

Determination of Thermophysical Properties of Alternative Motor Fuels as an Environmental Aspect of Internal Combustion Engines

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Abstract. The article analyzes the state of the global problem of the fuel and energy crisis and environmental pollution by the combustion products of hydrocarbon fuels of industrial and transport power plants. To ensure the energy security of the state, the Cabinet of Ministers of Ukraine developed and adopted the «Energy Strategy of Energy Saving of Ukraine for the period until 2030», which was updated in 2008, to protect the country from energy risks. In addition, the Cabinet of Ministers of Ukraine approved the «Concept of a targeted scientific and technical program for the development of the production and use of biological fuels». To increase the efficiency of using alternative motor fuels, as one of the aspects of solving the problem, an original method and results of calculating the thermophysical properties of a wide class of such motor fuels (hydrogen, natural gas, biogas, mine gas, coke, blast furnace and synthesis gas, etc.) are proposed. A description of the developed mathematical model for determining parameters of phase equilibria and thermophysical properties of dense molecular systems (dense gases and liquids) is given. Calculation procedures are based on the thermodynamic theory of disturbances without the involvement of empirical parameters. Features of the proposed method are: limitation of initial information, high accuracy, the possibility of application in any practically important ranges of states. Calculation errors are at the level of traditional experimental errors.

Introduction

In ecology, pollution is defined as a violation of the optimal state of the living environment. When considering environmental pollution [1, 2], a distinction is made between natural pollution caused mainly by catastrophic causes (volcanic eruptions, earthquakes, dust storms, mudflows, etc.), and anthropological pollution caused by human activity [3, 4]. As a result of human activity, 98 % of natural substances go to waste and only about 2 % constitute a useful social product.

Protection of atmospheric air [5], water resources [6, 7] and soil from contamination by various pollutants is one of the main tasks of preserving the quality [8, 9] of the environment for current and future generations of people [10, 11].

At the same time, the development and implementation of environmentally friendly technologies [12, 13], according to the world's leading forecasters, is a vital necessity of humanity, that is, it has a global character [2].

The main causes of anthropogenic environmental pollution in the industrialized countries of the world are the fuel and energy complex, industry [14, 15], and transport. Moreover, reciprocating internal combustion engines (RICE) used in motor vehicles are the main pollutants of the atmosphere of cities with carcinogenic and mutagenic ingredients. These substances can cause changes in hereditary properties in the human body, disrupting the genetic programs of cells [16].

The European Parliament made changes to the rules for controlling harmful emissions of RICE.

They provide for the introduction of a ban on the sale (not on the production) of cars with RICE on the territory of the EU from 2035. According to the approved changes, all new cars on the European market must produce zero CO₂ and NO_x emissions. So, all cars with diesel and gasoline engines, hybrids, in particular, will fall under the sales ban. Some car manufacturers have already supported this initiative of the European Commission aimed at protecting the climate. After all, road transport is responsible for approximately 20 % of all greenhouse gas emissions in the EU, and the most of the emission falls on passenger cars.

The products of fuel combustion, including the exhaust gas (EG) of automobile RICE, emit harmful substances in gaseous form (CO, CH, NO_x, SO₂, etc.) or in the form of aerosols (solid or liquid): carcinogenic hydrocarbons, particulate matters. The main consumers of petroleum fuels, the reserves of which are limited and close to exhaustion, are vehicles with RICE.

Therefore, their environmentalization (or ecologization, or greening) should be carried out taking into account the indicated two-faceted (consumption of non-renewable energy resources and the impact of combustion products on environment components) fuel problem.

Problem Formulation

In the source [17] the approach for numerical assessment of the working performance of city bus with diesel engine using alternative fuels was developed, in source [18] the prospects for the use of alternative fuels and methods of determining their thermophysical characteristics were described, in source [19] the main provisions of the theory of disturbances were determined, in source [20] the main prerequisites and preliminary calculations for this study were performed.

Approaches to solving the problems of accumulation of solid waste from the production activities of industrial enterprises by developing of EPT and utilization of combustible waste as materials for fuel briquettes are given in the article [21]. Issues of high-temperature utilization of carbon-containing solid waste are covered in the study [22, 23], the use of organic high molecular weight waste from the food industry – in the study [24], features the use of renewable fuel sources in energy-generating facilities studied in the study [25], issues of reliable, rapid and low-cost detection of urban air pollution – in the study [26, 27].

Additionally substantiate the relevance of the study presented in this article, the results of an analysis of the efficiency of using alternative fuels in vehicles from the source [28], as well as a calculated assessment of the thermophysical properties of biogas used as a fuel for transport, performed by the authors using a less perfect version of the mathematical model, improved in this study, described in the article [29].

Thus, the results of the analysis of current trends in the market of traditional and alternative energy carriers, in particular motor fuels, show that the main complex problem is the greening of piston engines as sources of mechanical energy (especially when they are used as part of power plants that generate electricity in blackout conditions in our country caused by energy shortage as a result of the armed aggression of the russian federation and the republic of belarus), consuming alternative motor fuels, which can be formulated in the following definition of the purpose of this study.

The purpose of the study is to improve the mathematical tools for determining the thermophysical properties of alternative motor fuels as a means of increasing the ecological safety level of using of power plants (PP) with RICE.

The object of the study is alternative motor fuels as a means of increasing the ecological safety level of the use of PP with RICE.

The subject of the study is thermophysical properties of alternative motor fuels.

Analysis of Publications

The analysis of scientific and technical literature shows that the main directions in the modern developments of leading foreign companies are focused on improving the environmental performance of diesel engines, reducing the toxicity of their EG, improving the organization of working processes, researching and improving the physical properties of alternative motor fuels

(AMF). Abroad, the production of gas engines is quite well developed, and a number of companies produce engines that run on conventional fuels and on biogas (BG) or natural gas (NG).

For example, the Austrian company Ienbacher Berke produces serial gas engines with an effective power of 30–2200 kW, the West German Maschinenwerke (Augsburg–Nuremberg) – engines running on NG, which are easily modified in the case of BG use. The power of the engines is 99–130 kW. Daimler-Benz (Stuttgart, Germany) produces the M407 medium-power engine, which runs on NG with the possibility of its modification for BG [18].

In Ukraine, there is still no mass application of AMF for power plants (PP) with RICE, therefore the development of this direction is urgent.

For research related to the specifics of the use of AMF for transport diesel engines, it is necessary to solve tasks that allow predicting the necessary thermophysical properties of various fuels. The creation of modern methods will make it possible to obtain these properties in a wide range of states – liquefied gas to parameters of combustion or thermal decomposition.

Based on the analysis of existing calculation methods [18], it was concluded that various model schemes and empirical dependencies (the theory of corresponding states, lattice models, group models) can give acceptable quantitative results in limited ranges of states. At the same time, significant initial information about the properties of components and their mixtures is required for calculations. As for the practically important area – the liquid phase of AMF, the methods mentioned here are usually not acceptable.

Presentation of the Main Material of the Study

The main directions in solving fuel and environmental problems of road transport are as follows.

1. Use of unconventional, including alternative, motor fuels. AMF include: NG, as the most efficient energy carrier; synthetic motor fuels (SMF); biofuels, including BG; hydrogen (H₂), which can be used as a highly effective additive to combustible mixtures and as a necessary component in the production of SMF, as well as the main energy carrier.

2. Improvement of work processes of RICE. At the same time, it is known that you should not expect a significant improvement in engine efficiency without making structural changes. This requires the development and implementation of technology for conversion of existing gasoline and diesel car engines, as well as the creation of modern «environmental engines».

The use of NG and BG as a motor fuel for transport helps to reduce the level of emissions of harmful substances with the EG flow. Thus, compared to gasoline engines, the content of toxic substances in the combustion products of gas engines decreases [17]: Pb from 0.42 to 0 g/dm³; SO₂ from 5.5 to 0 ppm; NO_x from 257.3 to 18.0 ppm; CH from 83.2 to 19.2 ppm; CO from 1.46 to 0.16 %. As can be seen, the use of PG and BG instead of gasoline allows you to significantly reduce the level of toxicity of EG, which is one of the important aspects of solving this problem. Its essence consists in the development of PP with RICE, adapted to AMF, and their partial replacement of traditional petroleum fuels.

Studying their thermophysical properties is important in the process of adapting engines to AMF. Information about the thermophysical properties of fuels allows for more accurate simulation of RICE working cycle processes, improvement of the design and characteristics of dosing devices of engine fuel supplying systems, characteristics of electronic control systems.

The analysis of scientific and technical literature shows that the main trends in modern developments of leading foreign companies are focused on improving the environmental performance of diesel engines, primarily reducing the toxicity of their EG, improving the organization of work processes, researching and improving the physical properties of AMF. Abroad, the production of gas RICE is quite well developed and a number of companies produce engines that run on traditional fuel and on BG or NG. In Ukraine, there is still no mass application of AMF for PP with RICE, therefore the development of this direction is urgent.

For theoretical and experimental studies related to the specifics of the use of AMF for transport diesel engines, it is necessary to solve tasks that allow predicting the necessary thermophysical properties of various fuels. The creation of modern methods will make it possible to determine these

properties in a wide range of states – from liquefied gas to parameters of combustion or thermal decomposition. Based on the analysis of existing calculation methods, it was concluded that various model schemes and empirical dependences can give acceptable quantitative results in limited ranges of states. At the same time, calculations require a significant amount of initial data on the properties of components and their mixtures. However, for use in a practically important area – the liquid phase of AMF, these methods cannot be applied.

This state of the issue necessitates the development of modern statistical-mechanical methods for describing the properties of AMFs, which use a minimum of initial data and parameters. The conducted studies are devoted to the application of the original modified scheme of thermodynamic perturbation theory (TPT) [18, 19] to describe the properties of AMFs, which are multicomponent mixtures (NG and BG).

The specific (per particle) free energy f_m of the n -component mixture within the TMT, which takes into account the second order, has the form of formula (1). The initial stage of property calculations in a two-phase n -component system is the determination of the density ρ_m^* of the mixture at the specified temperature T and pressure p . Calculations of phase equilibrium, i.e. determination of the compositions of the liquid (index L) and vapor (index V) phases and their density values, are performed based on formal system of equations of the form (2), in which p_m – pressure of the mixture; μ_i – chemical potential of the i -th component.

The numerical implementation of the developed mathematical model is carried out using a computer program for determining phase equilibrium and thermophysical properties of the liquid and vapor phases of multicomponent AMFs, which also includes a subroutine for calculating properties in the single-phase region (homogeneous state).

The properties of the following components and their mixtures are determined: marginal hydrocarbons (CH_4 , C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $i\text{-C}_4\text{H}_{10}$, $n\text{-C}_5\text{H}_{12}$, $i\text{-C}_5\text{H}_{12}$, C_6H_{14} , C_7H_{16} , C_8H_{18} , C_9H_{20} , $\text{C}_{10}\text{H}_{22}$); inert gases (He , Ne , Ar , Kr , Xe); nitrogen N_2 ; CO_2 carbon dioxide; CO carbon monoxide; hydrogen H_2 ; oxygen O_2 ; water H_2O ; hydrogen sulfide H_2S ; benzene C_6H_6 etc.

$$\beta f_m = \beta f_m^{(0)} + \sum_{i,k=1}^n x_i x_k \rho_{ik}^* (I_{ik}^{(1)} + I_{ik}^{(2)} / T^*_{ik}) / T^*_{ik}, \quad (1)$$

$$\begin{cases} p_m(v_m^L, T, \{x_i^L\}) - p = 0; \\ p_m(v_m^V, T, \{x_i^V\}) - p = 0; \\ \mu_1(v_m^L, T, \{x_i^L\}) - \mu_1(v_m^V, T, \{x_i^V\}) = 0; \\ \dots\dots\dots \\ \mu_n(v_m^L, T, \{x_i^L\}) - \mu_n(v_m^V, T, \{x_i^V\}) = 0. \end{cases} \quad (2)$$

where $f_m^{(0)}$ – free energy of an n -component mixture of hard spheres; x_i – concentration (mole fraction) of the i -th component; $\beta = 1/(kT)$; k – Boltzmann constant; $\rho_{ik}^* = \rho \sigma_{ik}^3$ – given particle number density; $T^*_{ik} = (\beta \varepsilon_{ik})^{-1}$; σ_{ik} and ε_{ik} – parameters of initial potentials of intermolecular interaction $u_{ik} = \varepsilon_{ik} \varphi(r/\sigma_{ik})$ (the Lennard-Jones potential is used $\varphi(x) = 4(x^{-12} - x^{-6})$); $I_{ik}^{(1)}$, $I_{ik}^{(2)}$ – generalization of group integrals of the first and second orders for mixtures [3].

If the coexisting phases are formed from the original mixture $\sum_{i=1}^n x_i^0 = 1$, where $\{x_i^0\}$ – set of initial molar concentrations, then system (2) is supplemented with material balance equations for phases $\sum_{i=1}^n x_i^L = 1$ i $\sum_{i=1}^n x_i^V = 1$, as well as the equation for the distribution of mixture components between phases $n^V(x_i^V - x_i^L) = x_i^0 - x_i^L$, $i = 1, \dots, n$. Value n^V – gas content, determines the mole fraction of the

vapor phase of the two-phase mixture. This allows to calculate the equilibrium compositions $\{x_i^L\}, \{x_i^V\}$ for such phases.

These sets provide, in particular, a description of NG, gas condensate, mine gas, energy carriers based on hydrogen, nitrogen, working bodies of fuel cells of electrochemical generators and other mixtures. Determined properties: equation of state (p, V, T – ratio, density); coefficients of thermal expansion and isothermal compression; phase equilibria «liquid-vapor»; energy (Gibbs, internal, free); enthalpy; entropy; heat capacity (C_p, C_v).

State ranges:

- liquid state: pressure – from the lines of paraliqid equilibrium to 1000 MPa (or to the lines of crystallization), temperature – from the triple point to the critical point;
- gaseous (fluid) state: pressure – up to 1000 MPa, temperature – up to 5000 K (or pyrolysis temperatures).

During the modeling of phases equilibrium, numerous new data were obtained on the phase diagrams of mixtures typical for working bodies, in particular, various basic binary mixtures. Their thermodynamic properties are determined taking into account the TMT formula (1).

Calculation of phases equilibrium parameters and thermophysical properties was performed for a wide range of model of working bodies of the hydrocarbon type. A comparison of the obtained calculated values with the experimental data available in the literature and with the calculated values determined by other methods allows us to conclude that the proposed model better identifies the existing experimental results. The property calculations in the software package do not contain fitted parameters and empirical correlations and are based only on the obtained data on the interaction potentials of substances. Average calculation errors are at the level of conventional experimental ones (for modern experimental methods). This eliminates the need for time-consuming and expensive experimental research, which gives a significant economic effect.

In Fig. 1 shows the diagram of phases equilibrium of liquid-vapor mixtures of methane-ethane at the indicated temperatures. In Fig. 1 also shows the phase diagram of the basic binary methane-ethane mixture for a set of isotherms. Comparison with experimental data (icons) allows us to estimate the errors in the description of the compositions of the liquid and vapor phases of about 4–5 mol. %. As a rule, there are no experimental data when approaching the critical points, so the calculated values predict the phase behavior of mixtures in these areas.

In Table 1, the values of the molar volume of the hydrocarbon mixture obtained by calculation, corresponding to the possible composition of NG or BG, are compared with experimental data given in the literature [18]. The calculation error shows a good agreement between the experimental and calculated values. As a result of solving the problem of liquid-vapor phase balance for hydrocarbon motor fuels of different fractional compositions, the density, enthalpy and entropy along the saturation line were determined (see Table 2).

The study analyzed the state of the global problem of the fuel and energy crisis and the pollution of environment by products of combustion of hydrocarbon fuels of industrial and transport PP equipped with RICE.

So, to increase the efficiency of using AMF, as one of the aspects of solving the problem, an original method and results of calculating the thermophysical properties of a wide class of AMF (hydrogen, natural gas, biogas, mine gas, coke, blast furnace and synthesis gas, etc.) are proposed. The paper describes the developed mathematical model for determining parameters of phase equilibrium and thermophysical properties of dense molecular systems (dense gases and liquids). Calculation procedures are based on the thermodynamic theory of disturbances without the involvement of empirical parameters. Features of the method are: limitation of initial information, high accuracy, the possibility of application in any practically important ranges of states. Calculation errors are at the level of traditional experimental errors.

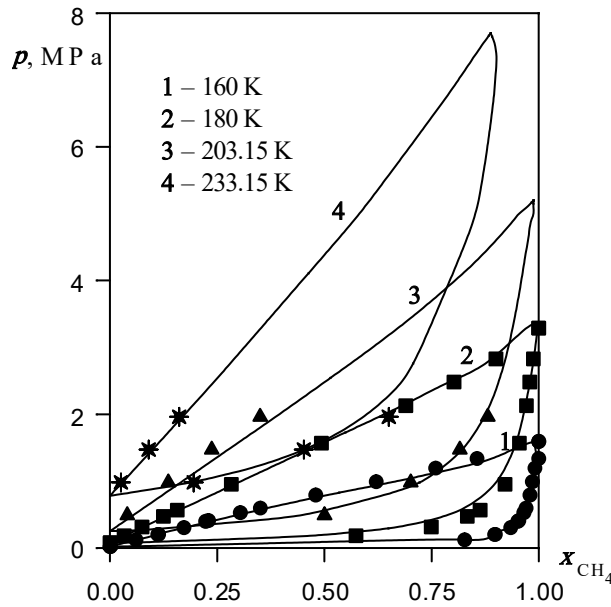


Fig. 1. Diagram of phases equilibrium of liquid-vapor mixtures of methane-ethane at the indicated temperatures

Table 1. Comparison of the experimental and calculated value of the molar volume of a hydrocarbon mixture

Composition of the mixture Mole fractions of components, [%]	T , [K] P , [MPa] V_{exp} , [m ³ /kmol]	Calculation according to TMT	
		V_{calc} , [m ³ /kmol]	Error, [%]
CH ₄ =72.27; C ₂ H ₆ =4.551; C ₃ H ₈ =2.474; n-C ₅ H ₁₂ =5.205; C ₇ H ₁₆ =3.65; C ₁₀ H ₂₂ =2.814; N ₂ =3.02; CO ₂ =3.015; H ₂ S=3.001	338.71 22.62 0.09469	0.096	1.38
CH ₄ =77.43; C ₂ H ₆ =5.74; C ₃ H ₈ =2.99; n-C ₅ H ₁₂ =4.66; C ₇ H ₁₆ =3.59; C ₁₀ H ₂₂ =2.63; H ₂ S=2.96	338.71 21.75 0.1003	0.1004	0.09
CH ₄ =80.97; C ₂ H ₆ =5.66; C ₃ H ₈ =3.06 n-C ₅ H ₁₂ =4.57; C ₇ H ₁₆ =3.3; C ₁₀ H ₂₂ =2.44	366.45 21.63 0.1134	0.1134	0.00
Average error $\bar{\delta} = \sum \delta/N , \%$			0.49

Table 2. Thermodynamic properties of AMF mixtures in equilibrium with the vapor phase

Composition of the mixture. Mole fractions of components, [%]	T , [K]	D_m , [kg/m ³] (mixture density)	$-H_m$, [kJ/kg] (mixture enthalpy)	S_m , [kJ/(kg K)] (mixture entropy)
CH ₄	105	431.37	308.60	4.729
	112	422.07	285.46	4.942
	120	410.27	257.62	5.181
CH ₄ =99.5, C ₂ H ₆ =3, N ₂ =1, CO ₂ =0.5	105	448.18	310.16	4.688
	112	438.71	288.05	4.891
	120	426.86	261.37	5.120
CH ₄ =99.5, C ₂ H ₆ =3, C ₃ H ₈ =0.5, N ₂ =1	105	446.35	311.86	4.695
	112	436.97	289.71	4.898
	120	425.22	263.01	5.127
CH ₄ =95, C ₂ H ₆ =3, C ₃ H ₈ =0.5, N ₂ =1, CO ₂ =0.5	105	450.78	311.04	4.675
	112	441.32	289.11	4.876
	120	429.50	262.66	5.103
CH ₄ =94, C ₂ H ₆ =3, C ₃ H ₈ =0.5, N ₂ =2, CO ₂ =0.5	105	453.80	306.18	4.676
	112	444.19	284.27	4.877
	120	432.19	257.91	5.104

Conclusions

Pollution of natural resources by carcinogenic substances, especially the atmosphere of large cities, is a global ecological problem of the second half of the XX – 20th of the XXI century. It is believed that 90 % of carcinogenic hydrocarbons contained in environment are related to energy, industry, transport, etc. At the same time, the biggest source of pollution of the atmosphere of cities with carcinogenic and mutagenic ingredients is motor vehicles with RICE.

Currently, the man-made load on the environment (the level of toxic substances in hydrocarbon fuel combustion products) in the cities of Ukraine exceeds the corresponding indicators of developed countries by 4-5 times. Since thermal RICE will remain the main types of car and PP in the near future, this leads to the need to find new solutions to the fuel-environmental problem of motor vehicles. One of these solutions is the transition to new, more efficient fuels.

At the same time, a set of scientific and technical measures aimed at reducing the man-made load on the environment includes the creation of ecological transport RICE, i.e., improving the environmental indicators of RICE, reducing the toxicity of their EG, improving the organization of working processes, researching and improving the physical properties of AMF. This paper proposes methods for calculating AMF parameters, which are used in mathematical modeling of the working processes of RICE with a low level of harmful substances in EG.

The possibilities of the TMT method for the study of phase equilibrium and thermophysical properties, implemented in the form of computer programs, demonstrate the results for binary and multicomponent mixtures (natural gas, gas condensate, biogas, mine gas, etc.). The average error in the description of the AMF density is, like that of the pure components, about 0.1 %. Similar results were obtained for a set of basic thermodynamic characteristics (enthalpy, entropy, heat capacity, etc.).

Thus, in general, the description of the properties of AMF can be successfully carried out within the framework of the proposed method. In the entire set of properties, this method has significant advantages over existing model and empirical schemes. Including, in particular, the minimum number of initial data required for calculations; lack of fitted parameters and empirical correlations; adequacy of the statistical-mechanical model, which is the basis of the method, and thus reliable determination of thermodynamic features of systems; applicability to a large class of substances and their mixtures; ability to work in a wide range of conditions; calculation errors at the level of experimental errors.

The developed method of prompt and reliable determination of the thermodynamic properties of multicomponent mixtures allows to exclude the implement of expensive and lengthy experimental studies, which gives a significant economic effect.

The scientific novelty of the results obtained in the research lies in the fact that the mathematical apparatus for determining the thermophysical properties of traditional and alternative types of motor fuel in both liquid and gaseous state, as well as mixtures of different types of such fuel, based on improved thermodynamic theory of perturbations, in terms of adaptation to computer calculation and reduction of calculation time and minimization of the error in determining the main thermodynamic parameters of motor fuels in comparison with reference and experimental data.

The practical significance of the results obtained in the study is that the improved mathematical apparatus for calculating the basic thermodynamic parameters of motor fuels is suitable for use for the entire range of types of traditional, alternative and mixed fuels in both liquid and gaseous states.

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