

## Formation of crystalline hydrates of hydrocarbon gases and selection of methods for combating it

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**Abstract.** The article presents the results of the analysis and study of hydrate vapors and considers the formation of hydrates in hydrocarbon gases, starting from pentane and moving upwards (hexane, heptane, octane, etc.).

The formation of hydrates in hydrocarbon gas is considered the most important complication in its transportation through pipelines. Methods of combating this complication are carried out in two directions: the development and application of measures to prevent the formation of hydrates; the development and application of measures to eliminate already formed hydrates.

As one of the first directions, methanol injection into the gas flow is carried out in the pipeline. At the beginning of the pipeline, gas heating is applied in order to prevent hydrate formation. At the same time, the turbulent motion of the gas flow creates certain conditions for the formation of hydrates. The equilibrium constants of gas hydrates were determined based on the experimental data of Carson and Katz.

As the second direction, the regulation of cleaning of hydrates deposited in the pipeline by various mechanical methods is carried out.

The formation of hydrocarbon gas hydrates is considered the most important complication in its transportation through pipelines. Methods of combating this complication are carried out in two directions: 1) development and application of measures to prevent the formation of hydrates;

2) development and application of measures to eliminate already formed hydrates.

As the first direction, methanol is injected into the gas flow in the pipeline; the gas is heated at the beginning of the pipeline where hydrate formation begins.

The turbulence of gas movement contributes to the formation of hydrates.

As the second direction, hydrate deposited in the pipeline is cleaned by various mechanical method. Three types of methods for combating hydrate plugs in gas pipelines are shown and five different methods for drying gas are mentioned.

**Keywords:** gas pipeline, crystalline hydrate, gas condensate, thermodynamic research, fractional composition of gas, flow turbulence.

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**1. Introduction.** Hydrocarbon gases saturated with water vapor at certain pressure and temperature form chemical compounds of hydrocarbons with water called gas hydrates. When water is present in the liquid phase of the gas hydrates are formed.

Gas hydrates were discovered in 1810 by G. Davy, and their properties were studied in depth much later.

Thermodynamic studies have shown that methane molecules combine with 7 (or 6) water molecules to form methane hydrate  $-CH_4 \cdot 7H_2O$ , respectively: ethane hydrate  $-C_2H_6 \cdot 8H_2O$ ; propane hydrate  $-C_3H_8 \cdot 18H_2O$ ; carbon dioxide hydrate  $-CO_2 \cdot 7H_2O$ ; propane hydrate  $-C_3H_8 \cdot 18H_2O$  are formed.

As a result of the analysis and study of hydrate vapors, it has been determined that starting from pentane and higher (hexane, heptane, octane, etc.), hydrocarbons do not form hydrates [1,6].

The peculiarity of hydrate formation is that its formation temperature is much higher than the ice formation temperature ( $0^\circ C$ ). Each hydrocarbon, starting from methane to butane, has a

certain temperature limit at which hydrates can form, for example,  $CH_4 - O \div 22^\circ C$ ;  $C_2H_6 - O \div 14,5^\circ C$ ;  $C_3H_8 - O \div 5,5^\circ C$ ; izzo  $C_4H_{10} - O \div 2,5^\circ C$ ; normal  $C_4H_{10} - O \div 1^\circ C$ .

At the indicated limits, hydrates are gaseous, slightly saturated and quickly decompose. At temperatures higher than these limits, hydrates do not form, even at high pressures [2,8].

**2. Methodological part.** The article also mentions five different methods of drying gas and explains their purposes. Hydrate is a yellowish solid substance resembling wet snow, which is formed in the form of crystals inside pipes and pipelines and settled on their walls, reducing their cross-sectional area and pipeline productivity [3,7].

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As the first direction, methanol is injected into the gas flow in the pipeline; the gas is heated at the beginning of the pipeline where hydrate formation begins.

**3. Results and discussion.** As the second direction, hydrate deposited in the pipeline is cleaned by various mechanical methods.

The following empirical formula was proposed by Gammer-Schmidt to determine the melting temperature of hydrates depending on pressure:

$$t = 10,633 \cdot p^{0,285} - 17,78, ^\circ C \quad (1)$$

However, the formation of hydrates depends not only on pressure and temperature, but also on the fractional composition of the gas, its humidity, the physical conditions of the gas, that is, the flow velocity, pulsation, flow turbulence, the presence of  $CO_2$ ,  $N_2$ ,  $H_2S$  and other gases in its composition.

The temperature of the gas in the pipeline is found by the following formula [4,9]:

$$\lg \frac{t_i - t_g}{t_i - t_g} = -10,4 \frac{k\pi DL}{V\gamma C_p} \quad (2)$$

where  $t_g$  - the temperature of the gas pipeline at a distance  $L$  m from the first temperature measurement point,  $^\circ C$ ;  $c$  - the coefficient of heat transfer from the gas pipeline to the soil surrounding the pipe, in  $kkal / saat \cdot m^2$ ,  $D$  - the outer diameter of the gas pipeline in  $m$ ;  $V$  - the volume flow of gas in  $m^3 / day$ ;  $\gamma$  - the specific gravity of the gas, in  $kq / m^3$ ;  $C_p$  - the heat capacity of the gas at constant pressure, in  $kkal / kq$ .

The law of pressure change, i.e. (dispersion) through the gas pipeline is expressed by this equation:

$$P_x = \sqrt{P_1^2 - (P_1^2 - P_2^2) \cdot X} \quad (3)$$

where  $P_1$  is the pressure at the beginning of the pipeline, atm;  $P_2$  pressure at a distance of  $X$  atm.

The distance of hydrate fall in a gas pipeline, depending on its temperature of fall is determined by the following formula of V.G. Shukhov:

$$t_x = t_g + \frac{t_i - t_g}{l} \frac{k\pi DX}{V\gamma C_p} \quad (4)$$

Where  $l = 7,22$  is the base of the natural logarithm.

Formula (4) can also be written as

$$\lg \frac{t_i - t_g}{t_x - t_g} = 0,434 \frac{k\pi DX}{V\gamma C_p} \quad (5)$$

Methods of combating hydrate plugs in gas pipelines can be divided into the following three groups:

1. Methods of only decomposing crystalline hydrates by reducing the pressure in the gas pipeline.
2. Methods of preventing decomposition of hydrates and their formation by heating the gas pipeline and injecting chemical reagents into the pipeline.
3. Methods of warning against the formation of hydrate plugs, that is, methods of partially drying the gas before feeding it into the pipeline [5,10].

The methods of drying gas are as follows:

- 1) The method of using the throttle effect (choke) in the expansion of the gas (or cooling it to a low temperature).
- 2) The method of compressing and cooling the gas.
- 3) The method of absorption by wet hygroscopic products.
- 4) The method of absorption by wet solid sorbents.
- 5) The method of drying the gas by injecting a hygroscopic liquid into the gas flow.

Gas drying has the following purposes:

The presence of water vapor condensate in the gas creates the following complications:

1. Formation or increase of water vapor condensate in gas pipelines;
2. Formation of ice plugs in gas pipelines;
3. Formation of crystal hydrates in gas pipelines;
4. Corrosion and erosion of metal parts of pipes, apparatus and devices.

#### **4. Conclusion.**

1. The article provides detailed information on the development of effective measures to combat crystalline hydrates formed during the transportation of hydrocarbon gases through main pipelines.

2. It is shown that hydrates are formed as a result of a chemical reaction between hydrocarbon gases and the water vapor contained in them.

3. Gas hydrates are formed by combining one molecule of each of methane, ethane, propane, isobutane and normal borosilicate gases with various numbers of water molecules, and carbon dioxide hydrates are also formed.

4. Hydrates are not formed from pentane and higher natural hydrocarbons.

5. Each hydrocarbon gas, from methane to butane, has a temperature limit at which hydrates are formed. At temperatures higher than these, hydrates are not formed.

6. The Gammer-Schmidt formula determines the pressure-dependent melting temperature of hydrates.

7. The turbulence of gas movement contributes to the formation of hydrates.

8. The article provides a formula for determining the temperature of gas in pipelines.

9. The formula for the law of pressure dispersion in a gas pipeline is also provided.

10. The distance at which hydrate begins to fall in a gas pipeline, based on the temperature of its fall, is determined by the formula of V.G. Shukhov, for this purpose, the second formula is also presented.

11. Three types of methods for combating hydrate blockages in gas pipelines are shown.

12. The article also mentions five different methods of drying gas and explains their purposes.

#### **Conflict of interest**

The authors declare that they have no conflict of interest in relation to this research.

## References

1. Salavatov, T.Sh., Ibrahimov, Yu. A //Comparative analysis of drill pipes with the API standard and pipes with two thrust locking connections//”Azerbaijan Journal of Oil Industry”, 2021, No.06-07, pp.28-38, [www.adnsu.edu.az](http://www.adnsu.edu.az)
2. Aliyeva, O.A. //Nequality of gas consumption and methods of their regulation//8th International Icontech Congeress on Innovative Surveys in Positive Sciences Azerbaijan Cooperation University, mart 16-18, Congress Program, 2024, pp. 222 -225, <https://www.icontechsurveys.org/books>
3. Akhundova, N.R, Aliyeva, O.A. //Determination of the exact daily gas intake volume of an unfinished flatbed gas injection well according to the degree of opening of the formation in the underground gas. Today we finally received the third review for your article. Storage (GAS)//, The review is positive so, the article will be published Nafta-Gaz, 2023, no 9, Pp. 592-595, 10.18668/NG.2023.09.04, <https://www.inig.pl/en/nafta-gaz/en/abstracts> [www.expo-gas.pl](http://www.expo-gas.pl)
4. Mammadova, G.G., 2023. //Determination of the formula for the exact oil flow rate of a production well in thick Newtonian oil reservoirs\\ Proceedings Of Azerbaijan High Technical Educational Institutions, Volume 25, issue 4(144), pp.10-16, [www.adnsu.edu.az](http://www.adnsu.edu.az)
5. Akhundova, N.R., Rza zade, S.A., Bahshaliyeva, S.O., Aliyeva, O.A.// Compression of liquids from the operating wells to the surface applying the sequential approximation//Today we finally received the third review for your article. The review is positive, so the article will be published Nafta-Gaz 10.18668/NG.2023.03.04,2023, no.3, pp. 184-189, <https://www.inig.pl/en/nafta-gaz/en/abstracts> [www.expo-gas.pl](http://www.expo-gas.pl)
6. Iskandarov, E., Ismayilova, F., Shukurlu, M., & Nagizadeh, A. (2025). The effect of filling the gas pipeline with condensate on transport pressure. Rudarsko-geološko-Naftni Zbornik 40, (317-24) <https://doi.org/10.17794/rgn.2025.3.2>
7. Ismayilov, G., Ismayilova, F., & Nagizadeh, A. (2025). Advanced Resource Operation of Main Natural Gas Pipeline Using Cfd Modeling Methods. Energy Technologies & Resource Saving, 83(2), 168–175. <https://doi.org/10.33070/etars.2.2025.13>
8. Gamidov, N.N. Development of a rational method of water injection for the extraction of Light hydrocarbon liquid that fell in the reservoir at the last stage of development, “Azerbaijan Journal of Oil Economy”, No. 11, pp. 30-36, 2020.
9. Aliyeva, O.A. // Determination of technological indicators of underground gas storage facilities (UGS) // Proceedings of Azerbaijan Highn Technical Educational Institutions, Azərbaycan Ali Texniki Məktəblərini Xəbərləri, 2024, Bakı, c. 262(148) Səh. 22-28 [www.adnsu.edu.az](http://www.adnsu.edu.az)
10. Aliyeva O.A. Congress Application Form Meetcon Mezopotamya II. Beynəlxalq Elmi-Tədqiqatlar Konfransı, 12-14 Mart 2026, Yer: Mardin, Türkiyə (Onlayn və canlı iştirak), saytı: <https://www.meetcon.org/meetcon-mezopotamya> (sertifikat). Gas Injection to the Dome of the Water Supply System Compression of Water to the Ground.