Heat transfer enhancement in superheated hydrocarbon fluids due to traces of water

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Abstract
For the specific mode of pulse heating of a wire probe immersed in a test liquid (saturated hydrocarbon), the effect of enhancement of the heat transfer through the probe surface has been revealed. The characteristic heating time is from 10 to 20 ms. The objects of research are n-hexane, n-decane, and n-hexadecane. It is shown that the addition of 0.003% water increases the heat transfer to 10% in the course of approaching the boiling-up temperature of liquid. Simulation of the experimental conditions shows the possibility of microconvection in the most heated boundary layer of a liquid about 10 μm thick.

1. Introduction
The known studies on the water addition effect on the hydrocarbons’ thermophysical properties revealed monotonic properties depending on the impurity concentration [1-3]. In the observed articles on the effect of water additives on the thermophysical properties of hydrocarbons, the monotonic dependences of the properties on the impurity concentration were obtained. For example, in [1], experimental results of a study of a binary mixture of water-hexane at various concentrations of these components near the critical point of water are presented, and critical lines and phase equilibria for the water-hexane system are calculated.

Moisture can negatively affect the properties of the process fluid, forming polar bonds with the components of the system, thereby changing the thermophysical properties of fuels, transformer and turbine oils and other process fluids [4, 5]. Water can be present in these process fluids in various states, such as dispersed, dissolved, and others. A change in the operating modes of technological units or the movement of process fluid from one section of a technological unit to another (change in temperature, pressure) can lead to a transition of water from a “bound” state to a “free” state.

Devices for monitoring the level of moisture in oil products were developed at our research group. These devices used the technique of pulsed thermal control [5, 6] which based on the general method of controlled pulse heating of the wire probe [7]. This method differs from the well-known THW-method [8] due to the relatively high level of heat generation in the probe. The idea of the technique [5, 6] is based on the results of studying the phenomenon of attainable superheating of mixtures (with respect of liquid-vapor equilibrium temperature) having limited mutual components’ solubility, in the processes of their pulsed heating [9, 10]. Among the methods of physical control, the method of pulse heating of the wire probe is distinguished for its high sensitivity, ease of implementation, and suitability for organizing monitoring of the moisture content of hydrocarbon liquids in the laboratory and industrial conditions.
The study of the water addition effect on the thermophysical properties of hydrocarbons is usually carried out on laboratory equipment using stationary methods. However, in real technological installations, thermal processes often occur under non-stationary regimes and the addition of small amounts of water can have unexpectedly strong effects on the thermophysical properties of hydrocarbon liquids [5].

The methods of wire probe’s pulsed heating are sufficiently sensitive to qualitatively detect heat transfer changes in superheated hydrocarbon liquids. This fact allows respond to the presence of moisture impurities in thousandths of a percent. However, the total measurement uncertainty in previously developed devices and techniques is large for quantitative assessment of heat transfer from the probe to samples with similar properties. The quality of measurements was improved by creating close temperature-time conditions for heating the probe in samples with different moisture content. Software and hardware have been developed for fine digital adjustment of the probe heating mode in order to minimize the methodological uncertainty in setting the heating mode. The purpose of the article is to develop a technique for reliably resolving the effect of moisture traces on heat transfer in pulse-heated hydrocarbon liquids. The objects of research are n-hexane, n-decane, and n-hexadecane with water addition form 5 ppm to 35 ppm.

2. Compensatory technique
The use of the two-pulse heating method previously revealed the effect of the increased influence of small moisture addition on the intensity of heat transfer from the probe’s surface in liquid hydrocarbons near the boiling-up point [5, 6]. The development of the two-pulse heating technique has shown that the signal from the first (powerful) pulse is not very informative, since impurities practically do not affect it. Therefore, the main research was aimed at analyzing the signal on the second pulse.

The similarity of the time dependences on the thermograms made it possible to assume the appearance of an additional heat loss by the convection mechanism with an increase in the heat transfer coefficient of the probe to the moistened sample. The use of the method of controlled heating on the second pulse allows, by changing the preset value of the heating current, to "compensate" the observed changes in the thermogram. Compensating part of heating power \[ \Delta P = \delta R(T - T_0) \] for relatively small temperature changes on the second pulse will repeat the dependence pattern of the compensated heat flux on temperature changes for the convection component of heat transfer \[ q = \alpha(T - T_0) \], in the first approximation.

The developed technique is used to select the current on the second pulse for one of the two samples, which differ only in the impurity content, in order to compensate for the difference in the heating thermograms (figure 1).

On the second current pulse \( I_2 \), there is a difference between the samples: the dried sample is heated to the temperature \( T_1 \) in the time \( t_0 - t_c \), the moistened sample - in the time \( t_0 - t_w \). In this case, it is possible to select a current \( I_{2w} \), at which \( (t_0 - t_c) \approx (t_0 - t_w) \). Thus, the thermograms for both samples will be the same. The similarity of the thermograms makes it possible to compare the intensity of heat loss from the probe surface in different samples under similar temperature-time conditions.

The proposed method makes it possible to introduce a relative quantitative characteristic of the effect of the addition of small amounts of moisture under non-stationary conditions of heating the wire probe. The proposed technique will be further referred to as the “compensation heating technique”.

The compensation heating technique is similar to the differential scanning calorimeter technique. Comparison of the heating curves makes it possible to reveal the difference between the samples in their thermal response to a given effect.
3. Measuring cell and probe

The scheme of the measuring cell is shown in figure 2. The measuring cell is made of inert material - fluoroplastic. The walls of the cell are thin and easily deformable; from the outside (from the outer part), they come into contact with the hydraulic fluid, and from the inside (from the inner part), they contact with the test fluid. Inside the cell, altogether with the liquid under study, there is a probe with a thin platinum wire and a sensor for the average temperature of the liquid volume. The top of the cell is closed by a scaled cover with fastening bolts and current leads. This design allows the application of pressure up to 10 MPa. The piston regulates the pressure in the cell. The pressure is monitored using a pressure gauge.

Figure 1. Compensation heating technique.

Figure 2. Measuring cell. 1 - current leads, 2 - mounting bolts, 3 - pressure chamber cover, 4 - liquid volume temperature sensor, 5 - probe board, 6 - wire probe, 7 - test fluid, 8 - fluoroplastic cup, 9 - hydraulic fluid, 10 - pressure chamber, 11 - pressure gauge, 12 - piston.
The measuring probe is installed in a textolite board, which is located inside a fluoroplastic cup and immersed in the test liquid (figure 2). This board also contains a temperature sensor that measures the temperature of the volume of the test liquid.

4. Results
The compensation technique is carried out automatically using specially developed software. The algorithm of the program is based on the cyclic loading of the experiment parameters from the table of the experiment parameters into the device. This table is generated automatically before the beginning of the experiment based on the data loaded by the experimenter. The data from this table are cyclically uploaded into the device, thus changing the parameters of each heating. After loading the parameters, the device performs heating and measurement. Automatic selection of the current allows quite accurately (0.3%) to select close temperature-time heating conditions.

The ratio of the heat transfer coefficients of the probe ($K_{hw}/K_h$) to the moistened (35ppm) and dried (5ppm) samples after the compensation procedure is practically independent of time (figure 3). This effect was observed for all studied samples (n-hexane, n-decane, n-hexadecane). Thus, the relative characteristic of the non-stationary heat transfer process at the second heating pulse of the probe, which does not depend on time, has been experimentally revealed. Should the average ratio of the heat transfer coefficients of a humidified hydrocarbon to a dried hydrocarbon be taken into consideration, it can be assumed that there is such a temperature for a given amount of moisture at which moisture begins to influence heat transfer.

The change in pressure significantly affects the average value of the ratio of the heat transfer coefficient of the watered ($K_{hw}$) and the original samples ($K_h$), which is clearly seen in figure 4 on the n-hexadecane example. It can be also seen that the effect of moisture on heat transfer practically disappears at a pressure of about 700 kPa. Similar effects are also observed with n-hexane and n-decane [11]. According to the relative increment of heat transfer from a moistened hydrocarbon to a dried one, it is possible to determine the pressure at which the effects of the influence of moisture become invisible under given heating conditions.

![Figure 3](image-url)

**Figure 3.** The ratio of the coefficients of unsteady "instantaneous" heat transfer from the probe to the moistened and dried samples of n-decane is stable over time at different temperatures of the probe heating. The weak dependence on time for a temperature of 260 °C is explained by compensation errors.
5. Conclusions
A comparative method for measuring the temperature dependence of the heat transfer from a pulse-heated probe to dielectric liquids with impurities has been developed and tested on samples of hydrocarbon liquids with traces of water. A main feature of the technique developed is the ability to create similar heating conditions for the wire probe in various samples under discussion. It has been shown experimentally that the ratio of the heat transfer coefficients from the probe to the moistened and dried samples after compensation for the difference in heating can serve as a stationary characteristic of a non-stationary heat transfer process. The dependences of the relative heat transfer coefficient on the probe’s temperature and external pressure are obtained. It is shown that the addition of 0.003% water increases the heat transfer to 10% in the course of approaching the boiling-up temperature of \(n\)-hexane, \(n\)-decane, and \(n\)-hexadecane. However, the application of an external pressure of several units of bar practically neutralizes this unexpected effect. The observed intensification of heat transfer manifests itself in pulsed experiments with a wire probe. Simulation of the experimental conditions shows that the effect of a heat transfer mechanism similar to microconvection in the most heated liquid layer with a thickness of about 10 \(\mu\)m is highly possible. The approximate values of the temperature gradient and heat flux in this thin layer are \(10^7\) K/m and \(10^6\) W/m\(^2\), respectively. Probably, the addition of water has a destabilizing effect on the interface between the solid surface of the probe and the hydrocarbon liquid directly in the course of approaching the boiling-up temperature and promotes the development of microconvection in the boundary layer.

![Figure 4. Temperature dependence of the \(K_{hw}/K_h\) ratio of the watered and dried \(n\)-hexadecane samples under specified temperature-time conditions at various pressures (1 - 0.084 MPa, 2 - 0.1 MPa, 3 - 0.212 MPa, 4 - 0.372 MPa, 5 - 0.692 MPa).](image)

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