

Predictive estimate of the calorific value of substances with negative oxygen balance depending on the value of oxygen balance

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Abstract: In recent years, it has become necessary to determine the calorific value of pure combustible substances, since the error of the previously used formula by D.I. Mendeleev reaches 20 %, which is not acceptable. The method for determining the calorific value by M.S. Karash is also widely known. This method is based on the interaction principle between the electron fields of atoms and atomic groups – any interaction of the atom fields is accompanied by a change in the energy of the system. According to the Karash method, the calculated calorific value refers only to the liquid state, while for each class of organic compounds its own calculation formula is proposed, taking into account correction factors for all atomic groups. The need for at least a quantitative account of the molecule structure and the mutual arrangement of atomic groups complicates the calculation. The authors of this work have found a relationship between the calorific value of substances with a negative oxygen balance and the value of oxygen balance. The formula calculated by the authors has the form $Q_L = 0.1387 \cdot OB$, MJ·kg⁻¹ and only one variable (oxygen balance). The determination accuracy is not worse than using the well-known formula by D.I. Mendeleev (6 variables), but the calculation is much simpler.

Keywords: calorific value; oxygen balance; forecast; fuel; calculation formulas.

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Прогнозная оценка теплотворной способности веществ с отрицательным кислородным балансом в зависимости от величины кислородного баланса

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Аннотация: В последние годы появилась необходимость определения теплотворной способности (ТС) чистых горючих веществ, так как погрешность ранее применяемой формулы Д. И. Менделеева доходит до 20 %, что не приемлемо. Широко известен и метод определения ТС М. С. Караша. В основе метода лежит принцип взаимодействия электронных полей атомов и атомных группировок – всякое взаимодействие полей атомов сопровождается изменением энергии системы. По методу Караша подсчитываемая ТС относится только к жидкому состоянию, при этом для каждого класса органических соединений предлагается своя формула расчета с учетом поправочных коэффициентов для всех атомных группировок. Необходимость хотя бы количественного учета структуры молекулы и взаимного расположения атомных группировок затрудняет расчет. Авторами настоящей работы найдена взаимосвязь между ТС веществ с отрицательным кислородным балансом и величины кислородного баланса. Рассчитанная авторами формула имеет вид $Q_H = -0,1387 \cdot \text{КБ}$, $\text{МДж} \cdot \text{кг}^{-1}$, и только одну переменную (КБ). Точность определения не хуже, чем известной формуле Д.И. Менделеева (6 переменных), но расчет значительно проще.

Ключевые слова: теплотворная способность; кислородный баланс; прогноз; топливо; формулы расчетов.

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1. Introduction

The issue of assessing the calorific value of fuel Q with sufficient accuracy without experimental determination, given its complexity, is quite acute.

D.I. Mendeleev proposed his empirical formula for the lowest calorific value of all types of natural fossil fuels, for which it is necessary to know the elemental composition, i.e. the percentage of the following elements in it: oxygen (O), hydrogen (H), carbon (C), sulfur (S), ash (A) and water (W) [1]. For the calculation, the lowest thermal conductivity Q_L is usually used, which takes into account heat losses with water vapor. For solid and liquid fuels, the value of Q_L ($\text{MJ} \cdot \text{kg}^{-1}$) is approximately determined by the formula:

$$Q_L = 0.339[C] + 1.025[H] + 0.1085[S] - 0.1085[O] - 0.025[W], \quad (1)$$

where parentheses indicate the percentage (wt. %) content of the corresponding elements in the fuel composition. Comparison of calculated and experimental data on the calorific value of various fuels (wood, peat, coal, oil) showed that the calculation by D.I. Mendeleev formula gives an error not exceeding 10 %. Checking the calculated Q_L for individual combustible compounds (alcohols, gases, aliphatic and aromatic compounds, sugars) by D.I. Mendeleev formula in comparison with the experimentally determined Q_L gave a spread of errors up to 20 %.

The paper [2] describes the most used method for calculating the combustion heat of substances (the method of M.S. Karash). The Karash method is based on the interaction principle between the electron

fields of atoms and atomic groups: any interaction of the atom fields is accompanied by a change in the energy of the system. The fundamentals of the method are given by Karash in the form of five postulates.

1. The combustion heat is a consequence of the energy release during the movement of electrons between atoms and molecules. Oxidation is the result of the movement of electrons. Therefore, it is possible to relate the combustion heat to the total number of electrons moved.

2. The combustion heat of an organic compound is a function of the total number of electrons moved. It is a quantity equal to the amount of heat corresponding to the movement of one electron, multiplied by the number of moved electrons:

$$Q_L = x \cdot n, \quad (2)$$

where x is a constant equal to the amount of heat released when an electron moves; n is the number of transferred electrons.

3. The amount of energy released in the form of heat when one electron moves from the position that exists in the hydrocarbon molecule (for example, in methane) to the position characteristic of the CO_2 and H_2O type is approximately equal to $x = 26.05 \text{ kcal} \cdot (\text{mol} \cdot \text{electron})^{-1}$. The constant $x = 26.05$ is determined from normal octane, which, according to numerous and verified data, has a calorific value of $1302.9 \text{ kcal} \cdot \text{mol}^{-1}$, and the number of displaced electrons in the combustion process is 50. Then

$$x = \frac{Q_{cv}}{n} = \frac{1302.9}{50} = 26.05. \quad (2a)$$

Octane is taken as the basis for calculating x , not only because the calorific value is known exactly, but also because it has a sufficiently long chain and the influence of terminal methyl groups does not distort the value, which is mainly characteristic of the CH₂ increment. In addition, according to the Karash method, the calculated calorific value refers to the liquid state.

4. The movement of electrons from a location in methane to an arrangement like CO₂ and H₂O occurs in stages. The farther the electrons are from the carbon atom and closer to the oxygen atom, the less energy is released during combustion.

In methyl alcohol, the position of the hydrogen atom in the OH group is exactly the same as in water, i.e. the entire energy of moving one electron (26.05 kcal) has already been released. The position of the electron in the C—O bond is only partially shifted, therefore, with a complete shift its amount will be less than 26.05 kcal·(mol·electron)⁻¹, although heat will be released. In the carboxyl group, all the electrons have already been completely moved, and during the combustion of formic acid, energy is released from the movement of only two electrons in the C—H bond. The final movement of these two electrons results in the formation of finished oxidation products.

This example shows that any partial movement of electrons from the position in CH₄ to the position of CO₂ and H₂O leads to an increase in the formation heat and reduces the combustion heat. When considering the structural formula of a substance, this provision allows drawing qualitative conclusions about the order of the combustion heat.

5. A pair of electrons common to two carbon atoms is not displaced, and during combustion the movement of this pair gives the same amount of heat as a pair of electrons in a position like methane. Based on these postulates, Karash offers calculation formulas for each class of organic compounds.

1. Limit hydrocarbons

$$Q_{cv} = 26.05n. \quad (3)$$

2. Unsaturated ethylene hydrocarbons

$$Q_{cv} = 26.05n + 13a, \quad (4)$$

where a is the number of double bonds.

3. Primary alcohols

$$Q_{cv} = 26.05n + 13b, \quad (5)$$

where b is the number of OH groups.

4. Secondary alcohols

$$Q_{cv} = 26.05n + 6.5b. \quad (6)$$

5. Tertiary alcohols

$$Q_{cv} = 26.05n + 3.5b. \quad (7)$$

6. Polyhydric alcohols

$$Q_{cv} = 26.05n + 13b + 6.5c, \quad (8)$$

where b and c are the numbers of primary and secondary alcohol groups, respectively.

7. Ketones

$$Q_{cv} = 26.05n + 6.5. \quad (9)$$

8. Acids

$$Q_{cv} = 26.05n. \quad (10)$$

9. Nitro compounds

$$Q_{cv} = 26.05n + 13d, \quad (11)$$

where d is the number of —NO₂ groups.

When all electrons are taken into account, the formula should be written as follows

$$Q_{cv} = 26.05n - 13d. \quad (11a)$$

10. Primary amines

$$Q_{cv} = 26.05n + 13e, \quad (12)$$

where e is the number of NH₂ groups.

11. Amides, anilides, amino acids

$$Q_{cv} = 26.05n. \quad (13)$$

In polyfunctional compounds, a combined formula, which includes correction factors for all atomic groups, is used. In this form, the use of the Karash method is cumbersome and inconvenient, since it is necessary to have a set of formulas and coefficients. M.Kh. Karapetyants [3] proposed a generalized formula for calculating the combustion heat of any organic compound

$$Q_{cv} = 26.05(4C + H - p) + \sum_{i=1}^i k_i \xi_i - q_f, \quad (14)$$

where 26.05 kcal·(mol·electron)⁻¹ is the electron displacement energy equal to the total heat of C—H and C—C bonds breaking and subsequent formation of CO₂ and H₂O; C is the number of carbon atoms in a substance molecule; H is the number of hydrogen atoms in a substance molecule; the sum $4C + H$ is the number of moving electrons for normal hydrocarbons ($4C + H = n$ in Karash formulas); p is the number of partially or completely displaced electrons in a substance molecule (C—O and O—H bonds); k_i is the number of identical i -substituents; ξ_i is thermal correction, taking into account the change in the energy of the substance due to changes in the electronic structure (polarization) caused by the introduction of this substituent; q_f is the latent heat of the substance fusion.

The combustion heat according to the formula (14) is calculated at $p = \text{const}$ for a liquid substance.

If the experimental value q_f is not known, the latter can be calculated approximately using the Walden formula:

$$q_f = 56.5T_f \text{ kJ}\cdot\text{kg}^{-1}. \quad (15)$$

V.O. Kulbakh notes that the nature of the correction factor is more complicated than Karash originally believed.

The correction factor is the net effect of the partial displacement of the electron pair and the substituent-induced displacement of the electronic field of the entire organic compound.

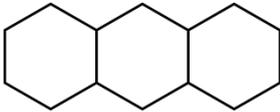
Thus, the correction factors make it possible to clarify the changes that occur in the energetics of a molecule with the introduction of one or another

atomic group. Such corrections are inevitable, since at present the change in energy with a change in structure cannot be expressed analytically. Therefore, any new attempts to create a calculation method based on some other principle always lead to a whole range of correction factors. Moreover, if in the Karash method the issue of corrections as a whole is solved quite simply and corrections are known for many types of compounds, this is not the case in other methods, so the calculation accuracy is much less and applicability is limited.

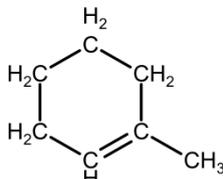
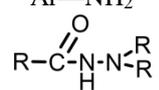
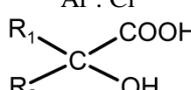
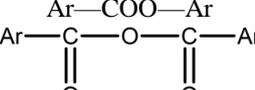
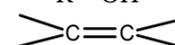
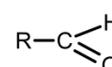
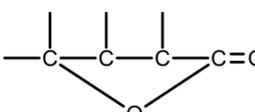
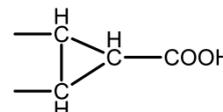
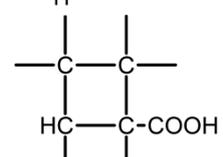
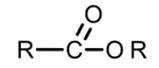
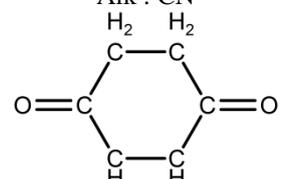
Table 1 shows the correction values proposed by Karash et al.

When using the Karash method, a template should be avoided, since disregard of the interaction of groups in a molecule can lead to incorrect data. A typical example is the correction for the nitro group.

Table 1. Values for thermochemical corrections

Correction number	Groupings and bonds	Structure	Thermochemical correction		
			kcal·mol ⁻¹	MJ·kmol ⁻¹	$n\Delta$
1	2	3	4	5	6
1	Sulfo group in aromatic hydrocarbons	Ar—SO ₃ H	-23.4	-98	-7Δ
2	Bonding of condensed aromatic nuclei		-20.0	-84	-6Δ
3	Nitro group in aliphatic and aromatic compounds	R—NO ₂	-13.0	-54.4	-4Δ
4	Carboxyl group in aromatic acids	Ar—COOH	“	“	“
5	Nitro group in heme-dinitro compounds	R—CH(NO ₂) ₂	-10	-41.8	-3Δ
6	Bonding of aromatic radicals	Ar : Ar	-6.5	-27.2	-2Δ
	Aromatic radical with vinyl radical	Ar : C = C	“	“	“
	Aromatic radical with acetylene radical	Ar : C ≡ C	“	“	“
	Nitro group in trinitromethane	Alk—C(NO ₂) ₃	“	“	“
	Aromatic radical and nitrile	Ar : CN	“	“	“
	Urea group	C = ON =	“	“	“
7	Aromatic and aliphatic radicals	Ar : Alk	-3.5	-14.6	-1Δ
	Aromatic radical and nitrogen (such as ammonia)	Ar—N =	“	“	“
	Quaternary carbon atom	(R) ₄ C	“	“	“
	Acid amides	R—CONH ₂	“	“	“
8	Carboxyl group in acids	Alk—COOH	0	0	0
	Alcohol nitrates	R—ONO ₂	“	“	“
	Nitro group in tetranitromethane	C(NO ₂) ₄	“	“	“
9	Tertiary alcohols	(R) ₃ —C—OH	+3.5	+14.6	+1
	Phenols	Ar—OH	“	“	“
	Nitroamines	R—NHNO ₂	“	“	“

Continuation of the Table 1

1	2	3	4	5	6
10	Secondary alcohols	$(R)_2CHOH$	+6.5	-27.2	+2
	Ethylene bond in the ring		"	"	"
	Aliphatic and aromatic ketones	$(R)_2C=O$	"	"	"
	Aromatic primary amines	$Ar-NH_2$	"	"	"
	Substituted amides		"	"	"
	Aromatic radical and chlorine	$Ar : Cl$	"	"	"
	Hydroxy acid type		"	"	"
	Esters of aromatic acids	$Ar-COO-Ar$	+10	+41.8	+3
	Anhydrides of carboxylic acids		"	"	"
11	Alcohols primary	$R-OH$	+13	+54.4	+4
	Ethylene bond		"	"	"
	Aliphatic and aromatic aldehydes		"	"	"
	Aliphatic primary amines	$Alk-NH_2$	"	"	"
	Aliphatic secondary amines	$Ar-NH-Ar$	"	"	"
	Lactones		"	"	"
	Aliphatic radical and chlorine (bromine)	$Alk : Cl(Br)_5$	"	"	"
	Aromatic radical and bromine	$Ar : Br$	"	"	"
	Esters of aromatic acids	$Ar-COO-Ar$	"	"	"
	C=C bond in transconnections	—			
	Trimethylene and cyclobutane rings in carboxylic acids		"	"	"
			+16.5	+69.1	+5
	Aliphatic esters		"	"	"
	Aliphatic radical and nitrile	$Alk : CN$	"	"	"
	Quinone group		"	"	"
	C=C bond in cis compounds	—	"	"	"

Continuation of the Table 1

1	2	3	4	5	6
12	Simple ethers	R_1-O-R_2	+19.5	+91.6	+6 Δ
	Secondaryaliphaticamines	$(Alk)_2NH$	“	“	“
13	Tertiaryaromaticamines	$(Ar)_3N$	“	“	“
14	Tertiaryaliphaticamines	$(Alk)_3N$	+26	+108.8	+8 Δ
	Oximes				
15	Acetylenebond (fully substituted)	$R-C\equiv C-R$	+33.1	+138.5	+10 Δ
	Isonitriles in the aliphatic series	$R-N=C$	“	“	“
16	Iodine derivatives of aliphatic and aromatic glyoximes	$R-I$	+40.1	+167.8	+12 Δ
17	Acetylene bond	$H-C\equiv H(R)$	+46.1	+192.2	+14 Δ

Correction for the primary nitro group is $R-NO_2\xi = -13$ kcal, however, in the case of gem-di-, three-tetra- and nitro groups, the corrections should be different.

The greatest corrections are given by such groups as OH, NO₂, amines, double and triple bonds. In some cases, when it is impossible to take into account the mutual influence of groups or the isomerization effect, these corrections can be neglected, since usually they do not exceed 3–5 kcal. It is more difficult to calculate heterocyclic compounds, especially those containing several nitrogen atoms (triazoles, tetrazoles, etc.).

The need for at least a qualitative account of the molecule structure and the mutual arrangement of atomic groups complicates the calculation, and this is undoubtedly a disadvantage of the Karash method.

This work is devoted to the rapid determination of the calorific value of compounds and carbon used in pasty, solid and gaseous fuel systems. Priority is given to fully gasified combustion products. Such an important additive to fuels as carbon in the form of detonation nanodiamond is reflected in articles [4–6, 8], in the form of graphenes – [11–13] and in the form of nanotubes – [14–16].

2. Methods

In carrying out this work, the authors used the known reference data on the calorific value of substances, the calculation of oxygen balance (OB) of substances and finding the relationship between them in the form of a graphical dependence.

The authors used a well-known mathematical apparatus to find the mathematical relationship between the calorific value and oxygen balance, and also calculated the calorific value of substances

according to the formula they proposed and the formula by D.I. Mendeleev.

3. Results and Discussion

The Q_L approximate value of fuel with a smaller error (as a rule, no more than 6 %) can be determined from the OB of the substance, determined for $C_aH_bN_cO_d$ compounds, according to the well-known formula [17]:

$$OB = \frac{[d - (2a + b/2)] \times 16}{M.w.} \times 100\%, \quad (16)$$

where M.m. is the molecular weight of the substance. Table 2 shows the experimental calorific value of various substances and carbon with a negative oxygen balance, which is then reflected together with OB in Figure 1, with which it is not difficult to determine Q_L of other substances. In addition, the table shows the calculated calorific value according to D.I. Mendeleev formula and the proposed formula and their errors in relation to the experimental Q_L (where it is available).

The calculation of the OB is based on the assumption that the fuel in a substance molecule (carbon and hydrogen) is oxidized during combustion or explosion by an oxidizer (oxygen in a molecule) to higher oxides – carbon to CO₂ and hydrogen to H₂O. Unlike the explosives, where only oxygen molecules are used, the combustion process is accompanied by the supply of an oxidizer (oxygen) from the outside – due to oxygen in the air or an oxygen-containing oxidizer in the fuel composition. In reality, some of the carbon is oxidized to carbon monoxide, releasing less energy. In addition, the experimentally determined Q_L is not constant, the accuracy of their

determination is affected by the method of determination, the features of the equipment and the qualifications of the experimenter, sometimes Q_L differs from each other (in various reference books) significantly. Taking into account the “ideality” of the calculating the OB, it should be expected that the calculation of Q_L , as a rule, should give a higher value than the experimentally determined calorific value. It should be expected that the smaller the difference between the calculated value Q_L (according to OB) from the experimentally

determined one, the more accurate the experimental data.

Table 2 (and Figure 1) shows the possible components of various types of fuels, their experimental and theoretical calorific value (calculated according to D.I. Mendeleev formula and the formula proposed in this work). In D.I. Mendeleev formula, it is necessary to take into account (and determine) up to 6 variables, while in the proposed formula – only oxygen balance. Table 1 also shows the calculation errors in relation to the experimentally determined Q_L .

Table 2. Dependence of the calorific value (Q_L) of organic substances on the OB

No.	Substance	Aggregate state of matter under normal conditions	Empirical formula and molecular weight	Experimental calorific value Q_L , kJ·kg ⁻¹	Calculated calorific value (D.I. Mendeleev formula), Q_L , kJ·kg ⁻¹	Error by D.I. Mendeleev formula, %	Oxygen balance, %	Calorific value calculated in the work, kJ·kg ⁻¹	Error according to the formula (in this work), %
1	2	3	4	5	6	7	8	9	10
1	Adamantane*	Solid	C ₁₀ H ₁₆ , 136	no data	41974	–	–329.4	45688	–
2	Amyl acetate	Liquid	C ₇ H ₁₄ O ₂ , 130	29874 [18]	30272	+1.3	–233.8	32428	+8.5
3	1-Aminoanthraquinone	Solid	C ₁₄ H ₉ NO ₂ , 223	29814 [19]	28124	–5.7	–21.88	30348	+1.8
4	3-Aminobenzoic acid	Solid	C ₇ H ₇ NO, 137	24484 [19]	23487	–4.1	–181	25105	+2.5
5	Ammonia	Gas	NH ₃ , 17	18585 [20]	18091	–2.7	–141.7	19654	+5.8
6	Aniline	Liquid	C ₆ H ₇ N, 93	36466 [19]	33963	–6.9	–266.3	36935	+1.3
7	Acetaldehyde	Gas	C ₂ H ₄ O, 44	27102 [19]	23864	–12	–181.8	25216	–7.0
8	Acetone	Liquid	C ₃ H ₆ O, 58	31403 [21]	28620	–8.9	–220.7	30611	–2.5
9	Benzoic acid	Solid	C ₇ H ₆ O ₂ , 122	26455 [20]	25520	–3.5	–196.7	27282	+3.1
10	Benzene	Liquid	C ₆ H ₆ , 78	40576 [20]	39183	–3.4	–307.7	42678	+5.2
11	Hydrazine	Liquid	H ₄ N ₂ , 37	14644 [18]	12813	–12.5	–100	13870	–5.3
12	Glycerol	Liquid	C ₃ H ₈ O ₃ , 92	16120 [18]	16523	+2.5	–121.6	16866	+4.6
13	1,4-diaminobenzene	Solid	C ₆ H ₈ N ₂ , 108	30836 [19]	30196	–2.1	–237	32872	+6.6
14	1,5-diamino-naphthalene	Solid	C ₁₀ H ₁₀ N ₂ , 158	34625 [19]	32235	–6.9	–253.2	35119	+1.4
15	1,2-diaminopropane	Liquid	C ₃ H ₁₀ N ₂ , 74	no data	30340	–	–237.8	32983	–
16	3,5-dimethylbenzoic acid	Solid	C ₉ H ₁₀ O ₂ , 150	29115 [19]	28931	–6.3	–224	31069	+6.7
17	1,2-dimethylhydrazine	Liquid	C ₂ H ₈ N ₂ , 60	29962 [19]	27223	–9.1	–213.33	29589	–1.2
18	N,N-dimethylurea	Solid	C ₂ H ₈ N ₂ O, 88	20986	21212	+1.1	–163.6	22691	+8.1
19	Dimethyl sulfoxide	Liquid	C ₂ H ₆ SO, 78	20623 [20]	22570	+9.4	–164.1	22761	+10.4
20	Dioxane	Liquid	C ₄ H ₈ O ₂ , 88	24887	23865	–4.1	–181.8	25216	+1.3

Continuation of the Table 2

1	2	3	4	5	6	7	8	9	10
21	Dimethylformamide	Liquid	C ₃ H ₇ NO, 73	26220 [20]	24180	-7.8	-186.3	25840	-1.4
22	Isopropanol	Liquid	C ₃ H ₈ O, 60	34190 [19]	31109	-9.0	-239.6	33233	-2.8
23	Methane	Gas	CH ₄ , 16	55688 [19]	51050	-8.3	-400	55480	-0.4
24	Methanol	Liquid	CH ₄ O, 32	23869 [19]	22359	-6.3	-150	20805	-12.8
25	Methylamine	Gas	CH ₅ N, 31	33350 [19]	29656	-11.1	-232.3	32220	-3.4
26	Urea	Solid	CH ₄ N ₂ O, 60	10528 [21]	10723	+1.9	-80	11096	+5.4
27	Naphthalene	Solid	C ₁₀ H ₈ , 128	39390 [18]	38187	-3.1	-300	41610	+5.6
28	3-nitroaniline	Solid	C ₆ H ₆ N ₂ O ₂ , 138	21685 [22]	19629	-9.5	-150.7	20902	-3.6
29	2-nitro-1,3-dimethylbenzene	Liquid	C ₈ H ₉ NO ₂ , 151	27700	25364	-8.4	-196	27185	-1.9
30	Nitronaphthalene	Solid	C ₁₀ H ₇ NO ₂ , 173	no data	26787	-	-198.8	27574	-
31	Pyridine	Liquid	C ₅ H ₅ N, 79	33360 [23]	32235	-3.4	-253.2	35119	+5.3
32	Polypropylene	Solid	[-CH ₂ -CH(CH ₃)-] _n [C ₃ H ₆] _n , 42	47140 [20]	43703	-8.5	-342.9	47560	+0.9
33	Polystyrene	Solid	[CH ₂ CH(C ₆ H ₅)-] _n (C ₈ H ₈) _n , 104	40700 [22]	39175	-3.7	-307.7	42678	+4.9
34	Polyethylene	Solid	[-CH ₂ -CH ₂ -] _n (-C ₂ H ₄ -) _n , 28	47140 [20]	43703	-7.3	-342.9	47560	+0.9
35	Polyethylenepolyamine*	Liquid	[-CH ₂ -CHNH] _n (C ₂ H ₅ N) _n , 43	no data	30840	-	-203.9	28281	-
36	Sugar	Solid	C ₁₂ H ₂₂ O ₁₁ , 342	16500 [18]	15283	-7.4	-112.2	15562	-5.7
37	Styrene	Liquid	C ₈ H ₈ , 104	42640 [20]	39175	-8.1	-307.7	42678	+0.1
38	Toluene	Liquid	C ₇ H ₈ , 92	40954 [20]	38869	-2.6	-300	41610	+1.6
39	Carbon	Solid	C, 12	33820 [20]	33900	+1.8	-266.7	36991	+9.4
40	Urotropin*	Solid	C ₆ H ₁₂ N ₄ , 140	no data	26240	-	-205.7	28531	-
41	Cyclohexan	Liquid	C ₆ H ₁₂ , 84	43825 [18]	43703	-0.3	-342.9	47560	+8.8
42	Cyclohexanol	Liquid	C ₆ H ₁₂ O, 100	35170 [22, 23]	34972	-0.6	-272	37726	+7.3
43	Ethyl acetate	Liquid	C ₄ H ₈ O ₂ , 88	25400 [18]	20101	-20.9	-181.6	25188	-0.8
44	Ethylene glycol	Liquid	C ₂ H ₆ O ₂ , 62	19351 [20]	15870	-17.9	-121.2	16810	-13.1
45	Ethanol	Liquid	C ₂ H ₆ O, 46	30562 [20, 22]	27248	-10.8	-208.7	28947	-5.3

Analysis of the data in Table 2 shows that 23 samples (No. 3, 4, 6–8, 11, 14, 17, 20–23, 25, 28, 29, 32–34, 37, 38, 43–45) have much higher accuracy calculation according to the proposed formula, compared with the experimentally determined Q_L , than by D.I. Mendeleev formula; for six samples, the calculation error by D.I. Mendeleev formula and the proposed formula is close (9, 16, 19, 31, 33, 36), and in thirteen samples (No. 2, 5, 10, 12, 13, 18, 24, 26, 27, 31, 39, 41, 42) the calculation accuracy according to the proposed formula is lower than by

D.I. Mendeleev formula. However, for samples No. 5, 10, 12, 26, 27, 31, the error is quite acceptable – up to 6%. For samples No. 1, 3, 40, which are one of the most interesting substances for further use, it was not possible to find reference data on Q_L .

Table 3 shows the dependence of the calorific value of explosives on their oxygen balance. It is impossible to determine the calorific value of explosives due to the rapid transition of their combustion to detonation. A slight difference is visible in the calculated calorific value of explosives

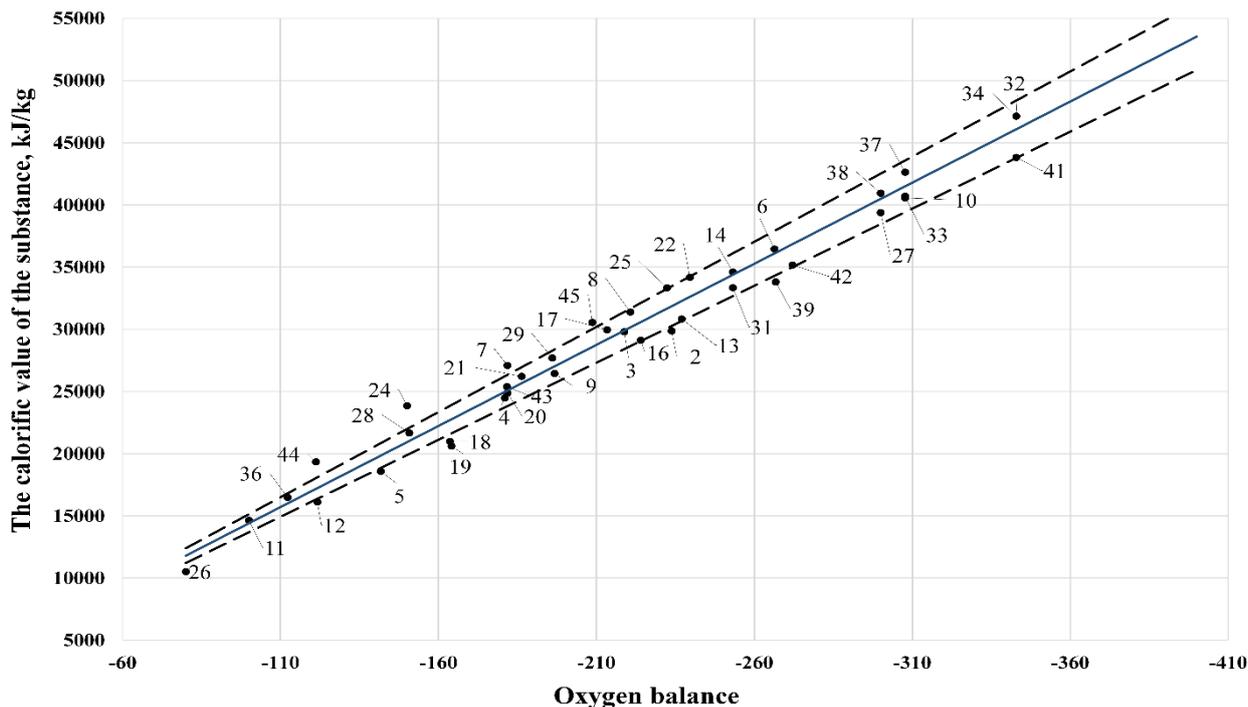


Fig. 1. Dependence of the calorific value of fuels on their oxygen balance.

26 – urea; 11 – hydrazine; 36 – sugar; 44 – ethylene glycol; 12 – glycerol; 5 – ammonia; 24 – methanol; 28 – 3-nitroaniline; 18 – N,N-dimethylurea; 19 – dimethylsulphoxide; 4 – 3-aminobenzoic acid; 43 – ethyl acetate; 7 – acetaldehyde; 20 – dioxane; 21 – dimethylformamide; 29 – 2-nitro-1,3-dimethylbenzene; 9 – benzoic acid; 45 – ethyl alcohol; 17 – 1,2-dimethylhydrazine; 3 – 1-aminoanthraquinone; 8 – acetone; 16 – 3,5-dimethylbenzoic acid; 25 – methylamine; 2 – amyl acetate; 13 – 1,4-diaminobenzene; 15 – 1,2-diaminopropane; 22 – isopropanol; 14 – 1,5-diaminonaphthalene; 31 – pyridine; 6 – aniline; 39 – carbon; 42 – cyclohexanol; 38 – toluene; 27 – naphthalene; 33 – polystyrene; 37 – styrene; 10 – benzene; 32 – polypropylene; 34 – polyethylene; 41 – cyclohexane

Table 3. Dependence of combustion heat of explosives on their OB

No.	Substance	Aggregate state of matter under normal conditions	Gross formula and molecular weight	Explosion heat, $\text{kJ}\cdot\text{kg}^{-1}$ (charge density, $\text{g}\cdot\text{cm}^{-3}$)	Calculated calorific value (D.I. Mendeleev formula), $Q_L, \text{kJ}\cdot\text{kg}^{-1}$	Oxygen balance, %	Calorific value calculated in the work, $\text{kJ}\cdot\text{kg}^{-1}$
1	RDX (cyclotrimethylene-trinitramine)	Solid	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$, 222	5401 (1.5) [25]	3575	-21.6	2996
2	o-dinitrobenzene		$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$, 168	3643(1.5) [25]	12835	-95.2	13204
3	1,5-dinitronaphthalene		$\text{C}_{10}\text{H}_6\text{N}_2\text{O}_4$, 218	2985 (1.5) [26]	18295	-139.4	19335
4	Tetryl (2,4,6-trinitro-N-methyl-N-nitroaniline)		$\text{C}_7\text{H}_5\text{N}_5\text{O}_8$, 287	4554 (1.6) [25]	6864	-47.4	6574
5	TATB (1,3,5-triamines, 2,4,6-trinitrobenzene)		$\text{C}_6\text{H}_6\text{N}_6\text{O}_6$, 258	3973 (1.854) [25]	7813	-55.8	7740
6	2,4,6-trinitroaniline		$\text{C}_6\text{H}_4\text{N}_4\text{O}_6$, 228	4266 (1.72) [25]	7931	-56.1	7781
7	1,3,5-trinitrobenzene		$\text{C}_6\text{H}_3\text{N}_3\text{O}_6$, 213	4606 (1.66) [25]	6568	-58.3	7809
8	2,4,6-trinitrophenol (picric acid)		$\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, 229	4103 [25]	6694	-45.4	6297

by D.I. Mendeleev formula and by the formula proposed in this work. Column 5 of Table 3 shows the empirical value of the explosion heat, which, as a rule, is 1.5–6.0 times less than the combustion heat of the same substances. The substances presented in Table 3 are the most interesting for preparation of fuel compositions (tens of mass percent), and even the theoretical determination of their calorific value is decisive for the formation of such fuel compositions

Both formulas – D.I. Mendeleev and the one proposed in this paper, are competitive, however, using the latter, it is much easier to determine Q_L (one variable) and, in general, it is more accurate. In addition, in the absence of reference data on Q_L or the presence of doubtful data (a large scatter in value in various reference manuals), it is advisable to calculate Q_L using both formulas and determine the arithmetic mean. Indeed, according to the proposed formula, the Q_L value, as a rule, is slightly overestimated, and according to D.I. Mendeleev formula, on the contrary, it is usually underestimated.

The calorific value of carbon strongly depends on its allotropic form, for example, carbon in the form of diamond under normal conditions burns mainly to CO, and activated carbon to CO₂, thus the thermal effect of combustion reactions can be very different.

Variance analysis: each experimental point is obtained as a result of multiple measurements, in order to determine the variance it is necessary to know the results of each specific measurement. This can only be done by the person who actually carried out these measurements.

In the table in column 10, “the error according to the formula proposed in this work, %” is defined – this is an analogue of the relative error.

The abscissa shows the oxygen balance, which is, in fact, a mathematically accurate value. As for the y-axis, the situation is different there. It contains the calorific value taken from reference books, and this is a purely empirical value. And although it is determined on hosted instruments, sometimes the numbers differ greatly in different reference books, so on average we determine the error at 5 % (the maximum correct error).

This means that the relative root mean square error is:

$$\delta = \sqrt{(\delta x)^2 + (\delta y)^2} = \sqrt{(5\%)^2 + (1\%)^2} = \sqrt{(26\%)^2} \approx 5\% . \quad (17)$$

On the graph, the boundaries of the confidence region at the selected significance level are given by lines:

$$y + \Delta = -k(1 + \delta)x = -1.05 \cdot 0.1387x [\text{MJ} \cdot \text{kg}^{-1}] = -0.1456x [\text{MJ} \cdot \text{kg}^{-1}]; \quad (18)$$

$$y - \Delta = -k(1 - \delta)x = -0.95 \cdot 0.1387x [\text{MJ} \cdot \text{kg}^{-1}] = -0.1317x [\text{MJ} \cdot \text{kg}^{-1}]. \quad (19)$$

Points located outside the boundaries of the trust area are indicated in the Figure.

The confidence region is enclosed between the thin dotted lines in the Figure.

Points 26, 12, 44, 5, 24, 18, 19, 7, 45, 2, and 39 were outside the confidence area.

The correlation line is sought in the form $y = kx + b$, but it turned out that b is small.

Even for the smallest values of x from the table, taking into account b changes y within the error.

The coefficient k was obtained by linear regression using the least squares method [24].

A line approximating a system of points on a plane is called a line passing through the origin of coordinates and, therefore, satisfying the equation $y = kx$, if the sum of the distances from the points to this line is minimal.

When counting, we find

$$k = -0.1387 \text{ MJ} \cdot \text{kg}^{-1}. \quad (20)$$

The correlation coefficient is the value of the found k .

Thus, a directly proportional dependence of the calorific value of a substance on its oxygen balance has been demonstrated. A negative oxygen balance of a substance indicates a quantitative lack of oxygen until the substance is completely burned. The more negative the value of oxygen balance, the more oxygen is necessary for the complete oxidation of the fuel – hydrogen and carbon in the molecule due to extramolecular oxygen. Consequently, the more oxygen is needed for the complete oxidation of the fuel, the greater will be the thermal effect from redox reactions (combustion reactions). This is also indicated by the slope of the ascending line on the chart.

The dependence found is the total effect of numerous and complex combustion processes of organic and inorganic substances. A step-by-step study of such processes is a separate problem, the solution of which may be carried out in the future. A positive result of this work is a very simple way to calculate the calorific value of a substance.

4. Conclusions

A new method for calculating the calorific value of substances with a negative OB suitable for organic, inorganic compounds and elements is proposed.

Compared to the well-known formulas for calculating Q_L according to formulas by D.I. Mendeleev and M.S. Karash, where the calculation error can reach up to 20 %, while according to the method proposed by the authors, the error, as a rule, does not exceed 6 %.

To determine the oxygen balance, the formula to calculate the oxygen balance of explosives of the universal formula $C_aH_bN_cO_d$ is used:

$$Q_L = -0.1387 \cdot OB, \text{ MJ} \cdot \text{kg}^{-1},$$

where M.w. is the molecular weight of the substance.

Calculation of the oxygen balance is based on the assumption that the fuel in a substance molecule (carbon and hydrogen) is oxidized during combustion by an oxidizer (oxygen) to higher oxides – carbon to CO_2 , and hydrogen to H_2O .

It became possible to quickly and fairly accurately calculate the calorific value of explosives as well; it is impossible to determine the calorific value in a practical way due to the rapid transition of combustion to detonation.

The directly proportional dependence found by the authors is satisfactorily described by the formula $y = 0.1387x$, where y is the calorific value of the substance, $\text{MJ} \cdot \text{kg}^{-1}$; x is the absolute value of the oxygen balance, %.

The accuracy of the calculated calorific value of substances is not lower than according to the empirical formula by D.I. Mendeleev, and the calculation is simpler (one variable – oxygen balance).

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6. Conflict of interests

The authors declare no conflict of interest.

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