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CREATION OF TEMPERATURE INHOMOGENITIES WITH THE USE OF PELTIER ELEMENT FOR THE MASS-EXCHANGE PROCESSES INTENSIFICATION OF THE OIL AND GAS INDUSTRY

Vitalii G. AFANASENKO, Yuliya L. YUNUSOVA
Ufa State Petroleum Technical University, Ufa, Bashkortostan Republic, Russia

The intensification of technological processes in the oil and gas industry is an urgent task for industrial production. Improving the efficiency of the processes leads to a decrease in the consumption of materials by the apparatus and the cost of their manufacture, an improvement in the quality of the produced product, and simplifies the transportation and installation of equipment. To achieve these goals, a new highly efficient equipment is being developed based on the use of various physical and chemical phenomena, their combinations, and new technological approaches. One of the most effective ways to solve such problems is pulse impact on the materials being processed, in which inhomogeneities of the process driving force are artificially created. The challenge of intensifying the processes occurring during the direct contact of the phases is the need to influence the system being processed locally - in the area of the interface, since it is there that the substances transfer from one phase to another.

The object of article's scientific research – mass-exchange process, which is most widespread in oil and gas technology. As a model, the process of liquid evaporation is chosen, on which the separation of mixtures by rectification is based – the main process of the oil and gas processing industry. The heterogeneity of the driving force of the mass transfer process was created using a thermoelectric converter, the principle of which is based on the Peltier effect, in a series of experiments. Such converters allow creation of higher temperature gradient and, consequently, a greater temperature heterogeneity in the investigated system compared with traditional resistance electric heaters at the same energy expenditure.

The article discusses the influence of the temperature inhomogenities location on the efficiency of mass-exchange processes, specifically the evaporation process. In experimental studies, the evaporation rate was estimated by measuring the mass evaporation velocity of a liquid. It is noted that the creation of a temperature gradient on the free surface of the liquid phase using a Peltier element with a specific power of 1.8 kW/m^2 leads to a twofold intensification of the evaporation process.

***Key words*:** oil and gas industry; mass-exchange processes; phase boundary; temperature gradient; Peltier element

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Introduction. Mass-exchange processes are accompanied by the transition of substances from one phase to another. The speed of mass transfer at a given temperature depends on the intensity of molecular diffusion, i.e. the ability of spontaneous penetration of one substance into another due to the random movement of molecules [2, 3, 10].

The driving force of the mass transfer process is determined by the difference in the phase concentrations between the working and equilibrium concentrations of the component to be distributed in the first and second phases, respectively. The amount of mass transferred from one phase to another also depends on the area of the interface and the time of interaction [18, 19, 27].

The interface between the phases of various media is of interest to researchers because of insufficient knowledge. The forces of interaction between the particles of the surface layer and the particles of the inner layers of each phase are not the same due to the different nature or state of aggregation of these phases. The arising asymmetry of the force fields near the phase boundary leads to the manifestation of a number of surface phenomena that can be of a purely physical nature or accompanied by chemical transformations [11].

The larger the interface between the phases (or the surface of a system volume unit), the greater its excess free energy concentrated on the phase boundary. Consequently, all heterogeneous systems have a greater amount or excess of free energy concentrated on the surface of the dispersed phase than ordinary massive bodies. The condition for a stable equilibrium of a system is a minimum of free energy. Systems with a large amount of free energy are non-equilibrium, thermodynamically unstable, processes will spontaneously run in them, accompanied by a decrease in the amount of free energy, which always tends to the minimum value [15]. It can be stated that in order to effectively intensify mass-exchange processes it is necessary to achieve a local excess of energy in the system, namely, at the phase boundary.

The main factor influencing the magnitude of the specific surface energy that prevents interfacial transitions is the surface tension due to the uncompensated field of molecular forces on the interfacial surface. With increasing temperature or pressure, the surface tension of the fluid decreases due to the weakening of intermolecular forces [8]. It should be noted that the value of free surface energy depends on the physical and chemical properties of the fluid, specifically on its surface tension, therefore, along with the increase in the internal energy of the heterogeneous systems' phases, it is also necessary to consider ways to reduce surface tension as a means of intensifying interfacial transitions.

Having considered in more detail the transformation mechanisms occurring at the interfaces of different phases, it can be concluded that the use of unsteady by the temperature profile modes of interfacial exchange, ensuring the achievement of high instantaneous values of heat and mass transfer coefficients due to the transition of excess energy into heterogeneous system, is one of the promising ways to intensify the mass-exchange processes [6, 12, 13, 16, 22].

Non-stationary impact is used to increase the efficiency of exchange processes and with discrete-pulse input and transformation of energy (DPIE), the main idea of which is to accumulate (concentrate) previously stationary introduced and freely distributed in the working volume energy in locally situated discrete points of the system and then pulse-implement to achieve the necessary physical effects [7].

In the experiment, thermoelectric converters were used as an instrument to achieve the nonstationary effect by the temperature profile, which allows introducing additional thermal energy into the considered liquid-gas (air) binary systems. The tool was chosen based on the analysis of previously conducted experiments: the paper [14] describes the contact device, which is a regular mesh nozzle with built-in heat exchange modules and without them, characterized by high gas and liquid performance; article [9] substantiates the expediency of using thermal rectification, which is accompanied by the transition of heat to the contact stages, or its removal by heat exchangers to influence the processes of evaporation and condensation in the system.

Description of the test-bench and methods of conducting experimental research. The evaporation process was chosen as a model mass-exchange process. To create a temperature gradient in the experiment, thermoelectric converters were used, the principle of which is based on the Peltier effect, which consists in transferring heat from one material to another when electric current passes through the connection of two dissimilar conductors. The amount of thermal energy transferred depends on the type of contacting substances, the direction and value of the flowing electric current. [5, 17, 20, 21, 23-26, 28, 29].

For research purposes, the following equipment was used: Peltier thermoelectric element SP1848 27145 SA (dimensions 40×40×4 mm); DC generator with a voltage of 5 V; two-channel contact thermometer TK-5.11 with a replaceable submersible probe ZPG 500; analytical scales GR 202; heat visor Ti55 IR Flexcam.

The following liquids with different boiling points were chosen as test samples for the liquid phase: acetone (t_{boil} = 56.1 °C), ethanol (t_{boil} = 78.3 °C), water (t_{boil} = 100 °C), butanol-1 (t_{boil} = 117.4 °C) [1, 4].

Heat transfer in continuous liquids or gases is carried out mainly through the process of convective mixing. The occurrence of convection in a substance happens spontaneously and is intensified with an increase in the temperature gradient between individual areas of the system. When exposed to external forces, forced convection arises, which in the experiment was created by using thermoelectric converters based on the Peltier effect.

Table 1

The results of experimental studies

Medium	Thermoelement position (lower / upper)		
	Initial mass, g	Heating speed, K/s·10^3	Rate of mass change, g/s·10^3
Acetone	165.42/160.81	40.67/30.17	6.88/9.90
Ethanol	166.13/187.9	41.50/21.17	3.40/7.40
Water	196.91/195.10	22.67/19.00	1.15/2.26
Butanol-1	186.11/188.29	28.44/18.11	1.32/2.93

Two types of experiments were carried out at an average room temperature of 20.4 °C, differing by the localization of the thermoelement relative to the interface between the «liquid-gas» phases. In the first case, the specified element was placed in the volume of the liquid phase; in the second, it was installed at the phase boundary.

The experiment was conducted in the following order:

• measurement of fluid temperature, °C;
• measurement of liquid's mass, mg;
• installation of Peltier thermoelement in a predetermined position;
• supplying a direct electric current to the thermoelement and conducting the experiment in a stationary mode (without external mixing of media) for a specified time;
• measurement of fluid temperature, °C;
• measurement of liquid's mass, mg.

The results of experimental studies and their analysis. The experiment for each variant of the thermoelectric converter position and each type of liquid was repeated under similar conditions five times. The presence time of the Peltier element in ethanol and acetone was 10 min, in distilled water – 25 min, in butanol-1 – 30 min. The time of the experiment for water and butanol-1 is increased to improve the accuracy of the determined heating rate and the change in mass at the initial stage. Table 1 shows the average values of the experimental studies' results of the heat and mass exchange process using the Peltier element.

In the course of the experiment, electrical energy was transformed into thermal energy using a thermoelectric converter and transferred to the test liquid. In this case, part of the energy was expended on the heat exchange, and part on the mass exchange process. Energy losses were neglected.

The energy spent on the heat-exchange process increases the average temperature of the tested system and is determined by the formula

$$Q_{\text{ТО}} = C_{\text{ср}} m_{\text{ср}} \Delta T,$$

where $C_{\text{ср}}$ – specific heat, J/(kg·K); $m_{\text{ср}}$ – average initial mass at five tests for each group of substances, kg; ΔK – temperature difference before and after the test, K.

The energy spent on carrying out the mass-exchange process leads to a decrease in the total mass of the liquid due to evaporation and is determined by the formula

$$Q_{\text{МО}} = L\Delta m,$$

where L – specific heat of vaporization, kJ/kg; Δm – the difference in mass before and after the test, kg.

To assess the effectiveness of the target process – mass exchange, a conditional value is introduced – the efficiency of the expended energy:

$$K = \frac{Q_{\text{МО}}}{Q_{\text{МО}} + Q_{\text{ТО}}} \cdot 100\ \% .$$

Table 2 presents the results of processing experimental data on the distribution of thermal energy to the heat and mass exchange process.

A comparative characteristic of the efficiency of the expended energy with a different location of the thermoelement relative to the phase boundary showed that the creation of a temperature gradient in the volume of the liquid phase (lower position of the Peltier element) is less effective than at the phase boundary (upper position of the Peltier element). This is explained by the need for active molecules to overcome some distance to the phase boundary, and therefore part of the energy required for evaporation is lost. With the thermoelectric converter in the lower position, the efficiency of the expended energy evenly decreases with increasing boiling point of the liquid phase. This is due to the fact that in this position the Peltier element works like a normal thermoelectric heater, increasing the total system enthalpy.

Table 2

Energy distribution between heat and mass exchange processes

Medium	Thermoelement position (lower / upper)		
	Power expended for heat transfer, J/s	Power expended for mass transfer, J/s	Efficiency of the expended energy, %
Acetone	4.851/1.205	3.480/1.733	19.7/33.1
Ethanol	5.678/0.952	2.850/2.072	14.0/41.8
Water	5.963/0.834	4.978/1.634	13.1/24.9
Butanol-1	7.558/0.469	4.871/1.041	5.9/17.7

The installation of a thermoelectric converter at the «liquid – air» phase boundary (upper position of the element) leads to intensification of mass-exchange processes, but the magnitude of the effect significantly depends on a larger number of factors, which results in an abrupt distribution of the efficiency of the expended energy. Thus, when creating temperature inhomogeneities at the phase boundary, in addition to the boiling point, other physical and chemical properties of liquids affect the rate of mass-exchange processes, so in more detailed studies more attention should be paid to the properties of the surface layer.

These conclusions are confirmed by thermal imaging of the vessel with the sample of the liquid phase during the experiment. At the lower position of the element, the liquid heated by the thermoelectric converter loses some of its energy when it moves to the phase boundary and is evenly distributed over the entire free surface (Fig.1, *a*). In the upper position of the thermoelement, the areas of temperature inhomogeneities are formed directly at the phase boundary, which due to this receives local zones with a significantly higher driving force and, accordingly, with an increased speed of the mass-exchange process (Fig.1, *b*).

Recommendations for the practical application of research results. The assessment of the temperature gradient influence on the intensity of mass-exchange processes is complicated by the fact that heat transfer between two bodies with the same temperature is impossible without compen-

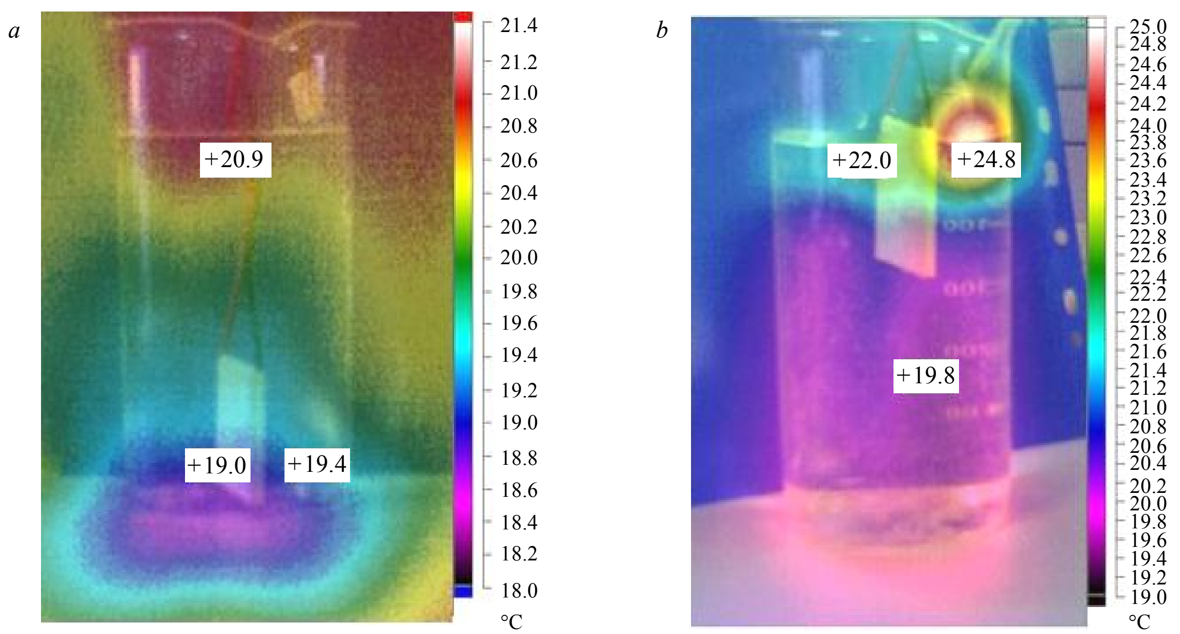

Fig.1. Thermal imaging of the experiment at the bottom (*a*) and top (*b*) position of the Peltier element

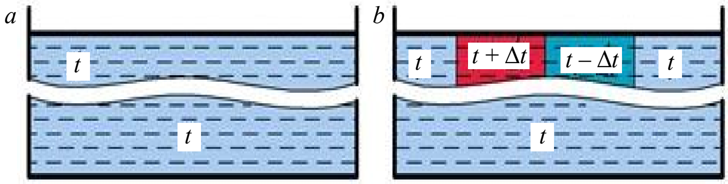

Fig.2. Temperature profile of the free surface of the liquid phase: *a* – constant; *b* – variable

sation. Furthermore, the efficiency of the thermoelectric converter essentially depends on the efficiency of heat removal from the working surfaces of the element.

Let us consider an idealized abstract experiment in which part of the internal energy without resistance and losses is transferred to another arbitrary volume of fluid, i.e. the total enthalpy of the system at the initial moment of time remains unchanged (Fig.2). In this case, according to the results of the research, the intensity of the evaporation process will change only when the indicated volumes approach the phase boundary (Fig.2, *b*) and remain unchanged when temperature heterogeneities form inside the liquid volume (Fig.2, *a*).

Thus, in the manufacture of mass-exchange apparatus, in which a substance or its component passes from a liquid phase into a gaseous one, to increase efficiency, it is necessary to transit from a system with a constant temperature of the phase boundary (Fig.2, *a*) to systems with temperature inhomogeneities on the free surface of the liquids (Fig.2, *b*).

Conclusion. The study of the mass-exchange process of the substance transition from one phase to another showed that the creation of temperature inhomogeneities at the phase boundary leads to an increase in the intensity of evaporation by a factor of 1.6-3 compared with temperature changes in the volume of one of the interacting media. The intensification of mass-exchange processes occurs due to the appearance of local zones with high mass transfer coefficients when creating a temperature gradient of interfacial surface, which must be taken into account when improving traditional designs of contact devices of mass-exchange apparatus, as well as developing new high-performance equipment.

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***Authors*: Vitalii G. Afanasenko,** *Candidate of Engineering Sciences*, *Associate Professor*, *afanasenko.v.g@yandex.ru* (*Ufa State Petroleum Technical University*, *Ufa*, *Bashkortostan Republic*, *Russia*), **Yuliya L. Yunusova,** *Postgraduate student*, *nedra.ugntu@gmail.com* (*Ufa State Petroleum Technical University*, *Ufa*, *Bashkortostan Republic*, *Russia*).

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