Experimental research of 134a hydrate formation in cyclic boiling-condensation process with variation of working volume

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Abstract. On the basis of researches on examination of gas hydrates previously made in Kutateladze Institute of Thermophysics SB RAS the new method was developed. That method is based on cyclic boiling-condensation process of gas-hydrating agent in enclosed volume. This method compares favorably with previously developed ones by its simplicity. There is no need in constant gas supply and mixing device.

1. Introduction

All the researches in the field of gas-hydrates can be roughly divided into fundamental and applicative. They examine general conditions as well as the most important lines. Those lines include the research of the structure of gas-hydrates, their physical-chemical, thermophysical, mechanical and other properties as well as general conditions and patterns of their formation, schemes and types of growth of the hydrate mass etc.[1–3]. A big attention is paid to methods of research of artificially made as well as natural gas-hydrates [4–7]. A big part of works is dedicated to experimental and mathematical simulation of processes of formation and dissolution of gas-hydrates [8–12].

Before the experimental researches of making of gas-hydrates of different gases by different ways were made. All those researches were mainly based on shock action on gas-liquid mediums. Their outstanding feature was a high speed of hydrate formation that can be explained by the essential intensification of heat and mass exchanging processes.

The logical extension of those researches was the creation of the boil-off method: the freon gas under the pressure is fed into the hermetic vessel halfway filled by the water cooled to 2-4°C. Freon creates the pressure, its temperature goes down to the environment temperature and it becomes liquefied. Since the liquefied freon is significantly heavier than water, it goes down and creates a layer on the bottom of the vessel. When freon is on the bottom of the vessel depressurizing begins by opening of the valve. As the result the liquefied freon on the bottom of the vessel explosively boils and mixes with the water. The boiling process is accompanied by creation of shock waves that crushes gas bubbles and creates a developed interfacial area. Bubbles move with respect to water but the water around them is significantly cooler. This combination of factors leads to a big formation of freon hydrate in the whole volume of water. It should be noted that the speed of formation of hydrate depends on the heat transmission and is not limited by diffusion of the gas into liquid. Along with the
crushing of the gas phase a significant importance has a heat transfer from interfacial area on which the gas hydrate forms. According to researches carried out by Japanese scientists the enthalpy of hydrate formation of freon R-134A is 124 kJ/mole. Therethrough when 1 kg of freon gas converts into gas hydrate creates 296 kcal of heat energy.

This piece of work describes the method of creation of gas-hydrate freon based on boiling-condensation of gas-hydrating agent in enclosed volume. This article shows the influence of height of water column on the process of formation of hydrates. This method is not so fast as the one described above but has the advantage of its simplicity and low energy consumption.

2. Experimental setup

The working area constituting a hermetic vessel of 740 mm height and with 150x150 mm section (fig. 1). Two vessel walls are made of optical transparent material that allows to observe processes taking place inside the working area. Maintenance of required temperature inside the unit is provided by the built in cooling system (water jacket). The bottom of the unit has no heat insulation and gets heat from external environment. Measurement of temperature was taken by the sensor ДТС204-РТ100, measurement of pressure was taken by the sensor ПД-100. The unit allows to make the research in the wide range of temperatures (from -10 to 60°C) and pressure (from 0.1 to 10MPa).

3. Method and results

The experiment: the reaction vessel is filled with water from 2 to 10 liters. The water is cooled down to 7 °C. Then 0.3 kg of R-134A freon is fed into the chamber. Since the walls of the vessel have subzero temperature freon liquefies and goes down to the bottom. After the delivery of the gas into the working area is cut off the pressure alines and boiling on the bottom of the vessel begins. Due to intensive boiling a big number of freon bubbles appear. When the gas goes up it cools down and it...
creates conditions for formation of freon hydrates. The hydrate film becomes to appear on walls of bubbles. When bubbles reach the free liquid surface they destroy and leave hydrate flakes. Freon gas which wasn’t converted into hydrate is condensed on walls and then goes down to the bottom of the vessel and takes part in boiling process again. As you can see from the description the process is cyclic and goes until all gas is converted into hydrate (fig. 2). Intensity of the process depends on heat exchange on side walls and heating of the bottom of the vessel as well as on the distance that bubbles go during the boiling on every cycle. The fig. 3 shows dependence of growth of gas-hydrate “hat” from the distance that bubbles go from the bottom of the unit to the water surface. As you can see from the chart the more distance bubbles go the slower gas-hydrates forms. It can be explained in the following way: the longer bubbles go to the surface the more gas-hydrate film forms and the harder gas-hydrates contacts with water. Also the boiling-condensation process takes more time.

Figure 3. Chart of growth of hydrate mass R-134A in the vessel depending on the level of water:
1 – Height of water column is 80 mm, 2 - Height of water column is 420 mm.

4. Conclusion

A method for obtaining a gas hydrate of Freon 134a was described, which is based on the cyclic boiling-condensation process of the gas-hydrate-forming agent in a closed water volume. The influence of the height of the water column on the hydrate formation process is shown. This method of hydrate formation is characterized by its simplicity and low energy consumption.

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References

[1] Makagon Y F 1997 Hydrates of Hydrocarbons (Tulsa, Oklahoma. Pennwell publishing company)
[2] Yakushev V S, Istomin V A 1993 Gas-hydrates self-preservation effect Physics and Chemistry of Ice pp 136-139
[3] Sloan E D, Koh C A 2008 Clathrate hydrates of natural gases 3rd ed Chemical industries series p 721
[4] Nakoryakov, V.E., Mezentsev, I.V., Meleshkin, A.V., Elistratov, D.S., Manakov, A.Y. 2015 Experimental investigation of gas-hydrate formation by underwater boiling of a condensed gas layer Journal of Engineering Thermophysics Vol. 24 № 4 pp. 335-337
[5] Nakoryakov, V.E., Mezentsev, I.V., Meleshkin, A.V., Elistratov, D.S. 2015 Visualization of physical processes occurring on liquid nitrogen injection into water Journal of Engineering Thermophysics Vol. 24 № 4, pp. 322-329
[6] Chernov A.A., Pil’nik A.A., Elistratov D.S., Mezentsev I. V., Meleshkin A.V., Bartashevich M.V., Vlasenko M.G. 2017 New hydrate formation methods in a liquid-gas medium Scientific Reports Vol. 7, 40809
[7] Chernov A.A., Elistratov D.S., Mezentsev I.V., Meleshkin A.V., Pil’nik A.A. 2017 Hydrate formation in the cyclic process of refrigerant boiling-condensation in a water volume International Journal of Heat and Mass Transfer Vol. 108 Part B P. 1320–1323
[8] Nakoryakov V E, Dontsov V E, Chernov A A 2006 Gas hydrate formation in a gas-liquid mixture behind a shock wave Doklady Physic Vol. 51 № 11 P 621-624
[9] Dontsov V E., Chernov A A 2009 Dilution and hydrate forming process in shock waves Int. J. Heat Mass Transfer Vol. 52 № 21-22 P 4919-4928
[10] Chernov A A, Dontsov V E 2011 The processes of dissolution and hydrate forming behind the shock wave in the gas–liquid medium with gas mixture bubbles Int. J. Heat Mass Transfer Vol 54 № 19-20 P 4307-4316
[11] Misura S Y 2013 Effect of Heat Transfer on the Kinetics of Methan hydrate dissociation Chem. Phys. Lett. Vol. 583 pp 34-37
[12] Nakoryakov V.E., Misyura S.Y., Elistratov S.L. 2013 Methane combustion in hydrate systems: water-hydrate and water-hydrate-isopropanol Journal of Engineering Thermophysics Vol. 22 №3 P. 169-173.
[13] Misyura SY. 2016 The influence of porosity and structural parameters on different kinds of gas hydrate dissociation Scientific Reports Vol. 6, 30324
[14] Misyura S.Y., Donskoy I.G. 2016 Dissociation of natural and artificial gas hydrate Chemical Engineering Science Vol. 148 P. 65-77
[15] Shagapov V.Sh., Musakaev N.G., Khasanov M.K. Formation of gas hydrates in a porous medium during an injection of cold gas // Int. J. of Heat and Mass Transfer. 2015. V. 84. P.1030-1039.
[16] Shagapov V.Sh., Khasanov M.K., Musakaev N.G., Ngoc Hai Duong Theoretical research of the gas hydrate deposits development using the injection of carbon dioxide // Int. J. of Heat and Mass Transfer. 2017. V.107. P. 347-357.
[17] V. Sh. Shagapov, G. R. Rafikova, M. K. Khasanov On the theory of formation of gas hydrate in partially water-saturated porous medium when injecting methane // High Temperature. 2016. V.54, №6. P. 858–866.
[18] M. K. Khasanov, I. K. Gimaltdinov, M. V. Stolpovsky Specific features of the formation of gas hydrates during the injection of a cold gas into a porous medium saturated with a gas and water // Theoretical Foundations of Chemical Engineering. 2010. V.44, №4. P. 424–431.