadily. The heat flux on the combustion boundary is greater than on the solid–liquid interface at the start of decomposition, so the heat transfer on the combustion boundary causes the dissociation of hydrate [103]. The heat flux on the solid–liquid interface is greater than on the combustion boundary at a later stage. Water diffusion and extrusion with heat transfer through the transition region become the new driving force [103].

Despite a great potential of gas hydrates as an alternative fuel, there are engineering and technical challenges posed by their extraction, access to reservoirs and study of safe and energy-efficient combustion. Since the gas hydrate medium consists of several phases (gas, liquid, ice constituent), studies should include the mass and heat transfer correlated with their internal kinetics to determine the characteristics of complex formation and dissociation of hydrates. Therefore, investigating gas hydrates as a fuel composition is quite a complicated task. Another barrier to gas hydrate application as an energy resource is the problem of providing complete and environmentally friendly burnout of the fuel while minimizing the cooling of combustion chamber walls due to the fuel self-preservation and underburning. A possible solution to this problem is to produce an environmentally friendly and energy-efficient composite fuel by adding available biofuel to gas hydrate. In-depth experimental and theoretical research is required for deeper insight into the area.

Despite the fact that gas hydrates have been actively studied recently, there are still many unsolved problems, the solution of which determines the effectiveness of technologies in practice. There are no models of ignition of gas hydrates that take into account the processes of dissociation or the effect of self-preservation. There is a lack of research in the field of co-combustion of hydrated and conventional fuels. There are not enough theoretical studies to establish the ignition characteristics of gas hydrates with varying key parameters that are promising for industrial applications. Moreover, the combustion of gas hydrate over the entire layer of the sample was not considered in detail, due to its inhomogeneity.

5. Hydrate-Based Carbon Dioxide Capture

The need for carbon dioxide disposal has been gaining more attention in the past decades due to the deteriorating environmental situation on the planet and high warming rate. Climate changes are linked to greenhouse gases. In addition to natural methane, considerable emissions of carbon dioxide are caused by the combustion of hydrocarbons in general. The geological disposal and storage of carbon in the form of gas hydrate is a promising technology to cut down carbon dioxide emissions [107]. To estimate the carbon dioxide amount on the planet, it is important to consider two storage states: CO_2 is stored as a separate phase; carbon dioxide is fully dissolved in liquid brine. With this in mind, modeling should take account of the ability of carbon dioxide to dissolve in brine. According to [108], a relatively small amount of an aquifer will be filled with carbon dioxide in the form of a separate phase due to the fluid dynamics and buoyancy of gas in the liquid phase. Even if almost all the carbon dioxide is dissolved in the brine due to interphase mass transfer, the solubility constrains the capacity. It is necessary to evaluate the dissolution kinetics and maximum amount of CO_2 that can be stored in a certain volume of a solution. Most technologies of geological storage of CO_2 utilize a depth ranging from 1000 m to 2500 m. The temperature and pressure at this depth may reach more than 373 K and several hundreds of bars, respectively [109].

Hydrate-based carbon dioxide capture is of the greatest interest to researchers because it reduces CO_2 emissions from the combustion of gases and their mixtures [110]. During capture, CO_2 molecules are enriched in the hydrate phase when the gas mixture undergoes hydrate formation. Other gases may also be trapped in the formation of a hydrate. However, the amount of CO_2 captured is much higher than for other gases since CO_2 hydrate has the lowest equilibrium phase pressure compared to other gases in the mixture. Then, the captured CO_2 molecules (guest gas molecules) are placed inside the cavity, the framework of which consists of water molecules linked by hydrogen bonds, which leads to the formation of a stable clathrate structure [110]. Studies related to the assessment of the cost of this technology are few [111,112]. Study [113] evaluated the processes of multistage separation for CO_2 trapping based on semiclathrate-hydrate adsorption media. A two-stage batch separation process allowed the CO_2 content to be increased to over 90 mole% from a 20 mole% CO_2 feedstock. A three-stage continuous countercurrent separation process resulted in approximately 90% CO_2 recovery. Carbon dioxide based on CO_2 hydrate was studied for the capture of synthesis gas from the combined cycle of complex gasification by the bubbling method using a set of visual equipment [114]. It has been found that a 50 µm gas bubble and a gas flow rate of 6.75 mL/min/L are ideal for capturing CO_2 from synthesis gas at 3.0 MPa and 274.15 K [114]. The hydrate-based gas separation process (HBGS) is seen as a promising new approach to capturing CO_2 from fuel and flue gas mixtures [115]. The basis for trapping is the selective separation of the CO_2 component between the crystalline phase of the solid hydrate and the gas phase during the formation of hydrate crystals [116]. Compared to competing technologies, high CO_2 capture performance and the use of water as a solvent are key advantages of the HBGS process for carbon dioxide capture [116].

In the industry, carbon dioxide is used for enhancing methane recovery from oil and coalbeds, underground storage of natural gas and acid gas (CO_2/H_2S mixtures), as well as for hazardous waste injection [117–120]. Hanisch et al. [121] explored the field-scale CO_2 injection into a deep offshore saline aquifer. One of the challenges of underground storage of carbon dioxide in deep saline aquifers is to provide safety and environmental protection. It is crucial to assess and investigate the environmental and societal risk involved with the long-term storage of CO_2 in receptor formations, as well as estimate the possible leaks of carbon dioxide.

The last two decades have seen a growing interest in the technologies of natural gas extraction from gas hydrates found in sediments. This interest stems from high efficiency of these technologies. Studies are conducted every year to increase natural gas production from gas hydrates via deep wells.

One of the most common techniques of producing natural gas from gas hydrates is to increase the temperature in the reservoir by injecting hot water or steam into it (thermal method) [122]. However, the thermal method requires high energy consumption associated with natural gas hydrate dissociation and the heating of the reservoir to the temperatures leading to gas hydrate dissociation.

Promising ways of improving the efficiency of gas recovery from methane hydrate using the cycling depressurization scheme and the electrical heating were demonstrated in [123,124]. The thermal impact method with carbon dioxide and N_2 injection was described in [125]. Adding low molecular weight gases (such as N_2 and H_2) into the injected gas can significantly increase the natural gas production coefficient and prevent carbon dioxide liquefaction. Adding 15% carbon dioxide to the nitrogen flow makes it possible to extract 25% of natural gas. The optimal mole ratio of carbon dioxide to methane is 1.3–1.45 [126]. The natural gas hydrate exploitation by the CO_2/H_2 injection was described in [127]. Natural gas production from gas hydrates by CH_4-CO_2/H_2 replacement was explored in [128].

The experimental research findings on the replacement of methane in a gas hydrate with CO_2 were reported in [28,129–132]. In the studies cited above, the samples had small sizes and were under thermostatic and barostatic conditions. Therefore, the kinetics of methane replacement by carbon dioxide does not reflect the real sizes of the reservoir and dissociation conditions. These constraints complicate the comparison of the experiment with the large-scale modeling of real non-isothermal processes. The modeling of gas hydrate formation by injecting gas into extended porous media was considered in [133,134]. A mathematical model of CO_2 injection into a reservoir with methane and water was presented in [135]. Guo et al. [136] elaborated an enthalpy model of CO_2-CH_4-H_2S-N_2-brine systems used to simulate non-isothermal multiphase and multicomponent flows with high pressure, temperature and salinity. Shagapov et al. [137] developed a model of carbon dioxide injection into a natural reservoir with methane hydrate. The modeling results revealed that two regimes are possible: (i) methane is recovered from hydrate without methane hydrate decomposition into gas and water; (ii) methane is recovered with the gas hydrate decomposition into gas and water. In the first regime, methane in the gas hydrate is replaced by carbon dioxide. In the second regime of gas hydrate decomposition, water and gas (methane) are produced with subsequent formation of CO_2 hydrate from water and carbon dioxide.

The formation of carbon dioxide hydrates in permafrost environments can occur at temperatures below the melting point of ice. Yet, the calculation of the growth and dissociation kinetics at negative temperatures differs from that at positive temperatures. In these environments, self-preservation is possible. By generalizing the experimental data on the dissociation of carbon dioxide hydrates (at low temperatures), the activation energy values were obtained [138,139].

The carbon dioxide hydrate formation by replacing CH_4 with CO_2 depends on a great number of factors. Therefore, it is essential to optimize these parameters depending on the physical and chemical composition of the porous reservoir. A change in the pore geometry, varying gas hydrate saturation, surfactants in the reservoir and varying compositions of elements are crucial for the gas hydrate dissociation and growth kinetics. Moreover, different dissociation regimes (formation of liquid phase and its absence) are also responsible for the reaction rate and affect the heat exchange. In actual practice, the heterogeneity of the composition, temperature and pressure may arise that will affect the heat and mass transfer to the porous medium. Thus, additional theoretical and experimental research on the contribution of the above factors to the phase transition kinetics is required to increase the rate of carbon dioxide hydrate formation and reduce the energy use. For risk assessment, the research should focus on long periods of gas hydrate storage.

6. Fire Safety

Carbon dioxide hydrates are a promising fire extinguishing agent owing to their composition and qualities [140]. CO_2 hydrate dissociation and water evaporation make it possible to reduce the temperature in the flame combustion zone [141]. There are several areas of CO_2 hydrate application at present [126]. Carbon dioxide hydrates are most commonly used for seawater desalination [142], CO_2 storage [27,143,144], cooling and production of carbonated solid foods [145–147], as well as in fire-extinguishing mixture compositions. Seawater desalination using gas hydrates relies on the conversion of water from the liquid phase to the solid one, e.g., by freezing. That is to say that the physical reaction associated with the exclusion of ions by the hydrogen bonding of water molecules during hydrate formation is the core of desalination [142]. Moreover, solids (hydrates) should be separated from the remaining liquid phase (brines) in the process following hydrate formation [142]. It was established [142] that CO_2 is a more suitable guest gas for seawater desalination than CH_4. An amount of 71–94% of each cation and 73–83% of each anion was removed from carbon dioxide hydrate [142]. Hydrate-based CO_2 capture and storage is believed to be an effective way to reduce greenhouse gas emissions and mitigate the global warming impact. Liu et al. [27] studied the effect of two carbon nanomaterials, an original multiwalled carbon nanotube (MWCNT) and modified herringbone carbon nanotube (MWCNT-HB), on the gas storage performance of carbon dioxide hydrate. MWCNT-HB was better at improving the gas storage performance. Secondary formation of hydrates in the MWCNT-HB system was observed, and the final gas storage capacity could be increased by 119.2% compared to the pure water system [27]. The CO_2 hydrate formation was examined by Zhang et al. [143] to explain the way varying liquefaction degrees affect the characteristics of CO_2 hydrate formation in porous media. The findings indicated that CO_2 liquefaction greatly facilitated hydrate formation, and the liquefied gas amount was a crucial factor for the carbon dioxide hydrate formation in porous media [143]. Carbon dioxide hydrates are also used to produce solid carbonated foodstuffs [145]. Carbonated drinks are popular worldwide because they are refreshing. However, very low solubility of CO_2 in ice, contrary to that in water, is an obstacle for producing solid carbonated food with refreshing qualities. This obstacle can be overcome by using clathrate hydrates formed with CO_2 and containing high concentrations of CO_2 [145].

CO_2-based firefighting systems are widely used to suppress the flame combustion of substances and materials [148,149]. They have their advantages and disadvantages [148,149]. Water mist provides a good three-dimensional cooling effect in firefighting. However, it is less effective with oil fires than firefighting foam. The study [148] dealt with improving the efficiency of extinguishing gasoline by using water mist with additives such as Tween-80 and a dissolved CO_2 solution with different suppression mechanisms. The extinguishing efficiency of different additives was assessed by measuring the fire extinguishing time. The experiments showed [148] that Tween-80 and the dissolved carbon dioxide reduced the flame height. It was also established [148] that Tween-80 and the dissolved carbon dioxide added to the water mist significantly improved the ability to extinguish a gasoline fire compared to pure water mist. Liu et al. [149] found that a CO_2 fire extinguisher is twice as effective as a common wind fire-extinguisher, which saves a lot of human and financial resources due to more efficient fire suppression.

Gas hydrates are ice-like crystalline solid substances, so the heat of hydrate formation and dissociation is usually 300–500 kJ/kg [150]. These values of hydrate dissociation heat are comparable or even above the ice melting heat (333 kJ/kg). Thus, if clathrate hydrate is formed with a noncombustible guest gas such as CO_2 and dissociates around the flame base, the flame temperature will decrease due to the hydrate dissociation heat. At the same time, hydrate dissociation in the fire will prevent the access of oxygen due to the production of noncombustible gases from the dissociating hydrate, and the fuel concentration will decrease as well. Less water is required to extinguish a fire when using gas hydrate than when pure water is sprayed, which is due to a greater dissociation heat of hydrate and noncombustible gas production [140]. Halon is traditionally used as a fire extinguishing agent in fires when it is impossible to spray water, for example, in a subway station [151]. It can be expected that hydrates will become an environmentally friendly alternative to halon gas, as hydrates can only form with water and nontoxic substances, such as CO_2. Carbon dioxide hydrates are undoubtedly less harmful to people's health and the environment. Another advantage of hydrates worth mentioning is that they are dense and solid, unlike traditional fire-extinguishing agents that are in the liquid form [140]. Sugahara et al. [152] conducted experimental research into extinguishing pool fires with methanol and 1-hexanol as fuels by using CO_2 hydrate powder and dry ice powder. It was established [152] that in a methanol pool flame, the critical mass of CO_2 hydrate should be higher than that of dry ice to supply the same mass of CO_2 gas. This suggests that CO_2 supply is crucial for the suppression of a methanol pool flame. It dilutes the methanol gas and weakens the mixing of methanol with air. As for 1-hexanol, the necessary critical mass of CO_2 hydrate is lower than that of dry ice. In this case, the water from the carbon dioxide hydrate dissociation dilutes and cools down 1-hexanol, which decreases its vaporization. Thus, the CO_2 hydrate can reach the flame base and extinguish the fire due to the endothermic reaction of the hydrate dissociation and production of noncombustible gases in the flame base. This would make the suppression of fierce forest fires or compartment fires highly effective.

Using CO_2 hydrates for the containment and suppression of fires is not widely used nowadays due to the lack of reliable data on what thermal conditions and concentrations of gas and water vapors are sufficient for effective application. It is instructive to investigate and define accurate characteristics of the containment and suppression of fires involving materials and substances, when using CO_2 hydrate as a new component for firefighting.

7. Conclusions

The analysis of known research findings revealed that gas hydrates have an enormous potential for a wide group of applications. As hydrates are being introduced into certain industries, national economy and safety control, interesting science and technology objectives emerge. Some of them have been highlighted in this research. The following conclusions have been derived:

(i) Gas hydrates are unique structures due to their multiphase and multicomponent composition. At present, the most common forms of gas hydrates are granules, tablets, clusters and layers of varying configurations. The most widely used gases in the hydrate composition are methane, propane, ethane, isopropanol, carbon dioxide, freon, etc. In this research, some threshold conditions of gas hydrate application have been identified;

(ii) The analysis of the results of experiments, mathematical modeling, bench and field tests indicates that a great number of issues are to be addressed for the efficient application of gas hydrates. The following issues are worth mentioning: the effect of gas concentrations on the dissociation kinetics, creating the conditions for safe and environmentally friendly combustion, enhancing the combustion efficiency, gasification and thermal decomposition of gas hydrates, development of physical and mathematical models to describe the full cycle of physical and chemical processes in hydrate application.

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