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Prediction of higher heating value based on elemental composition for lignin and other fuels

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ABSTRACT

Higher heating values (HHV), as well as carbon, hydrogen, sulphur, nitrogen and ash contents have been experimentally determined for eight lignin samples.

Systematization and analysis of equations for prediction of HHV for the different fuels (coal, wood, biomass, waste, etc.) based on the carbon, hydrogen, oxygen, sulphur, nitrogen, chlorine, phosphorus, and ash content were carried out.

The feasibility of 27 equations for predicting lignin HHV has been checked. A simple new equation for predicting lignin HHV based on the carbon content has been proposed; its accuracy is 2.4%.

1. Introduction

Lignin is the second most widely available biopolymer in the world, while its practical use is insignificant. This imbalance between the demand and supply of lignin stimulates its study. In addition, lignin is a renewable source of energy and raw material. The largest amounts of lignin are generated as waste at wood chemical plants [1]. Lignin is used to produce fuel [2,3], polymers [4,5], sorbents [6] and other chemical products [7–9]. The utilization of lignin typically involves thermochemical processes: direct combustion, pyrolysis, thermal liquefaction or hydrothermal conversion [10]. To evaluate the heat effects of such processes it is necessary to know the heating value of lignin or that of compounds modeling fragments of its structure.

In the current study "higher heating value at constant volume" (HHV) is considered, which is analogous to "gross calorific value at constant volume" according to ISO 1928:2009, ISO 18125:2017 or "gross heat of combustion at constant volume" according to ASTM D 240-17, ASTM D 4809-18 or "energy of combustion" in the definition of chemical thermodynamics [11]. The result of the experimental determination of HHV_w is recommended to be presented as HHV_d (sometimes HHV_{daf}) according to ISO 16993:2016. HHV_{daf} is used when discussing the maximal HHV value or HHV organic part of fuel.

Lignin species differ in the method of isolation from the wood or plant matrix: Kraft process, hydrolysis, extracting with organic solvents, etc. [9]. HHV_{daf} of the lignin depends on the origin of the raw materials (softwood, hardwood, straw, etc.), the degree of chemical modification of native lignin, and the ratio of aromatics (or lignin)/carbohydrates as well. The latter factor makes the main contribution to the value of HHV_{daf}, since the cellulose HHV_{daf} is less than that of lignin and has a constant value of 17.35 ± 0.05 MJ kg^{-1} [12] with the following elemental composition C_{daf} = 44.4 wt%, H_{daf} = 6.2 wt%, O_{daf} = 49.4 wt%. For lignin samples that do not contain carbohydrates the value of HHV_{daf} can reach 29.2 MJ kg^{-1} [13] with the elemental composition C_{daf} = 70.0 wt%, H_{daf} = 6.5 wt%, O_{daf} = 23.5 wt% [14]. Therefore HHV_{daf} of lignins (including lignocellulose samples) varies in a wider range than that of the biomass, from 17.3 to 29.2 MJ kg^{-1}, which makes it reasonable to develop a special equation for predicting HHV of the lignin.

HHV is determined experimentally using bomb calorimeter or by calculation based on proximate analysis, ultimate analysis, structural (or chemical) composition, or their combinations [15]. The first calculation method was based on the determination of HHV by the elemental composition [16]. It has been theoretically justified for coals by P.-L.Dulong (1785–1838) even before P.Vieille (1854–1934) created a calorimetric bomb. Since Dulong did not have reliable HHV values in due time, his postulates in the form of the equations were presented by other researchers much later [16,17]. Therefore, one can find various variants of Dulong's formula in the literature, as well as modifications of Dulong's formula [18].

The use of bomb calorimeters for HHV_w or HHV_d measurements designed at the end of the 19th century by P.Mahler and M.Berthelot led to the accumulation of reliable HHV_d values for different materials. This allowed D.I.Mendeleev (1834–1907) to propose the first universal formula for HHV_d calculation [16] based data points for 70 coals, 7

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Nomenclature

HHV	higher heating value (MJ kg^{-1})
wt%	weight percent
C	carbon content (wt%)
H	hydrogen content (wt%)
O	oxygen content (wt%)
S	sulphur content (wt%)
N	nitrogen content (wt%)
Cl	chlorine content (wt%)
P	phosphorus content (wt%)
A	ash content (wt%)
Q_C	coefficient at C (MJ kg^{-1} $wt\%^{-1}$)
Q_H	coefficient at H (MJ kg^{-1} $wt\%^{-1}$)
Q_O	coefficient at O (MJ kg^{-1} $wt\%^{-1}$)
Q_S	coefficient at S (MJ kg^{-1} $wt\%^{-1}$)
Q_N	coefficient at N (MJ kg^{-1} $wt\%^{-1}$)
Q_{Cl}	coefficient at Cl (MJ kg^{-1} $wt\%^{-1}$)
Q_P	coefficient at P (MJ kg^{-1} $wt\%^{-1}$)
Q_A	coefficient at A (MJ kg^{-1} $wt\%^{-1}$)
w	wet basis, not excluding ash
d	dry basis, not excluding ash
daf	dry basis, ash-free
waf	wet basis, ash-free
Const	absolute term (MJ kg^{-1})

liquid petroleum products, graphite and cellulose. A review of the theoretical criteria of Dulong, Mahler and Mendeleev, which form the basis of the formulas of the XIX century for calculation of the HHV, was considered by us previously [19], and a complete review has been fulfilled by [20]. Many similar and original dependencies were proposed in the twentieth century: relationships for coals until the middle of the twentieth century were analyzed in two reviews [21,22], while data from the second half of the twentieth century to 2010 were regarded in the review [23]; equations for biomass and waste have been published since the 1980s [24] and the equations up to 2011 were reviewed [25], recent developments are presented by two works [26] and [27]. Beginning from the second half of the twentieth century formulas based on different statistical processing of experimental data have dominated. Along with regression analysis Monte-Carlo method is used [28], and neural networks technique is especially widely applicable [29]. A new universal equation [20] based on data for 6 gaseous fuels, 40 liquid fuels, 49 coals and cokes, 95 biomass materials, 21 wastes including refuse derived fuel (RDF) and municipal solid waste (MSW), 14 chars. Recently several authors [27,30,31] have presented thermochemical models for calculation of the HHV_{daf} based on the use of the mass fraction of oxygen consumed by combustion. The dominance of the statistical approach in the development of equations for calculation of the HHV has led to an abrupt increase in their number in the twenty-first century, which now exceeds 250. Table 1 presents a sampling of 100 equations systematized in a chronological order and, as far as possible, they are brought to a single form regarding the contributions of individual elements (including ash) and fuels the equations are developed for. Principles of selection 100 equations from 250 were the following: at least 1 equation from each reference, author's recommendation, maximum correlation coefficient (R^2), minimum number of parameters. Such a number of equations require their comparative analysis to limit this variety and to offer a simple equation for lignin.

Although there are many data on determination of HHV and elemental composition for lignin in the literature, there are few works that provide both sets of data simultaneously. Thus, it seems reasonable to determine both HHV and elemental composition on dry basis for variety of lignin samples to check the applicability of the equations for calculating their HHV.

2. Materials and methods

2.1. Materials and sample preparation

Original samples of wood lignin from hydrolysis plants in Bobruisk, Belarus (LN-BBY), Rechitsa, Belarus (LN-R1BY, LN-R2BY, LN-R3BY, LN-R4BY), Kedainiai, Lithuania (LN-KLT), Kirov, Russia (LN-KRU) and lingosulphonate, Vyborg district, Russia (LS-VRU) were used as the test samples.

The preparation of general analysis samples for experimental measurements was performed according to ISO 14780:2017. Laboratory samples were pre-dried in the laboratory to an air-dry condition, ground in an electric mill to pass a sieve with mesh size of 0.25 mm.

2.2. Experimental measurements

Measurements of all experimental values were carried out with the same general analysis sample in parallel with its moisture content measurements.

Moisture was determined by drying 1–2 g at (105 ± 2) °C in the aluminum cylindrical container of 70 cm^3 to a constant weight for at least 3 h (ISO 18134–3:2015). Before removing the hot containers from the drying oven, they were tightly covered with lids, placed in a desiccator with anhydrous $CaCl_2$ and weighed after 15 min. The containers were opened for a few seconds before weighing.

A_w was determined by baking of ~1 g of preliminarily carbonized sample at 550 °C for 120 min in porcelain crucibles (ISO 18122:2015). The hot crucibles were kept in the air for 5 min after being removed from the oven, then placed in the desiccator and weighed after 15 min. In moisture determining the drying oven SNOL 24/200 was used, in the case ash the muffle furnace MIMP-3P was applied. The accuracy of temperature maintenance in the test chambers was ± 2 °C. Three parallel determinations were made during the measurements, with the maximum difference between the determinations not exceeding 0.2%.

HHV_w was determined according to ISO 18125:2017 using the bomb isoperibolic calorimeter BIC 100 with the water jacket described earlier [99]. Calibration of the calorimeter was carried out with a standard reference material – benzoic acid (calorimetric standard, trade mark K-3, VNIIM, St. Petersburg) which has a certified value of the specific energy of combustion equal to 26.454 ± 0.005 MJ kg^{-1}, when weighing in the air [100]. Certified conditions are T = 298 K, P = 2941955 Pa, m (benzoic acid), kg / V (bomb), m^3 = 3, m (water added to the bomb), kg/V (bomb), m^3 = 3. Samples of lignin weighing of 1.0–1.2 g were obtained with an accuracy of 0.1 mg with a Sartorius CPA 225D balance and burned as air-pressed pellets in heat-resistant stainless steel crucible. Copper wire of 0.5 mm diameter was used as a fuse. The correction for the combustion copper wire was made 0.013 kJ in all experiments. The repeatability of the measurement results averaged 0.05 MJ kg^{-1}, with a maximum discrepancy not exceeding 0.12 MJ kg^{-1}.

C_w, H_w and N_w were determined simultaneously according to ISO 16948:2015 using VarioEL III (Elementar Analysensysteme GmbH) and Flash 2000 (ThermoFisher Sci.). The weighted samples were 2–3 mg in the case of the Flash 2000 and 5–10 mg for the VarioEL III. The certified sample of sulfanilic acid was used to calibrate the instruments. Three parallel determinations were made during the measurements, with the maximum difference not exceeding 0.5 wt% for carbon, 0.2 wt% for hydrogen and 0.05 wt% for nitrogen.

S_w was determined by the gravimetric method through sulfate ions

Table 1
Equations for fuel HHV (MJ kg^{-1}) calculation.

Eq.	(1) HHV = *f* (C, H, O, S, N, Cl, P, A)	Basis	Fuel	Authors, year	Refs	*n*
(2)	HHV = 0.3383C + 1.443H − 0.1804O + 0.1047S	daf	coal	Dulong, 1820	[32]	1
(3)	HHV = 0.3408C + 1.444H − 0.1256O − 0.1256 N	daf	coal	Mahler, 1892	[16]	1
(4)	HHV = 0.339C + 1.256H − 0.109O + 0.109S	d	any fuel	Mendeleev, 1897	[16]	1
(5)	HHV = 0.3406C + 1.432H − 0.1532O + 0.1047S	daf	coal	Strache and Lant, 1924	[33]	1
(6)	HHV = 0.3391C + 1.444H − 0.1279O + 0.1047S	daf	coal	Steuer, 1926	[34]	1
(7)	HHV = 0.373C + 1.444H − 0.1444O + 0.1047S − 0.00026C^2	w	coal	Vondracek, 1927	[35]	1
(8)	HHV = 0.3391C + 1.4337H − 0.1273O + 0.0931S	daf	coal	D'Huart, 1930	[36]	1
(9)	HHV = (0.001486O + 1.0632)(C/3 + H − (O − S)/8)	daf	coal	Schuster, 1931	[37]	1
(10)	HHV = (0.0152H + 0.9875)(C/3 + H − (O − S)/8)	daf	coal	Grummel and Davis, 1933	[38]	1
(11)	HHV = 0.519C + 1.625H + 0.001O − 17.87	daf	coal	Seyler, 1938	[39]	1
(12)	HHV = 0.3403C + 1.2432H − 0.0984O + 0.1909S + 0.0628 N	daf	coal	Gumz; Michel, 1938	[40,41]	1
(13)	HHV = 0.3391C + 1.4445H − 0.2175O + 0.1047S	daf	coal	Sumegi, 1939	[42]	1
(14)	HHV = 0.3361C + 1.419H − 0.1453O + 0.0942S	daf	coal O < 15%	Mott and Spooner, 1940	[43]	2
(15)	HHV = 0.3361C + 1.419H − 0.1532O + 0.0942S + 0.0007O^2	daf	coal O > 15%			
(16)	HHV = 0.3517C + 1.1625H − 0.1109O + 0.1047S + 0.0628 N	daf	coal	Boie, 1953	[44]	2
(17)	HHV = 0.3517C + 1.1626H − 0.111O + 0.1047S	daf	liquid fuel			
(18)	HHV = 0.3414C + 1.4445H − 0.125O + 0.093S − 0.125 N + 0.125	daf	coal	Dulong – Berthelot	[17]	1
(19)	HHV = 0.3279C + 1.5045H − 0.1384O + 0.0926S + 0.02419 N − 0.1485 C_i	d	MSW	Wilson, 1972	[45]	1
(20)	HHV = 0.3417C + 1.323H − 0.1194O + 0.068S − 0.1194 N − 0.0153A	d	coal	IGT, 1978	[46]	1
(21)	HHV = 0.4373C − 0.3059	d	wood	Tillman, 1978	[47]	2
(22)	HHV = 0.4373C − 1.6701	d	biomass			
(23)	HHV = 0.7523H − 0.4654O − 0.2674S − 0.2802 N + 0.3814Cl + 35.8368	daf	MSW	Chang, 1979	[48]	1
(24)	HHV = 0.328C + 1.4306H − 0.0929S − 0.0237 N + (40.11HC^{-1}) + (1 − 0.01A) + 0.3466	d	biomass	Graboski and Bain, 1979	[49]	1
(25)	HHV = 0.4791C + 0.6676H + 0.589O + 1.2077S − 8.42	d	RDF	Jenkins, 1980	[50]	1
(26)	HHV = 0.3578C + 1.1357H − 0.0845O + 0.1119S + 0.0594 N	daf	liquid fuel	Lloyd and Devenport, 1980	[51]	2
(27)	HHV = 0.3578C + 1.1357H − 0.0845O + 0.1119S + 0.0594 N − 0.974	n/a	coal			
(28)	HHV = 0.3530C + 0.8712H − 0.0732O + 0.0696S	d, daf	brown coal	King and Attwood, 1980	[52]	1
(29)	HHV = 0.4608C + 1.4429H + 0.188S + 0.105A − 11.99	d	coal	Mason and Gandhi, 1983	[53]	1
(30)	HHV = 0.3578C + 1.1356H − 0.0854O + 0.1195S + 0.549 N − 0.974	n/a	liquid fuel	Francis and Lloyd, 1983	[54]	1
(31)	HHV = 0.301C + 0.525H + 0.064O − 0.763	d	biomass	Jenkins and Ebeling, 1985	[55]	16
(32)	HHV = 0.306C + 0.703H − 0.016O + 1.177	d	wood			
(33)	HHV = 0.322C + 3.754	d	biomass			
(34)	HHV = 0.293C + 5.205	d	wood			
(35)	HHV = 0.3278C + 1.419H − 0.1379O + 0.0926S + 0.637	n/a	coal	Given et al., 1986	[56]	1
(36)	HHV = 0.3394C + 1.3249H − 0.1253O + 0.1002S + 0.01465A	d	coal	Neavel et al., 1986	[57]	1
(37)	HHV = 0.3391C + 1.4340H − 0.097O	n/a	biomass	Abe, 1988	[58]	1
(38)	HHV = 0.3484C + 1.1526H − 0.1080O + 0.0628 N + 0.0394Cl + 0.2721P	n/a	biomass	Corbitt, 1989	[59]	1
(39)	HHV = 0.352C + 0.944H − 0.106O + 0.106S	n/a	vegetable oil	Beckman et al., 1990	[60]	1
(40)	HHV = − 14.104O/C − 21.2929O/H + 37.4541	daf	coal	Singh and Kakati, 1994	[61]	4
(41)	HHV = 0.2322C + 0.7655H − 0.072O + 0.0698S + 0.0419 N + 0.0262Cl + 0.1814P	daf	sewage sludges	Niessen et al., 1995	[62]	1
(42)	HHV = 0.335C + 1.423H − 0.154O − 0.145 N	daf	biomaterial	Demirbas et al., 1997	[63]	2
(43)	HHV = 0.512C + 0.512H + 84.07H/C − 16.46	d	coal	Mazumdar, 2000	[64]	3
(44)	HHV = 0.3491C + 1.1783H − 0.1034O + 0.1005S − 0.0151 N − 0.0211A	d	any fuel	Channiwala and Parikh, 2002	[20]	1
(45)	HHV = 0.3553C + 1.1286H − 0.1087O + 0.1087S	n/a	any fuel	Vandralek	[65]	1
(46)	HHV = 0.3708C + 1.1124H − 0.1391O + 0.1391S + 0.3178 N	d	MSW	Meraz et al., 2003	[66]	1
(47)	HHV = 0.4166C − 0.5700H + 0.2590O + 0.5990 N − 5.8291	d	MSW	Kathiravale et al., 2003	[67]	1
(48)	HHV = 0.4084C − 0.459	d	lignocellulosic	Demirbas and Demirbas, 2004	[68]	4
(49)	HHV = 0.3699C + 1.3178	d				
(50)	HHV = − 0.232C − 2.230H + 0.131 N + 0.00355C^2 + 0.0512CH + 20.6	d	biomass	Friedl et al., 2005	[69]	3
(51)	HHV = SR/0.31	d	any fuel	Zhu and Venderbosch, 2005	[70]	1
(52)	HHV = 0.4912C − 0.9119H + 0.1177O	d	sewage sludges	Thipkhunthod et al., 2005	[71]	14
(53)	HHV = 0.4925C − 0.9260H + 0.1176O + 0.0193S	d				
(54)	HHV = 0.3137C + 0.7009H + 0.0318O − 1.3675	d	biomass	Sheng and Azevedo, 2005	[72]	2
(55)	HHV = 0.3259C + 3.4597	d				

(*continued on next page*)

Table 1 (*continued*)

Eq.	(1) HHV = *f* (C, H, O, S, N, Cl, P, A)	Basis	Fuel	Authors, year	Refs	*n*
(56)	HHV = 0.3897C + 0.2976	d	biomass	Toscano and Pedretti, 2009	[73]	5
(57)	HHV = 0.4011C + 0.2943H + 0.0423O + 0.298S + 0.3407 N − 4.311	d				
(58)	HHV = 0.468C − 3.147	d	vegetable biomass	Callejón – Ferre et al., 2011	[74]	20
(59)	HHV = 0.507C − 0.341H + 0.067 N − 3.939	d				
(60)	HHV = 0.2949C + 0.8250H	d	biomass	Yin, 2011	[75]	1
(61)	HHV = (C^2 + 0.60C) + 0.03CH − O + 0.53S + 0.11ON + CO^2 − 0.33SO	d	biomass	Moka, 2012	[76]	1
(62)	HHV = 0.3425C + 1.274H − 0.1500O	daf	MSW	Komilis et al., 2012	[77]	3
(63)	HHV = 0.0743C + 3.5710 N + 11.7136	d	rice straw	Phayom et al., 2012	[78]	1
(64)	HHV = 0.3315C + 0.5388H	d	any fuel	Lasek et al., 2013	[79]	3
(65)	HHV = 0.3848C + 0.2266H − 0.0247O + 1.9768S + 0.0010 N + 0.0102A	d	biomass			
(66)	HHV = 0.3719C + 0.6463H − 0.0656O + 0.3408S + 0.0010 N + 0.0304A	d	any fuel			
(67)	HHV = 0.3409C + 2.692	d	holocellulose	Toscano et al., 2013	[80]	4
(68)	HHV = 0.4537C − 2.032	d	lignin			
(69)	HHV = 0.6398C − 10.026	d	oil			
(70)	HHV = 0.621C − 10.216	d	biomass			
(71)	HHV = 0.879C + 0.3214H + 0.056O − 24.826	d	biomass	Elneel et al., 2013	[81]	4
(72)	HHV = 0.824C + 0.2894H − 19.427	d	palm oil			
(73)	HHV = 0.348C + 1.243H − 0.111O + 0.112S − 0.1 N − 0.408	n/a	coal	Chelgani and Makaremi, 2013	[82]	1
(74)	HHV = 0.335C + 1.423H − 0.154O − 0.145 N	d	biomass	Singh et al., 2013	[83]	1
(75)	HHV = 0.367C + 53.883O/(2.131C^2 − 3.299) + (CH − 115.971)/(10.472H + 0.129CO) − 91.531/(35.299 + N) + 232.698/(77.545 + S)	d	biomass	Ghugare et al., 2014	[29]	1
(76)	HHV = 0.9872$C^{0.7587}$ + 0.6831$H^{0.3645}$ + 0.1055 $N^{3.2688}$ + 0.8620	d	biomass	Christoforou et al., 2014	[28]	1
(77)	HHV = 0.326C + 1.242H − 0.0915O + 0.0408S − 0.264 N + 0.132	d	MSW	Abidoye and Mahdi, 2014	[84]	5
(78)	HHV = 0.3384C + 0.2442	w	biomass	Garcia et al., 2014	[85]	4
(79)	HHV = 0.1545C + 0.001592C^2 + 7.464	w				
(80)	HHV = 0.3198C + 0.0803O − 1.4502S + 0.4704 N + 0.9364	d	livestock waste	Choi et al., 2014	[86]	10
(81)	HHV = 1.508H − 0.192O + 0.575S + 0.102 N − 0.205A + 17.830	d	tropical peat	Setyawati et al., 2015	[87]	1
(82)	HHV = 0.3489C + 1.98198	w	fruit biomass	Pérez – Arévalo et al., 2015	[88]	15
(83)	HHV = 0.251C + 1.068H + 0.011O − 1.114S − 0.328 N + 0.644	d	biomass	Singh et al., 2015	[89]	1
(84)	HHV = 0.3480C + 1.2442H − 0.1306O	daf	any fuel	Schmidt– Rohr, 2015	[30]	1
(85)	HHV = 0.350C + 1.01H − 0.0826O	d	MSW	Shi et al., 2016	[90]	4
(86)	HHV = 0.4078C − 0.0506H	d	wood	Maksimuk et al., 2016	[11]	1
(87)	HHV = 0.34C + 1.26H − 0.155O_C + 0.11S − 0.126O_H	daf	any fuel	Kholmansky et al., 2016	[91]	1
(88)	HHV = 0.2914C + 0.8741H	d	biomass	Qian et al., 2016	[31]	2
(89)	HHV = 0.344C + 1.217H − 0.106O + 0.105S − 0.015 N − 0.02A	d	biopolymer	Ioelovich, 2016	[92]	2
(90)	HHV = 0.431C + 0.367H + 0.283S + 0.645 N − 4.542	w	coal	Matin and Chelgani, 2016	[93]	1
(91)	HHV = 0.35C + 1.20H − 0.16O	d	biomass C < 50%	Han et al., 2017	[94]	2
(92)	HHV = 0.33C + 1.20H − 0.16O	d	plastic C > 50%			
(93)	HHV = 0.3743C + 0.9287	w	wood	Velázquez – Martí et al., 2017	[95]	10
(94)	HHV = − 0.5321C + 2.8769H + 0.0608CH + 0.2401 N + 0.0053C^2 + 32.7934	d	biomass torrefied	Nhuchhen and Afzal, 2017	[96]	16
(95)	HHV = 0.3115C + 0.7823H	d	biomass	Ozyuguran et al., 2018	[97]	48
(96)	HHV = 0.3984C + 0.4030H − 0.03153O − 1.8644S + 0.2791 N	d				
(97)	HHV = 0.4114C + 0.6114H + 0.0210O + 0.3888S + 0.2611 N − 4.9140	d				
(98)	HHV = 0.3880C + 0.4022H − 0.0354O + 0.1987 N	d				
(99)	HHV = 0.4042C + 0.3189H	d, daf	RDF	Galhano and Bordado, 2018	[98]	2
(100)	HHV = 0.4531C	d, daf				
(101)	HHV = 0.3699C + 1.3279H − 0.1387O	daf	any fuel	Merckel et al., 2019	[27]	3

basis – basis of data set, used the authors of equation, n/a – not available, w – on wet basis; d – on dry basis; daf – on dry ash-free basis, *n* – total number of equations in Ref.; MSW – municipal solid waste, RDF - refuse derived fuel, SR – is the stoichiometrical ratio of air determined by complete combustion to fuel; C_i – inorganic carbon; O_C and O_H – oxygen bonded with carbon and hydrogen, respectively

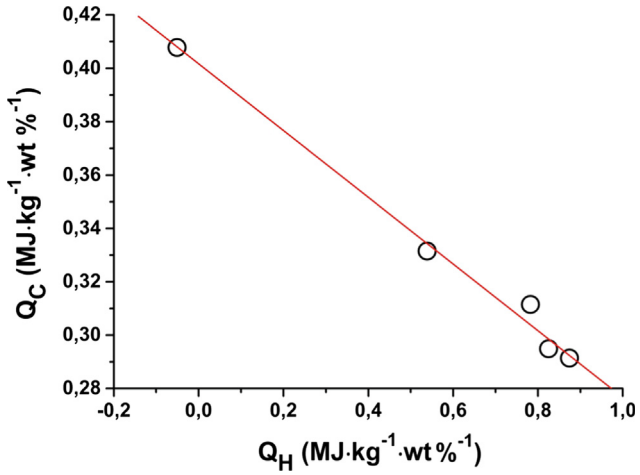

Fig. 1. Dependence of Q_C vs Q_H in equations of the type of (103) for Eqs. (60), (64), (86), (88), (95).

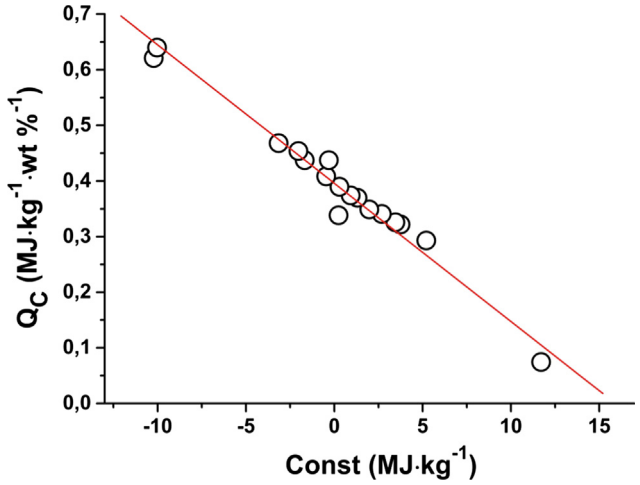

Fig. 2. Dependence Q_C vs. Const in equations of the type of (104) for Eqs. (21), (22), (33), (34), (48), (49), (55), (56), (58), (63), (67)–(70), (78), (82), (93).

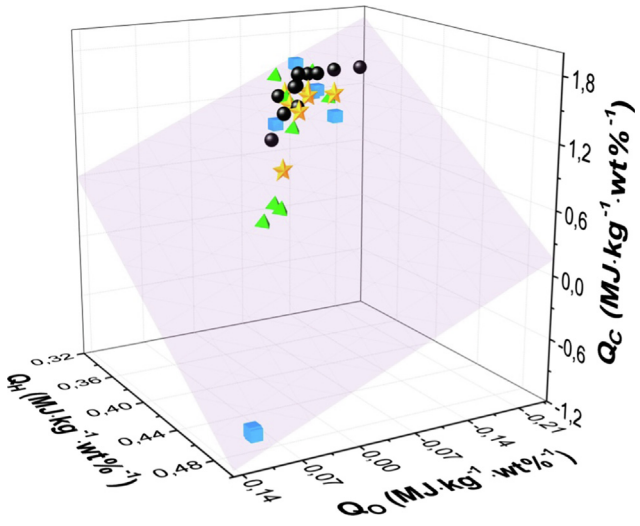

Fig. 3. Dependence of the Q_C, Q_H and Q_O (3D format) in the equations of the type of (105) for Eqs. universal ★ (4), (44), (45), (66), (84), (87), (100); coal ● (2), (3), (5), (6), (8), (12)–(14), (16), (20), (26), (28), (36); MSW ■ (19), (46), (52), (53), (62), (85), (92); biomass ▲ (37)–(39), (42), (65), (74), (89), (91), (96), (98).

precipitating from the calorimetric bomb washings with 10 wt% $BaCl_2$ solution.

Experimental values of HHV_w, A_w, C_w, H_w, N_w and S_w determined for the general analysis sample have been recalculated to HHV_d, A_d, C_d, H_d, N_d and S_d, respectively, taking into account moisture according to ISO 16993:2016.

3. Results and discussion

3.1. Analysis of equations for HHV calculation

It is reasonable to consider the questions of universality (applicability to different fuels) and independence of equations by checking the presence or absence of correlations between them. The basis is dropped from the predicting equations provided that the compositions and HHV are consistently used. The vast majority of equations are developed for a certain type of fuels (Table 1). *A priori*, the equations for coals are not applicable for calculation of HHV of the biomass and vice versa. However was found [49] that Eq. (20) [46] is quite acceptable for calculating HHV of the biomass and char. In the work [20] concluded that the equations for coals predict underestimated HHV values for biomass and overestimated values for MSW and sewage sludges. Rönsch and Wagner [101] confirmed that correlations developed for coals tend to underestimate HHV of the biomass, and was showed [23] that Eq. (54) for biomass [72] is not acceptable for calculating HHV of the coal. Peduzzi et al. [102] compared the HHV_d of the biomass values calculated from Eqs. (2), (15), (16), (20), (24), (44), (50), (54) and found that all models except Eq. (2) gave values close to the experimental data and average absolute error being within 1.9–2.4%.

A limited number of equations (4), (44), (45), (84), (87), (101), (16) apply for universal formulae. The most well-known and widely used empirical expressions belong to Mendeleev [16] and Channiwala and Parikh [20]. Calculated from these two Eqs., (4) and (44), HHV_d values for wood with C_d = 50 wt%, H_d = 6 wt%, O_d = 44 wt% differ by 0.3 MJ kg^{-1}, which corresponds to the reproducibility limit of the HHV_d calorimetric determination for solid biofuels according to ISO 18125:2017.

The equations from the Table 1, with the exception of Eqs. (7), (9), (10), (15), (24), (40), (43), (50), (51), (61), (75), (76), (79), (94) can be represented as

$$HHV = Q_C C + Q_H H + Q_O O + Q_S S + Q_N N + Q_{Cl} Cl + Q_P P + Q_A A + Const$$

The values of Q_C, Q_H, Q_O, Q_S, Q_N, Q_{Cl}, Q_P, Q_A and Const are independent of basis type (w, d, daf or waf). It means, that the basis of HHV in all equations will be determined by the type basis of C, H, O, S, N, Cl, P, A taken for HHV calculation, since the conversion HHV and C, H, O, S, N, Cl, P, A from one basis to another is carried out by the same formulas (ISO 16993:2016).

In our opinion, for comparative analysis of equations it is advisable to consider values of the first three coefficients (Q_C, Q_H, Q_O) and Const without reference to specific data sets. These values vary widely enough and Q_C, Q_H, Q_S are usually positive (+) and Q_O negative (−). The most "stable" is the Q_C, the numerical values of which are in the range from 0.29 to 0.48 MJ kg^{-1} wt%$^{-1}$ for 85% of the equations from the Table 1. This is due to the fact that HHV_{daf} of the carbon for the standard reference material Graphite EC-22 (VNIIM, St.Petersburg) is 32.792 ± 0.007 MJ kg^{-1}, which corresponds to Q_C = 0.33 MJ kg^{-1} wt%$^{-1}$. Equations obtained on the basis of statistical data processing only often contain Const and the coefficients, which have no physical meaning. For example, in the widely known Eq. (50) the main contribution is made by Const = 20.6 MJ kg^{-1}, while the Q_C, Q_H, Q_N and others, only slightly reduce it since HHV_d of the biomass varies in the range from 18.4 to 20.4 MJ kg^{-1} [102]. Thus, the applicability of the equation is determined not by the degree of "fundamentality" of its coefficients, but by the accuracy of the HHV values

Table 2
Composition (wt%) and HHV (MJ kg^{-1}) for lignin on dry basis.

Origin	C_d	H_d	S_d	N_d	O_d	A_d	HHV_d	Ref.
softwood (tree waste)	62.17	5.89	0.06	0.15	31.1	0.62	23.50	[103]
hardwood (yellow poplar)	51.20	5.70	0.24	1.07	38.4	3.40	21.45	
LignoBoost proccess	63.5	5.69	1.80	0.1	28.8	0.2	26.55	[104]
	66.0	6.18	3.19	0.2	23.0	1.4	27.23	
sulfuric/rape straw	58.2	5.62	1.54	3.29	29.7	1.62	24.70	[105]
hydrolytic/straw	57.8	5.7	0.14	1.2	23.0	12.1	22.8	[106]
H_2SO_4, pH 3/hemp, flax	63.64	5.93	0.49	1.18	28.3	0.43	25.88	[107]
Kraft Bukoza/H_2SO_4, pH 3	55.68	4.62	3.91	0.28	31.7	3.85	23.62	
HNO_3, pH 3/hemp, flax	62.06	5.91	0.01	1.85	28.3	1.91	25.23	
HCl, pH 3/hemp, flax	58.69	5.72	0.01	1.20	32.3	2.13	23.86	
CH_3COOH, pH 4.3/hemp	62.48	5.91	0.01	1.21	24.4	5.99	25.40	
CAS 8068–05-1	65.54	5.21	1.45	0.48	23.3	4.07	26.87	[108]
	56.82	5.21	1.32	0.11	34.6	2.92	23.25	[109]
	63	5.6	1.5	0.6	27	2.3	25.8	[110]
residue/rice straw	39	4.7	0.27	1.9	27	27.1	16.8	
	46	5.4	0.4	3.0	28	17.2	18.1	
	42	5.3	0.27	2.1	32	18.4	17.7	
alkaline liquor/rice straw	49	5.2	2.1	2.9	31	9.8	19.5	
Kraft, LignoBoost process	61.8	5.8	2.5	0.2	27.6	2.1	25.54	[111]
LN-BBY	55.6	5.26	0.89	0.19	28.0	10.05	22.98	this work
LN-R1BY	50.5	4.92	0.42	0.39	26.9	16.91	19.35	
LN-R2BY	56.3	5.27	0.17	0.29	32.2	2.79	22.50	
LN-R3BY	50.9	6.11	0.06	0.17	41.4	1.37	20.25	
LN-R4BY	55.8	5.66	0.06	0.23	35.7	2.52	21.75	
LN-KLT	57.6	5.14	0.32	0.38	24.4	12.20	22.88	
LN-KRU	64.2	5.26	0.10	0.07	28.4	1.92	25.98	
LS-VRU	43.4	4.61	5.27	0.59	26.2	20.0	17.74	

$O_d = 100 - C_d - H_d - N_d - S_d - A_d$.

obtained. Approximately half of the authors use the equations containing term Const, the value of which varies widely from −24.826 for Eq. (71) to 37.4541 MJ kg^{-1} for Eq. (40), and most of them are limited to Const value in the range from −6 to 6 MJ kg^{-1}.

In order to establish possible correlations between Q_C, Q_H, Q_O and Const we formed three groups of equations (despite the basis):

$$HHV = Q_C C + Q_H H \quad (103)$$

$$HHV = Q_C C + Const \quad (104)$$

$$HHV = Q_C C + Q_H H + Q_O O + (Q_S S + Q_N N + Q_{Cl} Cl + Q_A A) \quad (105)$$

Five Eqs. for biomass refers to the type of Eq. (103), 17 Eqs. for biomass - to Eq. (104), 37 Eqs. - to Eq. (105), of which 7 equations are universal, 13 for coals (including one liquid fuel), 10 for biomass, 7 for waste. We not considered Eq. (99) and Eq. (41) because of low accuracy [27].

A linear approximations $Q_C = f(Q_H)$, $Q_C = f(Const)$ and $Q_C = f(Q_H, Q_O)$ in equations of the type (103), (104), and (105), respectively was carried out by least square method. The following linear dependences are obtained

$$Q_C = (0.4011 \pm 0.0046) - (0.1240 \pm 0.0067)Q_H, R^2 = 0.99 \quad (106)$$

$$Q_C = (0.3961 \pm 0.0052) - (0.0242 \pm 0.0010)Const, R^2 = 0.97$$

$$Q_C = (0.4220 \pm 0.0036) + (0.0145 \pm 0.0748) Q_O - (0.0598 \pm 0.0088)Q_H, R^2 = 0.93 \quad (108)$$

and shown in Figs. 1–3, respectively.

The uncertainty of regression coefficients for the Eqs. (106) - (108) is calculated as a confidence interval at a probability of 95%.

Eqs. of the type (103) and (104) for calculation of HHV biomass are equivalent. Eq. (108) is obtained provided the inputs of other elements are small and can be neglected. Analysis of Fig. 3 and Eq. (108) shown that inputs of C, H and O are sufficient to estimate fuel HHV.

3.2. Development of the equation for prediction lignin HHV by the elemental composition

The results of experimental determinations for the lignin samples studied alongside with similar literature data are presented in Table 2.To check the applicability of different models for calculation of HHV_d of the lignin from Table 1, we chose 27 widely used and new equations developed for different fuels. Using the equations selected and taking elemental compositions from Table 2 we calculated HHV_d values and compared them with experimental ones. To estimate the deviations between the calculated and experimental values we used statistical parameters, which are usually applied in similar studies [69,75]: SER (standard error of prediction), AAE (average absolute error), ABE (average bias error). In addition, Table 2 data set was processed by the least squares method using one, two, three and five parameters. The results are shown in Table 3.To calculate HHV_d of the biomass, it is optimal to use equations with no more than two parameters [97]. The most appropriate way is to use the type of Eq. (103) taking into account the C and H, since in automatic analyzers carbon and hydrogen are determined simultaneously and H being used to calculate the lower heating value, which has practical significance [11]. From the equation Eq. (106) (Fig. 1) describing the dependence of the Q_C on Q_H in the equations of the type of Eq. (103), at $Q_H = 0$, we obtain the value $Q_C = 0.402 \pm 0.028$ MJ kg^{-1} $wt\%^{-1}$. Similarly, from Eq. (107) (Fig. 2) representing the dependence of Q_C on Const in the equations of Eq. (104) at Const = 0, we obtain the value of $Q_C = 0.396 \pm 0.025$ MJ kg^{-1} $wt\%^{-1}$. Both Q_C values agree (within the error of their determination) with the Q_C value from Eq. (109) obtained by linear processing of Table 2 data:

$$HHV_d = (0.4059 \pm 0.0024)C_d, R^2 = 0.999 \quad (109)$$

As it follows from the analysis of Table 3 the mutual consistency of experimental data for lignins from Table 2 with the value of AAE equal to 2.4% for Eq. (109) is at least 2 times worse than for wood fuels with AAE = 1.2% [11]. The lowest errors (AAE less than 3.2%) of Table 3 are obtained for three (Eqs. (4), (44), (66)) of the five universal equations; for all Eqs. (17), (20), (90) in the case of coal, for 6 Eqs. (22),

Table 3
Comparison of experimental and calculated HHV_d for lignin.

Eq.	Parameter	SER (MJ kg^{-1})	AAE (%)	ABE (%)	Ref.
	Eqs. for lignin				
(109)	C_d	0.68	2.41	–0.1	this work
(110)	C_d, H_d	0.68	2.38	0	
(111)	C_d, H_d, O_d	0.69	2.41	0	
(112)	C_d, H_d, O_d, S_d, A_d	0.64	2.33	0.1	
	universal Eqs.				
(4)	C_d, H_d, O_d, S_d	0.85	3.06	0	[16]
(44)	C_d, H_d, O_d, S_d, N_d, A_d	0.81	2.99	0.5	[20]
(66)	C_d, H_d, O_d, S_d, N_d, A_d	0.79	2.84	1.2	[79]
(84)	C_d, H_d, O_d	0.92	3.44	–1.4	[30]
(101)	C_d, H_d, O_d	0.99	5.44	4.9	[27]
	Eqs. for coal				
(17)	C_d, H_d, O_d, S_d	0.84	3.05	0.6	[44]
(20)	C_d, H_d, O_d, N_d, A_d, Const	0.90	3.18	–0.5	[46]
(90)	C_d, H_d, S_d, N_d, Const	0.75	2.88	–1.1	[93]
	Eqs. for biomass				
(60)	C_d, H_d	0.98	7.41	–7.4	[75]
(86)	C_d, H_d	0.68	2.58	–0.8	[11]
(88)	C_d, H_d	1.00	7.10	–7.1	[31]
(95)	C_d, H_d	0.91	4.95	–4.4	[97]
(22)	C_d, Const	0.73	2.59	0.2	[47]
(33)	C_d, Const	1.06	5.23	–4.7	[55]
(55)	C_d, Const	0.88	4.77	–4.3	[72]
(68)	C_d, Const	0.79	3.77	2.6	[80]
(93)	C_d, Const	0.71	4.16	–3.7	[95]
(24)	C_d, H_d, S_d, N_d, A_d	0.74	2.74	–0.6	[49]
(31)	C_d, H_d, O_d, Const	0.91	4.98	–4.5	[55]
(50)	C_d, C_d^2, C_dH_d, N_d, Const	0.77	2.60	–0.6	[69]
(54)	C_d, H_d, O_d, Const	0.94	7.41	–7.4	[72]
(79)	C_d, C_d^2, Const	0.87	6.65	–6.7	[85]
(83)	C_d, H_d, O_d, S_d, N_d, Const	2.17	14.7	–14.7	[89]
(89)	C_d, H_d, O_d, S_d, N_d	0.84	3.04	0.6	[92]
(97)	C_d, H_d, O_d, S_d, N_d, Const	0.67	2.46	–0.1	[97]
	Eqs. for MSW				
(77)	C_d, H_d, O_d, S_d, N_d, Const	0.86	3.50	–2.1	[84]
(85)	C_d, H_d, O_d	0.82	2.89	–0.3	[90]

(24), (50), (86), (89), (97) of the 16 equations for biomass and for one Eq. (85) of the 2 equations for MSW. This confirms the proposition that the main criterion for selecting an equation to calculate HHV_d of the lignin is the accuracy of the estimated values HHV_d, rather than the type of fuel for which the equation was originally developed.

4. Conclusions

1. The linear correlations $Q_C = f(Q_H)$, $Q_C = f(\text{Const})$ and $Q_C = f(Q_H, Q_O)$ indicate the equivalence of Eqs. (103), (104) and (105), respectively. The verification of applicability of 27 different equations and both with different number and type of parameters for calculation of the HHV_d for 27 lignins of different origin has shown that the accuracy of calculation of the HHV_d based on the elemental composition on dry basis is determined by numerical values of Q_C, Q_H, Q_O and poorly depends on the number of parameters and specificity of the equation according to the type of fuel.
2. It is possible to justify the adequacy of considering only C_d for prediction of HHV_d of the lignin as follows. In lignin, unlike wood or plant biomass, there are no extractives and its HHV_d is the sum of the HHV_{daf} of aromatic and carbohydrate parts. When hydrogen of carbohydrate part is burnt heat is not released because 50 wt% of hydrogen is in OH groups to which 50 wt% of hydrogen from C-H is added followed by the formation of water (H-OH), with C–H bond dissociation energy being approximately equal to H-OH bond energy. When hydrogen of aromatic part is burnt the heat released is added to the combustion heat of carbon of aromatic and carbohydrate parts, resulting in a higher value of $Q_C = 0.41$ MJ kg^{-1} wt $\%^{-1}$ in Eq. (109) as compared to $Q_C = 0.33$ MJ kg^{-1} wt$\%^{-1}$ for graphite.

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CRediT authorship contribution statement

Yury Maksimuk: Conceptualization, Investigation, Data curation, Methodology, Writing - original draft, Writing - review & editing. **Zoya Antonava:** Supervision, Writing - original draft. **Vladimir Krouk:** Formal analysis, Visualization. **Alina Korsakova:** Formal analysis, Visualization, Validation, Writing - review & editing. **Vera Kursevich:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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