Heat and mass transfer of multicomponent gas mixtures in cryogenic tank of automotive equipment

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Abstract. The use of liquefied gas as a motor fuel for automotive equipment has both certain advantages and significant problems. The paper deals with the solution of one of the main problems, reducing the speed of the phase transition of liquefied methane in a cryogenic tank in the mode of drainage-free storage. In solving the above problem, the process of convective heat and mass transfer caused by the chemical and physical state of natural gas and the external heat flow was investigated. The two-phase state of the gas is unstable in the event of an increase in heat input from the environment, which causes an imbalance of pressure and temperature in the volumes of the liquid and gaseous parts of the gas and creates the risk of an emergency. To prevent the formation of critical gas pressure in a cryogenic tank, a method is proposed for calculating the phase transition of liquefied methane to determine the volume fraction of vaporized gas using equilibrium constants, which will allow developing an algorithm for the technological process of gas recirculation in a specially designed tank design. This will also allow you to choose the best option for a thermal insulation layer that can reduce the rate of penetration of heat from the environment and increase the period of drainage-free storage of liquefied natural gas by 1.5-2 times.

1. Introduction

The use of natural gas as the main motor fuel in power plants when operating transport equipment in quarry conditions is of great importance for the entire mining industry in Russia. In the USSR, the active introduction of gas equipment for road transport began at the beginning of 1970, while there were the first attempts to convert cars, but its share was quite small. Currently, modern technologies make it possible to increase the energy intensity of the fuel system of power plants of land transport using already liquefied natural gas in the system and to indicate a stable position of the use of cryogenic technologies in the 21st century [2, 3, 4, 15].

2. Materials and methods

This work aims to study multicomponent mixtures based on liquefied methane in a cryogenic tank, as well as the used heat-insulating material that reduces the rate of phase transition of convective heat and mass transfer.

Multicomponent gas mixtures have a complex chemical composition and represent a combustible
mixture for which there are no experimental data in the form of dependencies, characteristics, or diagrams of equilibrium. Based on the obtained experimental data presented in [6], using mixtures of gases (propane, butane, ethane, methane, etc.), the calculated equilibrium constants $k_i$ of the individual gas components included in the mixture were obtained. This work also presents the graphs of the sought constants for some hydrocarbons. Under general conditions, these constants cannot be applied, but in calculations, concerning hydrocarbon mixtures, they are more convenient and reliable than the ratios of gas mixtures considered from the laws of ideal solutions.

During research, the considered constants of the equilibrium state of gas mixtures proved that they are a function not only of temperature and pressure, but the concentration composition of other components included in the gas, which are also presented in [6].

The critical pressure $P_{cr}$ of a mixture of hydrocarbons is higher than those included in the pure components, since nitrogen ($N_2$) and hydrogen ($H_2$), and in some cases, under certain conditions, reverse condensation is observed, according to the source [8]. An increase in the equilibrium constant $k$ with increasing operating pressure indicates the formation of reverse condensation of the gas. Various sources [9, 10, 13] present different approaches to determining the equilibrium constants using various kinds of dimensionless variables and reduced quantities, which in turn cause certain difficulties, mainly due to the chemical-physical state of the gas under study. The constant of phase equilibrium $k_i$ of the gas mixture, from the source [6], is the ratio of the molar fractions of the $i$-th components of the vapor phase $y_i$ of the gas to its liquid phase, respectively $x_i$:

$$k_i = \frac{y_i}{x_i}.$$ 

A certain difference from the laws of ideal solutions with the greatest deviation is observed with $CH_4$ with its low molecular weight and volume. If, for example, the equilibrium constants are applied to double gases, then the following expression can be used to calculate them with the subsequent construction of gas equilibrium graphs [11]:

$$x = \frac{1 - k_2}{k_1 - k_2},$$

$$y = k_3 x = k_4 \frac{1 - k_2}{k_1 - k_2}.$$ 

At the boundary of the phase transition, considering the saturation of the gas, the efficiency of the heat and mass transfer process is of great importance. Indicators of mass transfer of a two-phase methane medium in a closed volume of a cryogenic tank can be determined from the expression, [9].

$$\frac{1}{k_{Ga}} = \frac{1}{k_{Ga}} + \frac{1}{Hk_{La}},$$

where $k_{Ga}$ and $k_{La}$ are the mass transfer coefficient in two states of gas (vapor and liquid); $H$ - constant of phase equilibrium.

Due to insufficient information and data obtained on the mechanism and individual processes in the kinetics of mass transfer, as applied to multicomponent mixtures, the calculation of the mass transfer process in some cases is based on the concept of the effective efficiency of the object under study - cryogenic tank (CT).

It is known that under ultra-low temperature conditions, ferrous metal alloys do not tolerate shock loads, and non-ferrous metals under these conditions practically do not change their mechanical properties and are becoming more and more in demand for their widespread use in this environment [7]. In the works of academician A.F. Ioffe [5], numerous results of experimental studies of metals and alloys based on iron in various cryotemperature conditions have shown the ability of some steels and alloys (martensitic class) to impact resistance and brittle fracture, which indicates their use by the gas industry as a reliable material for various body products (containers, tubes, heat exchangers, etc.)

By the nature of the change in mechanical properties, if they work at low temperatures, metals can be conditionally divided into four groups [4, 12]:
- Non-ferrous metals and alloys based on them;
- Low alloy and carbon steels;
- Alloyed steels belonging to the austenitic class;
Alloyed steels belonging to the martensitic class.

During the research, the analysis of the following works [6,1] was carried out, which presents the experimental results of changes in the mechanical properties of carbon and low-alloy steels when exposed to cryogenic liquids: methane, hydrogen, nitrogen, helium, etc. The data presented in the sources well illustrate the picture of different indicators of impact toughness and strength, therefore, at temperatures close to minus 200 ° C, the yield strength and resistance increase by 1.5 – 2 times, and the impact toughness and, in general, the bending strength drops by tens time. The indices of the ultimate resistance and yield point of carbon steels similarly change when the temperature reaches close to minus 80 ° C. Similar properties in terms of changing the impact strength and resistance are also observed in carbon and low-alloy steels, in low-alloy steels such as chromium-nickel and chromium-molybdenum steels, the impact strength is slightly higher than that of the previous ones.

Studies have shown that at T = -80 ° C the impact toughness of carbon steel $ak \approx 0.5 \ldots 1.0 \text{ kgf} \cdot \text{m/cm}^2$, while for steels alloyed with chromium and nickel, $ak \approx 5.5 \ldots 7 \text{ kgf} / \text{cm}^2$ and more. It is necessary to consider the operating conditions of the materials under study, this steel is intended for operation in the temperature range (-150... -165 ° C), accordingly, it must contain carbon less than the limiting solubility of carbide in austenite. As shown by numerous experimental studies, the highest tensile strength and the lowest elongation during deep cooling are observed in martensitic steel.

According to the sources [3, 6], the most suitable material for the manufacture of body products of the developed cryogenic tank is 05Kh14N5DM steel, capable of operating in the temperature range (-196... +550 ° C). The purpose of the proposed tank is to increase the thermal conductivity resistance using various technologies, while maximizing the storage life of the liquefied methane in it, especially when the automotive equipment is not in operation and is in standby mode. The initial and boundary conditions, considering the thermal insulation layer of the outer and inner cryobank tanks, are set by an artificial heating and cooling process at the temperature range $T = -20 \ldots +25^\circ \mathrm{C}$.

An analysis of the temperature fields, obtained numerically earlier, showed the importance of determining the total heat capacity index of a cryogenic tank, which is determined by the following equation [11]:

$$\sum C(T_{CT}) = \frac{k_r a(T_{CT}-\sum T_{v_i})}{dr Ct} - 0.468 \sum C_{iS_i} \left( \sum T_{iS_i} \right)$$

Knowing the total heat capacity of a thermally insulated cryogenic tank, we can substitute it into the equation for determining the coefficient of thermal diffusivity through each wall with effective thermal insulation in the opposite direction, using the mathematical model developed for this purpose, presented earlier in [7, 14], which is based on the numerical simulation of a two-phase liquid methane medium in the computational grid of the control volume calculated in the Cartesian coordinate system, which gives a general representation of the phase transition of liquefied natural gas in the non-drainage storage mode in the developed cryogenic tank intended for agricultural automotive vehicles.

3. Results and its discussion

On the basis of the numerical modeling of the considered cryogenic fuel system, some conditions were considered:

1) studies of the state of liquid methane in a cryogenic tank at a level of 50% and 100% filling;
2) the studies were carried out under the following environmental conditions: transition period (autumn-winter, winter-spring), warm period (summer).

Having studied theoretically and experimentally the chemical and physical properties of some insulating materials, only seven were selected, among them the following materials:

- hydrophobic quartz airgel ($\rho = 2 \ldots 135 \text{ kg/m}^3$);
- hydrophobic cryogel ($\rho = 130 \text{ kg/m}^3$);
- foamed rubber Armaflex (Germany) ($\rho = 41-60 \text{ kg/m}^3$);
- mipora ($\rho = 21 \ldots 53 \text{ kg/m}^3$);
- silica gel ($\rho = 92 \text{ kg/m}^3$);
- mineral wool ($\rho = 96 \text{ kg/m}^3$);
- granular cork ($\rho = 73 \text{ kg/m}^3$).

The research results are shown in Figure 1. It shows the values of the heat capacity of the considered insulating materials, depending on the change in the thermal and physical properties of liquefied methane and structural elements of the cryogenic tank [7, 9].

![Figure 1](image1.png)

*Figure 1.* Dependence of the change in the values of thermal conductivity of the investigated heat-insulating materials of the cryogenic tank: Insulating (I) materials: 1) I1 – quartz airgel; 2) I2 – hydrophobic cryogel; 3) I3 – Foamed Armaflex rubber; 4) I4 – Mipora; 5) I5 – Kremnegel; 6) I6 – Granular cork; 7) I7 – Mineral wool

![Figure 2](image2.png)

*Figure 2.* Heat transfer indices of two-layer insulation of a cryogenic tank at pressures in the inter-vessel space from $p_1 = 0.1 \text{ MPa}$ to $p_2 = 1.0 \text{ MPa}$: 1 – I2 (0.1) - thermal insulation No. 2 at a gas pressure of $P = 0.1 \text{ MPa}$; 2 – I3 (0.1) - thermal insulation No. 3 at $P = 0.1 \text{ MPa}$; 3 – I2 (0.2) - thermal insulation No. 2 at a gas pressure $P = 0.2 \text{ MPa}$; 4 – I3 (0.2) - thermal insulation No. 3 at a gas pressure $P = 0.2 \text{ MPa}$; 5 – I2 (1) - thermal insulation No. 2 at a gas pressure $P = 1.0 \text{ MPa}$; 6 – I3 (1) - thermal insulation No. 3 at a gas pressure $P = 1.0 \text{ MPa}$.

According to the data obtained during the study (see Fig. 2), the most effective materials when used as a thermal insulation layer of the cryogenic tank shell were: I2 – hydrophobic cryogel and I3 – foamed Armaflex rubber, with fusion in the interlayer boundaries, for screening heat fluxes.
4. Conclusion

The obtained research results showed that the average phase transition rate is an adjustable indicator, which allows changing the main characteristics of the state of the liquefied gas in a wide range. Conditions that ensure a decrease in heat gain from the environment include:

- use of qualitatively selected two, three-layer insulating materials (hydrophobic quartz airgel or hydrophobic cryogel and foamed Armaflex rubber);
- fabrication of body products (external and internal cryogenic tanks) using martensitic steels.

The above conditions make it possible to reduce the heat flow from the environment through the walls of the thermally insulated tank by a factor of 1.5... 2. The technology used for gas recirculation in a cryogenic tank will increase the storage period of liquefied natural gas in a drainless mode by 19... 20 days in the summer and by 23... 30 days in the winter, which will significantly reduce the risks of an emergency.

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