

CALCULATION OF THE HIGH HEAT VALUE OF BIOFUELS

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Unique experimental data on the high heat value of biofuels – soy and rapeseed oils and methyl esters of the latter – which are in good agreement with the data of domestic and foreign researchers confirm the results of calculations: high erucic oil and its derivatives have a higher energy potential than low erucic oil. These data allow determining the indicator and effective indexes of operation of diesel (multifuel) engines with a high degree of reliability.

With the shortage of liquid energy carriers of petroleum origin and to reduce the environmental hazard of diesel exhaust gases, alternative fuels from renewable feedstock sources – vegetable oils and their derivatives, are beginning to be used.

In processing experimental data and calculations of the running cycle of diesel engines, it is important to know the precise value of the low heat value Q_1 of the fuel. The value of Q_1 is calculated with the high heat value Q_h , which is determined calorimetrically according to GOST 21261"91 in isothermal and adiabatic conditions in a constant volume.

The values of Q_h and Q_1 of petroleum fuels and the equations for calculating them are widely known [1], and the experimental values of these quantities were systematized in [2] for biofuels from plant feedstock. Although these values are in satisfactory agreement with the values calculated with Mendeleev's equation, Q_h was directly measured with a combustion calorimeter with a V-08MA liquid bomb.

Since GOST 21261 – 91 covers liquid fuels and hydrocarbon and oxygen-containing components, the recommended method for determination of Q_h can also be considered suitable for oxygen-containing (9-10% O_2) vegetable oils and their derivatives.

Calorimetric tests of samples of the following fuels [3] were conducted in the Laboratory of Thermal and Thermophysical Measurements at Khar'kov State Scientific-Research Institute of Metrology (KSSRIM):

Sample 1 – RME: German rapeseed oil methyl esters, erucic acid C22:1* = 0.6%; density of esters = 877 kg/m³ at 20°C;

Sample 2 – RHRO: refined high erucic rapeseed oil, C22:1 ≈ 30%, density = 916 kg/m³ at 20°C;

*Designation of the erucic acid used in the chemistry of fats: C22 – formula $C_{22}H_{42}O_2$; the figure 1 after the colon designates the number of double bonds in the molecule.

Table 1

Experiment 1: period						Experiment 2: period					
initial		main		final		initial		main		final	
measurement number	recorder readings, Hz	measurement number	recorder readings, Hz	measurement number	recorder readings, Hz	measurement number	recorder readings, Hz	measurement number	recorder readings, Hz	measurement number	recorder readings, Hz
1	0.519 (t')	1	5.787	1	8.625	1	0.660	1	4.516	1	9.465
2	0.533	2	8.173	2	8.631	2	0.677	2	8.908	2	9.471
3	0.549	3	8.433	3	8.637	3	0.691	3	9.265	3	9.476
4	0.563	4	8.487	4	8.644	4	0.705	4	9.325	4	9.481
5	0.578	5	8.504	5	8.650	5	0.720	5	9.344	5	9.487
6	0.592	6	8.512	6	8.656	6	0.735	6	9.353	6	9.492
7	0.607	7	8.517	7	8.662	7	0.750	7	9.361	7	9.498
8	0.621	8	8.521	8	8.669	8	0.767	8	9.367	8	9.504
9	0.636	9	8.525	9	8.675	9	0.781	9	9.373	9	9.509
10	0.651 (t_0)	10	8.530	10	8.681 (t'')	10	0.796	10	9.378	10	9.514
		11	8.535					11	9.384		
		12	8.541					12	9.389		
		13	8.546					13	9.395		
		14	8.552					14	9.400		
		15	8.558					15	9.405		
		16	8.564					16	9.411		
		17	8.570					17	9.417		
		18	8.576					18	9.421		
		19	8.582					19	9.427		
		20	8.588					20	9.433		
		21	8.596					21	9.438		
		22	8.601					22	9.444		
		23	8.606					23	9.449		
		24	8.613					24	9.454		
		25	8.619 (t_n)					25	9.459		

Sample 3 – SO: soy oil, density = 916 kg/m³ at 20°C;

Sample 4 – DF: winter diesel fuel, density = 826 kg/m³ at 20°C;

Sample 5 – RRO: refined rapeseed oil, C22:1 ≈ 10%, density = 915 kg/m³ at 20°C;

Sample 6 – ROME: RHRO fatty acid methyl esters, density = 874 kg/m³ at 20°C;

Sample 7 – ROME: RRO fatty acid methyl esters, density = 874 kg/m³ at 20°C.

Table 2

Sample No.	$t_k, ^\circ\text{C}$	$m \cdot 10^3, \text{kg}$	t_0, Hz	t_n, Hz	$S^a, \%$	$W^a, \%$	$\rho_s, \text{kg/m}^3$	$\sum_1^{n-1} t_i, \text{Hz}$
1	14.0	0.7748	0.670	8.764	0.01	0.03	877	214.930
	13.0	0.6872	0.726	7.974	DIN V 51606			195.232
2	13.5	0.6875	0.658	7.935	0.002	0.15	916	194.923
	14.0	0.6878	0.670	7.856	[4]	GOST 8988 – 77		191.858
3	14.0	0.6982	0.755	7.989	0	0.15	916	195.061
	13.0	0.7116	0.779	8.127	GOST 7825 – 76			198.499
4	18.5	0.6616	0.651	8.619	0.5	Отс.	826	210.647
	19.0	0.7209	0.796	9.459	DSTU 3868 – 99			229.529
5	18.0	0.6864	0.638	7.817	0.002	0.15	915	190.938
	18.5	0.6710	0.652	7.668	[4]	GOST 8988 – 77		187.682
6	15.0	0.6842	0.621	7.830	0.01	0.03	874	192.653
	15.0	0.6940	0.648	7.482	DIN V 51606			196.478
7	15.0	0.6830	0.620	7.798	0.01	0.03	874	191.590
	16.0	0.6845	0.679	7.913	DIN V 51606			194.099

Notations. t_k – ambient temperature in premises during thermotechnical measurements, $^\circ\text{C}$; m – apparent weight of fuel sample in air, kg; t_0 – thermometer reading corresponding to combustion temperature, Hz; t_n – thermometer temperature corresponding to final temperature, Hz; S^a and W^a – content of sulfur and water in tested fuel samples, wt. %; ρ_s – density of tested fuels, kg/m^3 ; $\sum_1^{n-1} t_i$ – sum of calorimeter temperatures in main period (see Table1), Hz.

Let us consider the basic stages and sequence of processing the results of determining Q_h .

In determinations of the effective heat capacity C_i (kJ/deg) of the calorimeter in the isothermal mode based on MI 2096, special-purity (minimum of 99.9%) benzoic acid (melting point $t_m = 122.4^\circ\text{C}$) is burned – the reference standard according to TU 6-09-49–85, certified for the heat value at 25°C . For this acid, the standard specific heat value is: 26,454 kJ/kg in weighing in air, 26,434 kJ/kg for the mass of an evacuated sample.

All temperature measurements were performed with a quartz thermometer for which the following constants were determined; coefficient of quartz thermometer $K_t = 3.856$ Hz/deg; frequency of quartz thermometer at 0°C : 100,678.5357 Hz.

As an example, the results of recording the calorimeter temperature (in Hz) with respect to the quartz thermometer for Sample 4 are reported in Table 1.

In determining the effective heat capacity of a calorimeter with an isothermal shell with an error of less than 0.1% (GOST 21261–91), the initial data reported in Table 2 were used for calculating the high heat value.

The accuracy of determination of Q_B was evaluated by the convergence of two successive measurement results by the same person. These results are considered reliable (with 95% confidence level) if the difference between them is no greater than 130 kJ/kg (GOST 21261–91).

Table 3

Sample No	$m_0 \cdot 10^3$, kg	t' , Hz	t'' , Hz	θ_0 , Hz	θ_n , Hz	K	Δh , Hz	Δt , Hz	Q_B^a , kJ/kg	$\overline{Q_B^a}$, kJ/kg	Q_S^a , kJ/kg	Q_S^d , kJ/kg
1	0.7758	0.558	8.797	0.614	8.781	0.001	-0.07338	8.02102	40070	40075	40074	40086
	0.6880	0.611	8.017	0.669	7.997	0.00095	-0.09785	7.15005	40080			
2	0.6883	0.551	7.973	0.605	7.956	0.00099	-0.085169	7.19150	40298	40268	40268	40328
	0.6886	0.580	7.885	0.625	7.872	0.00086	-0.061573	7.18423	40239			
3	0.6990	0.642	8.029	0.697	8.011	0.00103	-0.09014	7.14106	39402	39374	39374	39433
	0.7124	0.676	8.164	0.728	8.148	0.000956	-0.08047	7.26773	39346			
4	0.6625	0.519	8.681	0.585	8.653	0.000946	-0.14049	7.82751	45574	45604	45616	45616
	0.7218	0.660	9.514	0.728	9.489	0.001007	-0.12335	8.53975	45633			
5	0.6872	0.529	7.862	0.584	7.843	0.000976	-0.09689	7.08211	39747	39744	39744	39803
	0.6718	0.537	7.711	0.594	7.692	0.00109	-0.0945	6.92200	39740			
6	0.6850	0.527	7.822	0.574	7.842	0.00102	-0.04941	7.159387	40308	40340	40339	40351
	0.6949	0.550	8.009	0.599	7.997	0.000993	-0.06064	7.273158	40371			
7	0.6838	0.530	7.819	0.575	7.809	0.000978	-0.047207	7.130598	40216	40199	40198	40210
	0.6853	0.569	7.954	0.624	7.935	0.001001	-0.09348	7.14012	40182			

Notations m_0 – weight of fuel sample in vacuum; t' , t'' – initial temperature of initial period and final temperature of final period based on recorder readings (see Table 1); θ_0 , θ_n – average temperatures of initial and final periods of recording the calorimeter temperature; K – calorimeter cooling constant; Δh – correction for heat exchange of calorimeter with environment; Δt – corrected elevation of temperature in experiment; Q_B^a – heat value of tested fuel sample in calorimetric bomb; $\overline{Q_B^a}$ – arithmetic mean of two measurements; Q_S^a – high heat value for tested fuel sample; Q_S^d – high heat value for fuel with consideration of mass fraction W^a of water in it (see Table 2).

We note the features of recording quantities t_0 , t_n , and $\sum_1^{n-1} t_i$ in Table 2. For example, for fuel

Sample 1, first line: $t_0 = 100,774 + 0.670$ Hz, and $t_n = 100,774 + 8.764$ Hz. As a consequence, departing from the values of K_i and frequency of the quartz thermometer at 0°C indicated above:

$$t_0 = (100774.670 - 100678.535)/3.856 = 24.902^\circ\text{C}$$

$$t_n = (100782.764 - 100678.535)/3.856 = 27.030^\circ\text{C}$$

The real value of $\sum_1^{n-1} t_i$ for the first line in Table 2 is determined as $25 \cdot 100,774 + 214.930$ Hz

It is determined in the same way for all other lines.

For all fuel samples, the common initial data are: $t_{sh} = 27.5^\circ\text{C}$ – temperature of the calorimeter shell; $m_c = 7.98$ kg – mass of vessel with water; $m_2 = 0.006 \cdot 10^{-3}$ kg – mass of burning wire for igniting fuel sample, equal

to the difference in the masses of the wire before and after combustion; q_2 – specific heat value of ignition wire (for grade MM round copper electrical wire 0.1-0.15 mm in diameter, it is 2510 kJ/kg); ρ_w, ρ_a – density of the material for the weights for weighing the fuel sample and the density of ambient air (1.20), kg/m³.

Let us describe calculation for the quantities reported in Table 3.

The mass of the fuel sample in a vacuum is determined with the equation:

$$m_0 = m(\rho_a / \rho_s - \rho_a / \rho_w)$$

The calorimeter cooling constant is found from the expression:

$$K = (V_2 - V_1) / (\theta_2 - \theta_1)$$

where $V_1 = (t' - t_0) / n_0, V_2 = (t_n - t'') / n_n$ are the average rates of the change in the temperature (course of the temperature) in the initial and final periods after 30 sec; n_0, n_n are the number of measurements in the initial and final periods (see Table 1).

The correction for the heat exchange of the calorimeter with the environment is calculated with the equation:

$$\Delta h = K \left(\frac{t_0 + t_n}{2} + \sum_1^{n-1} t_i - n\theta_0 \right) + nV$$

where n is the number of measurements in the main period.

The corrected elevation for the temperature in the experiment is:

$$\Delta t = (t_n - t_0 + \Delta h)$$

The temperatures reported in Table 3 in Hz are converted to °C in the same way as the temperatures reported in Table 2.

Heat value Q_B^a of the fuel sample tested in the calorimetric bomb is calculated with the equation:

$$Q_B^a = (C_i \Delta t - q_2 m_2) / m$$

The term $q_2 m_2$ is not present in this equation, since polymer ampuls were not used in the experiments.

The high heat value Q_S^a of the fuel sample tested in consideration for the sulfur in it is calculated with the equation:

$$Q_S^a = \bar{Q}_B^a - 94S^a + \Delta Q_S$$

where 94 is the heat of formation of sulfuric acid from sulfur dioxide and dissolution of sulfuric acid in water for 1% sulfur converted to sulfuric acid during combustion of the fuel, kJ/kg; ΔQ_S is the correction, kJ/kg (GOST 21261–91, Table 2), for diesel fuel $\Delta Q_S = 59$ kJ/kg, and $\Delta Q_S = 0$ for biofuels in a first approximation.

High fuel heat value Q_s^d in consideration of the water in the fuel W^a is calculated with the equation:

$$Q_s^d = Q_s^a [100 / (100 - W^a)]$$

Using the data obtained on Q_b () for diesel fuel sample 4, we determine the low heat value:

$$Q_i = Q_i^a = Q_s^a - 24.42(8.94H^a + W^a)$$

where 24.42 is the heat of vaporization at a measurement temperature of 25°C allowing for 1% separated water, kJ/kg; 8.94 is the coefficient for conversion of the mass fraction of hydrogen to water; H^a is the mass fraction of hydrogen in the tested product ($H^d = H^a$ at $W^a = 0$), %.

We calculate $H^a(H^d)$ with the empirical equation:

$$H^d = 0.001195Q_s^d - 41.4 = 13.11\%$$

Thus,

$$Q_i^a(Q_i^d) = 45616 - 24.42 \cdot 8.94 \cdot 13.11 = 42754 \text{ kJ/kg}$$

According to GOST 21261-91, the result is founded to the nearest value divisible by 20 kJ/kg, i.e., $Q_i^a = 42760 \text{ kJ/kg}$

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