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DETERMINING THE PHYSICAL-CHEMICAL PARAMETERE OF FUEL MIXTURES OF NATURAL GAS WITH HYDROGEN IN GAS NETWORKS

The object of this study is a gas mixture of natural gas and hydrogen.

The physical and chemical parameters of fuel mixtures of natural gas with hydrogen have been investigated with the aim of further regulating the hydrogen content in the gas transmission system in accordance with the state standards of Ukraine and the European Union. The task addressed was the safe use of green hydrogen in a mixture with natural gas.

The permissible hydrogen content in municipal network gas was established at 7 mol %, which would allow efficient and safe use of existing gas transmission systems. Currently, a 4 % increase in pressure is recommended for low-pressure networks. This is because the calorific value of natural gas is regulated by the Code of Gas Transmission and Distribution Systems and must be within certain limits, and compliance with this particular hydrogen content in natural gas allows this indicator to be kept within the normal range. The 4 % increase in pressure is due to the preservation of the thermal power of gas burners when one gaseous fuel is replaced by another.

The content of the mixture of combustible gases at the lower and upper flash points was analyzed. It was found that at 7 % hydrogen content, the flash point range is 5.07–16.75 vol %, which is within the permissible range of 5–15 vol %. With an increase in the hydrogen content of the gas, an explosion may occur in a wider range of concentrations and require additional safety measures.

The defined hydrogen limit does not affect the explosiveness of network gas and ensures the safety of its use since the lower concentration limit of flammability (in terms of methane) in a mixture with air in volume percentage is 4.4, and the upper limit is 17.0 vol % according to Annex 2 of the technical regulations

Keywords: "green" hydrogen, network gas, calorific value, Wobbe number, flash point

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1. Introduction

The energy sector is the basis of the economic development of any country. A stable energy supply system is crucial for sustainable development and economic security, has enough environmental impact, can create new opportunities or, on the contrary, act as a constraint. The entire global energy industry is undergoing significant changes. However, changes in the national energy sector are taking place slowly and with a significant delay.

During the burning of natural gas, almost twice less CO_2 is released than during the production of electricity from coal. This is a significant incentive and advantage for the production of electricity based on natural gas.

As stricter emission standards, especially for CO_2, are expected to come into force around the world in the future, there will be increasing demand for the development of advanced and efficient technologies to convert natural gas into electricity with full carbon capture. The transition to a hydrogen economy is one of the promising strategies for reducing CO_2 emissions. The use of natural gas-hydrogen combinations could increase energy efficiency through the necessary increase in pressure in the gas pipeline with added hydrogen by 22 MJ/m^3 and reduce emissions of harmful substances by almost two times [1] and become a reliable source of low-carbon heat and energy, which is why the results of such studies are needed in practice.

Natural gas is a significant segment of the global energy portfolio (at least 40 %). As the least carbon-intensive fossil fuel (natural gas has a carbon concentration of at least 7 times that of light oil and 25 times that of coal) with abundant reserves worldwide, natural gas could become a “transition fuel” over the next few decades for the transition to a low-carbon energy economy without the need for major infrastructure changes. That is why scientific research on this topic is important and requires a greater study of the impact of the combination of natural gas-hydrogen on equipment, energy efficiency, safety at all stages of the use of natural gas; it is assumed that by 2050 green hydrogen will provide up to 24 % of global demand in energy resources.

2. Literature review and problem statement

In order to solve the issue of gas balance and reduce dependence on conventional imported energy sources, and to achieve global environmental goals, researchers have proposed a number of substances that partially or even completely replace conventional types of fuels in recent decades. In the case of natural gas (NG), it is proposed to use mixtures with biogas, synthesis gas, ammonia, hydrogen, and various process gases.

Paper [2] describes the model of mixing hydrogen with network natural gas. Different regimes of hydrogen mixing in the gas transportation network were analyzed. However, the question of using a safe concentration of hydrogen with natural gas and its impact on gas equipment and what parameters the existing gas transportation network should have for the application of the developed model remains open. All this allows us to assert the need to study the effect of hydrogen on the gas transport system, to establish the permissible parameters of the mixture of gases, to regulate it for safe use.

In addition to hydrogen-containing ones, it is also proposed to use mixtures of coke and blast furnace gases as well as in combination with natural gas [3]; however, for mass industrial use, the question of converting gas burners to the proposed gas mixture models arises. This is primarily due to the complexity of changing gas equipment on an industrial scale and their economic feasibility.

An alternative substitute for natural gas could be "green" ammonia in combination with hydrogen, which produces fewer emissions of harmful substances when burned compared to other types of fuel [4]. However, research on this issue continues since the characteristics of ammonia combustion are significantly different from the usual hydrocarbon fuels, there are specific difficulties during its use [5]. The paper shows the effectiveness of combining ammonia with other gases (hydrogen, methane) as a fuel substitute. However, the issue of the use of these gases in existing gas systems has not been covered since the effect of the mixture of gases on gas equipment has not been studied. All this points to the expediency of conducting a study on the impact of added "green" ammonia and hydrogen to natural gas on the gas transportation network, network operating conditions, and gas equipment.

An analytical review of the results of scientific research and applied development of the most pressing modern problem, such as hydrogen, hydrogen and nuclear-hydrogen energy, over the past 15–20 years has been reported in [6]. In the context of an argumentative statement of the problem, the main categorical and conceptual apparatus of the problem is defined. The main directions and issues of research on the step-by-step solution of the problem are outlined. Attention is focused on the peculiarities of the processes of storage, transportation, and use of hydrogen as an energy carrier and raw material for technologies. But the issue of the possible use of hydrogen in a mixture with natural gas was not covered since hydrogen was studied as an energy carrier in the field of heat supply; efficiency and profitability of methods for obtaining it.

Much attention is paid to the partial replacement of natural gas with the so-called "green hydrogen" [7]. The precise dosing of hydrogen to NG is indicated, as this is an important problem in some European countries. Existing regulations have not been adapted for the safe use of hydrogen in existing gas networks. Permitted hydrogen injection limits are low and green tariffs only apply to biomethane. The reason is legal barriers to mixing hydrogen with natural gas by harmonizing the concentrations of the mixture and setting thresholds based on physical restrictions in countries. All this allows us to talk about the expediency of revising the regulatory framework on this issue, and the possible development of new safety standards.

The growing role of "green" hydrogen in the formation of the future carbon-neutral society, as well as the transitional stage of both small and large countries, are also discussed and considered [8]. It is shown that renewable energy sources (RES) are dominant in the energy sector, energy storage, and their use is becoming key factors. One of the solutions is the addition of hydrogen to natural gas in existing gas networks as this affects its physical and chemical properties, which requires careful analysis and research.

Key issues related to the concept of hydrogen mixing in natural gas pipeline networks under appropriate conditions and relatively low concentrations of hydrogen mixing require only minor modifications in the operation and maintenance of the pipeline network [9]. Minor problems occur with mixtures containing less than 5–15 % hydrogen (by volume), depending on site-specific conditions and natural gas composition. More significant challenges need to be addressed for higher concentrations with natural gas in the 15–50 % range, such as appliance retrofits. A likely option to overcome difficulties is the conversion of household appliances or an increase in pressure along the distribution networks. However, optimal regulation of the hydrogen content in the gas transportation system from the point of view of efficiency and safety remains an unresolved issue due to the lack of legal regulations for mixing hydrogen with natural gas

Currently, the technical and economic indicators of the cogeneration system, which consists of a mixture of different percentages of "green" hydrogen with natural gas, are being widely studied. It was established that the energy efficiency of the natural gas–hydrogen system gradually increases with an increase in the percentage of hydrogen in the mixture from 0 % to 20 %, then slightly decreases at 50 % H_2 and again continuously increases both at 80 % H_2 and at 100 % H_2 [10]. The question of the recommended concentration of "green" hydrogen mixed with natural gas and its impact on gas equipment during transportation remains open since only the energy efficiency indicator was taken into account.

At present, a model has been built for simulating dynamic gas transportation in pipelines taking into account the composition of the gas mixture and their boundary conditions. The injection of hydrogen into the natural gas network infrastructure is modeled, taking into account the effect they have on the local properties of the gas. Studies on the impact of hydrogen added to natural gas on the transport system were also carried out: from the point of view of composition, flow rate, and pressure profiles in comparison with the reference case of natural gas. Research results show that the amount of hydrogen added to the gas transportation network should be limited as it has a direct impact on the pipeline and its safe use. Since the network could begin to receive several different gases, changes in their properties (thermal capacity, density) could significantly affect the management of the network [11]. The issue of normalizing the content of hydrogen in natural gas remains unresolved since the above indicators could change dynamically in each gas transportation system.

The use of mixtures of natural gas with hydrogen as an alternative fuel for industrial heat treatment furnaces and their economic potential for reducing carbon dioxide emissions in this field shows that such mixtures have a positive effect on the heating system without significant impact on the technological aspects of furnace heating [12]. Considerable attention has been paid to the determination of the gas flow rate of mixtures with different hydrogen content and combustion properties, such as the Wobbe index, but the question of the permissible hydrogen content in a mixture with natural gas and its standardization for safe industrial use has not been considered.

Under the conditions of the effect of hydrogen on the strength characteristics of the metal, studies on the effect of low hydrogen content in a mixture with natural gas on stretching, viscosity changes, and destruction of pipeline steel X70 were carried out [13]. It is shown that the mechanical properties of pipeline steel X70 change depending on the concentration of hydrogen and pressure in the network but the effect on other grades of steel on connecting elements of gas equipment requires additional research.

The concept of "power to gas", the essence of which is the transformation of excess electricity from renewable energy sources with the help of electrolyzers into ecologically clean fuel – "green hydrogen", has become widespread in the world. A technical and economic analysis of the system of hydrogen interconnections is carried out using methods of equalized cost of electricity/storage [14]. It is known that the system receives electricity from renewable energy facilities, converts it into hydrogen at an electrolysis plant, transports hydrogen to the consumption center through a pipeline, where it is again converted into electricity using a gas turbine or fuel cells. For such a system, it is proposed to use existing transport systems for hydrogen, and in its absence, the use of a gas transport network is possible, but it is not indicated under which parameters and regimes this is possible, and what the permissible concentrations of hydrogen transport are.

In addition, the replacement of gray hydrogen production with green hydrogen production using electrolysis and renewable energy sources for the EU-27 and Great Britain at the regional level, taking into account existing electricity consumption and hydrogen demand, was evaluated [15]. However, the issue of using "green" hydrogen with a mixture of natural gas in existing gas networks as one of the ways of using and preserving the excessively produced "green" hydrogen from renewable energy sources has not been considered.

Prospects for the use of hydrogen mixed with natural gas in the gas transportation system indicate significant differences in gas systems between European countries, which are critical for direct extrapolation of data obtained by European operators [16]. The reported results of the study on the influence of hydrogen on gas distribution networks show that a decrease in pressure in the system was observed on all studied models due to hydrogen leakage and the impossibility of taking into account all indicators that affect the determination of hydrogen rationing in the gas network.

"Green" hydrogen is not stored separately but is immediately pumped into gas networks. It is believed that the general understanding of the technical aspects of how to produce "green hydrogen" has already been resolved. However, issues related to the transportation of hydrogen to the direct consumer and the use of the gas-hydrogen mixture on site are still being researched. Currently, on the basis of experimental and industrial tests of gas equipment, the limits of the rational content of hydrogen in a mixture with natural gas have been established [17]. The possibilities of converting household appliances to natural gas heating devices with the addition of hydrogen have been identified. However, the authors recommend a hydrogen content range of 50 vol%. and this applies only to the energy efficiency of household gas appliances, where only the rate of laminar combustion of a mixture of gases is selected as the evaluation criterion, without taking into account thermobaric conditions.

In addition, complex studies on the influence of mixtures of hydrogen gas with natural gas on the operational and thermophysical characteristics of polyethylene pipes, as the most widespread in existing gas distribution networks, are being conducted. The relationship between the concentration of hydrogen in the mixture and the degree of its influence on the strength characteristics of the samples was established [18]. However, the research period was 6 months, which is not enough for an objective assessment in time. This is due to the narrow focus of the work, the results of which must be taken into account in a comprehensive analysis of the physical and chemical parameters of fuel mixtures of natural gas with hydrogen in gas networks.

Each element of the natural gas infrastructure has a different degree of acceptability with respect to hydrogen concentration, but the safety factor affects the overall permissible hydrogen concentration [19]. The effect of hydrogen injection on gas quality is also established, showing that introducing 2 % hydrogen into the distribution network has little effect, but 10 % hydrogen mixture affects the calorific value of the supplied fuel gas below the desired level. Mixing hydrogen with natural gas affects the quality of the gas, which is reflected by a change in its calorific value, and subsequently in the Wobbe number. This ultimately results in a higher gas flow rate to provide the same energy content to end users. Due to the high flow rate, the pressure in the pipeline drops, and therefore it affects the transportation and distribution network of the pipeline.

In the gas networks of the following countries and Japan, the maximum percentage of hydrogen content is limited by law [20], is standardized, and is within the range from 0 to 12 % by volume. Thus, in Great Britain, Belgium, Sweden, this indicator is up to 1 %, while in Italy, Switzerland, Austria, Spain, France, it is up to 10 %. The highest content of hydrogen in gas networks is allowed in Germany and the Netherlands, 10–12 % by volume, and in Japan it is not allowed at all. This is primarily related to the development of legislative norms for mixing hydrogen with natural gas by harmonizing the concentrations of the mixture and establishing threshold values based on the comprehensive consideration of all parameters that depend on the reliability and safety of use in existing gas networks.

Requirements for the composition and physical and chemical properties of natural gas (NG) are regulated by a number of regulatory documents. And only in DSTU EN 16726:2019 some attention is paid to permissible concentrations of hydrogen in natural gas systems. Also, state standards recommend considering this issue in each case separately. Thus, the hydrogen content in network gas is not regulated.

Another aspect is the excess capacity of gas transmission (GTS) and gas distribution systems (GDS). In 2020, the excess capacity of GTS was threefold [21]. Therefore, it is possible to continue to use the existing gas transmission system, while reducing the carbon emissions associated with the use of natural gas. In addition, mixing hydrogen with natural gas in the existing gas network could also be used as a way to store excess renewable energy. However, as our review of related studies on the specified topic demonstrated, it is complicated by a number of factors. Thus, based on the above, the main factors that do not make it possible to solve the task of increasing the energy efficiency of gas mixtures by adding hydrogen are as follows: the issue of the effect of different concentrations of hydrogen on the metal; maintaining the flash points of the mixture within acceptable limits; the possibility of using existing gas transportation systems; compliance with thermobaric conditions for safe use of the mixture.

3. The aim and objectives of the study

The purpose of our research is to determine the recommended limit of hydrogen concentrations in natural gas (NG), guided by the requirements of the current legislation in Ukraine for physical and chemical indicators and safety standards. This will make it possible to further develop hydrogen energy and organically integrate into the European energy space.

To achieve the goal, the following tasks were set:

– to perform chromatographic analysis of a number of natural gas mixtures; establishing their quantitative composition;

– to calculate PCP of real gas mixtures;

– to theoretically calculate the physicochemical parameters (PCP) of the NG-H_2 system in which the hydrogen content varies over a wide range;

– to calculate the change in the flash limit of the NG-H_2 mixture in air.

4. The study materials and methods

The object of our research is a gas mixture of natural gas and hydrogen.

It is assumed that the use of green hydrogen with the known composition of natural gas in a concentration of up to 7 % mol. could make it possible to use existing gas transportation systems with compliance with flash points within permissible limits.

Using hydrogen in a mixture with natural gas at higher and lower concentrations in the system may result in a discrepancy between the deviation of the flash points from the permissible limits and the impossibility of using the existing gas transportation network.

In this study, in order to simplify the calculations, natural gas is assumed to be 100 % methane.

The work employs the method of mathematical modeling to calculate the heat of combustion (higher and lower), density, relative density, and Wobbe number (higher and lower) of natural gas based on the known molar composition.

NG samples were taken at gas distribution stations in Kyiv, in accordance with the procedure established by DSTU ISO 10715:2009 and the Codes of gas transportation and gas distribution systems. Representative gas samples were collected by an indirect method so that the sample reflected the entire volume of gas at the time of sampling. The equipment, namely 2 L stainless steel metal containers, met the relevant sampling conditions: pressure, temperature, corrosion activity, flow rate, chemical compatibility, vibration, thermal expansion, and/or thermal compression. Before sampling, the containers were purged each time with argon, as the carrier gas on the chromatograph, to ensure the purity of the experiment. At the gas sampling points, lines were blown, and containers were filled through bypass loops made of stainless steel with a diameter of 3 to 10 mm. A pressure drop was created in the loop between the gas inlet and outlet points to ensure a constant flow rate through the sampling equipment located in the loop. During transportation and storage, safety caps were installed on cylinders, if provided for. The cylinders were marked with the capacity, working pressure, and test pressure (1.5 times higher than the working pressure).

After gas sampling, the cylinders were delivered to the laboratory within 4–5 hours.

Determination of component and PCP was carried out by the method of gas chromatography on a Kristallux 4000 M chromatograph. Calculations of physical and chemical indicators were performed according to DSTU EN ISO 6976:2020.

Determination of hydrogen (together with oxygen, helium, and nitrogen) on this chromatograph was carried out on a separating column with 13X molecular sieves using argon as a carrier gas on a thermal conductivity detector according to DSTU ISO 6974-3:2007.

Our research has made it possible to acquire an array of data that could be considered reliable, and which became the basis for further calculations.

5. Results of investigating the physical-chemical indicators of a mixture of natural gas and hydrogen

5. 1. Chromatographic analysis of a series of natural gas mixtures

As a result of our research, the characteristics of typical NG transported by the gas distribution system were determined. In a separate case, the situation in which “green” hydrogen is added to NG and passes through the gas distribution networks in the city of Kyiv was considered.

Table 1 gives summarized results of laboratory measurements of the component composition of natural gas, whose samples were taken weekly at the gas distribution stations (GDS) in the city of Kyiv during 2021.

Calculations were performed for dry NG at a temperature of 20 °C and a pressure of 101.325 kPa. Given in Table 1, the component composition could be called typical for the city of Kyiv in 2021. As a result of research, it was established that the main component of NG is methane, the content of which is almost 90 mol %. About 6.7 mol % of other hydrocarbons heavier than methane. About 3.8 % of inorganic components. Also, NG contains hydrogen sulfide and ethanethiol, but their content is not constant and very insignificant. Therefore, subsequently, their contribution was neglected. It should be emphasized that hydrogen was not registered in the selected natural gas samples.

Table 1

Average annual values of the component composition and physical-chemical parameters of natural gas by supply routes in 2021

No.	Indicator	Measurement unit	Requirements	GDS CHP-5	GDS-12	GDS-9	GDS CHP-6	Average value	Standard deviation
1	Methane (CH_4)	mol %	≥90	89.307	89.416	89.422	89.409	89.387	1.049
2	Ethan (C_2H_6)	mol %	≤7	5.071	5.060	4.961	5.027	5.030	0.577
3	Propane C_3H_8)	mol %	≤3	1.254	1.281	1.232	1.238	1.253	0.147
4	n-Butane (C_4H_{10})	mol %	≤2	0.215	0.222	0.217	0.212	0.217	0.023
5	Iso-Butane (2-methylpropane)	mol %	≤2	0.130	0.134	0.129	0.129	0.131	0.008
6	n-Pentane (C_5H_{12})	mol %	≤1	0.048	0.047	0.049	0.048	0.048	0.009
7	iso-Pentane (2-methylbutane)	mol %	≤1	0.052	0.052	0.052	0.052	0.052	0.006
8	neo-Pentane (2,2-dimethyl-propane)	mol %	≤1	0.005	0.005	0.006	0.006	0.006	0.001
9	n-Hexane (C_6H_{14})	mol %	≤1	0.043	0.042	0.045	0.045	0.043	0.009
10	Nitrogen (N_2)	mol %	≤5	1.509	1.543	1.506	1.442	1.506	0.197
11	Carbon dioxide (CO_2)	mol %	≤2	2.359	2.173	2.376	2.392	2.318	0.294
12	Oxygen (O_2)	mol %	≤0,02	0.009	0.008	0.007	0.009	0.008	0.003
13	Hydrogen (H_2)	mol %	–	absent					
14	Relative density	–	–	0.637	0.628	0.628	0.629	0.631	0.018
15	Absolute density	kg/m^3	–	0.758	0.756	0.757	0.757	0.757	0.009
16	Heat of combustion, higher	MJ/m^3	36,2–38,3	38.24	38.32	38.20	38.24	38.25	0.188
17		kWh/m^3	10,06–10,64	10.62	10.64	10.61	10.62	10.62	0.052
18	Heat of combustion, lower	MJ/m^3	32,66–34,54	34.55	34.62	34.51	34.54	34.55	0.177
19		kWh/m^3	9,07–9,59	9.60	9.62	9.58	9.59	9.60	0.049
20	Wobbe's number, higher	MJ/m^3	–	48.22	48.37	48.18	48.23	48.25	0.222
21		kWh/m^3	–	13.39	13.44	13.38	13.40	13.40	0.062
22	Wobbe number, lower	MJ/m^3	–	43.56	43.80	43.53	43.57	43.62	0.431
23		kWh/m^3	–	12.10	12.17	12.09	12.10	12.12	0.120

5. 2. Physical-chemical parameters of natural gas, methane, and hydrogen

Calculations of PCPs of natural gas were carried out on the basis of the obtained values of the component composition and are displayed in Table 1. High average values of relative and absolute density of 0.6307 and 0.7569 kg/m^3 were obtained, respectively. The average value of the higher heat of combustion (38.25 MJ/m^3) is close to the upper limit of the ranges established by the current Codes of gas transportation and gas distribution systems of Ukraine. The average value for the lower calorific value (34.55 MJ/m^3) does not significantly exceed the upper limit of the legal range. The high content of heavy hydrocarbons determines the high density and calorific value of the studied natural gas samples.

In all researched literature sources, to simplify the calculations, the physicochemical parameters of natural gas were assumed to be equal to methane. Therefore, calculations of the two-component hydrogen-methane system were actually carried out. It is important to emphasize that pure methane and especially hydrogen as combustible gases have quite different properties (Table 2) compared to natural gas (Table 1), which is transported and distributed by the gas networks in Ukraine.

The heat of combustion of "typical" natural gas is greater than that of methane by approximately ~3.5 %, the absolute and relative density are greater by ~12 %. Accordingly, other derivative parameters also change. At first glance, such differences may not seem significant, but everything changes dramatically from the point of view of gas transportation and gas distribution companies. When accounting for tens and hundreds of millions of cubic meters of transported NG, even small differences in density measurements could lead to significant financial discrepancies.

Table 2

Comparison of some physical-chemical parameters of methane and hydrogen

No.	Indicator: (20 °C/20.0 °C, 101.325 kPa)	Measurement unit	Methane (CH_4)	Hydrogen (H_2)
1	Higher mass heat of combustion	MJ/kg	55.54	141.87
2	Lower mass heat of combustion	MJ/kg	50.03	119.93
3	Relative density	–	0.5547	0.0696
4	Absolute density, kg/m^3	kg/m^3	0.6682	0.0838
5	Higher volumetric heat of combustion	MJ/m^3	37.11	11.89
6	Lower volumetric heat of combustion	MJ/m^3	33.43	10.05
7	Higher Wobbe number, MJ/m^3	MJ/m^3	49.83	45.08
8	Lower Wobbe number, MJ/m^3	MJ/m^3	44.88	38.11
9	Upper flash limit	vol %	15.40	80.00
10	Lower flash limit	vol. %	5.28	4.09

The situation is similar for the heat of combustion, especially against the background of the Law of Ukraine on the introduction of accounting and calculations for the volume of gas in energy units in the natural gas market [22].

5. 3. Theoretical calculations of the physical-chemical parameters of mixtures of natural gas with hydrogen

During the study, the changes in PCPs of the NG-H_2 system, in which the hydrogen content varies over a wide range (from zero to one hundred mol % in steps of one mol %), were calculated. The calculations were carried out based on the component composition and included the determination of changes in absolute and relative density, mass, and volume heat of combustion, as well as the Wobbe number at an increase in the hydrogen content. Changes in some PCPs are shown in Fig. 1.

Also, according to formula (1) [23], the extended Wobbe number was calculated taking into account the pressure in front of the burner:

$$W_N^p = H_N \cdot \sqrt{\frac{P}{G}}, \tag{1}$$

where W_N^p is the extended Wobbe number;

H_N – lower heat of combustion of the fuel mixture, MJ/m^3;

P is the pressure of the fuel mixture in front of the burner, kPa;

G is the relative density of the fuel mixture.

The necessary pressure of gaseous fuel, which must be maintained to ensure the thermal power of gas burner devices, was calculated according to formula (2):

$$P_2 = P_1 \frac{D_2}{D_1}\left(\frac{H_{N_1}}{H_{N_2}}\right)^2, \tag{2}$$

where P_2 is the pressure to be maintained in front of the burner, kPa;

P_1 – the pressure maintained in front of the burner, kPa;

D_1 – density of the fuel mixture to be replaced, kg/m^3;

D_2 – density of the fuel mixture to be replaced, kg/m^3;

H_{N_1} – lower calorific value of the fuel mixture being replaced, MJ/m^3;

H_{N_2} – lower heat of combustion of the fuel mixture with which it is replaced, MJ/m^3.

For calculations according to equation 2, the initial pressure P_1 is taken to be 1.27 kPa, as this is the minimum nominal pressure in front of the burner for utility devices [21]. The initial density of the fuel mixture that is replaced by D_1 and its lower heat of combustion H_{N1} are taken from Table 1. The results of our calculations are shown in Fig. 2. It should be added that in Fig. 2, for clarity, a curve corresponding to the change in the lower Wobbe number under standard conditions is plotted and that this curve has already been displayed in Fig. 1.

The differences between the ordinary Wobbe number and the extended Wobbe number calculated by formula (1) are insignificant. Both curves have the same shape, and the expanded Wobbe number value is 2.7 % larger. Calculated by formula (2), the excess pressure that must be maintained in front of the burner due to an increase in the hydrogen content in the mixture increases from 1.27 kPa, passes through a maximum (1.96 kPa) at a hydrogen content of 84 mol %, and sharply decreases to a value of 1.66 kPa.

It was established that the density and volumetric heat of combustion decrease in direct proportion to the increase in hydrogen concentration. To satisfy Wobbe's interchangeability criterion of 5 % deviation, the hydrogen content must not exceed 19 mol %. To meet the requirements for volumetric heat of combustion established by the legislation of Ukraine, the hydrogen content must be within 7 mol %.

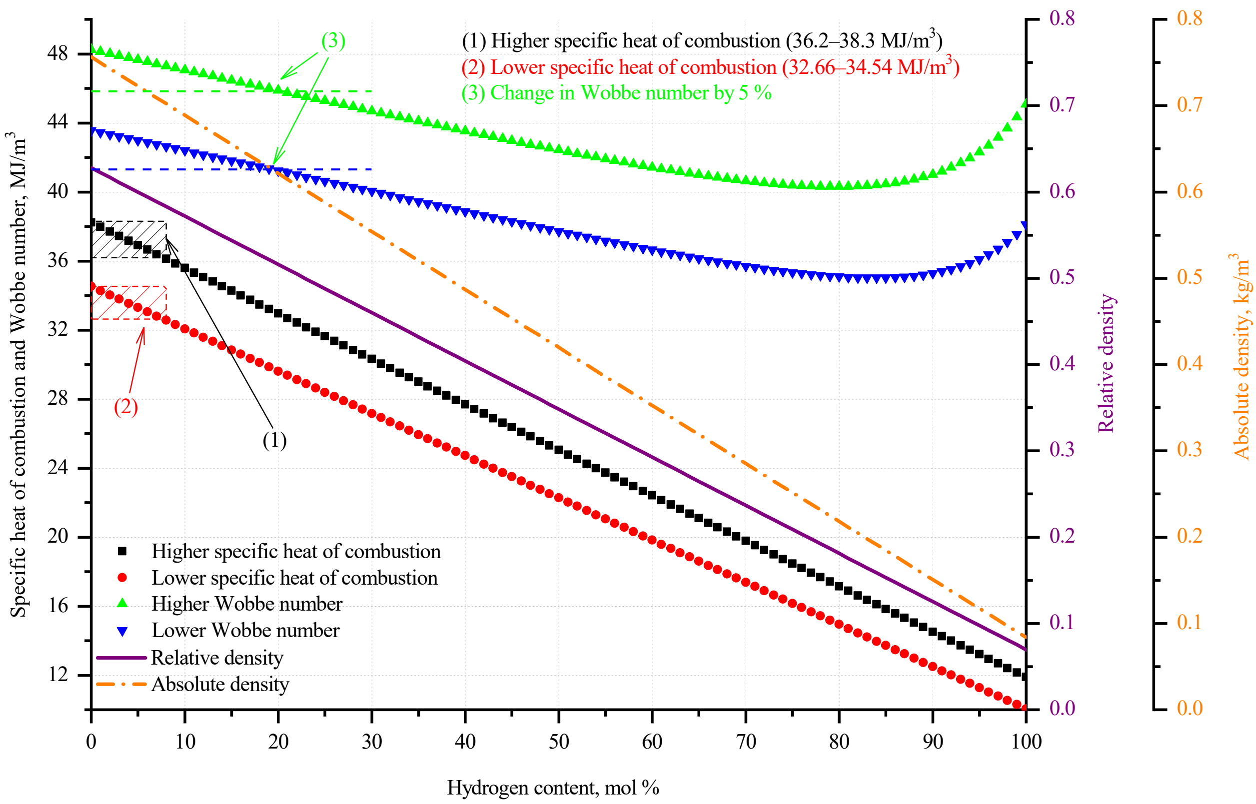

Fig. 1. Changes in the main physical-chemical parameters of natural gas when adding H_2

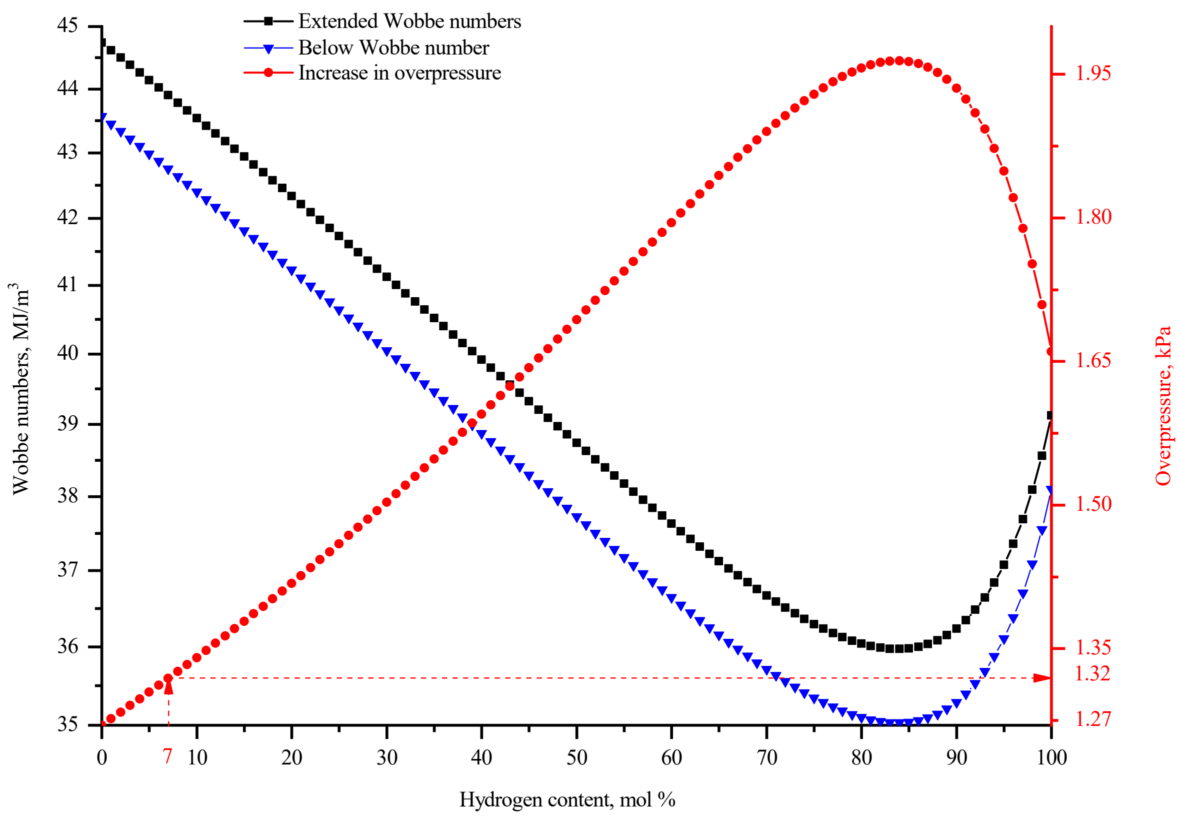

Fig. 2. Changes in expanded Wobbe number and pre-burner overpressure with addition of H_2

5. 4. Calculations of change in the flash limits of the NG-H_2 mixture in air

On the basis of our calculations (Fig. 3), it was determined that with an increase in the hydrogen content in the mixture, the lower flash limit decreases almost linearly from 5.16 to 4.09 volume percent. The upper flash point rises much faster from 15.81 to 80.00 vol percent.

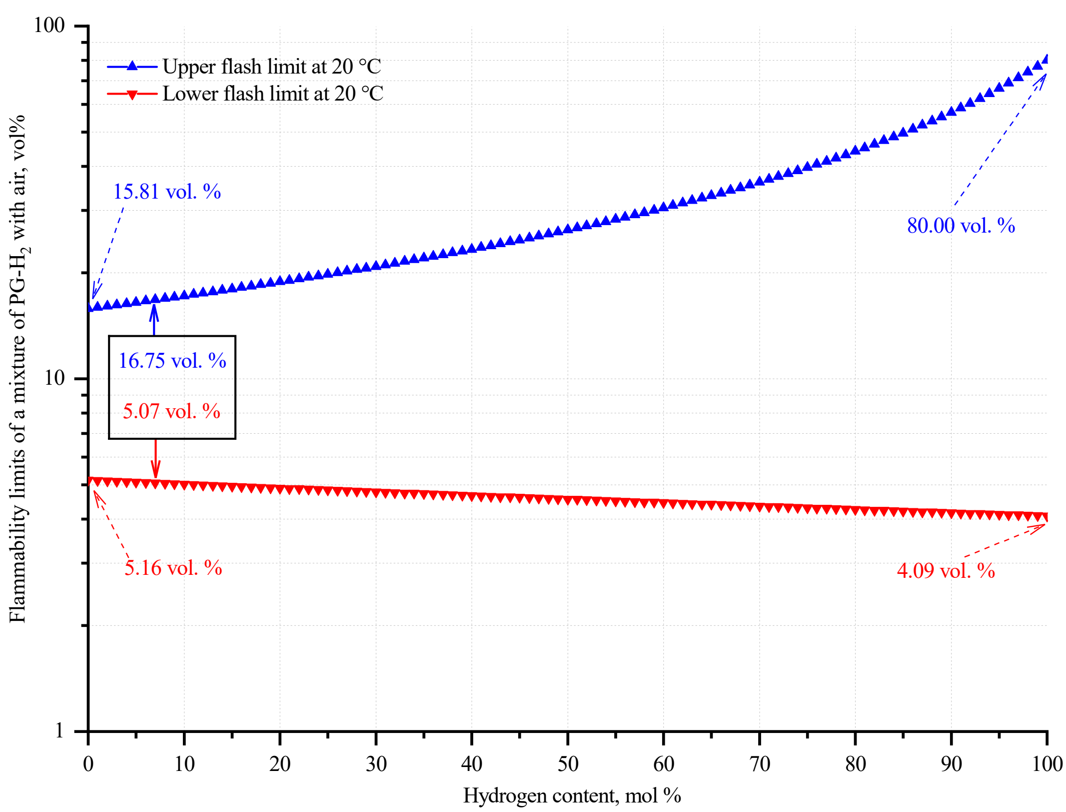

Fig. 3. Content of the mixture of combustible gases at the lower and upper flash limits

An increase in the hydrogen content leads to a gradual expansion of the range between the upper and lower flash limits. And at the permissible seven percent hydrogen content, the flash range lies within 5.07–16.75 volume percent, which is not significantly different from the conventionally accepted 5–15 vol. %.

6. Discussion of results based on investigating the physical-chemical parameters of mixtures of natural gas with hydrogen

For more accurate calculations of characteristics of the NG-H_2 system, the characteristics of a typical NG transported by the gas distribution system were first determined (Table 1). In a separate case, the situation in which "green" hydrogen is added to NG and passes through the gas distribution networks in the city of Kyiv was considered.

Fig. 1 shows that with an increase in the hydrogen content in NG, the higher and lower volumetric heat of combustion decreases linearly. This behavior is explained by the fact that the higher and lower volumetric heat of combustion of natural gas is more than three times higher than that of hydrogen (Table 2). Thus, with an increase in the hydrogen content, the volumetric heat of combustion decreases proportionally.

The higher and lower volumetric heat of combustion are regulated by the current Codes and under standard conditions correspond to 36.20–38.30 MJ/m^3 for the higher volumetric heat of combustion and 32.66–34.54 MJ/m^3 for the lower volumetric heat combustion; it has been calculated that with an increase in the hydrogen content of more than 7 mol %, the higher and lower combustion heat goes beyond the lower limits allowed by law (dotted lines in Fig. 1 mark the limits of higher (1) and lower (2) heat of combustion).

One of the main characteristics of NG is absolute and relative density. However, density is not regulated in any regulatory document in force in Ukraine concerning gas quality. The draft Technical Regulations for NG propose to limit relative density in the range of 0.555–0.750. The research has shown that with an increase in hydrogen content, the density of the NG-H_2 mixture decreases linearly. This is again due to the large difference in the absolute and relative densities of natural gas and hydrogen (Table 2). According to Fig. 1, with a hydrogen concentration of 13 mol %, the relative density of the NG-H_2 mixture will be below the permissible 0.555.

An important criterion for the substitution of one fuel for another without changes in the burner design and changes in its operating mode is the Wobbe index, which was calculated based on the heat of combustion and relative density of the fuel. Figure 1 shows the curves characterizing the change in the higher and lower Wobbe index with an increase in the hydrogen content in the mixture. Based on the calculations performed, it was found that in concentrations from zero to approximately 70 mol % above and below, the Wobbe number decreases almost linearly to 40.5 and 35.7 MJ/m^3, respectively, and then gradually begins to increase. This character is explained by the well-known formula for calculating the Wobbe number, in which the numerator (heat of combustion) changes linearly, and the denominator as the square root of the relative density.

Also, in Fig. 1, the dotted lines (3) indicate a decrease in the Wobbe number by 5 %. It is shown that the five percent limit is crossed when the hydrogen content increases by more than 19 mol %.

Based on the above, the Wobbe number imposes the smallest restrictions on the hydrogen content in a mixture with NG. Thus, with a hydrogen content of up to 19 mol %, it will not be necessary to change the design of the burners or significantly adjust their mode of operation. The addition of hydrogen to NG leads to a directly proportional decrease in the heat of combustion of the mixture, and therefore it is possible to comply with the requirements established by the legislation of Ukraine with a hydrogen content of no more than 7 mol %.

One of the available ways to preserve the thermal power of gas burner devices by replacing one gaseous fuel with another is to increase the pressure in front of the burner and change its operating parameters.

It was established that for increasing the hydrogen content in NG to the permissible 7 mol %, in order to maintain the thermal capacity of the burner, the nominal excess pressure in front of the burner must be increased within the range of 1270–1320 Pa.

Thus, it has been confirmed that in order to achieve the interchangeability of NG and its seven percent mixture with hydrogen, a small (about 4 %) increase in excess pressure in low-pressure gas distribution networks is required.

An important characteristic of combustible gases from the point of view of the safety of operation of gas networks and localization and liquidation of emergencies is their combustible characteristics, namely the limits of flame propagation. Calculations of the upper and lower flash limits under standard conditions were performed for NG-H^2 mixtures. The results of our calculations are shown in Fig. 3 in semi-logarithmic coordinates.

It was calculated that with an increase in the hydrogen content in natural gas, an explosion could occur in a slightly wider range of fuel concentrations in the air. The expansion of the range occurs mainly due to the increase in the upper flash limit.

The insignificant change in the lower flash limit is associated with fairly close values of the lower flash limit for the main component of NG – methane (5.28 vol. %) and hydrogen (4.09 vol. %) (Table 2). Therefore, with an increase in the hydrogen content, the lower flash limit does not shift significantly. Conversely, the upper flash limit of hydrogen is five times greater than that of methane, which induces a much larger shift of the upper flash limit for increasing hydrogen content in gas-hydrogen mixtures.

Another not-so-obvious obstacle is the complication of detecting "gas contamination" with gas analyzers, which are common and widespread at gas distribution companies. Their sensors react mainly to organic substances (although they have cross-sensitivity to carbon monoxide, hydrogen, etc.), the uncertainty of the results will increase. Even the chromatographic method for detecting city network gas leaks according to MVV 081/12-31-99 will not give reliable results. Therefore, the degree of gassiness displayed by the devices could be significantly distorted, which could lead to fatal consequences. It is necessary to improve existing or even devise new security measures. For example, use additional gas analyzers with hydrogen-sensitive detectors.

In the researched literature [17, 21], to simplify calculations, the physicochemical characteristics of NG were assumed to be equal to methane. Therefore, the authors caried out calculations of the two-component hydrogen-methane system. Thus, in [17, 21], calculations were performed only for three concentrations of 10, 30, and 50. In general, our results are close to the results reported by other authors for the indicated concentrations.

The limitations of this study are that the calculations could easily be performed only for certain temperatures (0, 15, 15, 55, 20, and 25 degrees Celsius) and a pressure of 101.325 kPa. At other temperatures and pressures, the correctness of the method was not determined. Also, it is important to determine the qualitative and quantitative composition of natural gas mixtures as accurately as possible because the "heavier" the component is, even with a relatively small content, it has a greater impact on the PCP of the mixtures, which in turn affects the subsequent calculated values.

The disadvantage of the work is that the moisture content of natural gas was not taken into account. For a more accurate study, this indicator should be taken into account.

In the future, our research may be advanced by studying the effect of hydrogen and other mixtures of natural gas (for example, with biogas, ammonia, carbon monoxide) on structural materials of gas networks. In addition, the study of factors affecting safe operation and environment is promising.

The share of renewable energy sources in the global energy supply is constantly growing, and the technology of converting electricity into gas is considered as a possible storage of excess renewable energy. Therefore, tackling this issue involves changing the composition of natural gas at the expense of renewable energy sources with the subsequent possibility of transporting it to European countries.

7. Conclusions

1. We have established that the main component of natural gas in the gas transportation network in the city of Kyiv is methane, the content of which is almost 90 mol %. Other, heavier than methane, hydrocarbons, account for about 6.7 mol %. About 3.8 % of inorganic components. Hydrogen is absent.

2. The investigated PCPs of natural gas showed that the average values of relative and absolute density are 0.6307 and 0.7569 kg/m^3, respectively. The average value of the higher and lower calorific value (38.25 MJ/m^3) and (34.55 MJ/m^3), respectively, are close to the limits of the ranges established by the current legislation. Considering the high heat of combustion of hydrogen, it could be stated that if it is added to natural gas, the energy intensity of the mixture would increase according to the concentration and thermobaric conditions.

3. Changes in the PCPs of the NG-H_2 system, in which the hydrogen content varies over a wide range (from zero to one hundred mol % in steps of one mol %), were calculated. It was established that the introduction of hydrogen into the gas mixture would require an increase in pressure in the network before the consumer. We have calculated excess pressure that must be maintained before the burner at an increase in the hydrogen content in the mixture from 1.27 kPa, it passes through a maximum (1.96 kPa) at a hydrogen content of 84 mol % and sharply decreases to a value of 1.66 kPa. Therefore, in order to maintain a constant power of gas burners of household equipment, it is necessary to raise the pressure in the low-pressure gas distribution network so that the excess pressure before the burner increases by about 4 %, which is not burdensome for the low-pressure gas distribution network.

4. Our calculations of changes in flash points showed that with an increase in the hydrogen content in the mixture, the lower flash point drops almost linearly from 5.16 to 4.09 percent by volume. The upper flash point rises much faster from 15.81 to 80.00 vol percent. Therefore, in order to maintain the safe flash limits of the gas-hydrogen mixture, the hydrogen content must be maintained at the level of 7 mol %, when the upper flash limit of the gas-air mixture increases by only 0.94 vol. %, and the lower limit will remain practically unchanged.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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