

Intensification of Hydrate Formation by Microbubbles

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Abstract. Industrial synthesis of gas hydrates is a promising area for storage, transportation and utilisation of natural gas. The aim of this work is to evaluate the factors that affect the efficiency of gas hydrate synthesis, in particular, the influence of gas microbubble generation. To achieve the goal, the following tasks were solved: the experimental unit was developed and assembled; the experimental research methodology was proposed; experimental data were obtained and their statistical analysis was performed; a mathematical model of hydrodynamic and heat and mass-exchange processes in the nozzle was developed; on the basis of the mathematical model, a calculation program was created which allows analyzing the nozzle operation in different thermobaric conditions under different hydrodynamic regimes. The most important are the results of experiments, which allowed us to determine the factors that have the greatest influence on the intensification of propane hydrate synthesis: the presence of gas microbubbles, liquid temperature, gas temperature, gas pressure in the reactor and others. The influence of individual factors and the presence of gas mixture microbubbles on the intensity of mass transfer processes of hydrate formation in the reactor was determined. The influence of nozzle design features on the efficiency of hydrate formation was analyzed. The significance of the obtained results is to expand knowledge about the influence of various factors on the intensification of gas hydrate synthesis. The research results can be used for designing industrial plants for gas hydrate synthesis.

Keywords: gas hydrates, experimental setup, microbubbles, heat and mass transfer processes, mathematical model, nozzle.

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Intensificarea formării hidraților prin intermediul al microbulilor

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Rezumat: Sinteza industrială a hidraților de gaz este un domeniu promițător pentru stocarea, transportul și utilizarea gazelor naturale. Scopul acestei lucrări este de a evalua factorii care afectează eficiența sintezei hidratului de gaz, în special influența generării de microbule de gaz. Pentru atingerea scopului, au fost rezolvate următoarele sarcini: a fost elaborată și asamblată unitatea experimentală; a fost propusă metodologia cercetării experimentale; s-au obținut date experimentale și s-a efectuat analiza statistică a acestora; a fost elaborat un model matematic al proceselor hidrodinamice, de schimb de căldură și masă în duză. Pe baza modelului matematic a fost creat un program de calcul care permite analiza funcționării duzei în diferite condiții termobarice în diferite regimuri hidrodinamice. Cele mai importante sunt rezultatele experimentelor, care ne-au permis să determinăm factorii care au cea mai mare influență asupra intensificării sintezei hidratului de propan: prezența microbulilor de gaz, temperatura lichidului, temperatura gazului, presiunea gazului în reactor și altele. S-a determinat influența factorilor individuali și prezența microbulilor de amestec de gaze asupra intensității proceselor de transfer de masă de formare a hidraților în reactor. A fost analizată influența caracteristicilor de proiectare a duzei asupra eficienței formării hidraților. Semnificația rezultatelor obținute este extinderea cunoștințelor despre influența diferiților factori asupra intensificării sintezei hidratului de gaz. Rezultatele cercetării pot fi utilizate pentru proiectarea instalațiilor industriale pentru sinteza hidraților de gaz.

Cuvinte-cheie: hidrați de gaz, montaj experimental, microbule, procese de transfer de căldură și masă, model matematic, duză.

Интенсификация гидратообразования при помощи микропузырьков

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Аннотация. Промышленный синтез газовых гидратов является перспективным направлением для хранения, транспортирования и использования природного газа. Целью работы является оценка факторов, которые влияют на эффективность синтеза газовых гидратов, в частности, влияния генерации

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микропузырьков газа. Для достижения поставленной цели были решены следующие задачи: разработана и собрана опытная установка; предложена методика экспериментальных исследований; получены экспериментальные данные и выполнен их статистический анализ; разработана математическая модель гидродинамических и тепломассообменных процессов в насадке; на основании математической модели составлена расчетная программа, позволяющая анализировать работу насадки в разных термобарических условиях при различных гидродинамических режимах. Наиболее важными являются результаты экспериментов, что позволило определить факторы, имеющие наибольшее влияние на интенсификацию синтеза гидрата пропана: наличие микропузырьков газа, температура жидкости, температура газа, давление газа в реакторе и другие. Выявлен характер влияния отдельных факторов и наличия микропузырьков газовой смеси на интенсивность массообменных процессов гидратообразования в реакторе. Проанализировано влияние конструктивных особенностей форсунки на эффективность гидратообразования. Значимость полученных результатов состоит в расширении знаний о влиянии различных факторов на интенсификацию синтеза газовых гидратов. Результаты исследований могут использоваться для проектирования промышленных установок синтеза газовых гидратов.

Ключевые слова: газовые гидраты, экспериментальная установка, микропузырьки, тепломассообменные процессы, математическая модель, насадка.

INTRODUCTION

The synthesis of gas hydrates is the basis for many promising technologies: gas storage and transportation [1], heat storage, separation of gas mixtures, and water desalination. Gas hydrates (GH) are also used as working fluids in various technological processes, such as: uncompressed gas compression, stamping of parts, etc. [2-7]. It is advisable to use gas hydrate technology to increase the efficiency of natural gas production and treatment in the development of gas and gas condensate fields during the period of reservoir pressure reduction [8]. One of the promising areas of application of gas hydrate technologies is the utilisation and disposal of carbon dioxide (CCS) [9, 10]. The relevance of this work is explained by the fact that the basis for many gas hydrate technologies is the industrial synthesis of gas hydrates, for which an important problem is to obtain gas hydrate in large quantities with minimal energy consumption.

Literature review and problem statement.

There are different ways to produce gas hydrates: on the surface of gas bubbles in water, on the surface of water droplets (aerosol), in porous media and on the surface of ice crystals. Many works in different countries have been devoted to the study of ways to produce gas hydrates in microstructures: in Japan [11], in China [12, 13, 14], in Switzerland [15] and others.

It is known that reducing the size of bubbles leads to a significant intensification of heat and mass transfer processes in bubbling units [16]. Hereinafter, the efficiency of the hydrate formation process will be understood as the ratio of the reagent (e.g. gas, water) that entered the hydrate formation reaction to the amount of the reagent supplied to the reactor in the absence of

recirculation. In particular, in this installation, for propane bubbles with a diameter of 5 mm, an efficiency of about 3% was obtained, which in terms of methane would be about 6%. The results of theoretical calculations for the synthesis of gas hydrates on the surface of water droplets in a gas environment show that the main ways to intensify the synthesis of GH are: obtaining a finer aerosol, maintaining the gas temperature at 0 °C and increasing the gas pressure. If we combine the influence of the above factors, we obtain the equation for determining the relative volume of synthesised GH, given in work [17]:

$$\bar{V}_{gg} = \frac{V_{gg}}{V_w} = \frac{\tau^{0,6} \sigma^{0,4869}}{D^{0,941}} (728,2P - 1655) \quad (1)$$

where V_{gg} is the volume of synthesised GH, m³; V_w is the volume of water used to produce GH, m³; τ is time, s; σ is the gas permeability of GH, m²/s; D is the size of droplets, mm; P is the gas pressure, MPa.

Taking into account all the factors, according to (1), for water droplets with an average diameter of 0.1 mm sprayed in a methane environment for 1 second at a pressure of 4 MPa, at least 0.16 m³ of methane hydrate can be obtained from each m³ of water. However, additional energy is required to spray the water.

The results of experimental studies of the synthesis of methane hydrate on the surface of water droplets in a pilot reactor with a volume of 0.248 m³ are presented in [18]. The authors note the important role of the following factors in the production of GH: water droplet size, spray quality, nozzle shape, and the use of surfactants. The operating pressure of the reactor is 5 MPa,

and the pressure of the liquid before the nozzle is 5-5.2 MPa. Quantitative characteristics of the hydrate formation process are not given.

The kinetics of hydrate formation for a mixture of CH₄ + tetrahydrofuran (THF) at different temperatures under steady-state conditions was studied in [19]. It was shown that when used, THF fills large cavities of the clathrate structure, and CH₄ fills small ones. At low pressures, a loose gas hydrate is formed, which is highly permeable to gas, which accelerates the hydrate formation process. The negative effects of using THF are its toxicity, high corrosiveness and cost.

The results of experiments at the pilot plant are presented in [20]. The synthesis of methane gas hydrate on the surface of ice crystals at a temperature of -4°C and a pressure of 4.0 MPa took 18.3 hours. Obviously, this is too slow a process for industrial use.

The production of methane gas hydrate in a fixed slotted bed reactor was discussed in [21]. A significant intensification of the hydrate formation process in slotted media (sand, activated carbon, sintered metal powders, zeolites, silica gels, etc.) is noted. The authors investigated the intensity of CO₂ hydrate synthesis in layers of activated sand with grain sizes ranging from 100 to 1400 µm.

The results of studies of the kinetics of methane hydrate formation in water with hydrochlorofluorocarbon R141b are presented in [22]. The formation of a binary hydrate R141b-CN₄ was detected. The results of the phase equilibrium study showed that the addition of R141b to liquid water significantly reduces the hydrate formation pressure (0.1-3.8 MPa) and increases the formation temperature (287.2-299.5 K).

In [23], an apparatus for studying the rate of hydrate formation on the surface of β-cyclodextrin was proposed. It was found that the use of cyclodextrin can approximately triple the rate of methane hydrate formation. However, the hydrate formation process lasts about 20 minutes.

The results of studies of methane hydrate formation with an aqueous solution of 1,3-dioxolane (DIOX) are presented in [24]. DIOX has the same water solubility as THF, but is less volatile and toxic. The authors studied the synthesis of methane hydrate in a reactor without stirring at a pressure of 7.2 MPa and a temperature of 283.15 K. Experimental data showed that 90% of methane was reacted within 1.5 hours. The authors also found that the addition of L-tryptophan (a hydrophobic amino acid)

accelerates the synthesis of hydrates by another 147%. The use of graphene-based materials to accelerate the synthesis of gas hydrates was analysed in [25]. Graphene activators have two main mechanisms of influence on the synthesis of GH. The first is high thermal conductivity, which allows for efficient heat removal from the reaction zone. The second mechanism is an increase in the number of germinal nanostructures on the basis of which GH crystals are built. Experimental results with different types of graphene materials prove that it is possible to reduce the time of hydrate formation by 96% compared to pure water. The gas content of synthetic gas hydrate also increases by 7.6%. The main problem with the use of graphene materials is their poor dispersion in water.

An analysis of the literature shows that most studies focus on increasing the intensity of hydrate formation in stationary reactors with batch operation. However, for the synthesis of GH on an industrial scale, flow apparatus in which hydrate formation continues continuously are more suitable. The issue of increasing the efficiency of the hydrate formation process in flow-through apparatuses has not been sufficiently studied and requires the study of the effect of gas microbubbles, thermobaric conditions in the reactor and the design of the nozzle on the efficiency of the hydrate formation process. The uniqueness of our paper we see in a comprehensive study of the influence of microbubbles of gas mixtures on the efficiency of the hydrate formation process in order to create an industrial technology for the production of synthetic gas hydrates.

The aim of the study is to improve the efficiency of industrial synthesis of gas hydrates by optimising the dispersion and thermobaric conditions in the reactor.

To achieve this goal, several tasks need to be performed:

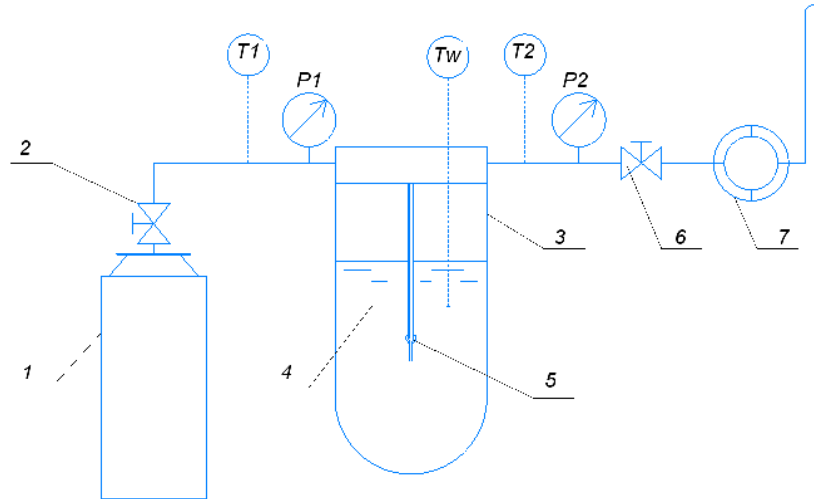
- to develop an experimental setup and technology for producing gas microbubbles in water under thermobaric conditions of hydrate formation;
- to conduct a series of experimental studies to determine the efficiency of hydrate formation using gas microbubbles;
- develop a mathematical model of hydrodynamic processes in the nozzle;
- to analyse the results of full-scale experiments using mathematical modelling methods. To determine the factors that have the

greatest correlation with the efficiency of hydrate formation and obtain regression dependencies.

I. METHODS OF RESEARCH

To conduct experimental studies of the synthesis of propane gas using microbubbles, we

have developed an installation, the scheme of which is shown in Fig. 1. The general view of the setup is shown in the photo, Fig. 2.



1 – gas cylinder, 2 – needle valve on the cylinder, 3 – reactor with a transparent flask, 4 – water, 5 – gas supply pipe with a replaceable nozzle, 6 – needle valve, 7 – gas flow meter.

Fig. 1. Schematic of the experimental setup.

The gas from the cylinder 1 flows through the valve 2 into the replaceable nozzle 5, and from it enters the transparent reactor 3, which is filled with water and ice 4. The gas flow rate is regulated by the needle valve 6 and measured by the gas meter 7. The gas pressure before the nozzle is determined by manometer P1, and the pressure in the reactor is measured by manometer P2. The temperature of the gas before the reactor, after the reactor and the water temperature are controlled by thermometers T1, T2 and Tw.

The efficiency of the gas hydrate synthesis process was determined by measuring the volume of gas released after its dissociation (V_{gg}) by the following equation

$$E = \frac{V_{gg}}{V_{\Sigma}} \cdot 100 \quad (2)$$

where V_{Σ} – the total volume of gas in the experiment, m^3 .



Fig. 2. General view of the experimental setup.

Preliminary studies conducted to assess the efficiency of the plant and identify the main factors affecting the hydrate formation process have shown that the intensity of hydrate formation depends on a number of factors: liquid temperature, gas temperature, gas pressure in the reactor, pressure difference before and after the nozzle, composition of gases in the gas mixture, type and concentration of surfactants, and the design of the nozzle.

The nature of the influence of individual factors was revealed. In particular:

- lowering the liquid temperature intensifies the hydrate formation process, but increases the probability of nozzle icing;
- at negative gas temperatures at the outlet of the nozzle, the icing process is sharply intensified;
- Increasing the overall pressure in the reactor leads to an intensification of gas hydrate synthesis, but part of the pressure must be lost at the nozzle to form microbubbles;
- the number of microbubbles in the water depends on the surfactant concentration and increases with the gas outlet rate from the nozzle. Thus, the design of the nozzle and the gas flow rate affect the size and number of gas bubbles in the reactor, which changes the intensity of hydrate formation.

Determining the size of bubbles. Bubbles smaller than 100 microns are called microbubbles. They are characterised by the absence of coalescence, the rate of rise exactly follows Stokes' law, and the Reynolds criterion does not exceed 1.

The rate of bubble rise was determined by high-speed videotaping of the transparent reactor followed by slow scrolling of the video. The displacement of the microbubble array was measured from a still image of the video (the interface between water and dispersed phase is quite well distinguishable). The bubble velocity (displacement divided by time interval) was determined as an average at different time moments.

After measuring the speed of bubbles in water, their size can be calculated by the formula

$$d = \sqrt{\frac{18Vv}{g\left(1 - \frac{\rho_g}{\rho_w}\right)}} \quad (3)$$

where d – the diameter of the bubble, m; V – the velocity of bubbles in water, m/s; v – the

kinematic viscosity of water, m²/s; g – the acceleration of free fall, m/s; ρ_g and ρ_w – the densities of gas and water, respectively, kg/m³.

According to the experimental data, the average size of microbubbles is in the range of 60÷70 μm.

The composition of the gas mixture. In experimental studies of the synthesis of propane gas, a propane-butane mixture from a cylinder was used. Since the proportion of its components is constantly changing during the evaporation of a liquid gas mixture, it is important to determine the propane concentration quickly.

At the saturation line, each gas has its own pressure value as a function of temperature, so the composition of the gas mixture can be calculated knowing its pressure at a known temperature. The total pressure is the sum of the partial pressures of the components, Pa

$$P = P_p + P_B \quad (4)$$

where P – the total pressure of the mixture, Pa; P_p – the pressure of pure propane at a given temperature, Pa; P_B – the pressure of pure n-butane at a given temperature, Pa. Having measured the total pressure of the gas mixture and its temperature, the fraction of propane (XP) can be determined by the formula

$$X_p = \frac{P - P_B}{P_p - P_B} \quad (5)$$

The use of dependence (5) to process the experimental data made it possible to determine the composition of the liquefied gas. In its initial composition, the gas mixture contains propane (C₃H₈) in the amount of up to 70% and n-butane (C₄H₁₀) in the amount of up to 30%. The total amount of other hydrocarbons (ethane, ethylene, butylene, etc.) does not exceed 7% and was not taken into account in the calculations. The final composition of the mixture is 30% propane and 70% n-butane.

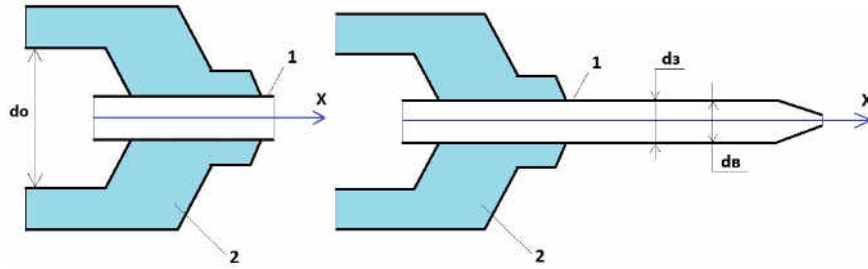
Surfactant concentration. The concentration of surfactant in the reactor water plays an important role in the production of microbubbles. In the experiments, a gel containing 10% sodium laureth sulphate and 5%

lauramine was used as a surfactant. A number of experiments were conducted to determine the minimum sufficient surfactant concentration. It was experimentally established that to obtain microbubbles at a water temperature of 0 - +5 °C, the minimum mass concentration of surfactant in water is 0.04%. Further increase in the surfactant

concentration does not lead to a significant increase in the number of microbubbles.

Study of the design of a nozzle for the synthesis of microbubbles of gas. The design of the nozzle plays an important role in the generation of micro gas bubbles in the water. In addition, it must not freeze and clog with solid particles. That is why special attention was paid to the study of the influence of the nozzle design on the synthesis of gas hydrates.

Steel tubes with a length of 7-44 mm and an internal diameter of 0.21-0.51 mm were used as a nozzle for the experiments. The part of the tube that is in direct contact with water is treated as a heat exchanger. Some of the tubes are made with a nozzle at the outlet. In general, all the considered types of nozzles can be divided into two types: a - short tubes without a confuser with a length of 22-26 calibres; b - long tubes with or without a confuser (50-86 calibres in length), Fig. 3.



1 – steel nozzle, 2 – part of the nozzle fastening.

Fig. 3. Design of different types of nozzles.

Mathematical model of hydrodynamic processes in the nozzle.

To study heat exchange and hydrodynamic processes in the nozzle, a mathematical model of the thermal and hydraulic regime of gas flow must be developed. The peculiarity of these processes is gas cooling with the possibility of partial condensation of vapours of each component of the gas mixture. Since the proportion of condensed gas is relatively small, it can be assumed to be evenly distributed in the gas flow.

Determining the pressure loss on a nozzle without a confuser.

The total pressure loss on nozzles of different types can be determined as the sum of individual components, Pa

$$\Delta P_{\Sigma} = \Delta P_1 + \Delta P_L + \Delta P_2 + \Delta P_C \quad (6)$$

where ΔP_1 – pressure loss on a sharp constriction of the flow, Pa; ΔP_L – pressure loss along the length of the nozzle, Pa; ΔP_2 – pressure loss on gas outlet to the external environment, Pa; ΔP_C – pressure loss to the gas outlet through the nozzle, Pa.

The total pressure loss on a short nozzle (a, Fig. 3) will consist of ΔP_1 , ΔP_L and ΔP_2 . For the nozzle type b, Fig. 3, it is ΔP_1 , ΔP_L and ΔP_S .

The pressure loss at the sudden flow constriction is calculated by the formula, Pa

$$\Delta P_1 = 0,5 \left(1 - \frac{d_B^4}{d_0^4} \right) \frac{V_1^2}{2} \rho_1 \quad (7)$$

where d_0 – the inner diameter of the nozzle mounting, mm; d_B – the inner diameter of the steel nozzle, mm; V_1 – the gas velocity in the nozzle, m/s. Diameter $d_0 = 2.5$ mm. The maximum internal diameter $d_B = 0.51$ mm. Consequently, the minimum value of the bracketed parameters in Formula 5 is 0.96, and with a decrease in d_i it approaches 1. If we assume that it tends to 1, Formula 7 takes the form

$$\Delta P_1 = 0,25 V_1^2 \rho_1 \quad (8)$$

At the nozzle outlet, we have hydraulic resistance, e.g. sudden expansion, for which the pressure loss can be calculated using the formula

$$\Delta P_2 = 0,55 V_2^2 \rho_2 \quad (9)$$

The nozzle also has gas flow areas in a **straight section of the pipeline**. Due to the large pressure loss along the straight section, the gas density and therefore the gas velocity can change significantly. Therefore, the pressure loss in such a section should be determined by integrating the Darcy equation, which is written in differential form

$$dP_x = -\lambda_x \frac{dx}{d_B} \frac{V_x^2}{2} \rho_x \quad (10)$$

where P – pressure, Pa; λ – friction coefficient; ρ – gas density, kg/m³; V – gas velocity, m/s.

In equation (10), the friction coefficient can be determined by the Altschul formula

$$\lambda_x = 0,11 \left(\frac{k_e}{d_B} + \frac{68}{\text{Re}_x} \right)^{0,25} \quad (11)$$

where $k_e/d_B=0,005$; Re – Reynolds number.

Reynolds number

$$\text{Re} = \frac{V_x d_B}{\nu_g} \quad (12)$$

where ν_g – the kinematic viscosity of gases, m²/s. Kinematic viscosity of gases: propane – 0,53 • 10⁻⁶ m²/c; n-butane – 0,6 • 10⁻⁶ m²/c. The gas velocity is determined by the formula

$$V_1 = \frac{4G_g}{\rho_g \pi d_B^2} \quad (13)$$

where G_g – mass rate flow of the gas mixture, kg/s; ρ_g – density of the gas mixture, kg/m³. The mass flow rate of the gas mixture can be determined from the meter readings, kg/s

$$G_g = L_1 \cdot \rho_1 \quad (14)$$

where L_1 – volumetric flow rate of the gas mixture through the meter, m³/s; ρ_1 – density of the mixture under thermobaric measurement conditions in the meter, kg/m³.

The density of a gas mixture of propane and n-butane can be determined by the formula

$$\rho_g = \frac{P}{RT} \left(X_p \frac{\mu_p}{Z_p} + (1 - X_p) \frac{\mu_B}{Z_B} \right) \quad (15)$$

where μ – molar mass, kg/mol; P – pressure, Pa; R – the universal gas constant, J/(mol·K); T is the absolute temperature, K; Z is the compressibility factor, respectively, for propane (P) and n-butane (B). The molar mass of propane is $\mu_P = 44.1$ g/mol, and that of butane is $\mu_B = 58.1$ g/mol.

The compressibility factor of each gas is determined by the formula

$$Z = \frac{V_M}{V_M - b} - \frac{1}{3(\sqrt[3]{2} - 1)^2} \frac{b}{V + b} F_{(\omega, T_r)} \quad (16)$$

where V_M – molar volume of gas, m³/mol; b – empirical constant; $F_{(\omega, T_r)}$ – the modifying function. The empirical constant is calculated as

$$b = \frac{\sqrt[3]{2} - 1}{3} \frac{RT_k}{P_k} \quad (17)$$

where T_k – the critical temperature of the gas, K; P_k – the critical pressure of the gas, Pa. For example, for propane, the critical parameters are $T_k=96,63$ °C, $P_k=4,3$ MPa, for n-butane – $T_k=151,94$ °C, $P_k=3,797$ MPa.

The modifying function depends on the acentricity factor (ω) and the reduced temperature. For light hydrocarbon systems, the modification by G. Soave is the most accurate in determining the parameters of liquid-vapour equilibrium:

$$F_{(\omega, T_r)} = \frac{1}{T_r} \left[1 + (0,48 + 1,574\omega - 0,176\omega^2) (1 - T_r^{0,5}) \right]^2 \quad (18)$$

The acentricity factors for propane and n-butane are given in Table 1.

Table 1

Acentricity factor for individual gases	
Gas	Acentricity factor (ω)
propane	0,152
n-butane	0,201

The reduced temperature is determined by the formula

$$T_r = \frac{T}{T_k} \quad (19)$$

Taking into account the acentricity factor, the modifying function for propane is

$$F_{(P)} = \frac{369,8}{T} \left[1 + 0,715 \left(1 - \frac{T^{0,5}}{19,23} \right) \right]^2 \quad (20)$$

Similarly, we find the modifying function for butane

$$F_{(B)} = \frac{425,1}{T} \left[1 + 0,789 \left(1 - \frac{T^{0,5}}{20,62} \right) \right]^2 \quad (21)$$

The determination of compressibility factors requires an iterative approach to calculations.

Determining the pressure loss on the nozzle.

Unlike the previous one, this nozzle contains a confusor that dramatically increases the gas outlet velocity.

Assuming an adiabatic flow of ideal gas from the nozzle, the gas outlet velocity is calculated by the formula, m/s

$$V_c = \sqrt{\frac{2k}{k-1} P_1 v_1 \left(1 - \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \right) + V_1^2} \quad (22)$$

where k – the adiabatic index ($k=C_p/C_v$); P_1 – the gas pressure at the nozzle inlet, Pa; P_2 – gas pressure at the nozzle outlet, Pa; V_1 – gas velocity before the nozzle, m/s; v_1 – the specific volume of gas, m³/kg.

The total pressure loss for a nozzle with a nozzle is therefore made up of the sudden narrowing, the frictional loss in the small diameter tube and the loss at the nozzle. The total pressure loss on this type of nozzle is determined by the formula

$$\Delta P_\Sigma = 0,25V_1^2 \rho_1 + \Delta P_l + \Delta P_c \quad (23)$$

Taking into account the heat exchange of the pipe with the environment, the following heat and mass transfer processes inside the pipe can be included

- gas cooling due to pressure reduction;
- temperature change due to heat exchange with the environment through the tube wall;
- condensation or evaporation of gas mixture components under suitable conditions.

The thermal regime of a gas mixture moving in a pipe along the x-axis under stationary conditions is described by the first law of thermodynamics.

$$dU_x = dQ_x - dA_x \quad (24)$$

From which, after the components are disclosed, we obtain the system of equations

$$dA_x = -\frac{G_g}{\rho_x k} dP_{g(x)} \quad (25)$$

$$dQ_x = K_x \cdot dx \cdot (T_w - T_{g(x)})$$

$$dU_x = c_g \cdot G_g \cdot dT_{g(x)} - r_p V_x \frac{dm_p}{dx} - r_b V_x \frac{dm_b}{dx}$$

$$K_x = \frac{1}{\frac{1}{\alpha_{1(x)} d_B} + \frac{1}{2\lambda_{CT}} \ln\left(\frac{d_z}{d_B}\right) + \frac{1}{\alpha_2 d_z}}$$

where c_g – the mass heat capacity of the gas mixture, J/(kg · °C); d_B – the inner diameter of the pipe, m; ρ_x – the density of the gas mixture in section X, kg/m³; T_g – the temperature of the gas mixture, °C; T_w – the temperature of the water in the reactor, °C; G_g – the mass flow rate of the gas mixture, kg/s; r_p – the heat of condensation of propane, J/kg; r_b – the condensation heat of n-butane, J/kg; m_p – the mass of liquid propane, kg; m_b – the mass of liquid butane, kg; $\alpha_{1(x)}$ – the heat transfer coefficient at the inner surface of the tube in section x, W/(m²·K); α_2 – the heat transfer coefficient at the outer surface of the tube, W/(m²·K); d_z – the outer diameter of the tube, m.

In the case of turbulent flow (Re>10000 in the experiments), the heat transfer between the gas and the pipe surface is mainly due to convection. For turbulent motion, the heat transfer coefficient at the inner surface of the heat exchanger tube can be determined by the formula, W/(m²·K).

$$\alpha_{1(x)} = 0,021 \frac{\lambda_g}{d_B} \text{Re}_{(x)}^{0,8} \text{Pr}_g^{0,43} \quad (26)$$

where λ_g – the thermal conductivity of the gas mixture, W/(m·°C); $\text{Re}_{(x)}$ – Reynolds number in section x; Pr_g – Prandtl number for the gas mixture.

To determine the heat transfer on the pipe surface, the following dependence is applied

$$\alpha_2 = C \frac{\lambda_w}{d_z} (Gr \text{Pr}_w)^n \quad (27)$$

where C, n – empirical coefficients; λ_w – the thermal conductivity of the heat carrier, W/(m·°C); Gr – the Grashof number; Pr_w – the Prandtl number for water.

Coefficients C and n in the equation (27) is determined depending on the mode of fluid movement, Table 2.

Table 2

Acentricity factor for individual gases		
Gr · Pr	C	n
<500	1,18	0,125

500...20000000	0,54	0,25
>20000000	0,135	0,33

The Grashof number is calculated by the well-known formula

$$Gr = \frac{g\beta l^3(T_W - T_S)}{\nu^2} \quad (28)$$

where g – acceleration of free fall, m^2/s ; β – coefficient of volumetric expansion of water, $^{\circ}C^{-1}$; l (d_z) – characteristic size, m ; T_W – water temperature, $^{\circ}C$; T_S – surface temperature, $^{\circ}C$; ν – viscosity coefficient of the liquid, m^2/s .

The thickness of the pipe and the material from which it is made allow us to calculate the heat transfer resistance. For example, stainless steel has a fairly low thermal conductivity $\lambda_s=15 W/(m \cdot K)$.

The mass of condensed propane and n-butane is determined only under thermobaric conditions when the partial pressure of the corresponding

component of the gas mixture is greater than the saturated vapour pressure at a given temperature:

$$P_B > P_{B(T)}^s \Rightarrow dm_B > 0 \quad - \quad \text{n-butane}$$

condensation;

$$P_P > P_{P(T)}^s \Rightarrow dm_P > 0 \quad - \quad \text{propane condensation.}$$

If the partial pressure of the gas in question is lower than the pressure of its saturated vapour at a given temperature and if condensed gas is present, it evaporates:

$$(P_B < P_{B(T)}^s) \wedge (m_B > 0) \Rightarrow (dm_B < 0) -$$

evaporation of n-butane condensate;

$$(P_P < P_{P(T)}^s) \wedge (m_P > 0) \Rightarrow (dm_P < 0) -$$

propane condensate evaporation.

II. RESULTS OF RESEARCH

A computer program was created based on equations 6-28 of the mathematical model. As a result of experimental studies, the initial data for the calculation were obtained (Table 3).

Table 3

Date	tg, $^{\circ}C$	tr, $^{\circ}C$	to, $^{\circ}C$	Pr ^{max} , bar	Pr, bar	P _{react} , bar	Ø internal, mm	Lg, l/s	Gg, kg/s	Nozzle Orifice
19.06	13	0	14	3,0	1,7	1,2	0,31	0,0170	$3,8 \cdot 10^{-5}$	orifice
07.07	15	0	16	4,6	3,46	3,1	0,535	0,118	$24,4 \cdot 10^{-5}$	orifice
09.08	16	0	17	4,0	3,4	2,4	0,795	0,0141	$3,03 \cdot 10^{-5}$	nozzle

The calculation results are shown in Table 4.

Table 4

Date	Xp1, %	Xp2, %	Gk/Gg, %	ΔP, bar	tg, $^{\circ}C$	Vg, m/c	E, %	Notes
19.06	44,1	47,6	3,3	0,5	7,0	88,34	6,6	Butane condensation in the reactor
07.07	67,9	70,2	2,5	0,36	4,03	128,65	8,3	Butane condensation in the reactor and in the constriction
09.08	54,5	75,0	7,7	1,0	5,8	152,6	5,8	Butane condensation in pipe, nozzle, reactor

Thus, initial data were obtained to analyse the influence of various factors on the hydrate formation process.

III. DISCUSSION

Experimental studies allowed us to characterise the influence of various factors on

the hydrate formation process. Let us highlight the factors that have the greatest impact on the

hydrate formation efficiency based on the results of pilot experiments.

Mass transfer processes. Correlation between the efficiency of gas hydrate synthesis and the mass fraction of condensed n-butane in the gas mixture at the inlet to the reactor is very high -0.940. Analysis of the expansion of the gas mixture in the nozzle shows that partial liquefaction of n-butane occurs during the cooling

of the gas mixture. This process uses part of the energy that would otherwise lead to a decrease in the temperature of the gas mixture. The condensation of n-butane vapours can be avoided by reducing its initial concentration in the gas mixture.

Gas temperature. The correlation between the hydrate formation efficiency and the gas temperature at the nozzle outlet (-0.906) is in

second place (Fig. 4). The obtained regression dependence has the form, %

$$\eta = 8,16 - 0,247t_g \quad (29)$$

In general, lowering the gas temperature at the nozzle outlet has a positive effect on the hydrate formation process. However, negative gas temperatures often lead to nozzle icing.

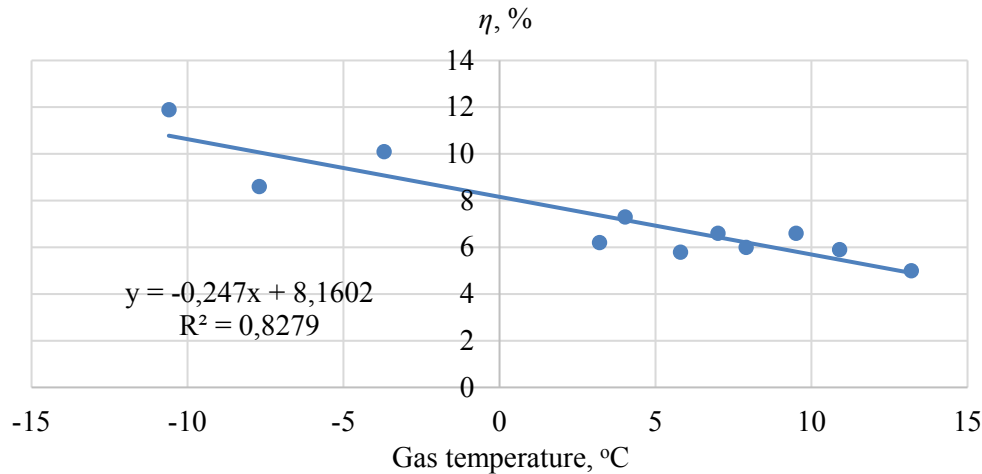


Fig. 4. Regression of hydrate formation efficiency with gas temperature at the nozzle outlet.

Propane concentration. The initial concentration of propane in the propane-butane mixture has a significant impact (correlation coefficient 0.836), Fig. 5. The results of the pilot experiments indicate that the propane concentration should be maximised to increase the process efficiency. The calculations also

indicate intensive condensation of butane vapours in the nozzle and sometimes in the reactor. Therefore, n-butane in this case acts as a ballast for the propane hydrate synthesis process.

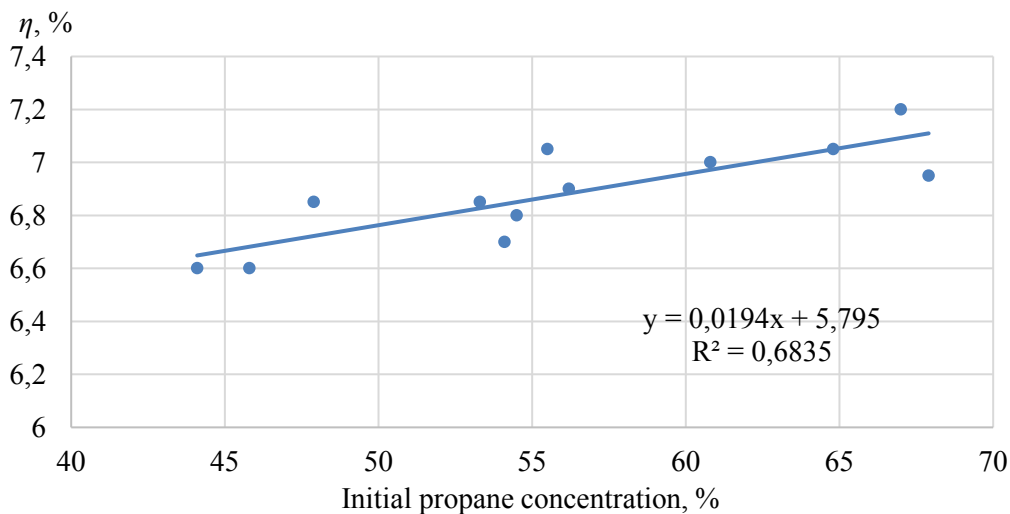


Fig. 5. Regression dependence of hydrate formation efficiency with the initial concentration of propane in the gas mixture (Xp1).

The velocity of the gas outlet from the nozzle has a significant positive correlation with

the hydrate formation efficiency (0.732) in the range of 50÷200 m/s, Fig. 6. An increase in the

gas mixture velocity at the nozzle outlet leads to an intensification of hydrate formation, but it is also influenced by other factors, such as n-butane condensation and nozzle icing. Therefore, there are significant differences in the results of similar experiments.

It has been experimentally established that a gas velocity of at least 50 m/s is required to initiate the formation of microbubbles in water. To obtain a significant number of microbubbles with a size of 60-70 microns, it is necessary to reach a speed of 80-120 m/s at the outlet of the nozzle.

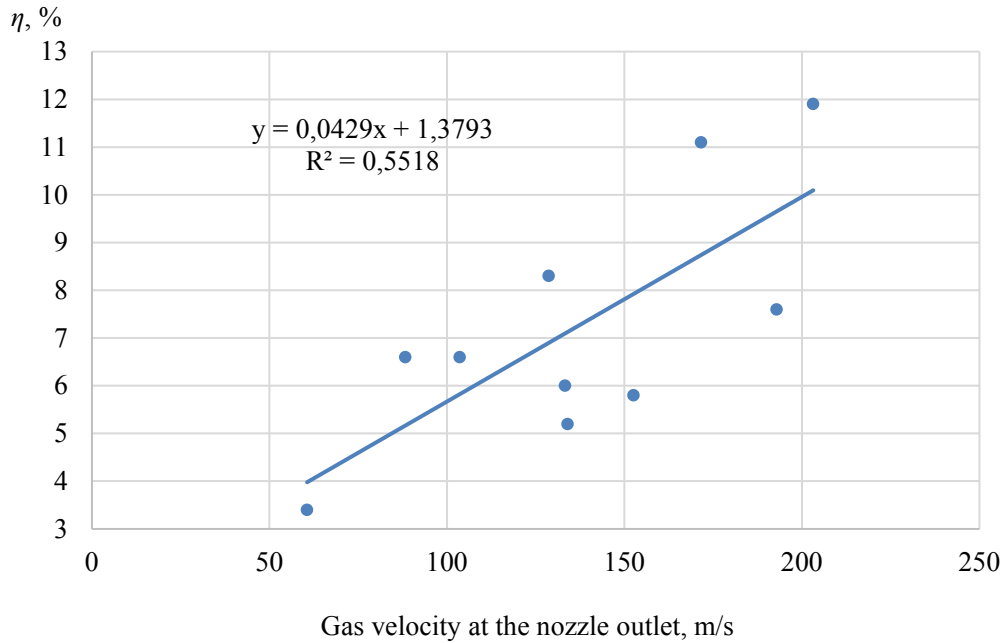


Fig. 6. Effect of gas mixture velocity at the nozzle outlet (V_g) on hydrate formation efficiency.

Pressure difference. The effect of the pressure difference in the reactor with the hydrate formation pressure has a weaker correlation (-0.694). Increasing the pressure in the reactor should intensify the hydrate formation process, but this is not the case with propane. An increase in the pressure drop in the reactor leads to a decrease in the pressure drop on the nozzle. This proves that the main hydrate-forming processes are mass transfer processes on the surface of microbubbles, rather than thermobaric conditions in the reactor. As a conclusion, it can be noted that for the synthesis of propane hydrate in the temperature range of 0-2 °C, it is necessary to maintain a gauge pressure of 1-1.5 bar in the reactor.

Water temperature. To achieve maximum hydrate formation efficiency, distilled water with ice at 0 °C was used in the experiments. As the gas temperature decreases as a result of throttling, the icing effect occurs, which leads to a sharp decrease in gas flow through the nozzle. Visually, when the nozzle is iced, an ice tube (sometimes branched) of small internal diameter with a length of 5-6 mm is formed. At the same time, the gas

flow rate decreases sharply, and instead of microbubbles, individual gas bubbles of 1-3 mm in size are formed.

According to the results of experimental studies, at a water temperature of +2 °C, icing of the nozzle is rare and the nozzle defrosts itself in a few minutes.

Nozzle design. The study of hydrate formation when using various nozzles made it possible to identify their characteristic features and optimise their design.

The long tube without a confusor (50-81 calibre) and nozzles with a minimum internal diameter ($d_v=0.21$ mm) are characterised by high pressure losses, which leads to intensive cooling of the gas mixture and nozzle icing at a water temperature of 0 °C. In addition, the pressure in the bubbles produced by this type of nozzles differs little from the pressure in the reactor, the bubbles expand poorly and do not have a sufficient internal source of "cold" for the synthesis of gas hydrate. As a result, the efficiency of hydrate formation is only 1-3%.

The nozzle with a confusor. At low gas flow rates, they operate in the subcritical mode and act

similarly to the previous ones. With an increase in the pressure drop, they switch to the critical mode, which is accompanied by an increase in the outlet velocity of the gas mixture by 2.5-3 times. Almost all the pressure is throttled in the part of the tube where the nozzle is located, which leads to its rapid cooling and almost instantaneous icing. At a water temperature of +2 °C, the nozzle defrosts itself in 1-2 minutes, the gas flow rate increases and it freezes again.

Short tube without a confusor. At the outlet of such nozzles, the gas mixture reaches a speed of 114-133 m/s, which creates numerous microbubbles in the water and increases the mass transfer surface area. With a length of 22-26 calibres, only 35-51% of the available pressure drop is used for throttling in the nozzle, which allows achieving two positive effects. Firstly, it reduces the influence of the Joule-Thomson effect, as a result of which the nozzle practically does not freeze. Secondly, the bubbles expand rapidly, which is accompanied by their cooling and a significant intensification of gas hydrate synthesis (efficiency of 5-12%).

Therefore, it has been experimentally established that the optimal nozzle design is a straight nozzle with a length of 22-26 calibres.

CONCLUSIONS

A mathematical model has been developed that allows determining the gas velocity and pressure loss in different parts of the nozzle. Its implementation in a computer program made it possible to perform gas-dynamic calculations of various nozzles in the experimental conditions of the pilot installation.

It has been established that the main hydrate-forming processes are mass transfer processes on the surface of microbubbles, rather than thermobaric conditions in the reactor. Regression dependences of the influence of the following factors on the intensity of gas hydrate synthesis were obtained: gas mixture composition, temperature, and gas velocity at the nozzle outlet.

The analysis of the results of experimental and theoretical studies allowed us to optimise the design of the nozzle and specify the thermobaric conditions in the reactor. In particular, it was found that the best nozzle shape is a 22-26 calibre nozzle. Such a nozzle practically does not clog and does not freeze at a water temperature of 0 °C.

It has been experimentally established that to obtain microbubbles, the optimal gas outlet velocity from the nozzle should be in the range of

100-130 m/s. At lower velocities, the number of bubbles with an average size of more than 100 microns increases, and at higher velocities, nozzle icing is observed. In order to avoid icing of the nozzle in water with a temperature of 0°C and to intensify hydrate formation, the optimum gas temperature at the nozzle outlet should be close to 0°C. The water temperature in the reactor at +2°C avoids nozzle icing in a wide range of gas mixture temperatures. It was found that n-butane in the gas mixture is a ballast. The minimum concentration of surfactant in water sufficient is 0.04% for the formation of microbubbles at a water temperature of 0...+5 °C.

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