Thermooptical Method and a Means of Measuring Mass Fraction Control of Liquefied Petroleum Gas Components

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Abstract—The paper presents the research results to increase the probability of mass fractions measuring control of liquefied petroleum gas components, which has various temperatures by defining the density of the liquid phase.

The thermo-optical method for measuring control of mass fractions of liquefied petroleum gas components is presented in the paper.

The measuring conversion function of the refractive index of liquefied petroleum gas was improved based on the proposed method. Based on research conducted it was developed the device of optoelectronic mass fraction measuring of liquefied petroleum gas components.

The estimation of static metrological characteristics of control device measuring channel for the liquefied petroleum gas components mass fractions.

The control device basic errors are defined as well.

Keywords—device for a measuring control; thermo-optical method; liquefied petroleum gas; propane; butane; unsaturated hydrocarbons; model liquid systems.

I. INTRODUCTION

Today the use of liquefied petroleum gas as a fuel in engines of motor transport, and units of municipal, industrial and agricultural facilities is widely spread [1]. Thus, there is a continuous growth in the consumption of this fuel, as a result, a problem of its quality increase arises. One of the ways to solve the problem is to control the mass proportion of the components of liquefied petroleum gas, as various mass and volumetric ratios of its components lead to a change in the basic characteristics of liquefied petroleum gas, particularly heat transfer, the composition of the emissions after combustion, and so on.

The known methods of mass fraction measuring control of liquefied petroleum gas components are chromatographic, chemical, radio wave, radio frequency, pyrolysis, hydrostatic weighing, evaporation and cooling [2 – 4]. Their main disadvantages are the complexity of the implementation of the measurement process, its high cost and low accuracy. For example, the error of the method of hydrostatic weighing is 5% [5, 6], pyrolysis – 5...10% [7], radio-wave and , radio frequency – 4% [8]. This is due to the definition of the ratio of only propane and butane, whereas the presence of unsaturated hydrocarbons is not considered.

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It was proved on the analysis of the peculiarities of the composition of the liquefied petroleum gas components that today in the CIS countries several brands of liquefied petroleum gas, depending on its basic components are widely used. For example, in propane-butane automobile gas, the proportion of propane can vary in the range from 40% to 60%, butane – from 34% to 60%, unsaturated hydrocarbons, from 0% to 6% [7,9]. The output of the mass fraction of at least one of the components of liquefied petroleum gas outside of the specified ranges is displayed on its quality. This eventually leads to significant economic losses. Therefore, the mass proportion measurement control of liquefied petroleum gas components is extremely important as the normalized ratio of mass fractions of each of the components defines not only the brand but also the quality of liquefied petroleum gas.

Thus, considering the continuous development of industry and high demands for gas quality standards [5, 7, 9 - 12], and, respectively, to the measuring equipment, an important and urgent task is the development of modern methods and means of mass proportion measurement control of liquefied petroleum gas components.

II. THE MAIN CONTENTS OF THE WORK

The density of liquefied petroleum gas, and, consequently, its components – propane, butane and unsaturated hydrocarbons, is characterized by a nonlinear dependence on temperature, as density gas components change differently. It is known that when the temperature changes for 1°C the density of propane is changed to 1.5 kg/m³, butane – 1,2 kg/m³, unsaturated hydrocarbons – 1.05...1.1 kg/m³ [13]. This means that specific ratio mass proportion of liquefied petroleum gas components corresponds to a specific feature of the dependence of density on temperature, which contains a linear site. This characteristic can be obtained by measuring the density of liquefied petroleum gas at several different temperatures. Based on the conditions of measurement it is appropriate to use the refractometric method, because the density of liquefied gas is in accordance with its refractive index.

On the basis of the above it is proposed thermooptical method of mass proportion measurement control of liquefied petroleum gas components, which is based on the differences in the temperature dependencies of refractive indices and, consequently, the densities of the components of liquefied petroleum gas. The density of the liquid phase of the liquefied petroleum gas can be defined by certain temperature as

$$\rho_{rid.f.} = 1 / \sum \frac{k_i}{\rho_i}$$

Fig. 1 shows the simulation results that take into account the mass proportions of liquefied petroleum gas components at the temperature T_1 =274 K. As the graph shows, there is ambiguity in the definition of the mass fractions of components of liquefied petroleum gas, as some of the ratio of the mass fraction give similar values of the total density or these values repeat.



Fig. 1. The ratio of mass fraction of propane, butane and unsaturated hydrocarbons at a temperature

To disambiguate it is proposed to measure the density of liquefied petroleum gas at different temperatures. In such case it is possible to write down a system of equations

$$\begin{cases} \frac{k_1}{\rho_1^1(T_1)} + \frac{k_2}{\rho_2^1(T_1)} + \frac{k_3}{\rho_3^1(T_1)} = \frac{1}{\rho^1(T_1)}; \\ \frac{k_1}{\rho_1^2(T_2)} + \frac{k_2}{\rho_2^2(T_2)} + \frac{k_3}{\rho_3^2(T_2)} = \frac{1}{\rho^2(T_2)}; \\ \frac{k_1}{\rho_1^3(T_3)} + \frac{k_2}{\rho_2^3(T_3)} + \frac{k_3}{\rho_3^3(T_3)} = \frac{1}{\rho^3(T_3)}, \end{cases}$$

according to its linear temperature dependence

$$\begin{cases} \rho^{1} = \rho_{0}^{1} (1 - \alpha_{1} (T - T_{0})); \\ \rho^{2} = \rho_{0}^{2} (1 - \alpha_{2} (T - T_{0})); \\ \rho^{3} = \rho_{0}^{3} (1 - \alpha_{3} (T - T_{0})), \end{cases}$$

where ρ_0^1 , ρ_0^2 , ρ_0^3 are the density of propane, butane and unsaturated hydrocarbons, respectively, for temperature T_0 ; α_1 , α_2 , α_3 are the thermal expansion coefficients of propane, butane and unsaturated hydrocarbons, respectively; k_1 , k_2 , k_3 are the mass fraction of propane, butane and unsaturated hydrocarbons, respectively; $\rho_1^1(T_1)$, $\rho_1^2(T_2)$, $\rho_1^3(T_3)$ are density of propane at temperatures of T_1 , T_2 , T_3 , respectively; $\rho_2^1(T_1)$, $\rho_2^2(T_2)$, $\rho_2^3(T_3)$ are density of butane at temperatures of T_1 , T_2 , T_3 , respectively; $\rho_3^1(T_1)$, $\rho_3^2(T_2)$, $\rho_3^3(T_3)$ are density of unsaturated hydrocarbons at temperatures of T_1 , T_2 , T_3 , respectively; $\rho_1^1(T_1)$, $\rho_2^2(T_2)$, $\rho_3^3(T_3)$ are density of liquefied petroleum gas at temperatures of T_1 , T_2 , T_3 , respectively.

The solution of the system of equations (1), and further experimental investigations allowed us to obtain a group of characteristics according to the mass proportion of the components of liquefied petroleum gas density at different temperatures.

Fig. 2 shows two temperature characteristics similar by values of the densities of liquefied petroleum gas at different ratios of the mass fraction of its components. As the graph shows, each feature corresponds to a particular ratio of mass fraction according to different angle of inclination.



Fig. 2. Temperature characteristics of liquefied petroleum gas similar values densities at different ratios of the mass fraction of its components

Thus, the uncertainty in the determination of mass fractions of liquefied petroleum gas components can be eliminated by measuring its density at multiple temperatures with a priory known values of the components densities.

Based on the proposed thermooptical method of mass proportion measurement control of liquefied petroleum gas components opto-electronic measuring transformer of the refractometric type is developed , which is described by the function $\left(2\right)$

$$U_{dv} = P_{in} P_i R_n f_{cf} \left(S(\Delta x(n(\rho(k)))) \right), \qquad (2)$$

where U_{dv} is differential voltage; P_{in} is the signal power at the input of composite photodetector; P_i is current sensitivity of the composite photodetector; R_n is a load resistance; f_{cf} is the conversion feature of the composite photodetector; S is illuminated area of the composite photodetector; Δx is the offset of the light spot; n is the refractive index.

Since the refractive index of liquefied petroleum gas is in accordance with its density ρ [6], their relationship can be described by a system of equations

$$\begin{cases} n = 1.3497 - \frac{9.591}{M/\eta + 9.5}; \\ \rho = \frac{PM}{RT}, \end{cases}$$
(3)

where R is universal gas constant; M is the molar mass; η is the coefficient of proportionality (10⁻³ kg/mol); P is the pressure of the liquefied petroleum gas at the temperature T.

A structured photodetector, on which falls a ray of light in the light spot, allows you to register the spatial distribution of illumination in the lighting of the area S_1 and S_3 of the opposite segments of the photodetector. The displacement of the light spot corresponds to the differential voltage U_{dv} , formed by the difference of electrical signals U_1 and U_3 , received from opposite segments of the photodetector.

Differential voltage is defined as

$$U_{dv} = U_1 - U_3, (4)$$

or

$$U_{dv} = P_{dv} P_i R_n (S_1 - S_3),$$
 (5)

and proportional to the displacement of the light spot Δx

$$U_{dv} = P_{dv} P_i R_n b \Delta x \,, \tag{6}$$

where b is the length of the strip light.

Fig. 3 shows the optical scheme of the opto-electronic transformer.

The displacement of the light spot Δx depends on the refractive index of liquefied petroleum gas and is defined as

$$\Delta x = d \cdot \left(\frac{n_g'' \sin \alpha}{\sqrt{n_c^2 - (n_g'' \sin \alpha)^2}} - \frac{n_g' \sin \alpha}{\sqrt{n_c^2 - (n_g' \sin \alpha)^2}} \right) + l \cdot \left(\frac{n_g'' \sin \alpha}{\sqrt{1 - (n_g'' \sin \alpha)^2}} - \frac{n_g' \sin \alpha}{\sqrt{1 - (n_g' \sin \alpha)^2}} \right), \quad (7)$$

where *d* is the thickness of the layer of liquefied petroleum gas; *l* is the distance of the photodetector from the composite to the glass; α is the angle of incidence of the beam; $n'_g \dots n''_{\epsilon}$ is the range of variation of the refractive index of liquefied petroleum gas; n_c is the refractive index of glass.



Fig. 3. Optical scheme of an optical-electronic transformer : 1 – light source; 2 – beam; 3 – optical system; 4 – lens; 5 – diaphragm; 6 – liquefied petroleum gas; 7 – glass cuvette; 8 – photodetector

The task was to get the same temperature throughout the volume of liquefied petroleum gas. Therefore, modelling of the process of the spread of warmth in the volume of liquefied petroleum gas was done . The modelling results are shown in Fig. 4.



Fig. 4. Temperature distribution tx in the amount of liquefied petroleum gas: 1 – from the Peltier element to the middle of the cuvette; 2 – from the middle cuvette to the Peltier element

It was found out to use two Peltier elements located on the opposite facets of the cuvette in the design of the cuvette. This allows you to achieve the same temperature throughout the volume of liquefied petroleum gas. This distribution is controlled by temperature sensors, which are located at different levels on opposite facets of the cuvette.

As shown in Fig. 5, the temperature of liquefied petroleum gas provides a significant impact on the source differential voltage of the transmitter.



Fig. 5. Dependence of the differential voltage measuring transformer from the density of liquefied petroleum gas

The sensitivity of optical-electronic transformer allows registering close values of density of liquefied petroleum gas by carrying out measurements at different temperatures.

In Fig. 6 is a block diagram of the measuring means of the mass fraction control of the of liquefied petroleum gas components , which contains opto-electronic measuring transformer 24 and the microprocessor 21, which receives the measurement information about the density and temperature, and it controls the operation of the Peltier elements.



Fig. 6. Block diagram of the measuring control mass fraction of the of liquefied petroleum gas components

The transmitter 24 includes a source of radiation 2, a light beam 6 which is focused by the optical system 5 and passes through a special glass cuvette 14 which contains liquefied petroleum gas at a certain pressure. The light beam 6 transmitted through the cuvette 14, is refracted due to the presence of the inclined walls 10', and comes as spots on the photodetector 15, which contains four segments, one of which the support 18 and the other two 16 and 17 allow to generate the differential voltage due to the displacement of the light spot, which is proportional to the refractive index of liquefied petroleum gas. The temperature of the liquefied gas is set by the Peltier elements 7 and is controlled by the temperature sensors 9 [14 - 16].

Mathematical model of the mass fraction control measuring means of the liquefied petroleum gas components in case of equality of temperature sensors $(T_1=T_2)$ described as

$$\begin{cases} N_U = K_n K_c \left(2^{n_0} - 1 \right) \left(1 - \frac{P_{ox} P_i R_n b}{U_{on}} \Delta x \right); \\ N_T = \frac{2^{n_0} U_T}{U_{on}}, \end{cases}$$
(8)

where N_U is ADC code, which corresponds to the measuring channel means; N_T is the ADC code, which corresponds to the temperature sensors; U_T is the temperature sensor voltage; K_n , K_c are the coefficients of amplification and conversion, respectively; U_{on} is the reference voltage; n_0 is number of ADC bits.

The measurement errors of the mass fractions of liquefied petroleum gas components are analyzed and found out that instrumental errors can be time-divided into the following: errors of temperature sensors δ_T and pressure δ_P ; error of Peltier elements δ_n ; a fotodetector δ_{fn} ; accuracy of conversion of current to voltage δ_{IU} ; the error

analog-to-digital conversion δ_{ADC} . The total instrumental error will be:

$$\delta_i = \sqrt{\delta_T^2 + \delta_P^2 + \delta_n^2 + \delta_{fn}^2 + \delta_{IU}^2 + \delta_{ADC}^2}, \quad (9)$$

and is 1,55%.

To methodological errors include: error δ_{nl} of nonlinearity of the temperature characteristics of density; the error δ_f arising from the exclusion from the calculation of the rate of scattering of radiation; the error δ_{nv} density unsaturated hydrocarbons; temperature error δ_m glass.

Thus, the total methodical error is defined as

$$\delta_M = \sqrt{\delta_{nl}^2 + \delta_f^2 + \delta_{nv}^2 + \delta_m^2}, \qquad (10)$$

and is equal to 0,44%.

Total measurement uncertainty of the mass fractions of liquefied petroleum gas components does not exceed 2%.

A study of the mass fraction measuring control of the liquefied petroleum gas components was investigated. The appearance of which is shown in Fig. 7. The studies were conducted using model liquid systems, since similar studies with liquefied petroleum gas in the laboratory is quite expensive and complex. In this regard, the method of model liquid systems was developed, where it was proposed to use toluene, hexane and isooctane based on the proximity of their temperature characteristics of composite liquefied petroleum gas. Temperature characteristics of toluene, isooctane and hexane are described using equations

$$\rho^{t} = \rho^{0} (1 + \gamma \cdot (t - t_0)),$$

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where ρ^0 is the density of hexane, isooctane and toluene at the temperature $t_0 = 273$ K; ρ^t is the density of hexane, isooctane and toluene at the temperature t; γ is the average temperature correction of the density.



Fig. 7. External view of the mass fraction control measuring means of the liquefied petroleum gas components

Fig. 8 shows the results of an experimental research of the mass fraction control measuring means of the liquefied petroleum gas components. The convergence of theoretical and experimental characteristics are received. Model error does not exceed 8%.



Fig. 8. Theoretical and experimental characteristics of density on temperature for several ratios of mass fractions of components of liquefied petroleum gas

According to the results of experimental studies the change in the mass fractions of components of the sample liquid model systems and their relative errors in time are carried out. 180 points of measurement are received. Dependences of the general law of the error distribution of mass fraction measuring of the liquefied petroleum gas components are given and it was found out that the distribution law is normal.

Research results and the dependences of errors of the first and second kind were analyzed. The probability of getting the correct result by this measuring means is D=0.97.

III. CONCLUSIONS

Thermooptical method of mass fraction measuing control of the liquefied petroleum gas components was developed, which is based on the differences in the temperature dependences of refractive indices and, consequently, the densities of the components of liquefied petroleum gas. The method of model liquid systems was developed, to prepare which it is proposed to use toluene, hexane and isooctane based on the proximity of their temperature characteristics of composite liquefied petroleum gas. Mathematical model of the mass fraction measuring means control of the liquefied petroleum gas components was improved , which allows on the basis of voltage values related to refractive index, and, consequently, densities of liquefied petroleum gas at given temperatures and a priori known dependence of the mass fractions of the liquefied petroleum gas components, which correspond to the obtained values of the density, to determine the mass fraction of the components of liquefied petroleum gas and to

increase the reliability of the control. The analysis of the experimental results of mass fraction measuring control of the liquefied petroleum gas components was carried out which showed the convergence of theoretical and experimental characteristics.

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