

Comparison of Methods for Calculation of Combustion Heat of Biopolymers

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Abstract: In this paper various methods for calculation of gross (Q) and net (q) heats of combustion for different biopolymers (lignin, cellulose, hemicelluloses, starch, pectin, proteins, lipids etc.) have been analyzed. The results showed that the calculation with use the energy released by combustion per gram of diatomic oxygen (E_q -parameter) is less accurate, because it gives a deviation from experimental values of about 4% for Q and more than 7% for q. In the case of calculations based on contribution of structural groups of polymers, the deviation may reach 3%. The lowest deviation of about 0.5% for Q and less than 1% for q was obtained using an improved method of calculation, which is based on elemental composition of the polymers. Calculation of gross and net heat of combustion for biomass samples by the improved method was very close to experimental calorific values. It was found that combustion of biomass waste supplemented with waste plastic is preferable, since such combustion technology provides more thermal energy than single firing of biomass and is accompanied by less emission of carbon dioxide in comparison with separate burning of plastic waste only.

Keywords: Biopolymers, Biomass, Plastics, Chemical Structure, Composition, Heat of Combustion, Calorimetry, Calculation Methods

1. Introduction

Mankind produces a huge amount of solid waste including several billion tons of plant-based waste (paper, cardboard, textile, sawdust, shavings, branches, straw, husk, etc.) and hundreds million tons of waste plastics annually [1, 2]. Currently, main population of the world living in underdeveloped and developing countries, especially in rural areas, uses solid residues and wastes of the plant biomass (straw, bushes, twigs, firewood, sawdust, etc.) to meet their energy needs [3]. In many countries, these resources account for over 90% of household energy consumption. In developed countries about 20% of solid organic waste is burned to generate the thermal energy [4]. The not-edible plant materials are related to abundant, renewable and inexpensive source of the solid biofuel. To improve fuel properties, it is preferable to use the pelletized form of plant material containing high-energy binders, such as plastics, rubbers, tars, waxes, lipids, etc. [1, 5].

In order to determine the true value of gross energy or enthalpy of combustion of organic materials, a special

apparatus is required such as precise, but complex and expensive calorimeter. Moreover, the calorimetric experiments are long and require the introduction of various corrections and laborious calculations. Therefore to characterize fuel properties of organic substances, e.g. combustible waste, the approximate calculations of calorific value are performed using equations of Mendeleev or other researchers [6, 7]. Estimating calculation method of combustion heat based on contribution of atoms and structural groups of polymers to thermal energy is also proposed [8]. Study of 49 synthetic polymers showed that the net heat (E_q , kJ) released by combustion per gram of diatomic oxygen has approximately constant value: $E_q = 13.10 \pm 0.78$ kJ per 1gr of O_2 [9, 10]. Then, net heat of combustion (q, kJ/g) of the polymer sample can be calculated by the equation:

$$q = E_q n_{O_2} M_{O_2} / M_p \quad (1)$$

where $M_{O_2} = 32$ is molecular weight of O_2 and n_{O_2} is number

of O₂ molecules consumed for complete combustion of one mole of the repeat polymer unit having molecular weight M_p.

As known, vegetable biomass is a complex of natural biopolymers such as cellulose, hemicelluloses, lignin, starch, pectin, proteins, lipids and some others. Therefore, to estimate fuel properties of the biomass waste it is advisable to know beforehand the calorific value of the individual biopolymers. For this purpose it is necessary to perform a comparative analysis of various methods for calculating the combustion heat value of different biopolymers to choose the most accurate and reliable method.

2. Experimental

2.1. Materials

Various samples of biopolymers and plant biomass were studied (Tables 1 and 2).

Table 1. List of used biopolymers.

Polymer	Abbr	Repeat unit	M _p
Glycine protein of wheat	GLP	C ₂ H ₃ O ₂ N	73
Gluten of wheat	GLT	C ₅ H ₆ O ₂ N	112
Xylan of birch	XYL	C ₅ H ₈ O ₄	132
Mannan of spruce	MAN	C ₆ H ₁₀ O ₅	162
Cellulose of cotton	CEL	C ₆ H ₁₀ O ₅	162
Starch of potatoes	STR	C ₆ H ₁₀ O ₅	162
Pectin of citrus	PEC	C ₆ H ₈ O ₆	176
Lignin of spruce	LIG-S	C ₁₀ H ₁₁ O ₃	179
Lignin of aspen	LIG-A	C ₁₁ H ₁₂ O ₄	208
Abietic acid	ABA	C ₂₀ H ₃₀ O ₂	302
Suberin of aspen bark	SUB	C ₇₂ H ₁₄₀ O ₆	1100

Note: Abbr is abbreviation; MW is molecular weight of repeat unit

Table 2. Chemical composition of biomass (wt. %).

Biomass	Cellulose	Hemi	Lignin	Extr	Ash
Softwood	0.48	0.20	0.28	0.02	0.02
Hardwood	0.45	0.25	0.23	0.03	0.04
Bagasse	0.40	0.31	0.20	0.03	0.06
Corn stover	0.38	0.33	0.2	0.02	0.07
Cardboard	0.60	0.12	0.18	0.03	0.07
Wr. paper	0.73	0.07	0.05	0.03	0.12

Note: Hemi is hemicelluloses; Extr is extractives; Wr is wrapping

2.2. Methods

Gross combustion heat (Q) of the samples was determined using a stainless steel calorimetric bomb having volume 0.320 dm³ at oxygen pressure of 3.05 MPa with 1.00 cm³ of deionized water added to the bomb [11]. The combustion measurements were carried out by an isothermal water calorimeter at 298.15 K with accuracy ±0.001 K. The value of the energy equivalent of the calorimeter determined by standard benzoic acid was 15802.3 ± 0.9 J/K. The true mass of the sample used in each experiment was determined from the mass of the produced CO₂. The system was thermostated for 1 h. After ignition, the temperature rise was measured within 1 h. All needed corrections were introduced. Conventional

procedure was used to adjust the experimental combustion energy to standard conditions: T=298.15 K and p= 0.1 MPa. For each sample five experiments were performed to calculate an average value of combustion enthalpy and standard deviation.

The net combustion heat (q) of the samples was calculated by the equation [10]:

$$q \text{ (MJ/kg)} = Q \text{ (MJ/kg)} - 0.22 H \quad (2)$$

where H is percentage of hydrogen in the sample.

The experimental results were compared with Q and q values obtained by various calculation methods based on equations of Mendeleev (eq. 3 and 4) [6], Parikh et al. (eq. 5 and 6) [7], improved eq. 7 and 8, on E_q-parameter (eq. 1 and 9) [9, 10], as well as on structural groups of polymers [8].

$$Q \text{ (MJ/kg)} = a_1 C + b_1 H - c_1 O - d_1 N - e_1 A \quad (3)$$

$$q \text{ (MJ/kg)} = Q - f_1 H \quad (4)$$

where a₁=0.339; b₁=1.255; c₁=0.109; d₁=0.015; e₁=0.02; f₁=0.226

$$Q \text{ (MJ/kg)} = a_2 C + b_2 H - c_2 O - d_2 N - e_2 A \quad (5)$$

$$q \text{ (MJ/kg)} = Q - f_2 H \quad (6)$$

where a₂=0.349; b₂=1.178; c₂=0.103; d₂=0.015; e₂=0.02; f₂=0.202

$$Q \text{ (MJ/kg)} = a_3 C + b_3 H - c_3 O - d_3 N - e_3 A \quad (7)$$

$$q \text{ (MJ/kg)} = Q - f_3 H \quad (8)$$

where a₃=0.344; b₃=1.217; c₃=0.106; d₃=0.015; e₃=0.02; f₃=0.210

In eq. 3-8: C, H, O, N is percentage of atoms in dry organic material; and A is percentage of ash in the sample.

Gross heat value can be also calculated using the parameter E_q:

$$Q = k E_q n_{O_2} M_{O_2} / M_p \quad (9)$$

where k ≈ 1.075 is coefficient of transition from net to gross heat of combustion.

To implement the method of structural groups, the contributions of these groups to the heat of combustion should be used (Table 3).

Table 3. Structural groups and their contributions to gross heat of combustion [8].

Group	Q _i , kJ/mol	Group	Q _i , kJ/mol
-CH ₃	775	-COO-	112
-CH ₂ -	670	-C=O	259
-CH-	518	-NH-	77
-C-	431	-O-	-132
-H	190	-OH	-108

Gross heat of combustion was calculated by the equation:

$$Q = \sum n_i Q_i \quad (10)$$

Then, the net combustion heat of the samples was calculated:

$$q = Q - f_3 H \quad (11)$$

The average relative deviation of calculated values from the experimental values was found by the equation:

$$RD (\%) = 100 \Sigma(MSD/X_e)/n \quad (12)$$

where the mean standard deviation is:

$$MSD = \sqrt{\Sigma(X_c - X_e)^2 / (n - 1)}$$

X_c and X_e are the calculated and experimental values of combustion heat, respectively; n is the number of samples.

3. Results and Discussion

Results of experimental determination of gross and net heat of combustion for investigated biopolymers are shown in Table 4.

Table 4. Calorimetric data for gross (Q) and net (q) combustion heat of biopolymers.

Polymer	Formula	M_p	$n(O_2)$	Q , MJ/kg	q , MJ/kg
PEC	$C_6H_8O_6$	176	5	13.73	12.76
XYL	$C_5H_8O_4$	132	5	17.80	16.38
STR	$C_6H_{10}O_5$	162	6	17.53	16.23
MAN	$C_6H_{10}O_5$	162	6	17.50	16.20
CEL	$C_6H_{10}O_5$	162	6	17.45	16.12
GLP	$C_2H_3O_2N$	73	1.75	11.41	10.55
GLT	$C_5H_6O_2N$	112	5.5	21.87	20.64
LIG-S	$C_{10}H_{11}O_3$	179	11.25	27.70	26.45
LIG-A	$C_{11}H_{12}O_4$	208	12	25.72	24.83
ABA	$C_{20}H_{30}O_2$	302	26.5	38.25	36.17
SUB	$C_{72}H_{140}O_6$	1100	104	41.67	38.92

The experimental values of the combustion heat (EXP) were compared with the results of calculations using various methods (Tables 5 and 6). Analysis of the results showed that the calculations by eq. (1) and eq. (9) with use the E_q -parameter is less accurate and reliable because they give the relative deviation from experimental values of about 4% for Q and more than 7% for q . In the case of calculations by eq. (10) and eq. (11) based on contribution of structural groups of polymers, the deviation for some samples may reach 3%. The lowest deviation of about 0.5% for Q and less than 1% for q was obtained using an improved method of calculation by eq. (7) and (8), which is based on elemental composition of the polymers.

Table 5. Comparison of experimental and calculated values of gross combustion heat of biopolymers (Q , MJ/kg).

Polymer	EXP	Eq. (3)	Eq. (5)	Eq. (7)	Eq. (9)	Eq. (10)
PEC	13.73	13.56	13.93	13.75	12.80	13.70
XYL	17.80	17.67	18.00	17.81	17.07	17.14
STR	17.53	17.43	17.67	17.50	16.69	16.49
MAN	17.50	17.43	17.67	17.50	16.69	16.49

Polymer	EXP	Eq. (3)	Eq. (5)	Eq. (7)	Eq. (9)	Eq. (10)
CEL	17.45	17.43	17.67	17.50	16.69	16.49
GLP	11.41	11.24	11.51	11.38	10.82	11.77
GLT	21.87	21.72	21.98	21.86	22.12	21.90
LIG-S	27.70	27.57	27.91	27.75	28.32	27.71
LIG-A	25.72	25.45	25.82	25.65	25.99	26.38
ABA	38.25	38.21	38.31	38.27	39.54	38.38
SUB	41.67	41.61	41.50	41.57	41.74	42.42
RD, %	0	1.4	0.8	0.5	4.0	2.9

Table 6. Comparison of experimental and calculated values of net combustion heat of biopolymers (q , MJ/kg).

Polymer	EXP	Eq. (4)	Eq. (6)	Eq. (8)	Eq. (1)	Eq. (11)
PEC	12.76	12.54	12.91	12.81	11.91	12.71
XYL	16.38	16.30	16.58	16.50	15.88	15.80
STR	16.23	16.00	16.23	16.21	15.52	15.18
MAN	16.20	16.00	16.23	16.21	15.52	15.18
CEL	16.12	16.00	16.23	16.21	15.52	15.18
GLP	10.55	10.31	10.69	10.52	10.04	10.86
GLT	20.64	20.51	20.80	20.74	24.33	20.71
LIG-S	26.45	26.17	26.52	26.45	26.35	26.34
LIG-A	24.83	24.15	24.51	24.43	25.18	25.10
ABA	36.17	35.98	36.10	36.10	36.78	36.30
SUB	38.92	38.76	38.62	38.90	38.83	39.63
RD, %	0	1.7	1.4	0.9	7.2	3.2

Calculation of gross and net heat of combustion for biomass samples was performed taking into account chemical composition of the samples (Table 2):

$$Q = \Sigma w_i Q_i \quad (13)$$

$$q = \Sigma w_i q_i \quad (14)$$

where w_i is weight part of individual components of the biomass; Q_i and q_i are gross and net combustion heat calculated by the improved method (eq. 7 and 8).

As can be seen, the calculated heat values for various biomass samples were close to experimental values in the RD range of 1.0-1.2% (Table 7).

Table 7. Comparison of experimental (EXP) and calculated (CALC) values of combustion heat of biomass samples.

Biomass	Q, MJ/kg		q, MJ/kg	
	EXP	CALC	EXP	CALC
Softwood	20.45	20.53	19.11	19.18
Hardwood	19.70	19.44	18.35	18.14
Bagasse	19.00	18.84	17.82	17.60
Corn stover	18.37	18.46	17.44	17.58
Cardboard	18.48	18.75	17.21	17.50
Wr. paper	16.69	16.54	15.56	15.38

The main problem for using the biomass waste as solid fuel is relatively low heat output. One of the ways to solve this problem is to obtain a mixed solid fuel containing along with biomass waste also an additive of widespread waste plastics such as PE and/or PP. On the one hand it allows to release the environment from solid waste, and on the other hand the use of mixed fuel provides a greater amount of thermal energy (Fig. 1 and 2).

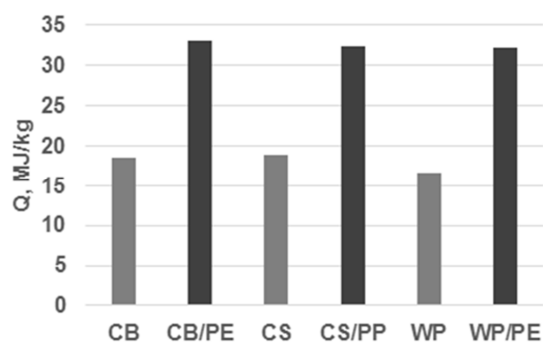


Figure 1. Gross heat value of waste cardboard (CB), corn stover (CS), wrapping paper (WP) and mixture of these biomass waste with waste plastics (1:1).

Further more, since the biomass is neutral for emission of carbon dioxide into the environment, burning of the mixed fuel results in reduction of carbon dioxide emission by half in comparison with a separate burning of plastic waste only (Fig. 3).

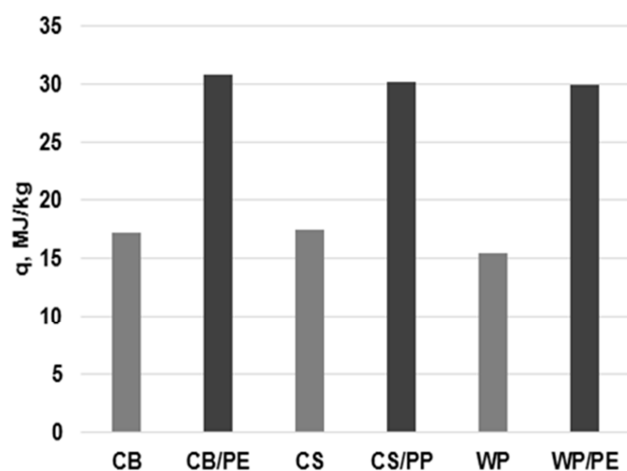


Figure 2. Net heat value of waste cardboard (CB), corn stover (CS), wrapping paper (WP) and mixture of these biomass waste with waste plastics (1:1).

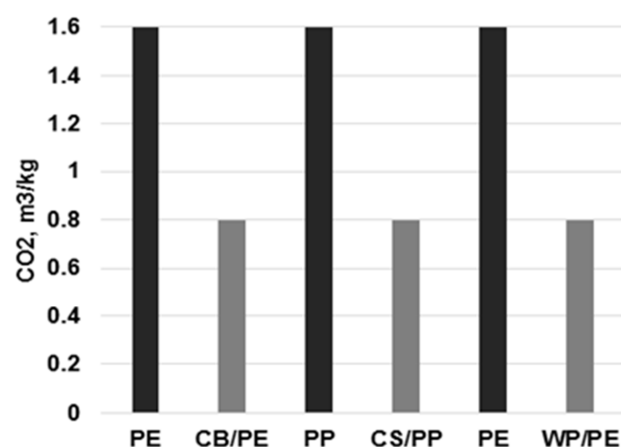


Figure 3. Emission of carbon dioxide after burning of waste plastics and their mixture with biomass waste (1:1).

4. Conclusion

Vegetable biomass is a complex of natural biopolymers such as cellulose, hemicelluloses, lignin, starch, pectin, proteins, lipids and some others. Therefore, to estimate fuel properties of the biomass waste it is advisable to know beforehand the calorific value of the individual biopolymers. For this purpose a comparative analysis of various methods for calculating the combustion heat value of different biopolymers was carried out in order to choose the most accurate and reliable method.

Gross and net heats of combustion for different biopolymers such as lignin, cellulose, hemicelluloses, starch, pectin, proteins, lipids, as well as some biomass have been determined. The experimental values of the combustion heat were compared with the results of calculations using various methods. The results showed that the calculation with use the energy released by combustion per gram of diatomic oxygen (E_q -parameter) is less accurate and reliable because this method gives the relative deviation from experimental values of about 4% for Q and more than 7% for q . In the case of calculations based on contribution of structural groups of polymers, the deviation for some samples may reach 3%. The lowest deviation of about 0.5% for Q and less than 1% for q was obtained using an improved calculation method of gross (Q) and net (q) heat values, which is based on elemental composition of the polymers:

$$Q = 0.344 C + 1.217 H - 0.106 O - 0.015 N - 0.02A$$

$$q = Q - 0.210 H$$

where C , H , O , N is percentage of atoms in dry biopolymer; and A is percentage of ash in the sample.

Values of combustion heat for biomass samples calculated by the improved method were close to experimental calorific values. To generate the heat energy it is preferable to burn the biomass waste supplemented with the waste plastic, since such combustion technology provides more thermal energy than separate firing of biomass, as well as less emission of carbon dioxide in comparison with separate burning of plastic waste only.

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