Effect of Surfactants on the Synthesis and Dissociation of Gas Hydrates

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Abstract: The synthesis and dissociation of methane hydrate and carbon dioxide hydrate were studied. Nonflammable gas hydrates can be used to extinguish flames in confined spaces. To increase the extinguishing efficiency, it is necessary to increase the dissociation rate (gas release rate) by using surfactant. The work investigates gas hydrates synthesized using sodium dodecyl sulfate (SDS). Experimental studies were carried out in wide ranges of surfactant concentration, the number of the stirrer revolutions and the initial water volume. To achieve the maximum rate of synthesis and dissociation, optimization of the specified parameters was performed. The influence of the key parameters on the dissociation rate was investigated experimentally and theoretically. The novelty of the work lies in solving a complex of interrelated tasks on the synthesis and dissociation of gas hydrate. It is shown that in order to achieve the maximum dissociation rate of carbon dioxide hydrate, it is necessary to optimize the following parameters: the diameter of the particles and their porosity, the porosity of the layer and the external heat flux.

Keywords: gas hydrate synthesis; dissociation; surfactant; mechanical stirring; combustion

1. Introduction

Gas hydrates are crystalline compounds consisting of water and gas [1,2]. Their outer frameworks consist of water molecules that form hydrogen bonds. The gas molecules are located inside the cell due to van der Waals dispersion forces. Depending on the shape and size of the gas hydrate framework, three crystal structures sI, sII and sH are formed [1,2]. The most common structure is sI.

The natural gas reserves in the form of gas hydrates, discovered to date, significantly exceed the reserves of natural gas extracted by traditional methods [1–3]. The prospect of developing the technologies dealing with gas hydrates is associated with an increase in energy needs, a decrease in the reserves of traditional energy sources, as well as environmental problems, including the need to counter global warming.

When combusting natural gas hydrates, harmful emissions that are inherent in coal fuels are eliminated [4,5]. At coal fuel burning, a high concentration of sulfate and nitrate particles accumulates in the atmosphere, posing a danger of cardiovascular diseases. Cleaning air and liquids from dangerous impurities with the aid of filtration technologies is extremely expensive [6]. Environmental and energy issues should be addressed in the following areas: technologies for the extraction of natural hydrate, technologies for the transportation and storage of natural and synthesized gas hydrates, as well as technologies for burning hydrates. The combustion of gas hydrates is considered in [7–11].

Hydrates of noncombustible gases for extinguishing flames are not used today due to high energy costs and the lack of developed technologies. However, today’s methods of high-speed synthesis of gas hydrates are rapidly developing. A significant reduction in the cost of their production and storage, as well as combined use with other methods and fire-fighting substances, will increase the efficiency of this technology.
CO₂ hydrate may be used to localize and suppress local fires due to the oxidizer displacement from the combustion zone and a significant decrease in the flame temperature [12]. The synthesis of such gas hydrates from flue gases can be realized during the combustion of traditional fuels. To date, there are practically no methods for calculating extinguishing technologies based on the use of carbon dioxide hydrate. Some experimental results on flame extinguishing using CO₂ hydrate were obtained in [13–16].

Another important application of CO₂ hydrate concerns the extraction of natural gas from gas hydrate deposits. The efficiency enhancement in methane recovery from natural gas hydrates using injection of CO₂ gas is discussed in [17–20]. Therefore, experimental and theoretical studies on the dissociation of gas hydrates and on the assessment of key factors affecting the efficiency of heat and mass transfer and the dissociation rate are important.

Since the issues of synthesis and dissociation of gas hydrates are related to various allied fields, it is important to enlighten these ideas in the Introduction. The rate of synthesis and dissociation of gas hydrates is determined by various key factors [1,2]: the deviation of temperature and pressure from equilibrium; the type of unit cell of the gas hydrate; the nature of the interaction of molecules; the diameter of the gas hydrate particles; as well as the textural parameters of ice during dissociation. Modeling the gas hydrate dissociation at a temperature below the melting point of ice is complicated due to the influence of temperature on the dissociation rate. In the temperature range from approximately 230 K to 268 K, the dissociation rate of the gas hydrate varies by several orders of magnitude, which extremely complicates the prediction of dissociation [21–23]. Abnormally low dissociation rates in this temperature range are called “self-preservation”. When the gas hydrate dissociates, an outer crust of ice is formed (at subzero temperatures), and gas is removed through porous ice. During dissociation and in the presence of self-preservation, a high-strength ice shell with closed pores or with pores having a very small diameter is formed on the surface of the particle, which leads to a significant filtration resistance of the gas through the porous ice crust [24]. The influence of key parameters on self-preservation and dissociation of gas hydrates is considered in [22–29]. The diameter of the gas hydrate particles, as well as the heat flux, have an important effect on dissociation [32–34].

Since the dissociation kinetics of the gas hydrate depends on the particle parameters—the porosity of the powder and the diameter of the particles and their porosity—it is important to consider how the properties of the powder are affected by the methods of its synthesis in a high-pressure reactor.

In [35], the synthesis of methane hydrate under static conditions was investigated. Explosive boiling leads to rapid crystal growth [36]. By changing the heating rate of the liquid, it is possible to influence the boiling rate of the gas and the rate of synthesis of the gas hydrate. In [37], the kinetics of the growth of methane gas hydrate crystals at a rotation speed from 0 to 800 rpm was investigated. The effect of liquid mixing conditions on the kinetics of CO₂ hydrate synthesis was investigated in [38].

The mechano-dynamic methods of accelerating the synthesis of gas hydrates due to the intensification of heat and mass transfer have been considered above. Other methods of accelerating the growth rate of gas hydrates are associated with the use of surfactant. Most often, the initial growth of gas hydrate particles in water without the addition of surfactant occurs at the phase boundary (water–gas). After the first stage of rapid growth of the hydrate crust, the growth rate decreases many times due to a sharp drop in mass transfer between water and gas [39]. To increase the synthesis rate, methods of forced mixing of gas with water are applied and various additives are used to reduce excess surface energy. The use of surfactants prevents the formation of a dense hydrate film at the phase interface. The formation of loose hydrate scales enhances the mass exchange between gas and water. Molecular dynamics study of surfactant-modified water–carbon dioxide systems was carried out in [40]. The use of sodium dodecyl sulfate (SDS) is considered in [41–48]. SDS increases both the methane hydrate formation rate and the amount of water converted into hydrate, when compared to pure water [49]. Excessive
addition of SDS beyond solubility leads to a decrease in the rate of hydrate formation and an increase in the final level of the water-to-hydrate conversion [50]. The addition of SDS to water significantly increases the wettability [51]. The increase in wettability is known to negatively affect the corrosion resistance of the material. It is worth noting the mechanisms of intensification of the gas hydrates growth due to the use of surfactant, which are most often considered in the literature [41–44].

The change in the structure of the hydrate crust (when using an aqueous solution with surfactant) is realized on the basis of the following factors: (1) formation of micelles; (2) enhancement of mass transfer between water and gas due to capillary phenomena; (3) reduction in free surface energy. The capillary model considers the adsorption of surfactant molecules on hydrate particles, which prevents the hydrate particles from adhesion with forming a solid hydrate crust. Water moves through a capillary-porous loose mass of gas hydrate, which ensures rapid and continuous contact of water with gas [52].

The study of macro- and micro-processes of hydrate formation was carried out in [52,53]. In [53], it was found that hydrate formation with surfactant application in a porous layer of quartz sand occurs much faster than in a solution without sand because of accelerated redistribution of the solution inside the pores of the sand. In the presence of surfactant, a loose hydrate mass forms on the walls, and vertical migration of water through the gas hydrate appears. The growth rate of the gas hydrate depends on the surfactant concentration [54]. When synthesizing CO\textsubscript{2} hydrate at surfactant concentrations from 0 to 3000 ppm, the highest rate of hydrate growth corresponds to a concentration of 1500 ppm.

The combined use of sodium iodide and surfactant in the growth of methane gas hydrate was investigated in [55]. The addition of sodium iodide led to a more rapid nucleation of the gas hydrate. However, at the same time, a decrease in the growth rate of gas hydrate was realized [56].

Nano-microparticles are also used as promoters affecting the induction time and the growth rate of the gas hydrate. The effect of metal particles and nanotubes on the synthesis of gas hydrates was investigated in [57]. The effect of reaction promoters in the form of graphene nanoparticles was studied in [58,59]. The use of graphene particles accelerates the synthesis of CH\textsubscript{4} hydrate.

An analysis of the existing literature has shown that most studies deal with individual parameters. There are limited experimental data obtained as a result of the studies of simultaneous influence of several parameters on the kinetics of gas hydrate synthesis realized within the frameworks of one work. Synthesis and dissociation are, as a rule, investigated in different works as well. Moreover, there are no experimental and theoretical studies on the dissociation of carbon dioxide hydrate in a wide range of particle diameters and porosity parameters. The main problem of modeling the combustion suppression using gas hydrates is not the study of the combustion kinetics, or the effect of hydrodynamics of the gas mixture on the combustion temperature, but the determination of the dissociation rate of carbon dioxide hydrate of the falling powder array at negative temperatures of the gas hydrate. The dissociation rate determines the rate of carbon dioxide flow, the rate of melting ice and evaporation of water, which lead to a decrease in the flame temperature below the stable limit.

Previous studies concerned the effect of air temperature and porosity of the powder layer on the kinetics of CO\textsubscript{2} hydrate dissociation. This research work on the influence of particle size and porosity of particles is a continuation of earlier studies.

Objective: to investigate the simultaneous effect of surfactant concentration, the number of revolutions of the stirrer and the initial water volume on the kinetics of the synthesis of methane hydrate and carbon dioxide hydrate, as well as the influence of key parameters (pore size and particle diameter) on the dissociation of gas hydrates. The efficiency of extinguishing the flame depends on the rate of dissociation of the gas hydrate, which in turn depends on the porosity and particle size. Therefore, dissociation and synthesis kinetics are interrelated and are investigated within the framework of one work.
The economic rationale for the use of gas hydrates in flame suppression is explained by modern promising methods of purification of harmful impurities of industrial flue emissions due to the synthesis of carbon dioxide hydrate. The problems of carbon dioxide hydrate utilization in this case concern transportation, storage and suppression of flame sources. These issues cannot be solved without creating an adequate physical and mathematical model that should take into account a large number of key parameters, which will ensure the implementation of high rates of dissociation of carbon dioxide hydrate in the presence of high flame temperatures.

2. Experimental Technique

For the synthesis of gas hydrates, a high-pressure reactor with mechanical mixing of liquid with gas was used (Figure 1a). Water was placed in the lower part of the working chamber. Methane was located above the water surface. The high-pressure chamber had a cylindrical shape (1). Cooling of the reactor walls at the time of hydrate formation was realized using a heat exchanger device (2) and a coolant entering the reactor from the thermostat (3) CRYO-VT-12-1. A thermocouple in a protective sleeve (10) was used to measure the temperature of the liquid. The temperature measurement error corresponded to 0.5 °C. Gas pressure measurements inside the chamber were carried out with a pressure gauge (Wika) (11), as well as a pressure sensor (Baumer) (12). With the help of a magnetic coupling, the mixing device was connected to an electric motor. To change the number of revolutions of the stirrer (from 0 to 1300 rpm), a frequency controller was used. The measuring values of pressure, temperature, as well as the revolutions of the stirrer were reflected on the control unit (9) and transmitted to the PC.

Figure 1. (a) Experimental unit for the gas hydrates synthesis: 1—high-pressure reactor; 2—heat exchanger for cooling water in the working chamber; 3—thermostat for cooling the working chamber of the reactor; 4—funnel for pouring water; 5—gas cylinder; 6—valve for supplying gas to the reactor; 7—magnetic stirrer for mixing water and gas; 8—electric motor; 9—temperature and pressure control unit; 10—temperature sensor; 11—pressure gauge; 12—gas pressure sensor; 13—gate for gas depressurization; 14—valve for gas depressurization. (b) The scheme of the unit to study the flame extinguishing of the liquid fuel layer: 1—cylindrical working unit; 2—kerosene; 3—CO₂ hydrate powder; 4—horizontal table; 5—thermocouples.

Initially, water was poured into the reactor through a funnel (4). The volume of water for different experiments varied in the volume range from 150 to 400 mL. Further, with the use of a thermostat (coolant), the temperature of the liquid in the working volume of the reactor was lowered to 5 °C. After that, the methane pressure in the reactor was set to 80 bar for a few seconds, and the revolutions of the magnetic coupling (mixing device) were
set in the range from 0 to 1300 rpm. In one experiment, the number of revolutions was kept constant. Due to the deviation of the system from equilibrium (pressure and temperature), the process of hydrate formation was realized until establishing the equilibrium state. During the growth of gas hydrates, the gas pressure decreased, as gas and water transited into a hydrated state. After synthesis, the hydrate was removed and placed in a Dewar vessel with liquid nitrogen for storage.

Samples of CH\textsubscript{4} and CO\textsubscript{2} hydrate have the cubic structure sI (the elementary cell is 2D·6T·46H\textsubscript{2}O; with consideration of crystal edges and faces 2(5\textsuperscript{12}) + 6(5\textsuperscript{12}·6\textsuperscript{2}) (the cell consists of 46 water molecules, two small and six large cavities).

To study the extinguishing of liquid fuel, experiments were performed on the installation, the scheme of which is shown in Figure 1b. Kerosene was poured into cylindrical working unit (1) (Figure 1b). In the experiments, the cylindrical section (1) with a diameter (D\textsubscript{1} = 40 mm) and the kerosene layer height (h = 3 mm) was used. The liquid fuel (2) was ignited and after that, a powder of carbon dioxide hydrate (3) synthesized in a high-pressure reactor was poured on top of the burning fuel. The experiments were performed at a fixed powder weight, as well as at a given particle diameter. The mass of the powder increased until flame extinguishing was realized within 1–2 s. The purpose of these experiments was to determine what minimum mass of CO\textsubscript{2} hydrate powder is necessary to completely extinguish the flame when the diameter of the particles (aggregates) changes. The experimental data on the minimum powder weight were compared with the simulation results. The performed experiments and modeling also allowed scaling the combustion process to a large mass of fuel with an increase in the size of the working area with a layer of liquid fuel. The flame extinguishing was recorded using a video camera.

3. Results and Discussion

3.1. Synthesis of Gas Hydrates Using Surfactant

In the Introduction, it was pointed out that inert gas hydrates can be effectively used to extinguish flames in confined spaces. The development of this technology requires the research of not only the kinetics of combustion suppression but also that of gas hydrate synthesis. Studies of synthesis and dissociation are interrelated. To reduce the cost of gas hydrate production technology, it is important to increase the rate of hydrate mass growth. In addition, the size of particles and aggregates, as well as the porosity of the layer, affect the effectiveness of combustion suppression. Therefore, Section 3.1 investigates the key issues of hydrate synthesis, and Section 3.2 shows how the specific parameters of synthesized hydrate affect the kinetics of dissociation and the efficiency of flame suppression. To increase the rate of synthesis of gas hydrate, it is effective to use surfactant. However, surfactant has different effects on the kinetics of synthesis of different hydrates. So, it is expedient to identify a specific type of surfactant for carbon dioxide hydrate for reaching the maximum synthesis rate.

To improve the understanding of surfactant’s effect on synthesis kinetics, the article examines the effect of SDS not only on the growth of CO\textsubscript{2} hydrate but also on the growth of methane hydrate. This comparison provides for a better comprehension of the physical mechanisms of hydrate growth and ways to increase the rate of hydrate mass growth. In addition, the extraction of natural gas from gas hydrate deposits is inextricably linked not only to energy issues but also the issues of combustion, spontaneous combustion and extinguishing of this fuel, which consists mainly of methane.

The influence of several key parameters on the kinetics of the gas hydrate synthesis was studied: at surfactant concentrations (anionic substance—sodium dodecyl sulfate SDS) in the range of 0–0.2 mass%, at rotation speed 200–1300 rpm, and at the water volume in the reactor of 125–400 mL. Figure 2 shows the curves of pressure and temperature changes when the SDS concentration changes. A faster synthesis of methane hydrate was accompanied by a stronger pressure drop and a faster temperature increase. Several characteristic pressure change modes were implemented for all curves (Figure 2a).
Figure 2. Changes in gas pressure (1–4—Various dissociation modes) (a) and liquid temperature (b) in the working chamber during the synthesis of methane hydrate in the SDS concentration range from 0 to 0.2% (200 rpm, initial water volume of 125 mL).

In the absence of SDS (curves—0%), the temperature decreases rapidly within 10 min, which indicates an extremely slow growth of gas hydrate. Conversely, surfactant addition demonstrates a significant temperature jump during the formation of a gas hydrate. At the same time, a decrease in temperature to 0 °C is realized within 50–70 min. A higher slope of the pressure curve (mode 1) was followed by a less slanting pressure change (mode 2) and an increased rate of pressure drop (mode 3).

Since there was no visualization of the hydrate formation process, one can only assume possible reasons for the change in these modes. In the first time section, a rapid capture of gas into water is realized when the stirrer rotates (Figure 3a). Large bubbles are broken into small ones due to hydrodynamic disturbances and surfactant. As a result, a high phase interface (gas–liquid) is formed relatively quickly, and a high rate of hydrate mass growth is realized. Moreover, the presence of surfactant leads to a smaller size of bubbles and to a larger total surface, which contributes to a higher rate of hydrate formation (a higher slope of the pressure curve to the horizontal time axis). Additional reasons for the acceleration of hydrate formation in the presence of surfactant may be associated with a decrease in the induction time of the appearance of crystal centers, as well as an increase in the growth rate of gas hydrates.

Figure 3. Different modes of mass exchange between gas and water: (a) An increase in the number of gas bubbles in the liquid during the stirrer rotation; (b) The formation of a gas hydrate crust on the free liquid surface (cessation of the gas phase flow into the liquid); (c) Disruption of the hydrate crust and increased mass exchange between gas and liquid.
The adhesion of colliding solid particles (mode 2) leads to an increase in the size of aggregates that accumulate at the free boundary of the liquid and form a porous crust of ice (Figure 3b), which is located between gas and water. As a result, the mass transfer between liquid and gas is significantly reduced, which leads to a sharp decrease in the rate of hydrate formation. Moreover, the more horizontal the curve in mode 2, the greater the share of the free liquid surface occupied by the hydrate crust.

Prolonged rotation of the liquid and gas hydrate mass leads to impacts of solid aggregates on the lower surface of the hydrate crust. With increasing time, cracks accumulate in the crust, and the hydrate film disintegrates into separate pieces (Figure 3c). As a result of the hydrate film destruction, mass transfer increases. In the third mode, the slope of the pressure curve is approximately the same as in the first (initial) mode.

A sharp decrease in the slope of the pressure curve in mode 4 (at the end of synthesis) is due to the fact that most of the liquid has passed into a hydrated state. Water with no gas remains between the units. The process of mixing the quasi-solid phase is realized with an extremely low mass transfer of gas inside the liquid.

Figure 4 shows curves of changes in the hydrate formation time $t_1$ depending on the initial volume of water $V_0$ ($t_1$ corresponds to the time when the pressure differs by 5–7% from the minimum pressure, corresponding to the cessation of hydrate formation). Time $t_1$ decreases with increasing surfactant concentration. With an increase in the value of $V_0$, the time $t_1$ increases. In the absence of SDS, this growth of $t_1$ is weakly expressed in the measured interval $V_0$.

![Figure 4](image)

**Figure 4.** Dependence of the hydrate formation time $t_1$ on the initial water volume in the reactor (750 rpm): 1—0% SDS, 2—0.02% SDS, 3—0.15% SDS.

Figure 5 shows curves for the change in gas pressure in the reactor during hydrate formation depending on the number of revolutions (SDS of 0.15% and initial water volume $V_0 = 125$ mL). With the increase in the number of revolutions from 200 to 1300 rpm, the time $t_1$ has decreased almost two times. At 200 rpm, there are several modes of hydrate formation, which are discussed in Figures 2, 4 and 5. With an increase in the number of revolutions, the nature of the pressure curve has changed.

Four hydrate formation modes are absent on the graphs in the rotation interval from 900 to 1300 rpm. The slope of the pressure curve continuously decreases with increasing time. This is probably due to quite strong dynamic disturbances during rapid rotations of the liquid (pressure surges, impacts of aggregates on the gas hydrate crust), which hinders the growth of a strong crust of gas hydrate on the free liquid surface. As a result, during the entire hydrate formation, there is a mass exchange between the liquid and gas phases, which is shown in Figure 3c.
The fast rotation velocity leads to rapid accumulation of a large number of gas bubbles in the liquid. At small times, there is a maximum specific surface of these bubbles. Further, with increasing time, this surface decreases due to the growth of methane hydrate on the surface of the bubbles, as well as due to aggregation. As a result, the slope of the pressure curve decreases with time.

It should also be noted that as the number of revolutions increases, the size of both gas bubbles and aggregates decreases. Optical microscope images show that at 200 rpm, the size of most of the aggregates is 0.5–1 mm, and at 1300 rpm, the size of the aggregates corresponds to 0.05–0.3 mm (Figure 6). Moreover, the methane hydrate aggregate (at 1300 rpm) with a size of 0.3 mm consists of a large number of particles of about 0.01–0.05 mm. When the liquid rotates, the aggregates collide with each other, which leads to their disintegration into smaller parts.

Let us consider various mechanisms of growth of gas hydrates. In the absence of liquid rotation, as well as with low saturation of water with gas, the growth of the hydrate crust is realized mainly on the free surface of the liquid. In this case (without surfactant, Figure 7a), the growth rate of the crust thickness drops sharply due to the lack of mass transfer. In the presence of surfactant, the hydrate crust has a porous appearance (Figure 7b). Water moves through the pores due to capillary forces, and gas moves through a porous space, which ensures mixing of gas with water and an increase in the thickness of the hydrate crust.
The mechanism of formation of aggregates of gas hydrates from smaller particles is shown in Figure 9. Between the larger parts of the gas hydrate, there are both small gas bubbles and small particles of gas hydrate. Gas bubbles, appearing on the surface of the gas hydrate, remain on it. The capillary bridges of the liquid in Figure 9b are formed between the solid and liquid phases, as well as between the gaseous and liquid phases. As a result, a force \( F \) retaining two different parts of the gas hydrate is formed. A hydrate crust grows on the surface of the gas bubble, additionally binding the two parts of the gas hydrate. The growth of the aggregate from smaller parts is realized until the dynamic disturbances (inertia forces \( F_i \)) do not exceed the adhesion forces \( F_a \) by \( k \) times, where \( k \) is the equilibrium criterion (stability of the aggregate, \( k = F_i/F_a \)).
The formation of micelles leads to an increase in the solubility of carbon dioxide in water (Figure 10). Further, these micelles are adsorbed onto growing crystals of methane hydrate. Methane is much less soluble in water than carbon dioxide. The poor solubility of methane contributes to the fact that methane molecules accumulate inside the micelles of SDS to form a porous hydrate of methane. SDS/CO\textsubscript{2} micelles are probably less stable than CO\textsubscript{2} micelles (there is no accumulation of a great number of CO\textsubscript{2} molecules inside SDS molecules, (Figure 11)) and do not contribute to the formation of branched porosity of CO\textsubscript{2} hydrate which determines the key role in accelerating the kinetics of gas hydrate growth. However, unlike water without surfactant, flat areas in the presence of SDS are more clearly visible, i.e., there is some growth of the hydrate crust on the free surface of the liquid.

Figure 9. (a) Formation of aggregates of gas hydrates; (b) The capillary bridges are formed between the solid and liquid phases, as well as between the gaseous and liquid phases.

Figure 10 shows graphs of changes in gas pressure and liquid temperature in the working chamber during the synthesis of CO\textsubscript{2} hydrate with various types of surfactant. The rate of synthesis of methane hydrate increased significantly with the addition of SDS, but the synthesis of CO\textsubscript{2} hydrate was practically not affected by SDS. It may be assumed that the molecular bonds between the “guest molecule” (gas) and surfactant molecules affect the formation of micelles, as well as the formation of porous structures in the gas hydrate. Methane is much less soluble in water than carbon dioxide. The poor solubility of methane contributes to the fact that methane molecules accumulate inside the micelles of SDS to form a porous hydrate of methane. SDS/CO\textsubscript{2} micelles are probably less stable (there is no accumulation of a great number of CO\textsubscript{2} molecules inside SDS molecules, (Figure 11)) and do not contribute to the formation of branched porosity of CO\textsubscript{2} hydrate which determines the key role in accelerating the kinetics of gas hydrate growth. However, unlike water without surfactant, flat areas in the presence of SDS are more clearly visible, i.e., there is some growth of the hydrate crust on the free surface of the liquid.

Figure 10. Changes in gas pressure (1–4—Various dissociation modes) (a) and liquid temperature (b) in the working chamber during the synthesis of CO\textsubscript{2} hydrate at various surfactant (1000 rpm, initial water volume of 150 mL, and surfactant concentration of 0.5%).
The formation of micelles leads to an increase in the solubility of carbon dioxide in water (Figure 11). Further, these micelles are adsorbed onto growing crystals of methane hydrate, making the gas hydrate porous. The presence of surfactant in water is known to lead to the forming of the porous (defective) gas hydrate.

It is interesting to note that with all surfactants applied, there are 4 modes of hydrate formation. Moreover, the flat Section 2 (Figure 10) is noticeably longer for CO$_2$ hydrate than for methane hydrate. This is probably due to the higher synthesis rates of the CO$_2$ hydrate crust and growth of the hydrate crust thickness on the free liquid surface, as well as the greater strength of the hydrate crust (its lesser looseness) due to its lower porosity. For methane hydrate, 4 modes (with a flat section) were formed only at low rpm (about 200 rpm). When synthesizing CO$_2$ hydrate, even at high stirrer rotation speeds, there are 4 modes of hydrate formation and a long flat section, which indicates a high strength of the hydrate crust. Its destruction takes a long time for a lot of large hydrate aggregates to form under the crust, pressing on the crust when the liquid rotates and destroying the crust into separate parts.

3.2. Suppression of Combustion by Increasing the Dissociation Rate of Carbon Dioxide Hydrate

When analyzing active fire extinguishing methods, the main attention is paid to the choice of the most optimal means, which has both high fire extinguishing efficiency and optimal costs for the creation of this means, its storage, transportation and delivery to the fire location [60]. The most commonly used methods and extinguishing agents include foam extinguishing agents [61,62]. However, with a high surface area of the fire source, complex geometry of premises, warehouses, industrial and residential buildings, it is difficult to quickly deliver foam extinguishing agent to all areas of the fire. The high rate of convection during a fire and the high temperature of the flame often create uneven extinguishing and hinder fast coverage of the entire area of the fire [63].

To date, fire extinguishing technologies are being effectively developed through the use of water spray. Water mist penetrates into the fire zone quite quickly, which is an advantage when extinguishing volumetric fires with the presence of a large number of volumetric combustible objects. Compared with commonly used foam compositions, water mist has a lower fire extinguishing efficiency for heavy hydrocarbon liquids, and it is also undesirable in the presence of electrical appliances and electrical circuits in the location of the fire. Water is effectively used to extinguish forest fires, as it is possible to quickly capture large volumes of water from natural water reservoirs. In addition, getting into the fire area, large volumes of water spontaneously quickly disintegrate into small droplets,
which, due to convection, spread to a large fire area. Optimization of the parameters of fire extinguishing agents is considered in [64]. By adding various additives to the water mist, it is possible to significantly increase the effectiveness of fire extinguishing.

One of the methods of increasing the efficiency of fire extinguishing with the use of water is water spray. However, various experimental and pilot studies, as well as our works [65], have shown that when extinguishing a volumetric fire, for example, a woodpile, fine water droplets do not have time to penetrate down the fire center, and all evaporation is realized over it. In addition, the high intensity of droplet evaporation leads to the instantaneous achievement of an equilibrium partial vapor pressure (generation of a vapor cloud), which excludes further evaporation of water droplets. The release of a large volume of water into the fire point (without spraying drops) leads to extinguishing only small areas of the fire, which reduces the economic efficiency of extinguishing and requires a lot of time. It was shown in [66] that the use of carbon dioxide hydrate powder serves to effectively extinguish a fire in a woodpile, i.e., to extinguish volumetric fires. Solid particles of carbon dioxide hydrate, unlike water spray, do not turn into water mist until they fall to the bottom of the volumetric fire point. Only after their fall, the bulk of carbon dioxide and water vapor is released, leading to rapid extinguishing of the flame. Thus, steam and gas do not come from the top down (as for clean water), which is not entirely effective, but from the bottom up. In addition, the phenomenon of self-preservation maximally slows down the gas hydrate dissociation at the moment of its fall (unlike ice powder) and ensures a decrease in the temperature of the flame along the entire height of the fire. The use of carbon dioxide hydrate to extinguish the flame also reduces harmful impurities due to the high concentration of water vapors that react with the products formed during combustion [67].

On the one hand, it is necessary to ensure the small size of the powder particles for the rapid dissociation of the gas hydrate. This allows achieving the maximum heat flux (the heat of ice melting and water evaporation). On the other hand, solid particles have to reach the very bottom of the fire, which may be ensured by the aggregation of particles and the rapid disintegration of aggregates into small particles when reaching the bottom. This problem cannot be solved without creating a physical model of dissociation taking into account the following factors: self-preservation, the size of the powder body and the distance between the particles, the particle size of the gas hydrate and the porosity of the particles. The rate of the gas hydrate dissociation depends on the external temperature, and the temperature near the array of falling CO₂ hydrate may drop with time.

Work [68] considers the effect of the powder layer porosity \(P\) on the change in \(V_{CO₂}\). At a fixed ambient temperature of 400 °C, a 2-fold increase in porosity from 0.3 to 0.6 has led to a 2.8-fold increase in \(V_{CO₂}\) (from 0.0124 to 0.035 mm/s). In this case, we obtain Equation (1).

\[
V_{CO₂} \sim (P)^{1.5}
\]  

The external temperature of the gas and the porosity of the layer affect the dissociation kinetics. To further develop the calculation methodology and improve the efficiency of flame extinguishing, studies were carried out on the effect of particle diameter and porosity on the dissociation rate. At negative dissociation temperatures, the porosity of the particles (the number of pores on the surface of the particle, the diameter of the pores and the diameter of the particle) determine the rate of gas filtration through the pores. Two completely different porosities are realized: the porosity of the particle layer (an array of falling particles) and the porosity of the particle itself due to meso-macropores. A decrease in the particle diameter leads to an increase in the specific surface area and an increase in the dissociation rate. However, the proximity of the particles to each other (low porosity of the layer) on the one hand leads to an increase in the integral gas flow, since it is proportional to the mass of the gas hydrate. On the other hand, low porosity leads to an increase in the filtration resistance of the layer (array of particles) and to a slower heating of the layer (thermal inertia due to an increase in the integral heat of dissociation, melting of ice and evaporation of water). Therefore, it is necessary to calculate dissociations in a wide range
of key parameters. In the future, this will help to choose a method for calculating flame extinguishing to optimize a large number of key parameters. The purpose of optimization is to ensure the maximum possible flow rate of carbon dioxide (when an array of particles enters the fire) at the time of the powder incidence on the combustible substance.

To achieve this goal, various samples of carbon dioxide hydrate were synthesized using surfactant and changing the number of revolutions of the stirrer in the reactor. The resulting powder was sieved using sieves to a fixed size.

Figure 12a shows experimental data on extinguishing a flame over a kerosene layer when using CO$_2$ hydrate powder with different average particle diameters. Both calculated and experimental data show that with a decrease in the particle diameter, the value of the powder mass $m_p$, required for rapid flame extinguishing, decreases. The calculated values show a lower mass value than in the experiment. This is due to the fact that, in reality, the particles aggregate (Figure 12b) when falling and drop extremely unevenly, which reduces the extinguishing efficiency, i.e., a larger value of the mass of carbon dioxide hydrate is required. The calculation was performed without the presence of aggregates at a constant porosity of the layer (Figure 12c). In addition to aggregating particles when falling, aggregates are also formed during synthesis. The minimum size of particles that have grown without adhesion with other particles is much smaller than 1 mm. So, from the photos in Figure 6, it follows that even with the size of the aggregates of 0.2–0.3 mm, the particle size may be many times smaller. Thus, there are two types of aggregation: during the synthesis of gas hydrate, as well as during storage and drop of powder. Taking into account the influence of aggregates, as well as the porosity of the powder array when falling, is the goal of further research.

![Figure 12](image)

Figure 12. (a) The mass of CO$_2$ hydrate powder required to extinguish the flame (extinguishing time of 1–2 s) depending on the diameter of the aggregates (extinguishing the flame above the kerosene layer, layer diameter of 60 mm; the experimental values are presented in the form of grey rectangles, and the calculated data are in the form of white rectangles); (b) the powder consists of a layer (array), aggregates of particles and individual particles; (c) the powder layer (array) consists of particles without the formation of aggregates.

The description of the model for calculating the dissociation of the gas hydrate powder layer at negative temperatures is considered in [22,32] and at combustion in [68]. In general, the dissociation rate of the gas hydrate depends on the kinetic and filtration resistance in the form of Equation (2),

$$
\frac{\partial Y_H}{\partial t} = -\frac{6k_R}{B\rho_H d_0} \left( \frac{P^{eq} - P^0}{1 + \gamma} \right)^{2/3} Y_H,
$$

where $Y_H$ is the dissociation rate of a spherical gas hydrate particle, kinetic parameter $k_R = k_0 \exp(-E_a/RT)$, parameter $B$ is the initial gas content in CO$_2$ hydrate, $\rho_H$ is the density of the particles hydrate, $d_0$ is the average diameter of the gas hydrate particles in the powder.
layer, $P^0$ is the equilibrium gas pressure into the gas hydrate, $P^0$ is the partial gas pressure, and the parameter $\gamma$ is the coefficient reflecting the impact of pore resistance. The method of calculating the boundary of the combustion stability is given in [69]. For all calculations, the following parameters were taken: the height of the powder layer of 6 mm; the area of the upper surface of the powder of $7.85 \times 10^{-5}$ $m^2$; the pore density (the number of pores on the surface of spherical particles) of $10^{10}$ ($1/m^2$); the powder layer porosity of 0.6; the heat flux through the side and bottom walls was neglected (heat-insulated material); the heat transfer coefficient was determined from the equality $Nu = 2$. The calculations took into account the thermal balance, the heat of melting ice, dissociation of gas hydrate, the heat of water evaporation, as well as the heat of radiation.

Figure 13 shows the calculated curves for the change in the dissociation rate of carbon dioxide hydrate powder. The dissociation rate depends on temperature, since the heat flux $q$ ($q = \alpha \Delta T$) coming from the outside air to the upper surface of the gas hydrate is proportional to the temperature difference $\Delta T = T_a - T_s$ ($T_a$—is the temperature of the outside air, $T_s$ is the temperature of the powder and $\alpha$ is the heat transfer coefficient in the gas mixture). With an increase in temperature $T_a$, the temperature difference $\Delta T$, the heat flux and the dissociation rate increase. With increasing time, $T_s$ increases from the equilibrium temperature at atmospheric pressure of 1 bar to the melting point of ice. The calculations were performed at a constant particle diameter $D$ and at a variable pore diameter $d$, as well as at constant $d$ and variable $D$. Here, the porosity is taken for the particles of the gas layer, which differs from the porosity of the particle layer.

During the transition from $T_a = 100 ^\circ$C to $T_a = 1200 ^\circ$C, the temperature difference $\Delta T$ increased 9.5 times, and the maximum dissociation rate $J_{\text{max}}$ increased 18 times. Then, during the transition from $T_a = 100 ^\circ$C to $T_a = 1200 ^\circ$C, an approximation Equation (3) will be performed.

$$J \sim (\Delta T)^{n_1} \ (n_1 \approx 1.29) \quad (3)$$

During the transition from $T_a = 20 ^\circ$C to $T_a = 100 ^\circ$C ($D = 1$ mm and $d = 10$ $\mu$m), $\Delta T$ increased 2.6 times, and the maximum dissociation rate increased 3.6 times. During the transition from $T_a = 20 ^\circ$C to $T_a = 100 ^\circ$C, an approximation Equation (4) will be performed.

$$J \sim (\Delta T)^{n_1} \ (n_1 \approx 1.35) \quad (4)$$

![Figure 13. (a,b) The rate of dissociation of CO2 hydrate (external air temperature $T_a = 20 ^\circ$C, the layer height of powder is 6 mm, $D$—particle diameter, $d$—pore diameter): (a) $D = \text{var, } d = \text{const}$; (b) $D = \text{const, } d = \text{var}$.](image-url)
According to Equations (3) and (4), the degree \( n_1 \) depends on \( \Delta T \). In the \( T_a \) range from 20 °C to 100 °C (\( \Delta T = 50–130 \) °C), \( n_1 \approx 1.35 \). In the \( T_a \) range from 100 °C to 1200 °C (\( \Delta T = 130–1230 \) °C), \( n_1 \approx 1.29 \). Thus, a decrease in the degree \( n_1 \) is realized during the transition to a high temperature difference (high heat flux (Figure 14)), which is realized at combustion temperatures.

![Graph showing the dependence of \( n_1 \) on \( \Delta T \)](image)

**Figure 14.** Dependence of the degree \( n_1 \) on the temperature difference \( \Delta T \).

A decrease in the degree of \( n_1 \) at high dissociation rates may be associated with different effects of thermal and kinetic resistance on the dissociation rate of a gas hydrate particle. At low temperature differences and low dissociation rates, the thermal inertia of the particles and the porous layer give the main resistance. At high dissociation rates, the thermal front moves quickly and the kinetics of dissociation plays a limiting role. In this case, a decrease in the degree \( n_1 \) is realized due to the inertia of gas filtration through the pores in the particle and the porous space in the powder layer.

With an increase in the particle diameter \( D \) (with a constant pore diameter \( d = 10 \) µm), the dissociation rate decreases. There are several modes of dissociation in Figures 13 and 15. At the beginning of the dissociation, \( J \) rises and reaches its maximum value. In this mode, the temperature of the powder and the temperature deviation from equilibrium increase, which leads to an increase in the dissociation rate. When the temperature range of self-preservation is reached, part of the powder shows a low dissociation rate, which leads to the fact that the total gas flow decreases. The sphericity of the granules, with the greatest effect at the final stage of dissociation, when the reaction surface in the particle tends to zero, also leads to a decrease. In addition, the temperature difference between the ambient medium and the powder surface decreases over time, which also leads to a decrease in the external heat flux and \( J \).

The decrease in \( J \) in the final stage is associated, as mentioned above, with the sphericity of the granules and with a decrease in the total reaction area (dissociation front inside the particles). A noticeable effect of the pore diameter (Figures 13 and 15) is observed only in the first mode of decomposition, when the dissociation rate increases and reaches a maximum.

The dissociation pattern of the gas hydrate at \( T_a = 1200 \) °C changes markedly (Figure 16a,b). After the extremum \( J \) during the first 0.1–1 s (Figure 16b), the dissociation rate drops sharply due to the appearance of the heat of water evaporation. Up to this point, the temperature of the powder was low, and the heat of evaporation practically did not affect the dissociation. The long plateau is associated with the establishment of a constant temperature of the water film. A small increase in \( J \) at the end of the dissociation is due to the fact that the temperature of the powder rises slightly after reaching the thermal front of the lower wall of the powder layer. The diameter of the pores at high heat flux (Figure 16c) has no effect on the gas hydrate dissociation.
The value of the extremum at D=6 mm, the values of the extremes are close to each other and closely coincide with the effectiveness of flame suppression. Experimental data show that with effective extinguishing, the flame disappears within 1 s. Thus, the particle diameter, D, of the granules and with a decrease in the total reaction area (dissociation front inside the particles). A noticeable effect of the pore diameter (Figures 13 and 15) is observed at the extremum indicates the effectiveness of flame suppression. Experimental data show the decrease in the rate of dissociation of the gas hydrate at D=6 mm, d=10 µm during the first 0.1–1 s (Figure 16b), the dissociation rate drops sharply due to the appearance of the heat of water evaporation. Up to this point, the dissociation pattern of the gas hydrate at D=6 mm, d=10 µm is associated, as mentioned above, with the appearance of the heat of evaporation. After the extremum during the first 0.1–1 s (Figure 16b), the dissociation rate drops sharply due to the appearance of the heat of water evaporation. Up to this point, the decrease in the rate of dissociation of the gas hydrate at D=6 mm, d=10 µm is associated, as mentioned above, with the appearance of the heat of evaporation.

**Figure 15.** (a,b) The dissociation rate of CO₂ hydrate (external air temperature Tₐ = 100 °C, D—particle diameter, d—pore diameter): (a) D = var, d = const; (b) D = const, d = var.

**Figure 16.** (a,b) The rate of dissociation of carbon dioxide hydrate (external air temperature Tₐ = 1200 °C, D—particle diameter, d—pore diameter); (c) D = const, d = var.
Since effective quenching is realized within 1 s, it is important to evaluate the time of occurrence of the maximum and its value rather than the average dissociation rate over time. As can be seen from Figure 16b, this maximum appears quite quickly. The value of the extremum indicates the effectiveness of flame suppression. Experimental data show that with effective extinguishing, the flame disappears within 1 s. Thus, the particle diameter of 0.1 mm allows for lowering the flame temperature with the maximum efficiency below the critical value of steady combustion. With a particle diameter in the range of 1–6 mm, the values of the extremes are close to each other and closely coincide with the values of the time–average dissociation rate J. The value of the extremum at D = 0.1 mm is almost 2.5 times higher than at D = 6 mm. The calculated data correspond to Figure 14, where the minimum mass of carbon dioxide hydrate corresponds to the minimum size of particle aggregates.

3.3. Dissociation Rate of Methane Hydrate during Combustion

Let us consider the effect of SDS on the dissociation of methane hydrate during combustion (Figure 17). The dissociation of methane hydrate during combustion occurs with the formation of a water film and gas bubbles, which significantly affect the dissociation rate of methane hydrate.

![Figure 17. Dissociation of methane hydrate during combustion: 1—clean water, 2—water with SDS concentration 0.1%, 3—water with SDS concentration 1%.

The lowest dissociation rate corresponds to the maximum concentration of SDS. SDS brings about foaming. As the foam thickness increases, the dissociation rate decreases (Equation (5)),

\[ J \sim (1/R)^{0.58} \sim (\lambda_v/\delta_v)^{0.58}, \]

where \( R \) is the thermal resistance, \( \lambda_v \) and \( \delta_v \) are the thermal conductivity of steam and the transverse thickness of the steam film, respectively.

The increase in foam thickness over time leads to a decrease in the dissociation rate of the gas hydrate. The maximum dissociation rate corresponds to clean water. No foam is formed during dissociation in clean water. The thermal resistance of a film of water is not significant. Then, the heat flux and the dissociation rate are controlled by the heat transfer coefficient in the gas phase due to the free convective air movement on the surface of the gas hydrate layer.

4. Conclusions

During the synthesis of methane hydrate and at low rpm (200 rpm), several characteristic pressure change modes are implemented. A higher slope of the pressure curve (mode 1) is followed by a more gradual pressure change (mode 2) and an increase in the rate of pressure drop (mode 3). At higher fluid rotation speeds, several of these synthesis modes are absent. The pressure in the reactor continuously decreases with time.
In the synthesis of carbon dioxide hydrate, there are several synthesis modes at both low and high speeds. The modes are associated with the formation of a crust of gas hydrate on the free surface of the liquid.

An increase in the number of revolutions of the liquid in the reactor leads to an increase in the rate of hydrate formation due to several factors: destruction of the hydrate crust, reduction in the diameter of aggregates, and intensification of heat and mass transfer.

Surfactant SDS significantly accelerates the growth of methane hydrate but practically does not affect the growth of carbon dioxide hydrate. The maximum growth rate of CO₂ hydrate takes place with the addition of surfactant OC-5 and Twin. The influence of micelles, gas solubility and porosity on the intensification of hydrate formation has been considered.

The conducted experiments on flame suppression show that it is most effective to use CO₂ hydrate powder with a minimum particle size (particle aggregates). In this case, the flame extinguishing is realized within 1 s. The simulation results also show that the maximum dissociation value is realized fairly quickly (in fractions of a second) and corresponds to particles with a minimum diameter of about 0.1–0.5 mm.

Experimental data and simulation results show that to increase the efficiency of extinguishing the flame, it is necessary to use a powder with a minimum particle size. In this case, the maximum rate of dissociation of carbon dioxide hydrate and the maximum heat flux are achieved, leading to rapid extinguishing of the flame.

As the particle diameter increases, the dissociation rate decreases. There are several characteristic dissociation modes. The diameter of the pores of the particles has a significant effect on the rate of dissociation of carbon dioxide hydrate only at low temperature differences and low heat flux. With an increase in the temperature difference, the exponent (linking the temperature difference with the rate of dissociation of CO₂ hydrate) decreases from a value of 1.35 to a value of 1.29. The decrease in the degree is due to the various effects of thermal and kinetic resistances (during dissociation of gas hydrate) with an increase in external heat flux.

Author Contributions: Conceptualization, S.M., P.S. and V.M.; methodology, S.M.; software, I.D.; validation, I.D.; formal analysis, S.M. and P.S.; investigation, S.M., V.M. and N.S.; writing—original draft preparation, S.M.; writing—review and editing, S.M. and V.M.; visualization, N.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by a grant from the Ministry of Science and Higher Education of Russia, Agreement No. 075-15-2024-543.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

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