

CALCULATION OF THE HEAT VALUE OF BIOFUELS WITH CALORIMETRIC AND CHROMATOGRAPHIC DATA

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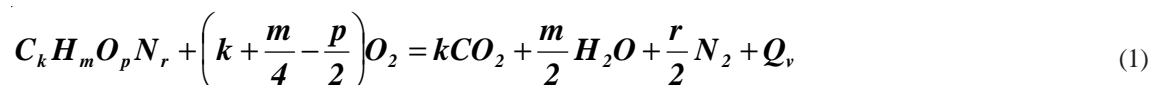
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The values of the gross (net) heating value were determined by burning samples of liquid biofuels – rapeseed and soy oils – and rapeseed oil fatty acid methyl esters manufactured in Germany and in Ukraine were determined. The experimental data obtained confirm the theoretical calculations that high erucic oil and its derivatives have the highest energy potential.

The heating value – high (gross) Q_h and low (net) Q_l – is the most important index of motor fuels, including alternative fuels.

The heating value (kJ or MJ) of liquid fuels usually refers to their mass in 1 kg in standard conditions: temperature of 0°C and pressure of 101.3 kPa. In thermal calculation of the operating cycle of internal combustion engines (ICE), quantity Q_l is used, since the temperature of the exhaust gases is higher than the condensation temperature of the water vapors in these gases, and it is consequently not possible to use the heat of vaporization [1].

The heating value Q_v of fuel combustion is experimentally determined in a calorimetric bomb of constant volume in compressed oxygen atmosphere. The reaction of combustion of an organic substance is expressed by the equation [2]:



The data on $Q_h(Q_l)$ of biofuels – vegetable oils and the fatty acid esters contained in these oils – are analyzed in [3]. We will compare our experimental data on Q_h^e of biofuels with the calculated Q_h based on the generalized dependences in [3, 4].

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The following samples of biofuels were investigated:

- sample 1 – RME (German rapeseed methyl esters, erucic acid C22:1 = 0.6%);
- sample 2 – RHRO (refined high-erucic rapeseed oil, C22:1 » 30%);
- sample 3 – RSO (soy oil);
- sample 4 – RRO (refined rapeseed oil, C22:1 » 10%);
- sample 5 – ROME (RHRO fatty acid methyl esters);
- sample 6 – ROME (RRO fatty acid methyl esters).

It is necessary to add correction ΔQ_s to the value of Q_h^e for determining the high heating value of the biofuel samples with the results of the calorimetric experiment in standard conditions (GOST 21261–91). The average value of $\Delta Q_s = 55$ kJ/kg was used for all of the biofuels investigated. The high heating value Q_h^e of a biofuel in standard conditions obtained in this way is rounded off to the nearest value divisible by 10 kJ/kg.

Bertram proposed the following equation for determining the heating value Q_h^B [4]:

$$Q_h^B = 4.1868(11380 - IN - 9.15SN) \quad (2)$$

where IN is the iodine number g I₂/100 g; SN is the saponification number, mg KOH/g.

The iodine number of the tested biofuel is calculated with the equation:

$$IN = \frac{(V - V_1)F0.01269}{m} 100 \quad (3)$$

where V , V_1 are the volumes of sodium thiosulfate solution in the concentration of 0.1 mole/dm³ consumed for titration in a control experiment ($V_{av} = 33.3$ cm³) and the tested biofuel, cm³; $F = 0.99$ is the factor of sodium thiosulfate solution of 0.1 mole/dm³ concentration; 0.01269 is the amount of iodine equivalent to 1 cm³ of sodium thiosulfate solution of 0.1 mole/dm³ concentration, g; m is the mass of the tested biofuel, g.

Table 1

Fuel sample No.	GOST 2070 – 82			GOST 5478 – 90			Q_h^e , kJ/kg	δ , kJ/kg
	V_1 , cm ³	m , g	IN, g I ₂ /100 g	V_1 , cm ³	m , g	SN, mg KOH/g		
1	22.8	0.1256	105.0	13.5	1.1688	182.7	40250	-110
	25.0	0.0998	104.5	14.0	1.1060	180.2		
			104.8			181.5		
2	26.7	0.0836	99.2	4.6	2.6011	179.5	40320	60
	26.3	0.0880	99.9	14.2	1.0693	181.1		
			99.6			180.3		
3	24.0	0.0933	125.0	7.0	1.9932	200.0	39370	120
	20.8	0.1210	129.8	17.0	0.5642	201.9		
			127.4			201.0		
4	22.9	0.0976	133.9	10.5	1.5975	187.2	39930	-70
	23.4	0.0950	130.9	6.8	2.1676	186.5		
			132.4			186.9		

The following equation was used to determine the saponification number of the biofuel:

$$SN = \frac{28.055(V - V_1)}{m} \quad (4)$$

where 28.055 is the mass of potassium hydroxide equivalent to 1 cm³ of hydrochloric acid solution with a concentration of $c = 0.5$ mole/dm³, mg; $F = 1.015$ is the ratio of the real concentration c of the hydrochloric acid solution to its nominal concentration; V, V_1 are the volumes of the hydrochloric acid solution of concentration c used for neutralizing the control ($V_{av} = 21$ cm³) and tested samples, cm³; m is the mass of the tested biofuel, g.

Table 1 reports the results of determining the iodine number according to GOST 2070–82 and the saponification number according to GOST 5478–64 and the calculated values of Q_h^e rounded to the nearest value divisible by 10 kJ/kg, as well as the experimentally found Bertram absolute error \bar{a} of determination of high heating value Q_h^e of the biofuels.

It is necessary to know the elemental composition of the biofuels – in mass fractions of carbon, hydrogen, and oxygen – to calculate the Mendeleev high (low) heating values [5]. The fatty acid composition (Table 2) of the fuels was determined by liquid chromatography [5].

It is necessary to note that samples 5 and 6 were obtained from samples 2 and 4 with methyl ester production technology [6]. They were placed in the chromatograph without preliminary methanolysis (GOST 30418–96). Samples 2 and 4 were first treated with methanol for determining their fatty-acid composition.

The insignificant difference in the qualitative and quantitative compositions of the fatty acid methyl esters for samples 2 and 5 and 4 and 6 can be attributed to the slight difference [6] in transesterification of the

Table 2

Fatty acid	Content (%) in sample of biofuel					
	1	2	3	4	5	6
C 16:0	4.5002	3.0856	10.7201	4.0760	3.0315	3.9912
C 16:1	0.2552	0.1425	–	0.1985	0.1386	0.2305
C 16:2	0.0615	–	–	–	–	0.0540
C 17:0	0.0598	–	–	–	–	0.0473
C 17:1	0.1103	–	–	–	0.0851	0.1490
C 18:0	1.9077	1.3781	4.1098	1.5680	1.3616	1.5724
C 18:1	61.9624	23.0861	24.7071	49.5419	23.6453	48.0660
C 18:2	18.1013	20.5419	51.7292	19.2891	20.1212	19.0328
C 18:3	10.5674	8.4299	7.3375	9.5142	8.2954	9.4281
C 20:0	0.5208	0.6349	0.3953	0.6058	0.6339	0.6366
C 20:1	1.2014	8.3155	0.2552	4.9161	8.2764	5.2588
C 20:2	–	0.5141	–	0.2468	0.5030	0.2624
C 21:0	0.0697	0.1232	–	–	0.1131	0.0514
C 22:0	0.2287	0.6345	0.5104	0.3511	0.6321	0.3992
C 22:1	0.2385	31.2772	–	9.0469	30.9616	10.8191
C 22:2	–	0.4211	–	0.1366	0.5848	–
C 24:0	0.0865	0.4105	0.2355	0.1471	0.4734	–
C 24:1	0.1285	1.0050	–	0.3619	1.1430	–

acylglycerins in the investigated biofuels. A similar difference in the fatty-acid compositions of initial rapeseed oil and the biodiesel obtained from it (ROME) was noted in [7].

The physicochemical properties of the biofuel samples were calculated with the data in Table 2 and are reported in Table 3. The Q_h^M and low Q_l^M heating values calculated with the equations of D. I. Mendeleev and the low heating value Q_l^e of the biofuels calculated with Q_h^e are also reported there. The results of the calculations are rounded to the nearest value divisible by 10 kJ/kg.

The following are also reported in Table 3:

the low heating value of 1 kmole of fuel mixture (for an air excess coefficient of $\alpha = 1.8$)

$$Q_l^{mi} = Q_l^e / M_l = Q_l^e / (\alpha M_0)$$

the low heating value of 1 m³ of fuel mixture

$$Q_l^{mim} = Q_l^e / (22.4 M_l) = Q_l^e / (22.4 \alpha M_0)$$

Table 3

Indexes	Fuel sample					
	1	2	3	4	5	6
Q_{hs}^e , kJ/kg	40086	40328	39433	39803	40351	40210
Q_h^e kJ/kg	40140	40380	39490	39860	40410	40270
Q_l^e kJ/kg	37420	37710	36890	37210	37650	37530
Q_h^B kJ/kg	40250	40320	39370	39930	–	–
Q_h^M kJ/kg	40100	40220	39530	39870	40570	40260
Q_l^M kJ/kg	37380	37540	36930	37230	37820	37530
Elemental composition, mass fraction						
C	0.7710	0.7803	0.775	0.7765	0.777	0.773
H	0.1205	0.1183	0.115	0.117	0.122	0.121
O	0.1085	0.1014	0.110	0.1065	0.101	0.106
Molecular mass M , kg/kmole	295.4	946.9	875.4	902.0	316.9	302.7
Approximate overall formula	$C_{19}H_{35.3}O_2$	$C_{61.5}H_{111.1}O_6$	$C_{56.5}H_{100}O_6$	$C_{58.3}H_{104.7}O_6$	$C_{20.5}H_{38.4}O_2$	$C_{19.5}H_{36.3}O_2$
L_0 , kg/kg	12.56	12.62	12.41	12.51	12.71	12.62
M_0 , kmol/kg	0.433	0.435	0.428	0.432	0.438	0.435
Q_l^{mi} kJ/kmol	48010	48160	47880	47850	47760	47930
Q_l^{mim} kJ/m ³	2143	2150	2138	2136	2132	2140
Q_l^{mik} kJ/kg	1585	1590	1581	1582	1577	1583
<p><i>Notation.</i> Q – heating value: Q_h^e – experimental high at 25°C; Q_h^e – same at 0°C; Q_h^B – Bertram calculated high; Q_l^e – experimental low; Q_h^M – Mendeleev calculated high; Q_l^M – Mendeleev calculated low; Q_l^{mi} – experimental low, per 1 kmole of fuel mixture; Q_l^{mim} – same, per 1 m³ of fuel mixture; Q_l^{mik} – same, per 1 kg of mixture; M – molecular mass, kg/kmole; L_0 – amount of air (kg) theoretically required for complete combustion of 1 kg of fuel; M_0 – same, kmole/kg.</p>						

the low heating value of 1 kg of fuel mixture

$$Q_l^{mik} = Q_l^e / (M_l + 1) = Q_l^e / (\alpha I_0 + 1)$$

The difference in the high heating values determined by the calorimetric method and calculated with the Bertram and Mendeleev equations does not exceed 0.4%.

The high (low) heating value of biofuels can be determined with the iodine number, saponification number, and fatty-acid composition.

The more erucic acid methyl esters in the biodiesel (samples 1, 6, and 5), the higher its low heating value, which is due to a decrease in the oxygen content of the ester molecule.

As a function of the fatty-acid composition of the biofuel (in the given series of experiments), the low heating value varies from 36,890 to 37,650 kJ/kg.

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