

THE DETERMINATION OF HIGHER HEATING VALUE BY CALCULATION BASED ON ELEMENTAL ANALYSIS

*Markéta Kalivodová^a, Marek Baláš^a, Pavel Milčák^a, Hana Lisá^a, Martin Lisý^a, Jakub Lachman^a,
Petr Kracík^a, Peter Križan^b, Karel Vejražka^c*

^a*Energy Institute, Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic*

^b*Institute of manufacturing systems, Environmental technology and quality management, Faculty of Mechanical Engineering STU in Bratislava, Slovak Republic*

^c*Agricultural Research, Ltd., Zahradní 1, 664 41 Troubsko, Czech Republic*

Marketa.Kalivodova@vut.cz

Biomass has increasingly been used as a renewable energy source, and the possibility of using waste materials for energy purposes has recently been highlighted. Therefore, it is necessary to know the properties of these fuels. The most important is the Higher Heating Value (HHV), and also the Lower Heating Value (LHV), which expresses the amount of energy stored in the fuel. These are determined by an experiment but can also be determined by calculation. This paper deals with the comparison of existing equations for the calculation of HHV with the value determined experimentally by a calorimetric method. The suitability of using the given equation for the given fuels is evaluated. Based on the results of the applied equations, some of them are selected and recommended for the calculation of certain fuels.

Keywords: higher heating value, lower heating value, biomass, calorific value

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1. Introduction

In the field of the environment, new requirements and problems are constantly emerging, associated with the negative impacts of electricity and heat production. Dealing with them requires changes in production and consumption systems. In the energetics, the use of renewable resources, including biomass, can be considered at least a partial solution to these problems [1]. Biomass is a substance of organic origin, whether animal or vegetable, produced by photosynthesis. For energy purposes, it is primarily used either from purpose-grown crops or waste from agriculture, food or forestry production [2]. When these crops are burned, combustion conditions are very important in terms of emissions produced. [3-5]. Recently, there has been a strong emphasis on sustainability, which includes the management of waste materials that have the potential for energy valorization [6]. Combustion is the most frequently applied processing technology in the energy sector. Therefore, it is important to know the properties of the biomass fuel, especially the Higher Heating Value and Lower Heating Value. [7].

In addition to proximate and elemental analyses, Higher Heating Value and Lower Heating Value are among the most important properties of the fuel. They provide information, regarding the energy content of the fuel, about the energy that is released during its combustion. Usually, these quantities are expressed in MJ kg⁻¹ for solid fuels, in MJ l⁻¹ for liquid fuels and in MJ m⁻³ for gases [8]. The definition for Higher Heating Value and Lower Heating Value is as follows. HHV is the amount of heat that is released by the perfect combustion of the fuel sample and the subsequent cooling of the flue gases to the original temperature, while the water released by combustion condenses and the energy of the chemical reaction does not need to be reduced by its latent heat. LHV

is defined in the same way, but in the value of the latent heat of the vapor is not included, as the water remains in the gas phase in the flue gases [9]. The use of HHV or LHV depends on the region; in Europe LHV is more common, the Anglo-Saxon world uses HHV.

Knowledge of these two properties is important for the energetic use of biomass, whether in the design, selection, planning and operation of the biomass energy processing facilities [10]. HHV can be determined by several methods. The first approach is experimental determination using a calorimeter. However, the measurement is a rather complex and time-consuming process requiring necessary instrumentation and a mastered method of experiment and calculation. To determine HHV, two analyses must be performed for the fuel. These are the proximate analysis and the elemental analysis. Both analyses provide a basic characterization of the fuel [11]. Chun Yang Yin [8] states that the elemental analysis is more accurate than the proximate one. However, the elemental analysis is much more expensive because it requires more expensive analyzers. The proximate analysis is more cost-effective, faster, easier and requires only standard laboratory equipment. Based on these two analyses, numerous mathematical models have been developed to predict HHV fuels [11,12]. However, most of these mathematical models are based on the elemental analysis, as they are much more accurate than models based on the proximate analysis.

1.1. Determination of HHV by calorimetric method

The heat of combustion is determined by burning in a calorimeter. A small sample of fuel is burned in an oxygen atmosphere at a pressure of 3 MPa in the instrument to ensure a perfect combustion. The released heat is transferred to a water bath. The temperature difference of the

water bath is measured. The amount of heat released in the calorimeter is given by:

$$Q = mc_p \Delta t \quad (1)$$

The values determined by the calorimeter represent GHV (Gross Heating Value), which is then converted into a basic mass unit:

$$\text{GHV} = \frac{Q}{m_1} \quad (2)$$

HHV (Higher Heating value) is then determined according to the following equation [13]:

$$\text{HHV} = \frac{\text{GHV}}{1 - \frac{M_{\text{ad}}}{100}} \quad (3)$$

Then, the calorific value can be calculated from the known value of HHV, fuel humidity and hydrogen content in the fuel according to the equation [13]:

$$\text{LHV} = \text{HHV} - r \cdot (W^f + 8,94 H_2^f) \quad (4)$$

For this method of determination, it is necessary to know the water content of the fuel (W^f). Water in the fuel is closely related to LHV. The higher the water content of the fuel is, the lower LHV of the fuel is. Water concentration is usually known from the proximate analysis [14].

Another parameter that is necessary for the calculation of LHV is the hydrogen content. The determination of the hydrogen concentration is usually part of the fuel analysis. However, this process is time and money consuming. The hydrogen content of different fuels can also be found in the tables.

1.2. Determination of HHV from elemental analysis

In the past, many studies dealt with the search for approaches to determine HHV or LHV by calculation. However, most of the studies were devoted to coal. Both quantities can be calculated, usually from the elemental analysis. The elemental analysis determines the percentage of single-individual elements in a sample. This analysis results in values for the elemental content of the raw sample, the combustible sample and the anhydrous sample. From known elemental analysis data, HHV values can be determined without using the calorimetric method [15].

There are several equations determining the HHV. Some of them state Tab. 1 and Tab. 2. The first relationship (5) was introduced by French chemist P. Dulong, who made several assumptions [16]. The first was that the oxygen found in the fuel combustible is completely bound to hydrogen. Furthermore, the burning of hydrogen which is not bound to oxygen releases as much heat as the burning of molecular hydrogen gas. The last assumption was that the fuel behaves like a mechanical mixture of carbon,

burnable and non-burnable sulfur. The simplification of these equations later led to the bundle equations (6).

These equations were further investigated by Mendeleev who found that the relationships were not very suitable for fuels with higher oxygen content and considered some of Dulong's assumptions to be incorrect. In particular, the heat released by the combustion of hydrogen, which is bound in the solid and liquid fuel in the form of complex organic compounds, was considered to be 144 MJ kg^{-1} , which is the value corresponding to the combustion of gaseous molecular hydrogen. According to Mendeleev only the value of 125.6 MJ kg^{-1} can be considered. In addition, the idea that oxygen is bound not only with hydrogen but also with carbon, which will affect the final value of HHV, was also incorrect. And another assumption that fuel is considered a mechanical mixture of combustible carbon, hydrogen, sulfur and incombustible water is refuted by Mendeleev with the explanation that heat is released or absorbed at the formation of each chemical bond so that the combustion of chemical compounds cannot release as much heat as the separate combustion of their initial components. Therefore, he proposed his own relationship (7).

Over time, the equations were refined. Many relations for the determination of calorific value and heat of combustion have been proposed and derived, the most important ones, including the assumptions for their origin, are given in Tab. 1. It summarizes the equations applicable to coal.

At present, there is more focus on biomass. Biomass has many more forms than coal, so finding a reliable model is more challenging. The equations of the current authors are given in Tab. 2. These relationships should be relevant for biomass.

Biomass is characterized by a variety of properties of individual fuels. It is composed mainly of elements C, H and O, elements N and S have a minority. Different types of biomass have a different molecular structure. They differ in the content of cellulose, lignin and hemicellulose. Also, the amount of inorganic matter that turns to ash during combustion depends on the type of fuel. For example, wood biomass is relatively poor in inorganic substances, while their concentration in waste materials can be relatively high. Not only is fly ash an inert material, but they even reduce the calorific value by consuming the energy generated during the combustion for thermal decomposition and phase transformation of several ash components. Some types of biomass have a high volatile matter content, which is associated with a low fixed carbon content. The latter is closely linked to calorific value and positively influences the energy potential of biomass. Conversely, volatiles do not guarantee a high calorific value because they can be formed from unburnable gases such as CO_2 and H_2O [17].

The variability of these characteristics is reflected in the calorific value of the fuel. Because of the great variety of biomass fuel properties, it is not possible to define only one general equation that will perfectly apply to all types of biomass [18].

Tab. 1 Historical equations for the determination of HHV from element analysis for coal.

Author	Source	Equation	Assumption	Unit
Dulong 1843	[19]	$\text{HHV} = 338.3C + 1443\left(H - \frac{O}{8}\right) + 94.2S \quad (5)$	The oxygen in the combustible is completely bound to hydrogen, the combustion of atomic hydrogen releases the same amount of heat as the combustion of gaseous molecular hydrogen, the fuel behaves as a mechanical mixture of carbon, atomic hydrogen, burnable sulfur and unburnable water.	
Simplified bundle equations	[9]	$\text{HHV} = 339C + 1440\left(H - \frac{O}{8}\right) + 105S \quad (6)$	Based on Dulong's equations.	
Mendeleev 1837	[9]	$\text{HHV} = 339C + 1254H - 109(O - S) \quad (7)$	Suitable for fuels with a higher oxygen content, such as wood and peat.	
Strache, Lant 1924	[19]	$\text{HHV} = 340.6C + 1432.4H - 153.2O + 104.6S \quad (8)$	Modified version of Dulong's equation.	[MJ kg ⁻¹]
Steuer 1926	[9]	$\text{HHV} = 339.1\left(C - \frac{3}{8}O\right) + 238.6\left(\frac{3}{8}O\right) + 1441\left(H - \frac{O}{16}\right) + 104.7S \quad (9)$	Modified version of the Dulong equation. The fusion of oxygen with both carbon and hydrogen is considered.	
Grummel, Davis 1933	[19]	$\text{HHV} = (15.22H + 987.5) \cdot \left(\frac{C}{3} + H - \frac{O - S}{8}\right) \quad (10)$	The amount of heat released in a perfect combustion is proportional to the amount of oxygen or air consumed, this dependence is based on the hydrogen content of the fuel.	
Michel 1938	[9]	$\text{HHV} = 340.3C + 1243.2H + 62.8N + 190.9S - 98.4O \quad (11)$		
Boie 1957	[9]	$\text{HHV} = 351.7C + 1162.6H - 110.9O + 104.7S \quad (12)$	A more general equation that is based on properties of hydrocarbon fuels.	
Schuster 1957	[19]	$\text{HHV} = (1.0632 + 1.486 \cdot \frac{O}{1000}) \cdot \left(\frac{C}{3} + H - \frac{O - S}{8}\right) \quad (13)$	The amount of heat released in a perfect combustion is proportional to the amount of oxygen or air consumed, this dependence is based on the hydrogen content of the fuel.	[MJ kg ⁻¹]
Vondráček	[15]	$\text{HHV} = (373 - 0.26C)C + 1444\left(H - \frac{O}{10}\right) + 104.7S \quad (14)$	For fuels with a higher hydrogen content.	[MJ kg ⁻¹]

Tab. 2 Newer relationships for HHV determination from elemental analysis for biomass - current authors.

Source	Equation	Unit
[20]	$HHV = 0.3259C + 3.4597$ (15)	[MJ kg ⁻¹]
[20]	$HHV = -1.3675 + 0.3137C + 0.7009H + 0.0318O$ (16)	
[21]	$HHV = 3.55C^2 - 232C - 2230H + 51.2C \cdot H + 131N + 20600$ (17)	[MJ kg ⁻¹]
[20]	$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211$ * Ash (18)	
[22]	$HHV = -0.763 + 0.301C + 0.525H + 0.064O$ (19)	[MJ kg ⁻¹]
[23]	$HHV = 0.4373C - 1.6701$ (20)	
[8]	$HHV = 0.2949C + 0.8250H$ (21)	
[21]	$HHV = 1.87C^2 - 144C - 2820H + 63.8C \cdot H + 129N + 20147$ (22)	
[21]	$HHV = 5.22C^2 - 319C - 1647H + 38.6C \cdot H + 133N + 21028$ (23)	
[24]	$HHV = 357.77C - 917.58H + 84.51O - 59.38N - 111.87S$ (24)	[MJ kg ⁻¹]
[25]	$HHV = 140.96C - 602.14 \left(H - \frac{O}{8} \right) - 39.82S - \frac{89.29 \left(H - \frac{O}{8} \right)}{2} - 42.74 \cdot \frac{O}{2} - 10.4N$ (25)	
[26]	$HHV = -3.147 + 0.468C$ (26)	
[26]	$HHV = -1.642 - 0.024Ash + 0.475(C + N) - 0.376(H + N)$ (27)	
[26]	$HHV = 23.668 - 7.032H - 0.002Ash^2 + 0.005C^2 + 0.771H^2 + 0.019N^2$ (28)	
[27]	$HHV = 0.335C + 1.423H - 0.154O - 0.145N$ (29)	[MJ kg ⁻¹]
[28]	$HHV = 0.879C + 0.3214H + 0.056O - 24.826$ (30)	
[28]	$HHV = 0.924C - 22.403$ (31)	
[16]	$HHV = 0.341C + 1.322H + 0.0686S - 0.12(O + N) - 0.153 \cdot Ash$ (32)	

2. Materials and methods

The aim of this work is to compare the calculated HHV from the above equations and HHV determined experimentally by the calorimetric method. Another aim of the research is to find for a group of fuels the most accurate relationship for the determination of HHV using the elemental analysis. All experiments were repeated so that the accuracy of the results met the requirements of the standards.

2.1. Fuels investigated

The determination was carried out on 34 types of biomass fuels (see Tab. 3). Fuels contain dendromass samples (wood pellets, softwood and hardwood, wood chips, sawdust), phytomass (mustard, rye, spelt, safflower, amaranth, sunflower, hay, straw, flax, camelina, quinoa, crambe), alternative fuel samples (digestate, sewage sludge). The individual types of fuels were in the form of both processed and unprocessed. Specifically, mustard, rye and safflower were examined for their grains.

Sunflower, hay, straw, spelt and wood were pelletized. Softwood and hardwood were crushed into chips. The remaining species such as amaranth, flax-waste and quinoa-waste were used unprocessed. Digestate, safflower and flare were examined in processed (pellets) and unprocessed state. In the case of safflower, the seeds and the husks were examined separately.

The plant biomass contains combustible components that affect the calorific value of the fuel. Three of them - cellulose, lignin and hemicellulose, all organic polymers - are of the greatest importance. They are most abundant in wood. Their proportion varies depending on whether the wood is softwood or hardwood. Hardwoods contain more cellulose and hemicellulose, while softwoods have a higher proportion of lignin. Their percentage in hardwood is approximately 43 % cellulose, 29 % lignin and 28 % hemicellulose [29,30]. Wheat straw contains 33-40 % cellulose, 20-25 % hemicellulose and 15-20 % lignin [31], sunflower 34 % cellulose, 5 % hemicellulose and 8 % lignin [32].

2.2. Calorimetric methods

First of all, the HHV was determined experimentally by the calorimetric method, which consists of the burning a precisely weighed amount of sample in a semi-automatic calorimeter. This was done according to the standard ČSN ISO 1928. The weighed sample is burned in a pressure vessel with oxygen at high pressure up to about 3 MPa. The amount of heat obtained from the sample is compared with the amount of heat obtained by burning a similar amount of benzoic acid. The energy released by the combustion of the sample is absorbed in the calorimeter by the absorption medium and the resulting temperature change is recorded in the calorimeter. The resulting calorific value of the sample is determined based on measurements taken during the process, the effective heat capacity of the calorimeter and other energy additions from the combustion of the ignited cotton fiber and thermal effects from chemical reactions such as the formation of nitric acid [33].

For fuels such as amaranth, flax, camelina, digestate and quinoa waste, the samples had to be pelleted for combustion because of their tendency to fly out of the combustion cup to the bottom of the pressure vessel during their combustion in the calorimeter.

2.3. Proximate analysis

For the determination of HHV of 34 samples by calculation, the equations (5)–(32) were used. In order to make calculations, it is necessary to know the proportion of moisture, ash and combustible in the fuel. Then the proportion of individual elements that the fuel contains. To determine properties of the fuel, the proximate analysis is used. To determine the elemental composition of the fuel, the elemental analysis is used. The proximate analysis means the determination of the mentioned properties – water content, ash content and combustible content of a particular fuel.

To determine the moisture content, the fuel samples were dried in an oven according to the standard ČSN EN ISO 18134-3 [34]. A weighed sample of 1 g is dried in an oven in an accurately weighed uncovered container with a lid at (105 ± 2) °C to constant weight. After removal from the drying oven, the sample is placed in a desiccator with the weighing container already covered, where it is cooled to laboratory temperature. After cooling, the weighing container with the lid and the sample must be weighed again. The resulting moisture content of the fuel is calculated from the relationship:

$$M_{ad} = \frac{m_2 - m_3}{m_2 - m_1} \cdot 100 \quad (33)$$

The description of the determination of the ash content of solid biofuels is included in the standard ČSN EN ISO 18122 [35]. The method consists of burning the weighed fuel sample in a crucible in the furnace at a temperature (550 ± 10) °C under well-defined conditions. The sample is heated uniformly to temperature of 250 °C for 30 to 50 minutes. It will remain at this temperature for

an hour. Then the heating lasts 30 minutes up to the temperature (550 ± 10) °C again, where it shall remain for at least 120 minutes. The ash content in the anhydrous state is again based on a formula containing proportions of changes in mass [35]:

$$A^d = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \cdot \frac{100}{100 - M_{ad}} \quad (34)$$

For solid biofuels, the content of volatile flammable matter in the fuel is determined according to the standard ČSN EN ISO 18123 [36]. The method consists of heating the sample contained in a refractory crucible with a lid in an oven heated to (900 ± 10) °C for approximately 7 minutes. After this time, the crucible is transferred to a refractory plate outside the oven to cool for 5-10 minutes. The crucible is then further transferred to the desiccator and cooled to laboratory temperature. Once cooled, the crucible with the sample and lid is weighed. The content of volatile matter in anhydrous sample is given by [36]:

$$V^d = \left[\frac{100(m_2 - m_3)}{m_2 - m_1} - M_{ad} \right] \cdot \left(\frac{100}{100 - M_{ad}} \right) \quad (35)$$

2.4. Elemental analysis of fuel

The elemental analysis requires good laboratory equipment. It determines the percentage of elements N, C, H, S and O in a fuel sample. The individual contents can be related to the original sample, the anhydrous sample or the combustible.

The sample thus prepared can be weighed and tested. This consists in oxidizing the sample and converting the elements into gaseous products. This is followed by a purification, separation and determination of the selected components of the gaseous mixture. The apparatus used for the analysis was Vario Macro cube CHNS (Elementar company), which works on the principle of burning the sample in a catalytic tube. The released gases are separated by adsorption-desorption on columns and subsequently detected by a thermally conductive detector [37]. The measured concentrations of the individual elements in the original sample were further converted to the proportion of the combustible material and dry weight of the analyzed sample as indicated in [38].

3. Results and discussion

This chapter summarizes the results of the proximate and elemental analysis of fuels, the results of HHV determined by the calorimetric method and the computational method based on the elemental analysis.

3.1. Proximate and elemental analysis of samples

Established values for fuels examined are in Tab. 3. The highest proportion of volatile matter was contained in the spelt, followed by the camelina seed and the safflower husks, while the lowest was the sewage sludge

Tab. 3 Proximate and elemental analysis of fuels.

Category	Fuel	Form	Proximate analysis [%]			Elemental analysis [%]				
			Water W ^r	Ash A ^r	Volatile matter V ^r	N ^r	C ^r	H ^r	S ^r	O ^r
Wood	BIOMAC	Pellet	9.49	0.33	75.45	0.80	48.30	5.02	0.00	36.09
Digestate	Digestate	Pellet	8.90	13.84	61.26	2.00	38.25	4.83	4.03	29.38
	Digestate	-	13.79	16.52	61.37	2.00	38.25	4.29	4.03	23.40
Sewage sludge	Sludge	-	6.52	49.10	44.36	0.36	22.51	2.95	0.00	21.77
	Sludge	Unrotted	4.06	37.62	53.90	4.05	25.15	4.42	0.99	25.24
	Sludge	Pellet	10.97	45.93	43.37	3.23	25.38	2.96	1.62	14.95
	Sludge	Ground	10.05	44.69	43.43	4.03	26.37	3.58	1.12	14.66
	Sludge	Tiny lumps	16.07	40.40	43.16	4.47	28.25	3.04	0.76	13.50
	Sludge	Large lumps	6.65	47.52	44.50	3.34	26.23	3.49	2.01	13.92
Oilseeds	Mustard	Seed	2.46	7.74	78.16	5.02	52.37	7.77	1.08	24.33
	Camelina	Pellet	8.91	5.32	74.15	6.17	47.21	6.41	0.90	25.58
	Camelina	Seed	7.10	3.69	80.36	4.66	54.81	7.65	0.66	21.69
	Crambe	-	5.49	6.16	78.82	3.13	54.48	7.67	0.67	22.74
Kind- leaved	Amaranth	-	6.69	7.70	73.58	0.89	40.16	4.96	0.09	40.09
	Quinoa-waste 1	-	8.32	5.34	71.82	2.87	42.99	5.91	0.18	34.95
	Quinoa-waste 2	-	10.75	11.80	84.80	2.95	38.47	4.42	0.18	32.61
	Quinoa-waste 3	-	8.43	5.20	74.77	3.05	43.62	6.02	0.13	33.99
Grasses	Hay 1	Pellet	12.88	9.21	78.39	1.03	41.63	4.28	0.24	31.91
	Hay 2	Pellet	12.25	6.33	67.21	1.20	44.71	5.40	0.84	30.05
	Hay 3	Pellet	10.10	6.05	67.28	1.20	44.71	5.64	0.84	32.08
	Hay 4	Pellet	9.37	9.46	67.02	1.52	41.96	4.99	0.25	33.34
	Straw	Pellet	7.16	6.64	71.37	0.76	43.81	5.29	0.11	36.71
Seeds	Flax-waste	-	3.10	20.03	72.41	3.41	46.78	6.40	0.17	20.73
	Sunflower	Pellet	9.52	28.20	47.49	2.21	35.69	3.76	0.30	23.00
	Sunflower-after press	Pellet	6.09	6.04	75.73	3.67	50.85	7.29	0.20	26.22
	Sunflower- husks	Pellet	9.31	3.31	69.43	0.76	47.21	5.24	0.04	34.44
	Safflower	Pellet	7.08	3.96	74.34	2.70	48.14	6.08	0.04	32.28
	Safflower	Seed	7.23	2.42	75.79	2.29	52.55	6.71	0.01	28.95
	Safflower	Husks	5.49	2.97	79.15	1.67	50.82	6.58	0.01	32.74
Grains	Rye	Grain	10.88	2.16	77.02	2.81	41.74	5.58	0.05	37.02
	Spelt-waste	Pellet	8.06	4.82	81.30	0.68	44.98	5.15	0.19	36.51
Wood products	Sawdust	-	13.53	4.40	76.88	0.13	45.03	5.03	0.10	32.38
	Softwood	Wood chips	7.67	3.01	76.44	0.43	46.65	5.51	0.00	36.98
	Hardwood	Wood chips	7.84	2.44	76.34	0.60	46.33	5.29	0.00	37.69

(dried, tiny lumps). Most of the ash is contained in the sewage sludge and a minimum in wood pellets. The moisture content was the highest in the sewage sludge (dried, tiny lumps), minimum in mustard seeds. The low moisture content was also observed in the flax.

The examined fuels were divided into nine categories (see Tab. 3), individual crops were grouped according to the taxonomy. The sewage sludge and the digestate were grouped separately. Wood pellets from the manufacturer BIOMAC were used as a reference fuel. Some of the fuels were tested in different qualities - e.g. the quinoa-waste 1-3, where the number 1 indicates the best quality and the number 3 the worst (higher impurity content). For the hay, on the other hand, the numbering indi-

cates that the samples differ, e.g. by the location of origin or content of herbs. For some biomass samples, individual parts were examined separately (seed, husk).

Within each category, similar results for the proximate analysis and the elemental analysis can be found among the single-individual fuels, except for the flax and sunflower pellets. Their ash and volatile matter differ quite significantly from the fuels in the rest of the category.

The HHV values determined experimentally (see Tab. 4), are also very similar within the defined categories for each fuel. The only exception are sunflower pellets whose determined HHV is 28.7 % lower than the average HHV for the rest of the fuels in the Seeds category.

Tab. 4 GHV determined by the calorimetric method and HHV

Category	Fuel	Form	GHV [MJ kg ⁻¹]	HHV [MJ kg ⁻¹]	LHV [MJ kg ⁻¹]
Wood	BIOMAC	Pellet	18.24	20.15	18.81
Digestate	Digestate	Pellet	15.45	16.96	15.68
	Digestate	-	15.69	18.21	16.93
Sewage sludge	Sludge	-	11.45	12.24	11.44
	Sludge	Unrotted	8.01	8.35	7.28
	Sludge	Pellet	6.55	7.36	6.44
	Sludge	Ground	6.98	7.76	6.73
	Sludge	Tiny lumps	7.01	8.35	7.29
	Sludge	Large lumps	7.10	7.61	6.68
Oilseeds	Mustard	Seed	24.13	24.74	22.97
	Camelina	Pellet	20.94	22.99	21.36
	Camelina	Seed	25.15	27.08	25.22
	Crambe	-	25.35	26.82	25.01
Kind-leaved	Amaranth	-	16.31	17.48	16.23
	Quinoa-waste 1	-	17.70	19.31	17.80
	Quinoa-waste 2	-	15.60	17.48	16.24
	Quinoa-waste 3	-	18.00	19.65	18.13
Grasses	Hay 1	Pellet	15.97	18.34	17.08
	Hay 2	Pellet	16.17	18.42	16.94
	Hay 3	Pellet	16.63	18.50	17.01
	Hay 4	Pellet	16.36	18.06	16.73
	Straw	Pellet	17.24	18.57	17.23
Seeds	Flax-waste	-	20.32	20.97	19.49
	Sunflower	Pellet	14.26	15.75	14.70
	Sunflower-after press	Pellet	22.32	23.77	22.02
	Sunflower-husks	Pellet	19.52	21.52	20.14
	Safflower	Pellet	20.13	21.66	20.15
	Safflower	Seed	23.22	25.03	23.38
	Safflower	Husks	22.68	23.99	22.42
Grains	Rye	Grain	16.84	18.89	17.40
	Spelt-waste	Pellet	16.95	18.43	17.10
Wood products	Sawdust	-	15.60	18.04	16.60
	Softwood	Wood chips	18.21	19.72	18.32
	Hardwood	Wood chips	18.04	19.58	18.23

3.2. HHV determined by the calorimetric method

The calorific values of the individual fuels were determined using the calorimetric method (see Tab. 4). From the known HHV, the known moisture content of the fuels and the hydrogen content in the raw state of the fuel, LHV can be calculated according to the equation (4). The highest value of HHV 27.08 MJ kg⁻¹ was present in the seed of camelina. This oilseed crop has a relatively low water content of 7.10 % and the second highest volatile combustible content of the fuels studied (80.36 %). Even the elemental analysis shows that the crop could have good energetic potential. The hydrogen content in the anhydrous sample is the highest of the fuels investigated for the camelina. The Sewage sludge group has the lowest HHV (7.61–12.24 MJ kg⁻¹), which corresponds to the proximate analysis and the lowest hydrogen content of all samples.

3.3. HHV based on the elemental analysis

Calculations were made for all analyzed fuels according to the equations (5)-(32). Subsequently, the calculated values were compared with the result of the experiment according to this equation:

$$\text{Deviation} = 100 - \frac{\text{HHV}_{\text{calculated}}}{\text{HHV}_{\text{calorimeter}}} [\%] \quad (37)$$

The result of the equation is considered satisfactory if it does not differ by more than 5 % from the value obtained by the calorimetric method. Average deviations of the relationships used (± 5 % from the experimental result) for each category are shown in Tab. 5. Based on the specified deviations, equations that provided the results with the greatest accuracy are selected (Fig. 1).

Tab. 5 Deviations of calculated HHV.

Equation No.	Wood	Digestate	Sewage sludge	Oilseeds	Kind-leaved	Grasses	Seeds	Grains	Wood products
(5)	-6.4 %	-2.8 %	41.8 %	0.7 %	-9.8 %	-1.7 %	-3.8 %	-6.5 %	-2.7 %
(6)	-6.2 %	-2.4 %	42.1 %	0.9 %	-9.7 %	-1.5 %	-3.6 %	-6.4 %	-2.5 %
(7)	2.7 %	4.3 %	49.6 %	2.2 %	-0.6 %	6.8 %	0.9 %	3.2 %	6.5 %
(8)	-0.7 %	2.3 %	48.3 %	3.6 %	-3.9 %	4.0 %	0.3 %	-0.4 %	3.2 %
(9)	-15.5 %	-17.7 %	13.5 %	-25.8 %	-22.3 %	-15.2 %	-22.9 %	-18.5 %	-14.6 %
(10)	-2.4 %	-0.7 %	38.9 %	1.4 %	-6.7 %	1.4 %	-2.4 %	-2.8 %	1.1 %
(11)	5.1 %	9.1 %	56.0 %	4.8 %	2.6 %	9.6 %	3.2 %	6.2 %	8.8 %
(12)	3.2 %	4.3 %	49.3 %	2.0 %	-0.7 %	6.9 %	0.9 %	3.1 %	6.7 %
(13)	2.2 %	3.2 %	44.9 %	0.8 %	-2.8 %	5.4 %	-0.4 %	1.3 %	5.3 %
(14)	6.3 %	9.4 %	59.3 %	8.8 %	3.4 %	11.3 %	6.4 %	7.0 %	10.5 %
(15)	3.5 %	-0.3 %	52.6 %	-15.1 %	-1.5 %	4.6 %	-7.5 %	2.2 %	5.2 %
(16)	1.9 %	-4.8 %	29.3 %	-12.1 %	-2.0 %	3.3 %	-7.9 %	2.4 %	4.7 %
(17)	5.4 %	-1.0 %	73.4 %	-4.9 %	-1.1 %	5.1 %	-3.0 %	2.8 %	6.3 %
(18)	4.3 %	3.3 %	39.0 %	1.8 %	-0.4 %	7.3 %	0.6 %	4.0 %	7.6 %
(19)	3.1 %	-4.2 %	31.4 %	-14.7 %	-0.6 %	4.2 %	-8.6 %	3.8 %	5.7 %
(20)	7.5 %	-2.1 %	29.3 %	-11.1 %	-2.2 %	6.1 %	-5.4 %	3.3 %	8.1 %
(21)	0.8 %	-3.4 %	37.8 %	-10.2 %	-2.0 %	3.3 %	-6.7 %	1.9 %	4.1 %
(22)	4.9 %	-1.2 %	71.0 %	-4.5 %	-1.2 %	5.0 %	-2.9 %	2.7 %	6.1 %
(23)	5.6 %	-1.1 %	75.4 %	-5.5 %	-1.2 %	4.9 %	-3.3 %	2.7 %	6.2 %
(24)	-14.0 %	-28.3 %	-4.8 %	-43.3 %	-24.5 %	-18.2 %	-32.0 %	-19.6 %	-15.2 %
(25)	-82.3 %	-85.4 %	-81.1 %	-90.9 %	-82.8 %	-82.9 %	-87.4 %	-81.9 %	-82.1 %
(26)	8.3 %	-3.0 %	22.1 %	-10.2 %	-2.7 %	6.1 %	-5.1 %	3.2 %	8.6 %
(27)	7.7 %	-4.5 %	17.4 %	-12.8 %	-4.2 %	4.2 %	-7.5 %	1.7 %	6.6 %
(28)	12.3 %	-4.0 %	5.2 %	25.1 %	5.0 %	11.4 %	9.3 %	10.9 %	14.7 %
(29)	-3.2 %	-4.0 %	37.6 %	-1.2 %	-7.9 %	0.8 %	-3.2 %	-3.9 %	1.0 %
(30)	29.5 %	-6.5 %	-69.9 %	9.4 %	2.0 %	17.5 %	7.1 %	14.9 %	26.2 %
(31)	33.6 %	-0.6 %	-52.4 %	13.3 %	4.3 %	21.4 %	11.6 %	17.1 %	29.5 %
(32)	2.4 %	1.1 %	36.8 %	0.7 %	-2.7 %	5.7 %	-0.4 %	1.9 %	6.3 %

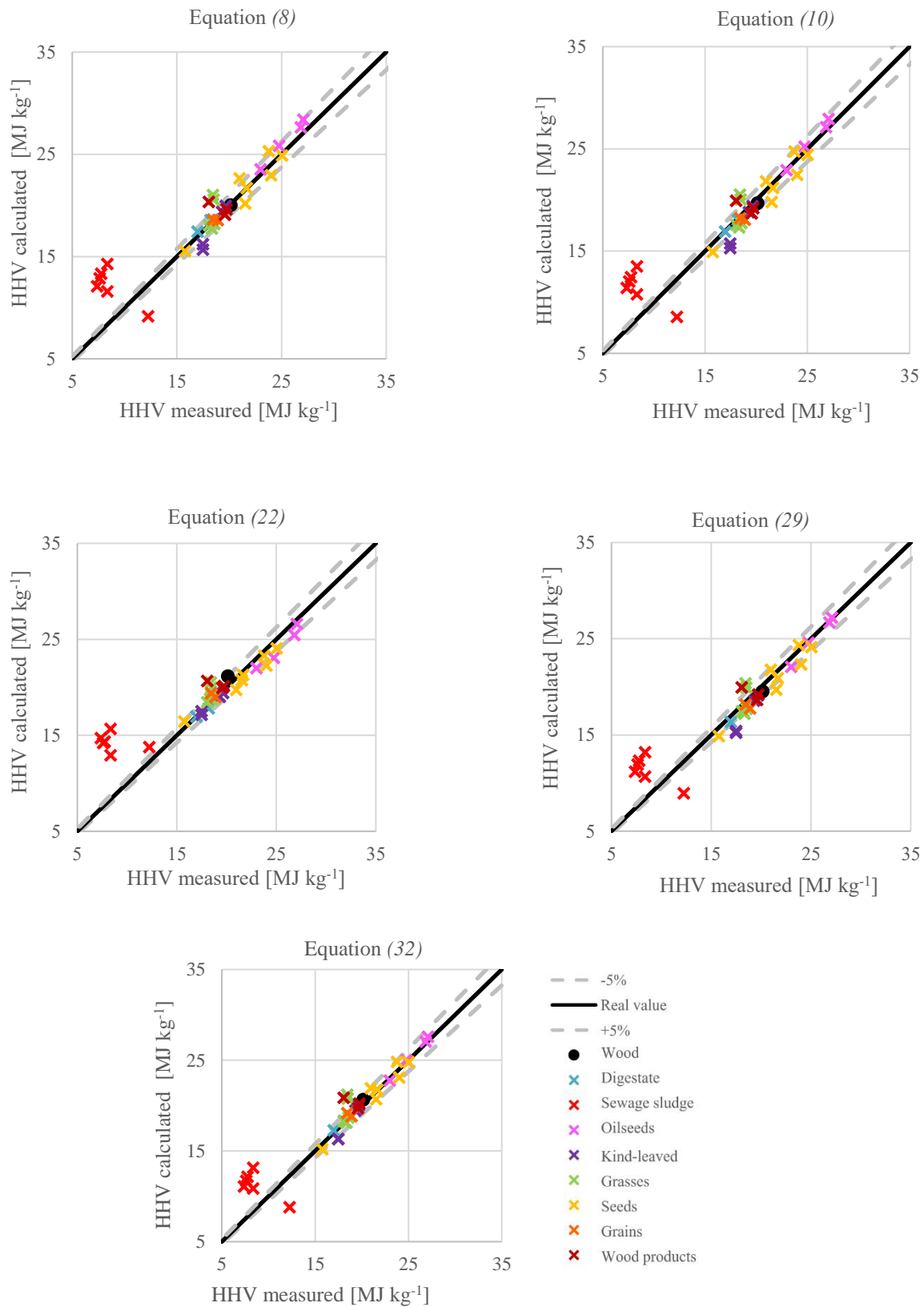


Fig. 1 Graphical representation of the results of the most accurate equations and their deviations.

The results of equations that do not differ from the measured HHV by more than 5 % are highlighted in Tab 5. It is noticeable that the most accurate results were provided by the equations (8), (10), (22), (29) and (32). Equation (8) by Strache and Lant, see Fig. 1, has, in terms of frequency of results in tolerance $\pm 5\%$, the highest success rate. However, in terms of accuracy, the largest frequency of results with the smallest deviations is shown in equation (10) by Grummel and Davis, see Fig. 1. The equation (32) by Milne also shows high accuracy, see Fig. 1. The latter equation is used most abundantly in practice to calculate HHV.

Results of equations (22) and (29), see Fig. 1, are also satisfactory for most types of fuels they work quite accurately, but not as much as the equation already mentioned (10). In the Fig. 1, it can be observed that the category of Sewage sludge forms a regular cluster, and it almost does not matter which equation is used for the calculation. Thus, it can be concluded that the equations used for the calculation of HHV are not suitable for the sewage sludge.

The surprising result is that the equations work much better for some biomass groups than for wood. For

wood pellets, which were used as a reference fuel, only 13 equations out of 28 show satisfactory accuracy in the calculation of HHV. For wood products, such as sawdust, softwood and hardwood chips, the satisfactory results are 7 of 28 which is much less. The lowest success of the calculations was for the group of sewage sludges, where any of equations came out within the required tolerance, which could be expected, because the used equations are primarily intended for the HHV calculation of the coal and biomass. The best results were achieved for the categories Digestate, Kind-leaved and Grains.

The selected equations that had the best results express the dependence on the content of C, H, O, S (equations (8), (10)); C, H, N (equation (22)); C, H, O, N (equation (29)), or on C, H, O, N, S, Ash (equation (32)). Fig. 2 shows the dependence of HHV on the different fuel components. Only for C, H and ash a certain linear dependence can be observed - higher C and H content precedes higher HHV values and the opposite is true for ash, whose high content means low HHV values. From the sensitivity analysis performed, no linear effect of O, N and S content on HHV values was clearly demonstrated.

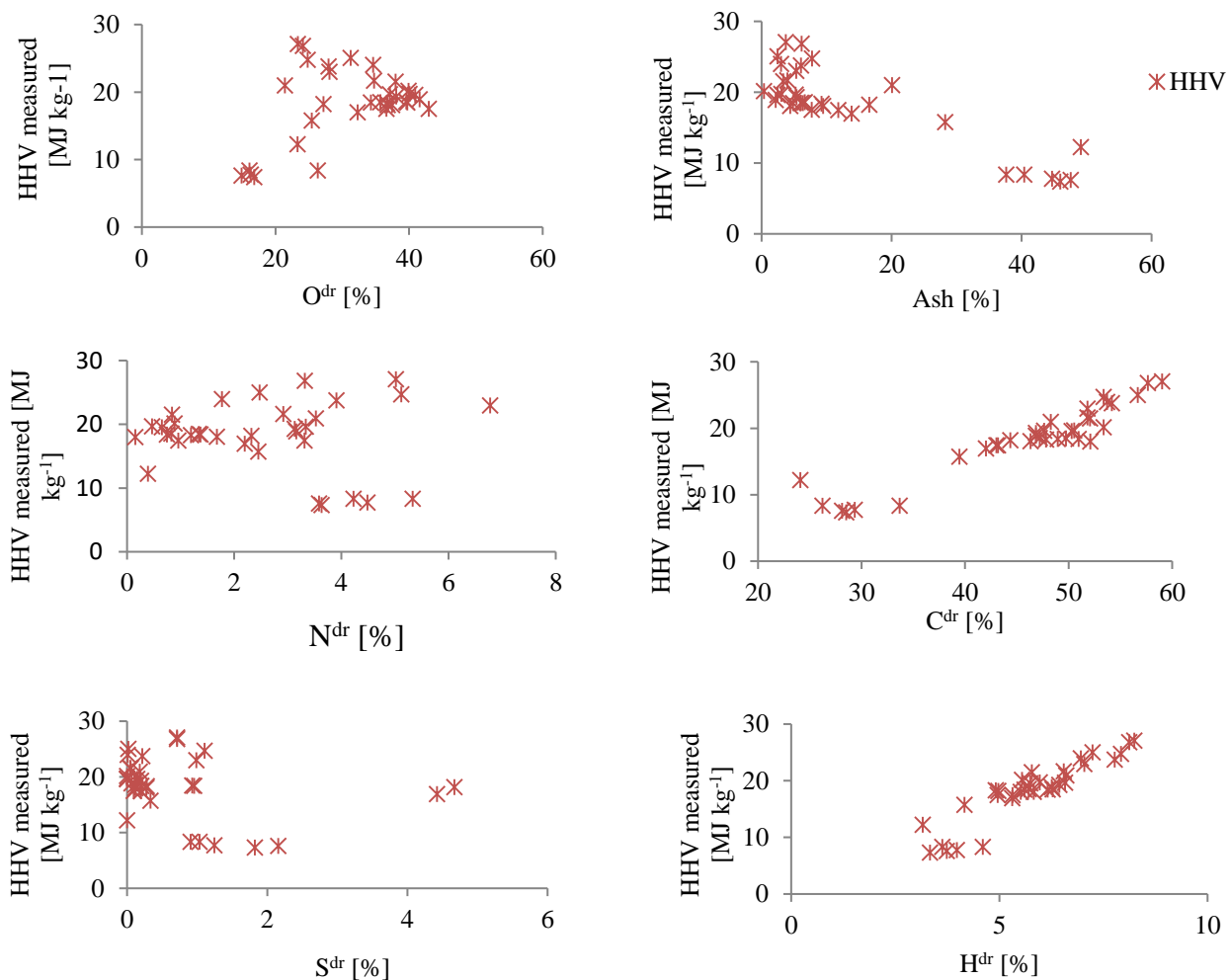


Fig. 2 Dependence of HHV on fuel composition.

4. Conclusion

For the calculation of HHV, 28 equations were selected with regard to their applicability for focusing mainly on the biomass. These equations are based on the dependence of HHV on the elemental analysis of the fuel (and in some cases the ash content). Most of these equations were reasonably well applicable to several biomass types. In the study, the investigated fuels were divided into different categories and for some of them (Kind-leaved, Grains and Digestate) the vast majority of used equations were suitable. The most accurate results were obtained using equations (8) and (10). However, only one equation out of 28 was suitable for calculating the HHV of the sewage sludge. Surprisingly, less than half of these equations were suitable for wood pellets, wood chips or the sawdust. Since the equations used were based on the elemental analysis, the dependence of calorimetrically determined HHV on the elemental and the ash content of the fuel was investigated. A linear dependence was demonstrated only for C, H and ash. Therefore, it is possible to use formulas involving only C, H and Ash with sufficient accuracy.

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List of symbols and abbreviations

A	Ash content in fuel (%)
c_p	Specific heat capacity ($J K^{-1} kg^{-1}$)
GHV	Gross Heating Value ($MJ kg^{-1}$)
HHV	Higher Heating Value ($MJ kg^{-1}$)
LHV	Lower Heating Value ($MJ kg^{-1}$)
m_1	Weight of empty crucible (g)
m_2	Weight of crucible with sample and lid before analysis (g)
m_3	Weight of crucible with sample and lid after analysis (33), (35); weight of crucible with ash (34)
M_{ad}	Percentage by mass of the water content of the analytical sample for general analysis determined in accordance with ISO 18134-3 (%)
Q	Heat required to heat the solid in the calorimeter (J)
r	Heat of vaporization of water ($MJ kg^{-1}$)
W^r	Water content of the fuel (wt. %)
x^d	Anhydrous fuel sample
x^h	Flammable content of fuel

x^r Fuel sample in its original raw state

Δt Temperature difference (K)

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