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ACTUAL PROBLEMS OF RENEWABLE ENERGY, CONSTRUCTION AND ENVIRONMENTAL ENGINEERING

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Promising renewable energy sources

FAST SYNTHESIS OF GAS HYDRATES

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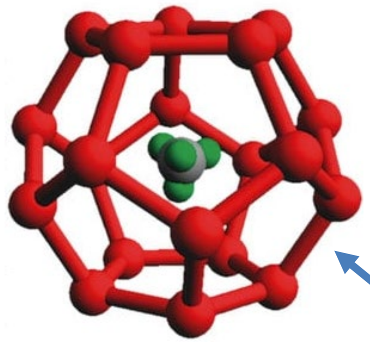
Natural Gas Hydrates

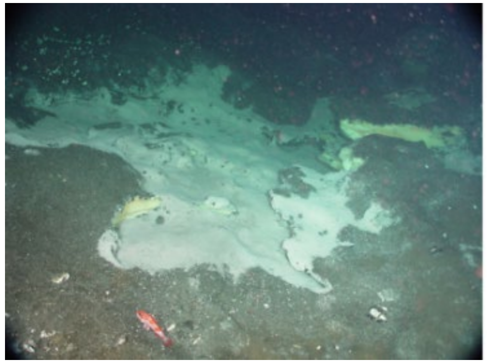
The Origin and Distribution of Gas Hydrates

Biogenic Hydrate ~99 %

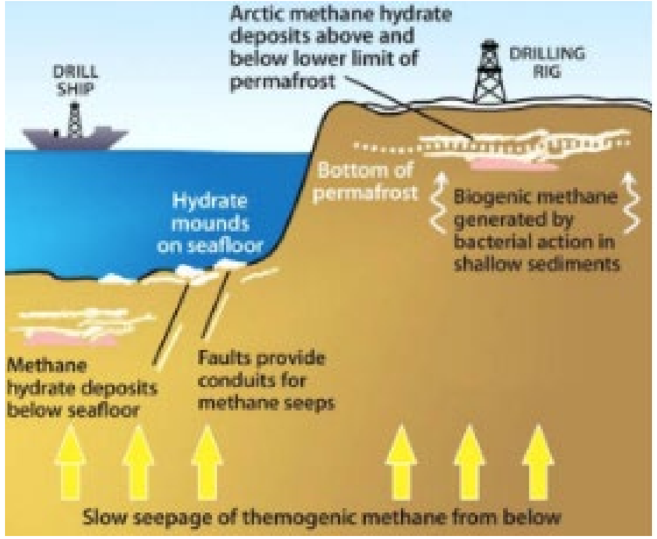
Thermogenic Hydrate



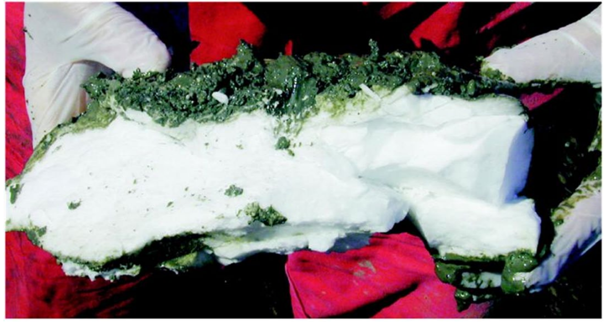
A model of methane hydrate's cage-like structure in which methane (the grey/green molecule) is enclosed inside a lattice of water (the red molecules)



A thinly-sedimented mound of exposed hydrate and associated clam community on the seafloor [1]



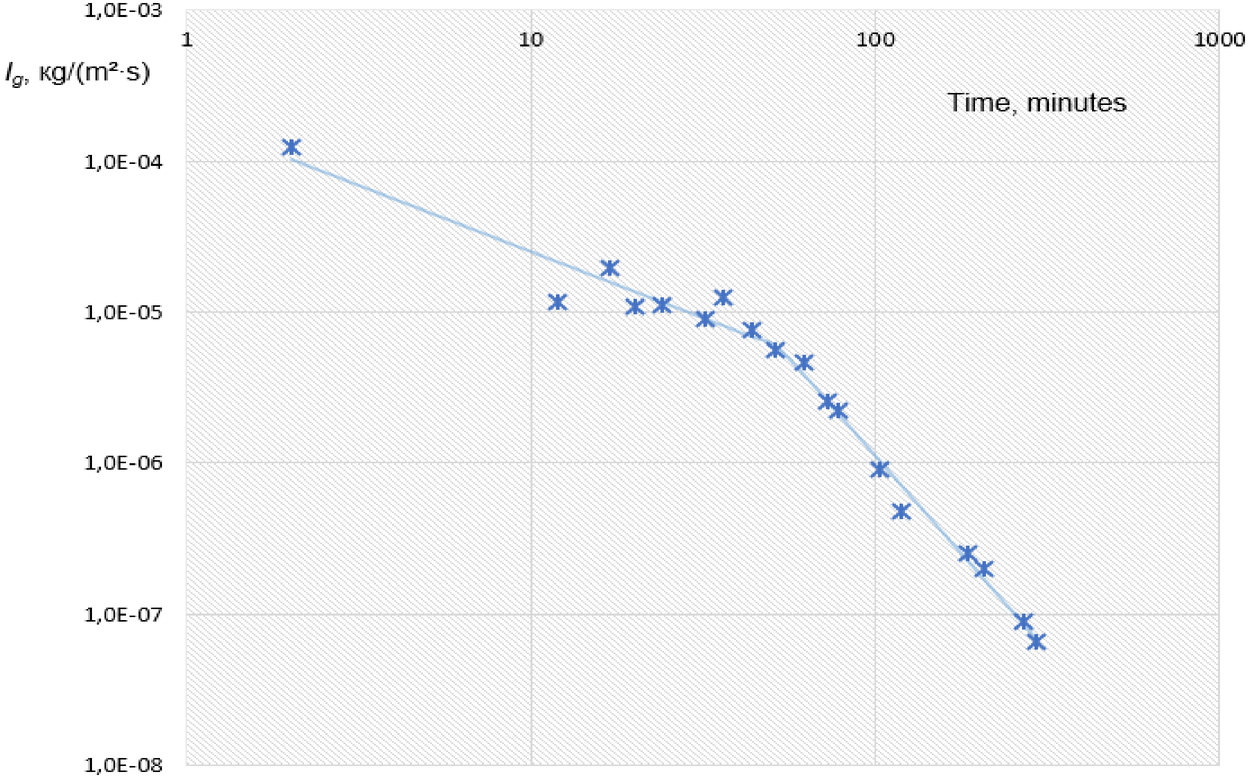
Synthesis of Gas Hydrates

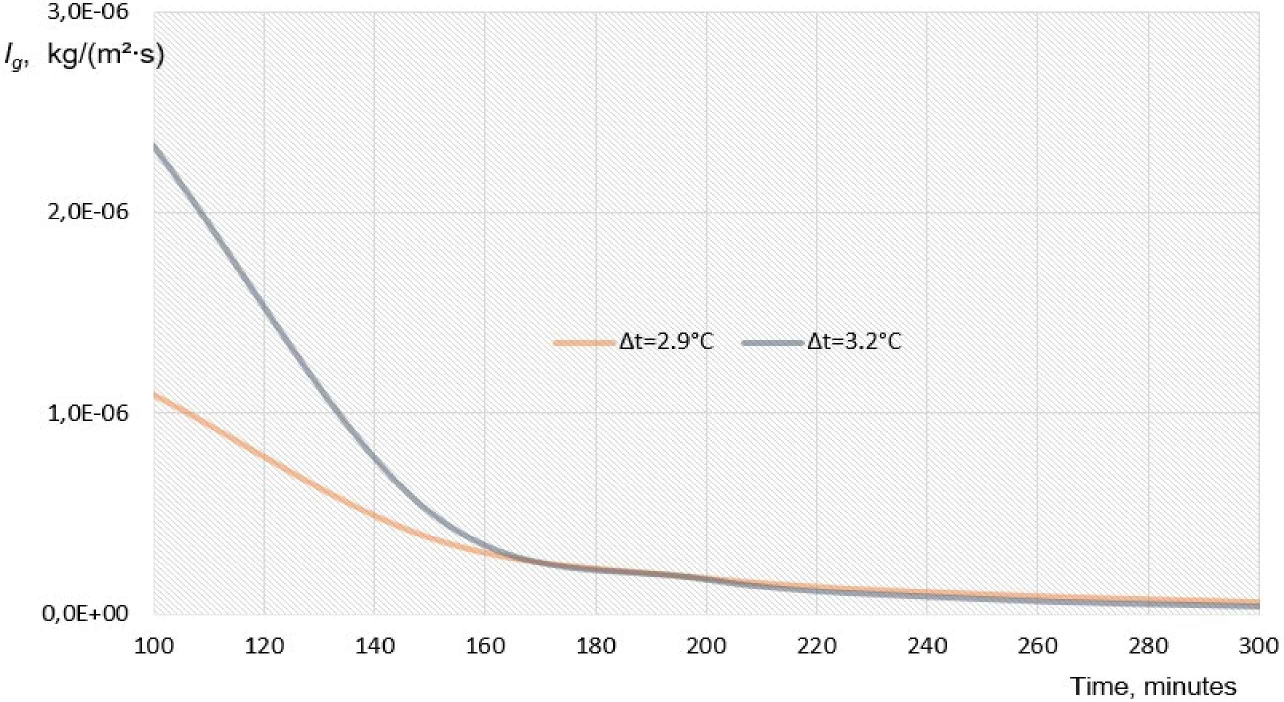


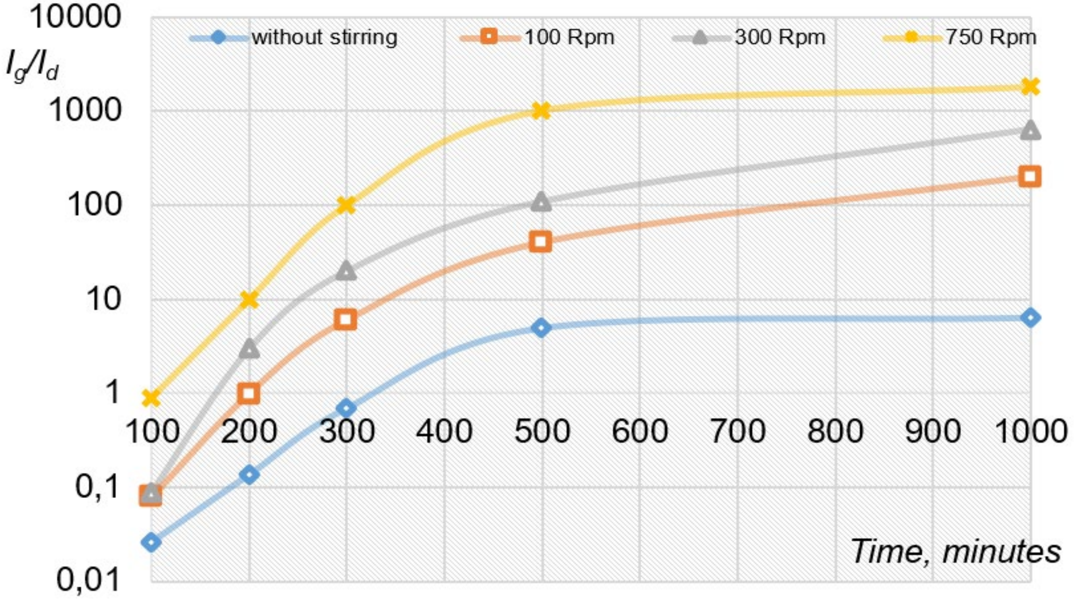
Problems in the Synthesis of Gas Hydrates:

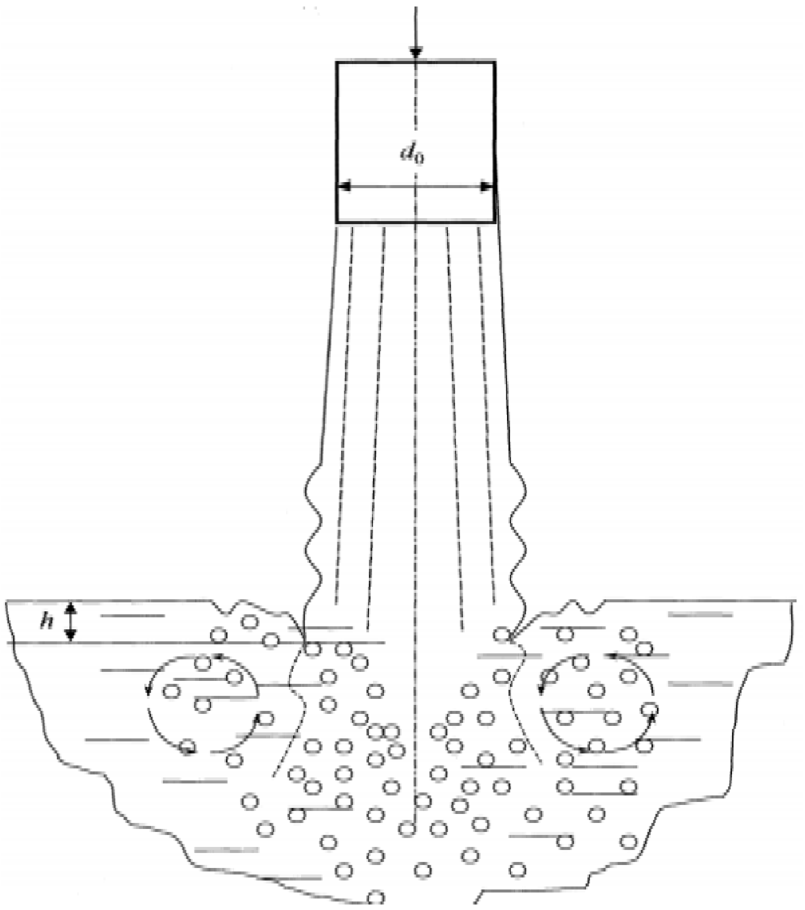
1. stochastic nature of hydrate nucleation
2. slow growth kinetics of hydrates
3. efficient heat removal from the reaction zone

Global estimates of the gas content of hydrate structures are in the range $\approx(1\text{–}5) \times 10^{15}$ (m^3)


I_g, кg/(m²·s)
1,0E-03
1,0E-04
1,0E-05
1,0E-06
1,0E-07
1,0E-08
1
10
100
1000
Time, minutes


I_g, kg/(m²·s)
3,0E-06
2,0E-06
1,0E-06
0,0E+00
Δt=2.9°C
Δt=3.2°C
100
120
140
160
180
200
220
240
260
280
300
Time, minutes


I_g/I_d
10000
1000
100
10
1
0,1
0,01
without stirring
100 Rpm
300 Rpm
750 Rpm
100
200
300
400
500
600
700
800
900
1000
Time, minutes


d_0
h

Experimental conditions

The following gas was used for the experiment:

CH_4—92.8%, C_3H_8—2.1%, C_2H_6—5.1%.

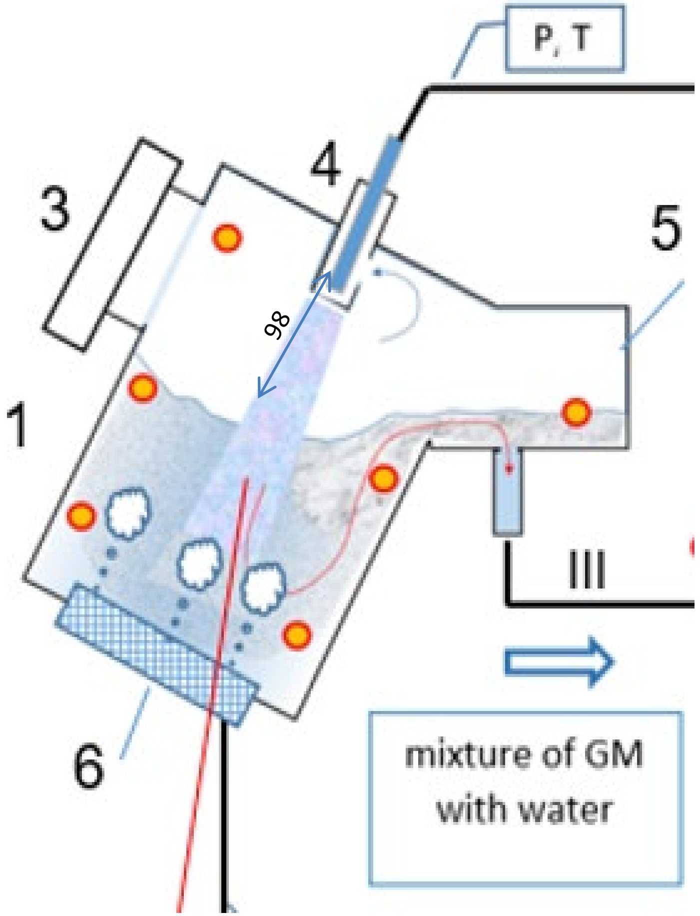
The nozzle diameter was 2.12 (mm).

Gas pressure in the reactor was maintained at 3.8 MPa.

The temperature in a plant thermal chamber was maintained
276.1 (K).

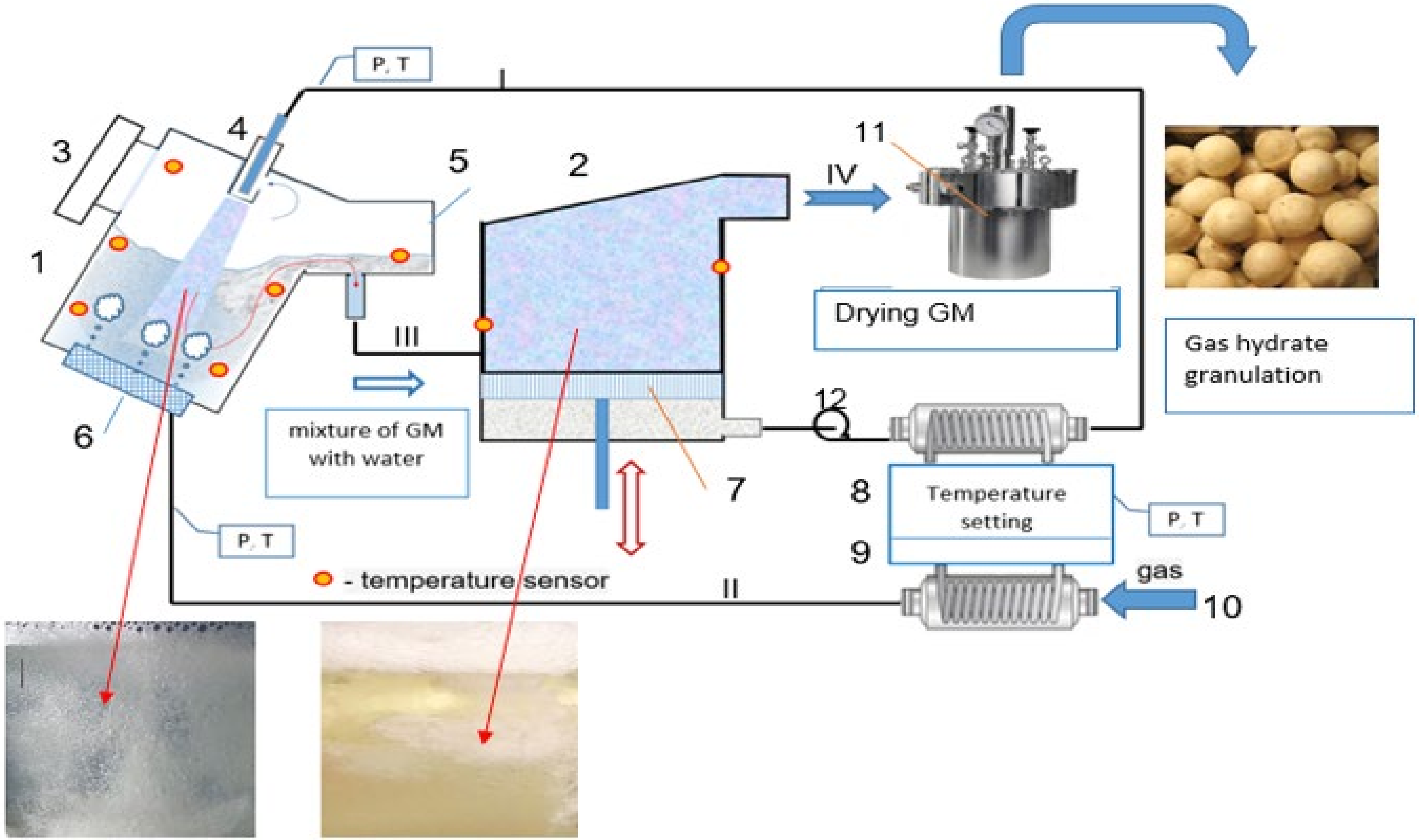
The distance from nozzle 4 (**Sl 4**) of the jet

apparatus to the liquid surface was 98 mm).

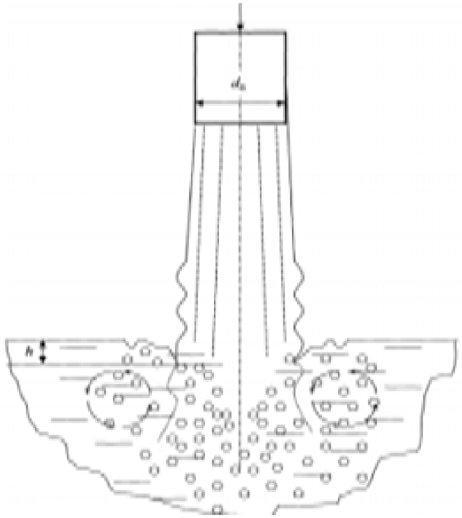


Main process steps

ESS



Scheme of a gas hydrate plant for continuous production of gas hydrate: 1– reactor; 2 - separator 2 - temperature sensors; 3, 5 - inspection windows; 4 - jet apparatus; 5 - removal of water-gas hydrate mixture; 6 - bubbler; 7 - filter; 8, 9 - thermostats; 10 - gas; 11 - thermal chamber for hydrate drying; 12- recirculation pump; flows: I - water under pressure; II - gas; III - water-gas hydrate mixture; IV - wet hydrate for drying



Scheme of gas-liquid mixture formation

a) b) c)

GM photos: a) 15% water content, morphology 1 (M1); b) 6% humidity, morphology 2 (M2); c) dry hydrate, morphology 3 (M3)

Formed hydrate (morphology 2 (M2))

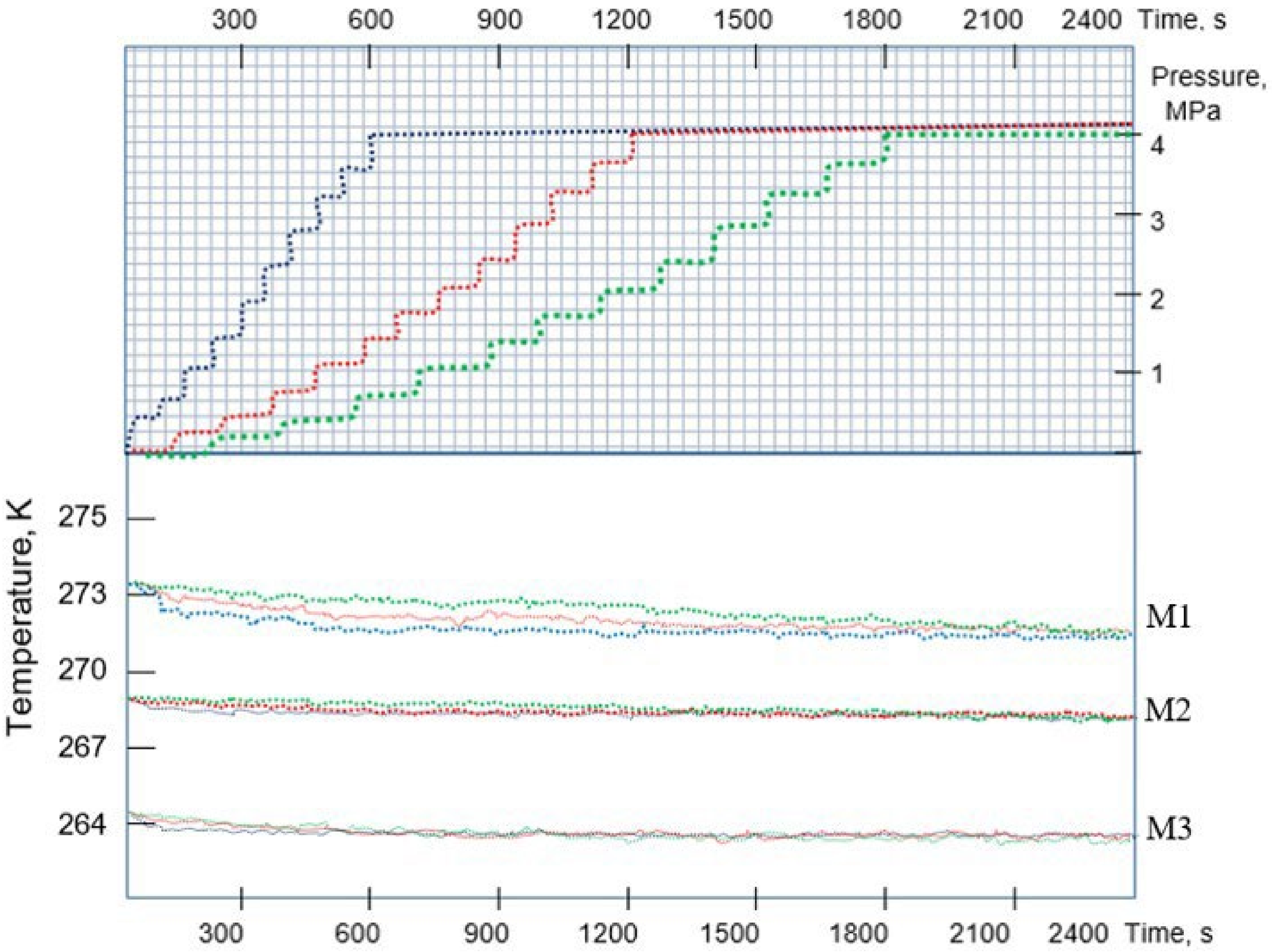
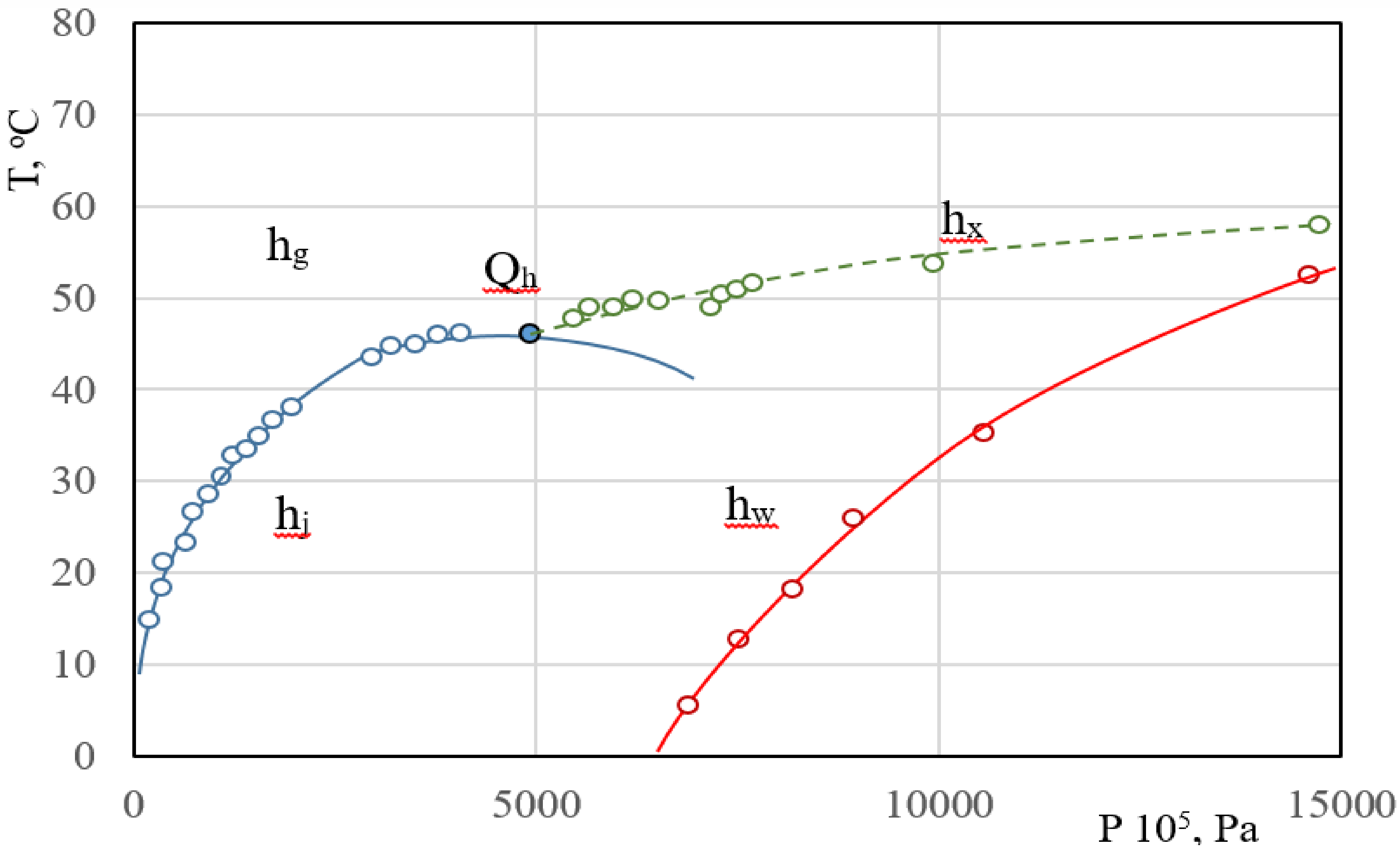


Fig. 5 Thermograms of hydrate formation at the final stage


80
70
60
50
40
30
20
10
0
T, °C
0
5000
10000
15000
P 10⁵, Pa
hg
Qh
hx
hj
hw

General Process of Synthesis GH

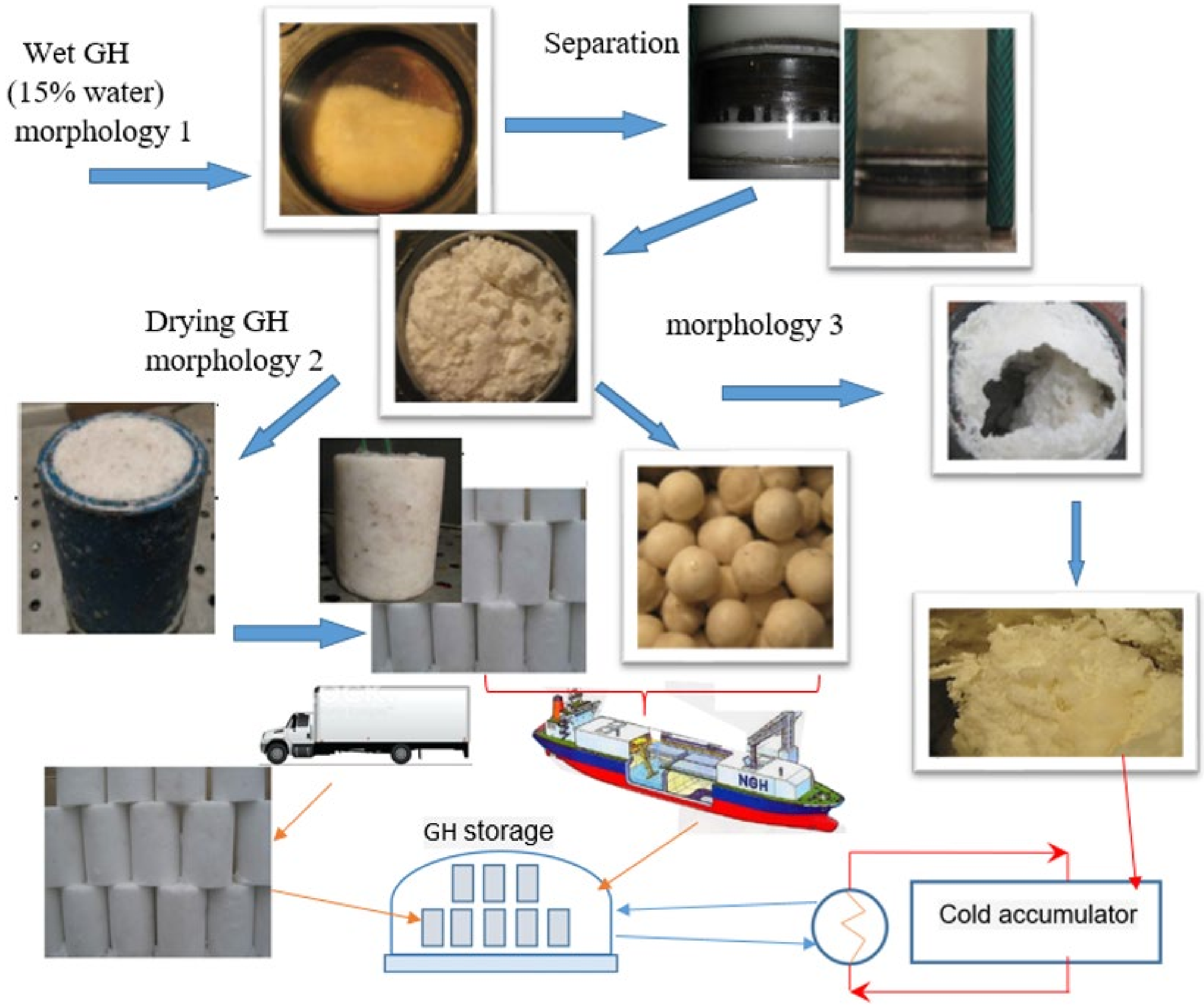
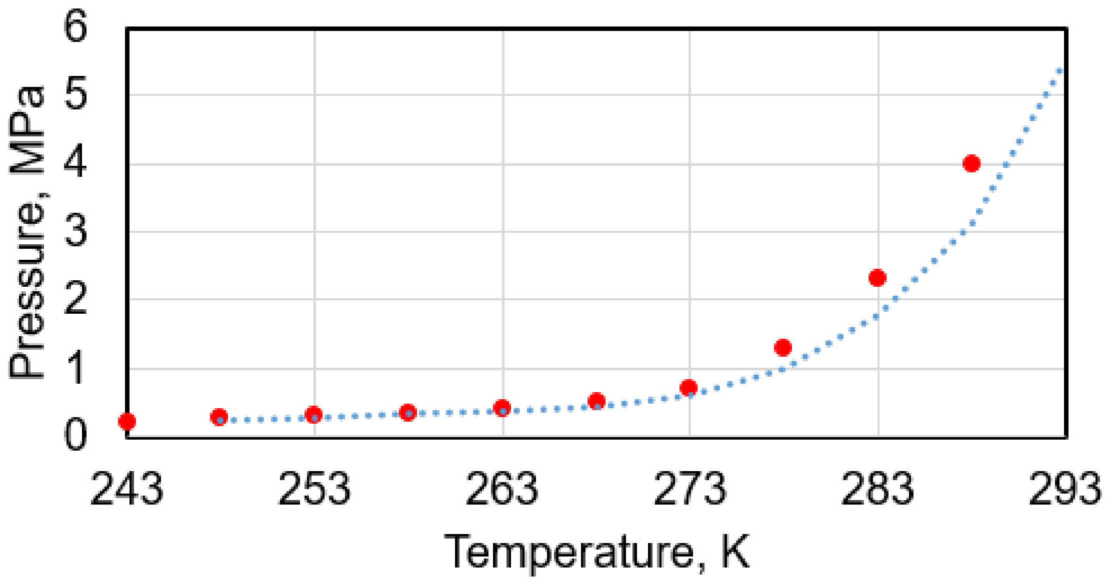
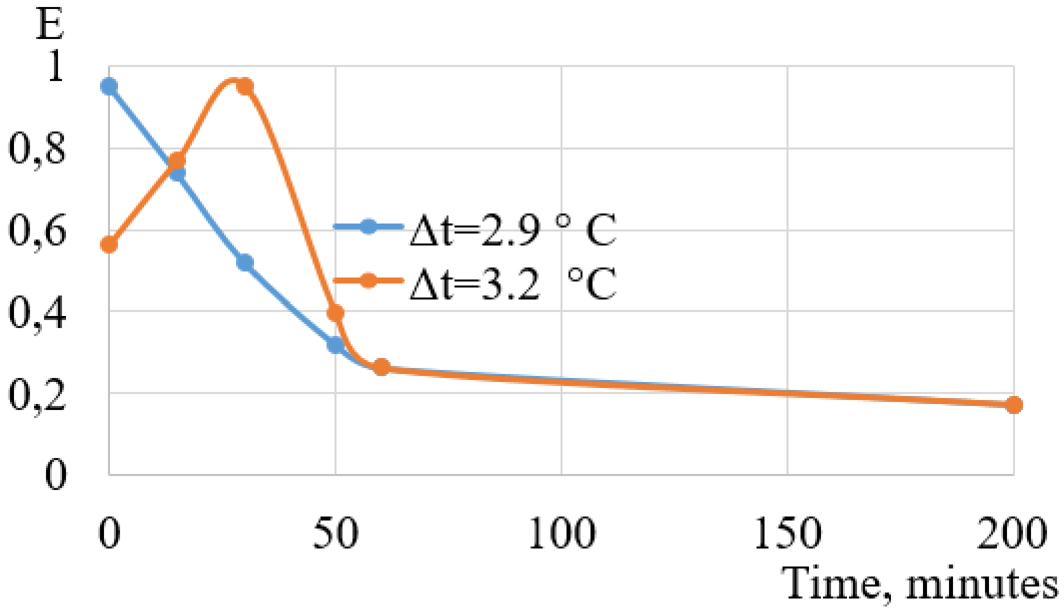


Fig. 6. GH synthesis diagram



Equilibrium curve of hydrate formation for the gas, entering the reactor



The efficiency of the hydrate formation process in diffusion mode (E) depending on gas supercooling (Δt) and time according to experimental study results

The optimization coefficient value for different gases.

Table 2. The optimization coefficient value for different gases.

Gas	K_S
Methane	36–40
Ethane	55–57
Propane	115–124
Isobutane	173–186

Ig - mass of synthesized hydrate per unit surface;

K_S - criterion for GH synthesis optimization;

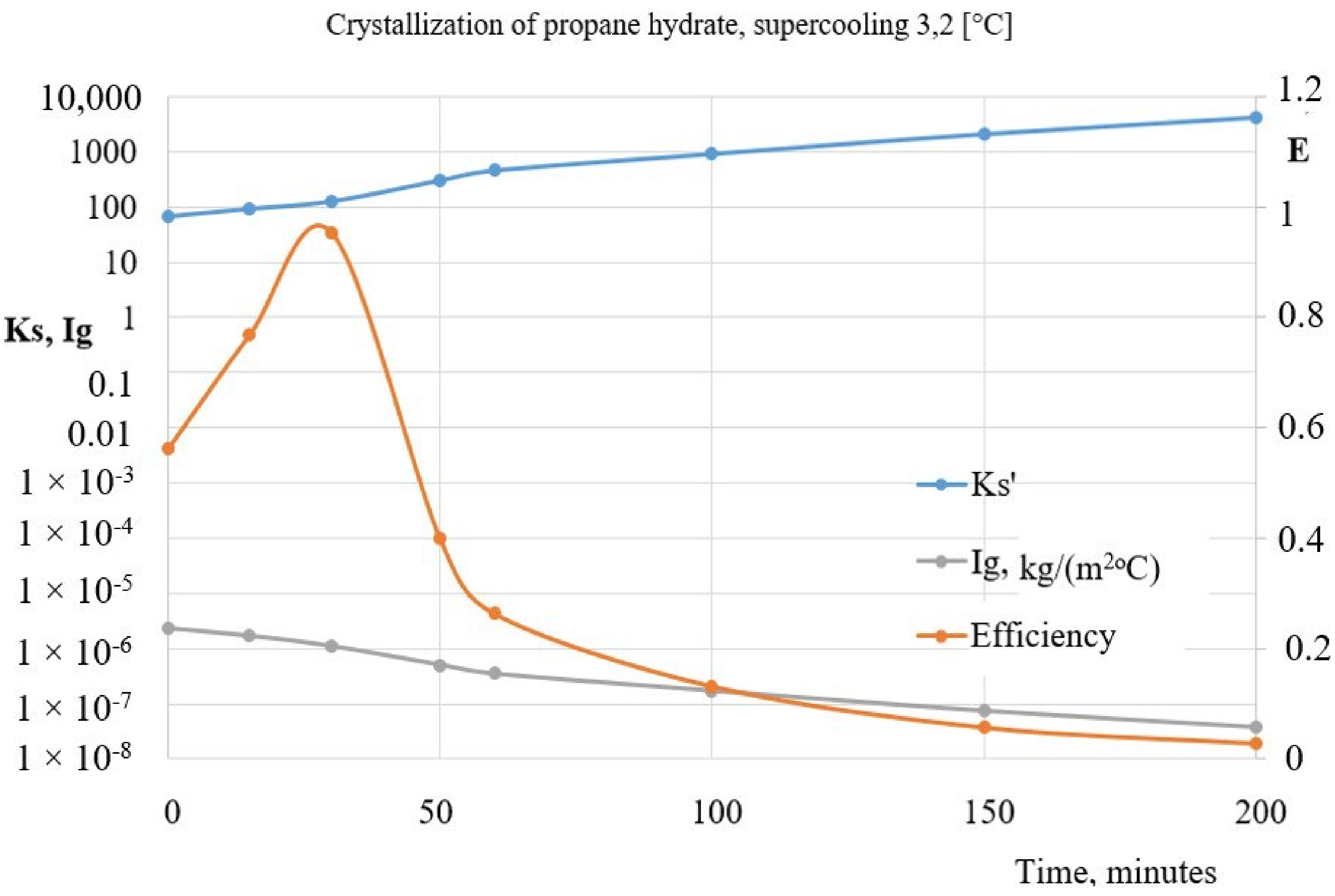


Fig. 9. Optimal characteristics of GH synthesis process

CONCLUSIONS

Diffusion phenomena underlying the processes of gas hydrate formation at the interface are slow, and practically all researchers use various tools to intensify these processes. In most cases, these techniques make it possible to implement a diffusion-convective mechanism for heat and mass transfer between gas and liquid. Clearly, the intensity of these processes is affected by the temperatures of contacting phases and pressure in the reaction zone. However, with the diffusion-convective mechanism of gas hydrate formation, as well as with the diffusion mechanism, the synthesis intensity decreases as a hydrate layer at the interface, generating resistance to mass gas flow and preventing intense heat removal from the reaction zone. Therefore, the formed hydrate layer will be destroyed and, thus, the phase interfacial contact will be renewed. According to our technology, this problem is solved using the hydrodynamic initiation of the synthesis process, resulting in a hydrodynamic and thermodynamic situation in the reactor; it contributes to the deformation of gas droplets and breaking of hydrate films. Hydrate removal from the phase interface also means a rather intensive heat removal from the reaction zone. The continuous destruction of the hydrate film provides a sufficiently high intensity of the GH synthesis process.

It was determined that at a certain optimal ratio of the intensity values of heat and mass transfer processes at the phase contact interface, the synthesis rate will be maximum, whilst continuous renewal of the contact interface allows for maintaining the maximum value of this parameter throughout the entire synthesis process. In this case, the optimal values of gas subcooling are recorded at 2.5–3.5 °C.

To assess the conditions for intensive GH synthesis, an optimization criterion was proposed to characterize the ratio of mass and heat transfer processes at the interface. Thus, the surface renewal and compliance with optimal ratios of heat and mass transfer processes will make it possible to achieve the maximum rate of hydrate synthesis. These ratios can be adjusted using our proposed method.

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Thank you for your attention