

1 **Spanish biofuels heating value estimation. Part I: Ultimate analysis data**

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5

6 **Abstract**

7 Due to the great variety of existing potential biomass fuels, measuring their heating
8 value accurately is a previous design requirement, since this is one of the most
9 important parameters regarding the evaluation of competitive energy generation from
10 biomass combustion. In this work, the higher heating value (HHV) of 100 different
11 biomass samples was experimentally determined. The list of biofuels tested includes
12 different kinds of solid densified commercial fuels, forest and agricultural industry
13 residues, woody and herbaceous residues, energetic crops and cereals.

14 Ultimate analysis-based equations were used to develop a correlation between data, in
15 order to quantify the detected dependence of HHV on mainly carbon and oxygen
16 content. A comparative study was carried out between our results and those predicted
17 from theoretical equations found in the bibliography.

18 The wide experimental database enables us to propose new predictive correlations, with
19 departures from experimental values below 6 % in all cases, as a contribution to the
20 characterization and normalization of solid biofuels.

21 Keywords: Biomass, higher heating value, elemental analysis.

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1. Introduction

The continuous increase in mankind's energy demand over the last few decades is a widely known and reported phenomenon [1]. This fact, combined with the unstable situation of traditional fossil fuels and some advantages of biofuels, such as their neutrality regarding greenhouse effect [2] and low NO_x and SO_2 emissions. In addition to the cheapness and autonomy of the resource [3], makes biomass an attractive feedstock to effectively complement fossil fuels in the energy mix. Because of that, biomass constitutes one of the most important energy sources, providing, more or less, a 14 % of the global energy requirements, contributing from a 9 to a 90 % of each country's energy consumptions, depending on whether they are industrial or developing ones [4].

In this way, a comprehensive characterization of biomass is required, in order to have reliable knowledge of its properties as a fuel, mainly by the experimental determination of its ultimate and proximate analysis and higher heating value by calorimetry. (See Fig.1, where FC qualitatively represents fixed carbon, VM volatile matter, X moisture content, I inerts and A ash, the chemical elements being expressed with their normalized symbols).

Other interesting experimental characterizations can be carried out, such as those based on thermal behaviour or gaseous emissions, which are developed in other works [5].

The heating value, or combustion heat, can be defined as the energy contained in a sample of a given material, and can also be defined with respect to two different references, higher heating value (HHV) and lower or net heating value (LHV).

“Higher heating value” (HHV) refers to the heat released in a combustion reaction, taking into account the fact that the original and process-generated water was in the condensed liquid state. These data are experimentally obtained using a calorimetric

51 bomb, with samples being at their initial moisture content (“as received”, a.r.). On the
 52 other hand, the “lower heating value” (LHV) is based on considering gaseous water as a
 53 product, with the energy needed to evaporate water not being computed as useful heat.
 54 Because of this, it is essential to measure the LHV value at dry base, if the value of the
 55 sample moisture content is not clearly indicated by researchers, heating value data
 56 cannot be compared [6]. Fig. 2 graphically shows the difference between HHV and
 57 LHV of fuels, ΔH being the heats of transformation as a variation in the internal energy
 58 at constant volume or as a variation in enthalpy at constant pressure.
 59 There exists a great amount of correlations based on the activity of water that enable the
 60 calculation of LHV from HHV data considering moisture at dry or wet base when
 61 moisture content is known.

62 Fig. 3, based on simple mass balances, is a guide for any conversion between these
 63 parameters, LHV_w and HHV_w , being respectively, the lower heating value and the
 64 higher heating value of the wet samples and LHV_d and HHV_d the lower and higher
 65 heating values corresponding to the dry samples. ΔH_b is the specific heat of
 66 vaporization of water in the experimental conditions (habitually, a value between 582
 67 and 665 kcal·kg⁻¹ [7]). X is the mass moisture content ratio in dry basis,

$$68 \quad X = \frac{m_m}{m_d} = \frac{m_w - m_d}{m_d} \quad (1)$$

69 being m_w the mass of the wet sample, m_m the mass of retained water as moisture
 70 content and m_d the mass of dry solid.

71 Thus, the most useful values in practice (water vapor is frequently lost, totally or in part,
 72 in full scale burners as exhaust flow) may be derived from the experimental data as
 73 follows, e.g.:

$$74 \quad LHV_d = HHV_w(1 + X) - \Delta \hat{H}_b X \quad (2)$$

$$LHV_w = \frac{HHV_d - \Delta \hat{H}_b X}{1 + X} \quad (3)$$

76 Among all the options to calculate HHV of different biofuels through correlations, there
77 are three kinds of models based on ultimate and proximate analysis, physical properties
78 and chemical composition.

79 Some years ago, due to the scarce information concerning heating values estimation in
80 biofuels, coal-formulated correlations were normally used, being Dulong's, Steuer's,
81 Scheuer and Kestern's or Boie's equations some of the most common ones. It seems
82 important to mention Channiwala's and Parikh's works [8, 9] which try to obtain a
83 general equation applicable to every kind of fuel, and made a review of the ultimate
84 and proximate analysis data-based equations, justifying more than twenty of the most
85 important ones, comparing and validating them for applications to other fuel types.

86 Then, newer correlations were obtained using biomass-specific data. This group
87 includes the ones developed for urban solid wastes (MSW) [10, 11, 12, 13], for example
88 plastic, wood, textile, paper and agricultural residues and sewage sludge.

89 This paper is envisaged as the first part of a global work including higher heating value
90 predictive equations obtained from ultimate and proximate analysis data and
91 correlations compressing both analyses, to compare the obtained results with the
92 previously mentioned 48 equations found in the bibliography. In this first part, only
93 ultimate analysis data are considered (this means carbon, hydrogen, sulphur, nitrogen
94 and oxygen composition), leaving proximate analysis based and hybrid expressions for
95 the second part. The main aim is to obtain a group of empirical equations as simple as
96 possible, this meaning, first or second order ones or a linear combination of data, which
97 **depend** on a low number of parameters. Thus, we can reduce the experimental process
98 as much as **possible**, avoiding complex calculations and may support the regulation of

99 the commercial solid single or mix biofuels. These equations were tested with our
100 experimentally obtained data bank of one hundred Spanish based samples.

101 2. Material and methods

102 2.1 Samples

103 The definition of solid biomass embraces a great variety of different raw materials and
104 wastes, and generates a wide range of criteria for the characterization of those potential
105 fuels. Thus, based in our experimental data, determinate reliable relationships between
106 composition in carbon, hydrogen, oxygen, sulphur and nitrogen and the heating value of
107 the Spanish woody and herbaceous biomass samples is of huge interest. Since the same
108 sample, for example pine, may have different composition depending on its sub-species
109 or origin.

110 The samples analyzed belong to different families of solid biofuels, such as commercial
111 fuels (CF), industry wastes (IW), forest wastes (FW), which includes two other groups,
112 branches (FW-B) and leaves (FW-L), energetic crops (EC) and cereals (CER) allowing
113 us to accurately formulate with high accuracy a predictive equation valid for a wide
114 range of Spanish based solid biomasses (see Tables 1.1. and 1.2).

115 The group of commercial fuels is made up of an average value of several commercial
116 brands of wood pellets, beet pellets, olive stones, pine cone leaves, pine kernel shells
117 and firewood, obtained from different suppliers of commercial solid biofuels in Spain.
118 Husks and stones were obtained from agricultural-industries. Shavings, sawdust and
119 firewood are all residues of the wood-transforming industry. Chestnut, hazel, alder,
120 eucalyptus and pine samples were obtained from local woods pruning. Energetic crops,
121 such as straw, miscanthus, oats and vetch straw, triticale, sainfoin and cereals were
122 supplied by some agricultural cooperatives also located in Spain too. Every sample was

123 air-dried to release external moisture and grinded and sieved to 1mm particle diameter
124 as indicated in the ASTM normative for HHV determination.
125 From all the available experimental databases of HHV, already published [3], enduring
126 the use of one hundred samples with known ultimate analysis were selected, making
127 sure to choose the same database in both parts of the research, which allows us to
128 compare the obtained results between ultimate and proximate obtained equations (see
129 Tables 2.1. and 2.2. where C,H, O, N,S are the weight percentage of carbon, hydrogen,
130 oxygen, nitrogen and sulphur respectively.)

131 **2.2 Calorimetry**

132 The experimental equipment used in this work was an IKA Werke C5000 Control
133 calorimetric bomb, suitable for routine HHV determinations. Determining this requires
134 the combustion to be developed under conditions established by standard normative, in
135 this case ASTM E-711 [20, 30, 31].

136 To perform the experiments, the ‘as received’ sample is grinded, sieved to 1 mm,
137 pressed into a tablet shape to avoid sparks and incomplete combustion and then
138 weighed.

139 To secure and reliable reproducibility, experiments are developed three times each,
140 obtaining an average value of the sample which is shown in Tables 2.1 and 2.2.

141 Obtained standard deviations are not mentioned again in this work, but they can be
142 consulted in the original research used as database [3]. Scientific names of the plant
143 where each sample comes from are also specified in these tables, except if the sample is
144 a mix of unknown origin, e.g. wood pellets, to make identification easier, trying to
145 assure data truthfulness and process reliability.

146 **2.3 Ultimate analysis**

147 Ultimate analysis of samples is expressed as C, H, N, O and S percent weight content of
148 the samples. C, H, O are the most important components of biomass. C and H are
149 exothermically oxidized to CO₂ and H₂O, in the expected case of complete combustion
150 so they contribute positively to HHV, while O is reduced and contributes negatively to
151 it. The necessary O is supplied by O bonds of biomass matter, and the rest of it is taken
152 from air injection. N is almost totally converted to gaseous N₂ and NO_x, the latter being
153 the last one of the most important environmental impact of biomass combustion. N₂O
154 amounts obtained are very low in modern biomass combustion chambers. On the other
155 hand, significant quantities of N are borne in the ashes. S contained in solid biofuels
156 produces gaseous SO₂, which is a contaminant emission, or sulphates, which condensate
157 on chamber walls and ashes [18, 32].

158 These analyse are carried out using a Perkin-Elmer 2004 elemental analyzer, in CHNS
159 mode, which enables the simultaneous determination of the carbon, hydrogen, nitrogen,
160 and sulphur content of organic samples, according to the Pergl-Dumas method. This
161 involves the complete combustion of the sample and reducing it to a group of gases
162 (CO₂, H₂O, N₂ and SO₂) which are captured, separated by frontal chromatography and
163 finally measured by a thermal conductivity probe. As oxygen determination is not
164 possible with this equipment, this element is determined by difference [20]. This
165 method is used by several author's [33, 34, 35, 36] with some differences when
166 calculating O%, such as considering ash percentage or not. In this work, finally,
167 Ghetti's experience [36] was followed, so oxygen apparent percentage was calculated
168 as:

$$O = 100 - (C + H + N + S) \quad (4)$$

169 where O, C, H, N and S represent the mass percentage of oxygen, carbon, hydrogen,
170 nitrogen and sulphur, respectively. Obtained data may present deviations between
171 $\pm 0.5\%$ of the presented value.

172 3. Calculation

173 The first step consists in determining which of the parameters are more influential on
174 the HHV estimation. With this aim in mind, Matlab's command *corrcoef* is used, to
175 obtain R and P values. R is a squared matrix of correlation coefficients, having as many
176 rows and columns as compared variables. P is the p-values matrix, the result of testing
177 the non-correlation hypothesis. Each p-value is the probability of obtaining the observed
178 correlation by hazard, its value being equal to 0 if there exists a phenomenological
179 dependence. So, if P(i,j) is small (e.g. less than 0.05), it can be assumed that the
180 correlation R(i,j) is significant, that means the "i" variable is related in some way with
181 the "j" variable. These values are presented in Table 3. Using the previous criteria, the
182 first row of the matrix shows the correlation level between HHV and C, N, H,O and S.
183 In this way, it can be concluded that C and O are meaningful in order to ascertain HHV
184 values. The other parameters must be considered in order of decreasing influence, that is
185 S, N and H, but *a priori* these have slight importance in the correlation.

186 Following the selection of the most relevant parameters the Matlab's tool *cftool* was
187 employed to determine linear and second order parabolic equations, using in both cases
188 the fitting option Linear Least Squares with the robust LAR method switched on to
189 improve the correlation. Linear combinations of C and O with other elements, in order
190 of importance were tested too, using Matlab's command *regress*. Combinations of C
191 and O with H were also tested, because there are quite common in coal's analysis.
192 Finally, *Tablecurve2D* software was used to determine pure second order relations.

193 4. Results and Discussion

194 Thirteen linear and second order combination were tested, and their results validated
 195 using three criteria, average absolute error (AAE), and average bias error (ABE),
 196 commonly used by several authors [6, 9, 13, 16, 37], which are relative errors. In
 197 addition to this, average absolute deviation (AAD) is shown. These three criteria are
 198 defined in the following way:

$$AAD = \frac{1}{n} \left[\sum (HHV_{calc} - \overline{HHV}) \right] \quad (5)$$

$$AAE (\%) = \frac{1}{n} \left[\sum 100 \frac{|HHV_{calc} - \overline{HHV}|}{HHV_{exp}} \right] \quad (6)$$

$$ABE (\%) = \frac{1}{n} \left[\sum \frac{100(HHV_{calc} - \overline{HHV})}{HHV_{exp}} \right] \quad (7)$$

199 where HHV_{calc} , HHV_{exp} and \overline{HHV} are, respectively, the calculated, experimental and
 200 average experimental values for HHV and n the number of elements, just one hundred
 201 in this work. All these values, both from the developed equations and the correlations
 202 found in the literature are attached in table 4.
 203 As can be seen, AAD consists in an absolute value, this means non-percentage, which
 204 makes it difficult to compare results between different equations. ABE does not imply
 205 absolute values, so results may be compensated, that is to say really large positive errors
 206 may be neutralized with really large negative ones, so this does not assure the accuracy
 207 of the methods. In this way AAE criterion will be considered in this work as the most
 208 important one, and equations with low AAE as the most reliable ones. Only in the case
 209 of the same AAE value, ABE may be a complementary criterion for choice. As can be
 210 determined in Table 4, any of the developed equations presents AAE values under 6%,
 211 which can be considered as quite a good estimation for HHV. Considering that fact,
 212 four equations are finally proposed, the three with the lowest AAE (these are linear and

213 second order polynomial versus carbon content, linear combination of carbon, oxygen
214 and sulphur values and first order straight line versus oxygen content) , and the
215 equation presenting the lowest ABE.

$$216 \quad f(C) \rightarrow HHV = 338.4 \cdot C + 244.2 \quad (8)$$

$$217 \quad f(C^2, C) \rightarrow HHV = 1.59 \cdot C^2 + 154.5 \cdot C + 7464 \quad (9)$$

$$218 \quad f(C, O, S) \rightarrow HHV = 303.81 \cdot C + 81.62 \cdot O - 490.68 \cdot S + 159.92 \quad (10)$$

$$219 \quad f(O) \rightarrow HHV = -150.6 \cdot O + 24660 \quad (11)$$

220 Where C, O and S are the mass percentage of carbon, oxygen and sulphur of each
221 sample respectively and HHV is the higher heating value in $\text{kJ} \cdot \text{kg}^{-1}$, which are the
222 international units provided by the experimental equipment.

223 **Figure 4** presents the results obtained when representing the experimental HHV versus
224 the calculated HHV for these four equations. As can be seen, most of the results
225 approach the **diagonal, representing** perfect fit between expected and calculated data
226 quite well. Otherwise, it can be easily detected that some group of data's approach is not
227 so accurate. In that way, **vegetable coal** presents a wide dispersion between data
228 obtained using carbon-based correlations, which perfectly fit the diagonal, and the ones
229 obtained using oxygen-based correlations **[f(O) and f(C,O,S)]** ..In fact these correlations
230 **may be useful by their simplicity and reliability when a direct procedure for O**
231 **determination is available in the laboratory.** On the other hand, peach tree and black
232 poplar leaves, lemon tree branches and horse chestnut burr calculated data is much more
233 reliable for oxygen containing than for carbon-based correlations. Lastly r three other
234 samples, cypress fruit, rice husk and sorghum present quite unexact and disperse results
235 for all the proposed equations. All these considerations must be taken into account to
236 determine the range of samples for which the developed equations can be accurately
237 used.

238 In addition to this, the five bibliographically found equations with the best AAE (S&A,
239 TIM, PLS, OPS, CAL₁) and ABE (STE, CAL₂, CAL₃, BOI, L&D) were selected and
240 their results graphically compared with our four proposed correlations. These results
241 are presented in Figure 5 showing
242 AAE errors obtained by using the nine equations (the four developed by us and the five
243 bibliographical ones that presented best average results) for each samples. As can be
244 seen a vast majority, more or less an 80 %, of the samples present AAE values under 10
245 % and are quite homogeneous. The difference with the average results can be explained
246 when studying the results of the remaining 20 % of them, where much more disperse
247 results can be observed. For example, when observing some samples such as black
248 poplar leaves, cypress fruit, horse chestnut burr, lemon tree branches, peach tree leaves,
249 rice husk, straw pellets or wheat a wide dispersion of results can be determined. In all of
250 these cases the AAE obtained from our developed expressions improves those to be
251 expected from the the bibliographical equations. These improvements may vary from
252 slight ones observed in straw pellets or wheat where every error are included between a
253 10 and a 20 % to wide improvements such as the observed in black poplar leaves,
254 cypress fruit, peach tree leaves or rice husk where errors vary from 10 % to nearly a 60
255 % in some cases. Usually, the equations that provides the best fit for the disperse
256 samples are the ones based only on oxygen f(O) or carbon, oxygen and sulphur f(C,O,S)
257 , but for some specific cases, with high carbon content, such as vegetable coal the
258 expressions that best fit, with an error of nearly under 1 % are the ones based on carbon
259 f(C) and f(C²,C).

260 On the other hand, a group of samples, such as chestnut shell, peach stone, pomegranate
261 peel, sorghum or wood chips, present high precision but low accuracy. This means a

262 low dispersion of predicted values among the nine tested equations but quite large
263 errors. These samples can only be qualified as difficult to predict.
264 If ABE is considered, most of the samples are included in the range of $\pm 10\%$ error. A
265 number of samples, such as apple tree branches, black poplar leaves and branches,
266 cypress fruit, grapevine waste, horse chestnut burr, lemon tree branches, peach tree
267 leaves, rice husk, sorghum or tomato plant waste again present much worse results than
268 the vast majority of them. The results obtained for these “complex” samples are usually
269 better for our developed equations than for the ones obtained in the bibliography, and
270 for C, O and S-based ones than for only C-based ones. Vegetable coal results are again
271 much better for C-based ones, as determined in Figure 5 useful to choose the most
272 adequate correlation for a given group or for a single material

273 5. Conclusions

274 Our purpose is not to describe a single material, where the best equation undoubtedly
275 would be a phenomenological model developed for the specie sub-specie or variety – in
276 the very frontier between Botanic and Engineering -, but to provide a general
277 approximation to the macroscopic and global energetic evaluation of a wide range of
278 materials dealing with the main objective of needed normalization of vegetable biomass
279 a single combustible or, more frequently, as a commercial mix. In this case, this type of
280 empirical wide purpose equations may be a usable tool.

281 Thus, this work was developed trying to obtain some reliable wide range equations to
282 relate HHV and elemental composition for, mainly, Spanish based biomass samples and
283 some conclusions were obtained thanks to it. The first one is that error comparison
284 confirmed that including a high number of experimental parameters does not necessarily
285 improve the correlation. Our equations based on five parameters (C, O, S, N and H)
286 resulted in higher errors than the ones based on a simple parameter (C or O). In general

287 terms, it can be assumed that both our developed equations and some of the
288 bibliographically obtained ones produces quite good fit with most of the studied
289 samples. Anyway, a number of “complex” samples, this is with high errors for nearly
290 every equation, appeared. In most of these cases our developed equations -specially
291 $f(C,S,O)$ and $f(O)$ - presented much better results than the bibliography ones, with
292 average errors under 6%, which can be assumed as quite good taking into account the
293 wide range and heterogeneity of the studied samples. On the other hand, high carbon
294 content samples, such as vegetable coal, were much more accurately predicted with
295 carbon-based equations, like $f(C)$ and $f(C^2,C)$ ones.

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Ref	Sample	Latin name	N	C	S	H	O	HHV
COMMERCIAL FUELS								
1	Almond shell	Prunus dulcis	0.30	46.35	0.22	5.67	47.46	18275
2	Beetroot pellets	Beta vulgaris	1.19	38.94	0.51	5.23	54.13	15095
3	Briquette		1.24	46.74	0.10	6.39	45.52	18498
4	Holm oak branch chips	Quercus ilex	0.76	45.65	1.99	5.75	45.84	17181
5	Olive stone	Olea europaea	1.81	46.55	0.11	6.33	45.20	17884
6	Pine and pine apple leaf pellets		0.40	42.26	0.27	4.81	52.27	18147
7	Pine chips	Pinus pinea	0.09	48.15	0.28	5.59	45.90	19427
8	Pine cone leaf	Pinus pinea	0.27	47.65	0.44	5.43	46.21	18633
9	Pine kernel shell	Pinus pinea	0.31	47.91	0.60	4.90	46.28	18893
10	Pine pellets	Pinus pinea	0.28	46.83	0.31	5.30	47.28	18840
11	Pinne cone heart	Pinus pinea	0.29	42.22	0.84	5.06	51.59	16440
12	Sawdust		0.53	45.34	1.07	6.02	47.05	18016
13	Straw pellets (grass)		0.56	47.89	0.17	5.51	45.87	16584
14	Vegetal coal		0.65	79.34	0.30	2.74	16.97	29712
15	Vine shoot chips	Vitis	0.61	40.15	0.31	5.02	53.91	14631
16	Wood chips		0.13	42.20	0.27	5.51	51.88	15162
17	Wood pellets		0.60	46.79	0.32	6.13	46.15	18218
INDUSTRIAL WASTES								
18	Barley straw	Hordeum vulgare	1.64	40.69	0.23	6.95	50.50	17369
19	Bean husk	Vicia faba	0.66	39.66	0.31	5.38	53.98	15114
20	Building wastes chips		0.08	47.26	0.17	6.45	46.04	18279
21	Cherry stone	Prunus avium	0.43	48.57	0.19	6.21	44.60	19069
22	Chestnut shell	Castanea sativa	0.42	42.31	0.33	5.17	51.77	14310
23	Cocoa beans husk	Theobroma cacao	2.64	43.25	0.29	5.89	47.93	17313
24	Coconut shell	Arecacae/palmae	0.15	47.93	0.24	6.05	45.63	18875
25	Coffee husk	Coffea	2.53	45.06	0.48	6.42	45.51	18326
26	Corn cob	Zea mays	0.22	44.78	0.21	6.02	48.77	17692
27	Date stone	Phoenix dactylif	1.03	43.37	0.32	6.23	49.05	18150
28	Grapevine waste	Vitis	1.35	35.74	0.30	5.95	56.67	16467
29	Hazelnut shell	Corylus avellana	0.27	47.80	0.16	6.14	45.64	18872
30	Lemon rind	Citrus limon	1.08	42.95	0.42	6.56	48.98	17184
31	Nectarine stone	Prunus persica	0.50	48.57	0.23	6.22	44.48	19560
32	Pea husk	Pisum sativum	1.24	39.62	1.82	6.54	50.78	15464
33	Pea plant waste	Pisum sativum	0.90	44.06	0.39	4.73	49.91	17351
34	Peach stone	Prunus persica	3.94	40.72	0.30	6.96	48.07	19590
35	Peanut shell	Arachis hypogaea	1.05	49.35	0.24	6.40	42.96	20088
36	Pepper plant waste	Capsicum	3.66	36.56	0.83	5.27	53.67	13656
37	Pistachio shell	Pistacia vera	0.11	44.69	0.18	5.16	49.87	17348
38	Plum stone	Prunus prunus	0.87	48.22	0.17	6.60	44.14	19136
39	Pomegranate peel	Punica granatum	0.69	42.19	0.33	5.11	51.68	15173
40	Potatoe plant waste	Solanum tuberosum	1.13	38.33	0.44	5.07	55.03	15070
41	Rice husk	Oryza sativa	0.21	26.69	0.17	2.88	70.05	15899
42	Rye straw	Secale cereale	1.16	40.18	0.32	6.85	51.48	17113
43	Sunflower Seed husk	Helianthus annuus	0.38	45.33	0.24	5.91	48.14	17998
44	Tomato plant waste	Solanum lycopersicum	1.19	36.63	1.48	0.68	60.01	14154
45	Vine orujillo	Vitis	1.91	44.15	0.58	5.31	48.04	17742
46	Vine shoot waste	Vitis	0.63	34.60	0.24	5.61	58.91	13292
47	Walnut shell	Junglans regia	0.22	46.97	0.10	6.27	46.44	18378
48	Wheat straw	Triticum	1.18	45.58	0.59	6.04	46.60	17344
49	Wood sawdust		0.12	45.97	0.24	5.13	48.53	18207
FOREST WASTES								
50	American oak acorn	Quercus rubra	0.60	44.68	0.18	5.98	48.55	17372
51	Black poplar bark	Populus nigra	0.42	43.25	0.34	6.33	49.66	17406
52	Black poplar wood	Populus nigra	0.18	46.19	0.56	5.70	47.36	18392

Table 1.1 – Raw data used to develop the proposed correlations.

Ref	Sample	Latin name	N	C	S	H	O	HHV
FOREST WASTES								
53	Chestnut tree chips	Castanea sativa	0.23	45.30	0.17	6.10	48.20	17485
54	Chestnut tree shaving	Castanea sativa	0.12	45.88	0.27	5.00	48.73	17616
55	Cypress fruit	Cupressus	0.35	27.81	0.18	5.70	65.96	20172
56	Eucalyptus bark	Eucalyptus	1.69	46.53	0.30	5.87	45.61	16237
57	Eucalyptus chips	Eucalyptus	0.14	44.77	0.15	6.33	48.60	16494
58	Eucalyptus fruit	Eucalyptus	1.14	46.81	0.39	5.81	45.84	18522
59	Hazelnut and alder chips	Alnus sorbus	0.40	45.47	0.20	5.94	47.99	17555
60	Horse chestnut burr	Aesculus hippocast.	0.45	53.38	0.23	7.16	38.77	17165
61	Oak acorn	Quercus robur	0.80	41.84	0.25	6.82	50.28	16165
62	Oak tree pruning	Quercus robur	0.73	37.89	0.21	5.94	55.23	17592
63	Olive tree pruning	Olea europaea	1.47	45.36	0.28	5.47	47.42	17342
64	Pine and eucalyptus chips		1.59	45.90	0.19	6.30	46.03	16987
65	Pine shaving	Pinus pinea	0.07	48.67	0.26	5.08	45.92	19793
Forest wastes-LEAVES								
66	Almond tree leaves	Prunus dulcis	2.85	43.25	0.34	5.50	48.06	17560
67	Apple tree leaves	Malus domestica	1.61	44.45	0.23	6.15	47.56	17510
68	Black poplar leaves	Populus nigra	1.03	58.30	0.35	8.41	31.92	18165
69	Cherry tree leaves	Prunus avium	1.49	45.52	0.19	6.25	46.55	17734
70	Chestnut tree leaves	Castanea sativa	2.21	47.82	0.27	6.24	43.46	18757
71	Feijoa leaves	Acca	1.23	45.28	0.20	6.03	47.25	17805
72	Hazelnut tree leaves	Corylus avellana	2.05	45.14	0.31	6.79	45.71	17870
73	Oak tree leaves	Quercus robur	3.04	46.90	0.38	5.47	44.20	18312
74	Orange tree leaves	Citrus sinensis	2.59	41.11	0.40	5.28	50.62	16170
75	Peach tree leaves	Prunus persica	2.03	59.59	0.77	9.76	27.86	18336
Forest wastes-BRANCHES								
76	Almond tree branches	Prunus dulcis	0.65	47.35	0.16	6.36	45.47	18351
77	Apple tree branches	Malus domestica	0.81	46.24	0.39	11.55	41.01	17821
78	Black poplar branches	Populus nigra	0.33	45.62	0.59	0.03	53.43	18411
79	Cherry tree branches	Prunus avium	0.52	46.42	0.17	6.21	46.68	19361
80	Grapevine branches	Vitis	0.76	45.00	0.46	6.95	46.83	16818
81	Horse chestnut tree br.	Aesculus hippocast.	1.05	43.71	0.43	6.27	48.54	17469
82	Kiwi branches	Actidina deliciosa	1.06	46.41	2.44	6.09	43.99	17812
83	Lemon tree branches	Citrus limon	0.54	54.74	0.33	5.72	38.68	17564
84	Medlar tree branches	Mespilus germ.	0.52	44.36	0.18	6.17	48.77	17645
85	Mimosa branches	Acacia dealbata	0.75	45.81	0.17	6.19	47.08	17752
86	Oak tree branches	Quercus robur	2.87	48.26	0.33	6.28	42.26	17717
87	Orange tree branches	Citrus sinensis	0.56	45.76	0.21	6.12	47.34	16305
ENERGY CROPS								
88	Gorse	Genista hirsuta	1.49	43.49	0.33	5.53	49.16	18599
89	Miscanthus	Miscanthus	0.10	47.09	0.10	6.30	46.42	18072
90	Oats and vetch	cceratonia siliqua	0.92	41.69	0.29	5.82	51.27	16661
91	Sorghum	Sorghum	0.73	40.79	0.23	4.38	53.87	11872
92	Triticale	Triticosecale	1.23	42.14	0.76	5.80	50.07	16645
CEREALS								
93	Barley grain	Hordeum vulgare	1.79	41.59	0.35	6.08	50.18	16519
94	Maize grain	Zea mays	1.17	40.96	0.23	6.92	50.71	16429
95	Oats bran	Avena sativa	2.17	44.01	0.29	7.17	46.36	18058
96	Rye grain	Secale cereale	1.20	41.11	0.21	6.76	50.72	16141
97	Sainfoin	Onobrychis viciif.	1.80	41.68	0.57	5.90	50.05	16412
98	Soya grain	Glycine max	1.16	44.42	0.24	6.33	47.86	16711
99	Wheat grain	Triticum	0.24	49.22	0.26	6.52	43.76	16325
100	Wheat bran	Triticum	2.34	42.74	0.31	6.62	47.98	17370

Table 1.2 – Further raw data used to develop the proposed correlations.

Beckman (BEC) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow biomass derived oils [8]	Dulong-Petit for coals (DPC) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [14, 22]
Boie (BOI) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow hydrocarbon fuels [6, 8, 11, 14, 15]	Dulong-Petit variation (DPV) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [23]
Callejón-Ferré 01 (CAL_1) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [16]	Dulong-Berthelot (D&B) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Coals [8, 18]
Callejón-Ferré 02 (CAL_2) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [16]	Francis and Lloyd (F&L) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Biomass [24]
Callejón-Ferré 03 (CAL_3) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [16]	Friedl's Ordinary Least Squares regression model (OLS) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Biomass [25]
Callejón-Ferré 04 (CAL_4) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [16]	Friedl's Partial Least Squares regression model (PLS) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Biomass [25]
Callejón-Ferré 05 (CAL_5) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [16]	Friedl's average of both methods (OPL) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Biomass [17, 25]
Chung-Yang (CHU) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [17]	Gumz (GUM) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]
Channiwala and Parikh (C&P) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow General [8]	Grummel and Davis (G&D) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8],
Demirbas 1997-1 (DEM_{97-1}) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [18]	Jenkins 1980 (JEN_{80}) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [8]
Demirbas 1997-2 (DEM_{97-2}) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [6, 13, 18, 19]	Jenkins 1985 (JEN_{85}) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [6, 8]
Demirbas 2004 (DEM_{04}) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Biomass [20]	Kathiravale et al. (KAT) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Municipal solid wastes [11]
D'Huart (DHU) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]	Lloyd and Davenport (L&D) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Coal char [14]
Dulong (DUL) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Coals [8, 10, 13, 16, 21]	Meraz et al. (MER) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Municipal solid wastes [12, 13]
Dulong (DUL_2) ($\text{Btu}\cdot\text{lb}^{-1}$) \rightarrow Coals [11, 18]	Mott and Spooner (M&S) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coal/wastes [8, 14, 26, 27]
Dulong (DUL_3) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Coals [11, 14]	Ruyter (RUY) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [28]

Table 2.1. Empirical equations based on ultimate analysis data selected from the cited literature (original units)

Schuster (SCH) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]	Thipkhunthod et al. 2 (THI ₂) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Sewage sludge [13]
Seyler (SEY) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]	Thipkhunthod et al. 3 (THI ₃) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Sewage sludge [13]
Steuer (STE) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Coals [8, 10, 12, 16, 21, 26]	Thipkhunthod et al. 4 (THI ₄) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Sewage sludge [13]
Sumegi (SUM) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]	Thipkhunthod et al. 5 (THI ₅) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Sewage sludge [13]
Sheng and Azevedo (S&A) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [6, 17]	Tillman (TIL) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [8]
Scheuer and Kestern (S&K) ($\text{kcal}\cdot\text{kg}^{-1}$) \rightarrow Coals [10, 11, 12, 16, 21]	Tillman's modified (TIM) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Biomass [6, 8]
Strache and Lant (S&L) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]	Vondreck (VON) ($\text{kJ}\cdot\text{g}^{-1}$) \rightarrow Coals [8]
Thipkhunthod et al. 1 (THI ₁) ($\text{kJ}\cdot\text{kg}^{-1}$) \rightarrow Sewage sludge [13]	Wilson (WIL) ($\text{Btu}\cdot\text{lb}^{-1}$) \rightarrow Municipal solid wastes [6, 29]
	— — —

Table 2.2. Empirical equations based on ultimate analysis data selected from the cited literature (original units)

R values					
HHV	C	N	H	O	S
1.0000	0.6779	-0.0835	0.0268	-0.6280	-0.1461
P values					
HHV	C	N	H	O	S
1.0000	0.0000	0.4089	0.7914	0.0000	0.1470

Table 3. P and R values for HLV selected from the Matlab® squared matrix

DEVELOPED EQUATIONS							
EQ.	AAD	AAE	ABE	EQ.	AAD	AAE	ABE
f(C)	1200	5.33	1.00	f(O)	558	5.96	0.50
f(C²)	744	5.53	0.60	f(O²)	668	5.92	0.74
f(C²,C)	1061	5.31	1.19	f(O²,O)	805	5.90	2.31
f(C,H)	783	5.55	0.63	f(O,H)	742	5.78	0.66
f(C,O)	803	5.52	0.63	f(C,O,S,N)	825	5.46	0.62
f(C,O,H)	801	5.53	0.63	f(C,O,S,N,H)	826	5.46	0.62
f(C,O,S)	840	5.44	0.62				
EQUATIONS FOUND IN BIBLIOGRAPHY							
EQ.	AAD	AAE	ABE	EQ.	AAD	AAE	ABE
BEC	2076	9.83	-4.98	KAT	5003	29.82	29.78
BOI	2042	8.93	-0.65	L&D	1881	8.00	-0.70
CAL₁	1693	6.39	1.96	MER	2236	10.09	-3.72
CAL₂	1697	6.60	0.39	M&S	2392	11.45	-5.89
CAL₃	1735	6.89	-0.63	OLS	1379	6.49	2.99
CAL₄	1966	7.43	2.57	OPS	1378	6.35	3.37
CAL₅	3675	17.54	12.11	PLS	1366	6.32	3.51
CHU	1503	7.79	3.71	RUY	2776	14.33	-9.88
C&P	5825	33.77	32.58	SCH	2191	9.92	-3.80
DEM₉₇₋₁	2645	13.39	-8.71	SEY	2058	9.42	-1.22
DEM₉₇₋₂	2727	14.02	-9.56	SUM	4937	27.37	-24.42
DEM₀₄	2191	11.81	9.86	STE	2190	9.86	-0.06
DHU	2251	10.06	1.45	S&A	1281	6.30	3.67
DUL	2691	14.27	-13.36	S&K	8570	49.72	49.70
DUL₂	2188	10.18	4.01	S&L	3341	17.92	-14.00
DUL₃	2243	10.54	-3.52	THI₁	6417	37.73	37.33
DPC	2105	9.49	1.73	THI₂	7604	44.56	44.56
DPV	2234	10.29	-2.68	THI₃	7065	41.45	41.45
D&B	3418	18.42	-14.58	THI₄	4810	28.54	28.03
F&L	2021	8.79	1.51	THI₅	4791	28.43	27.90
GUM	2100	9.27	2.14	TIL	2275	12.40	10.50
G&D	2582	13.04	-8.36	TIM	1613	6.32	2.61
JEN₈₀	3132	17.79	16.15	VON	2477	11.94	-6.49
JEN₈₅	1692	10.18	8.56	WIL	2244	10.52	-3.33

Table 4. Statistical criteria AAD, AAE and ABE for the evaluation of the tested equations

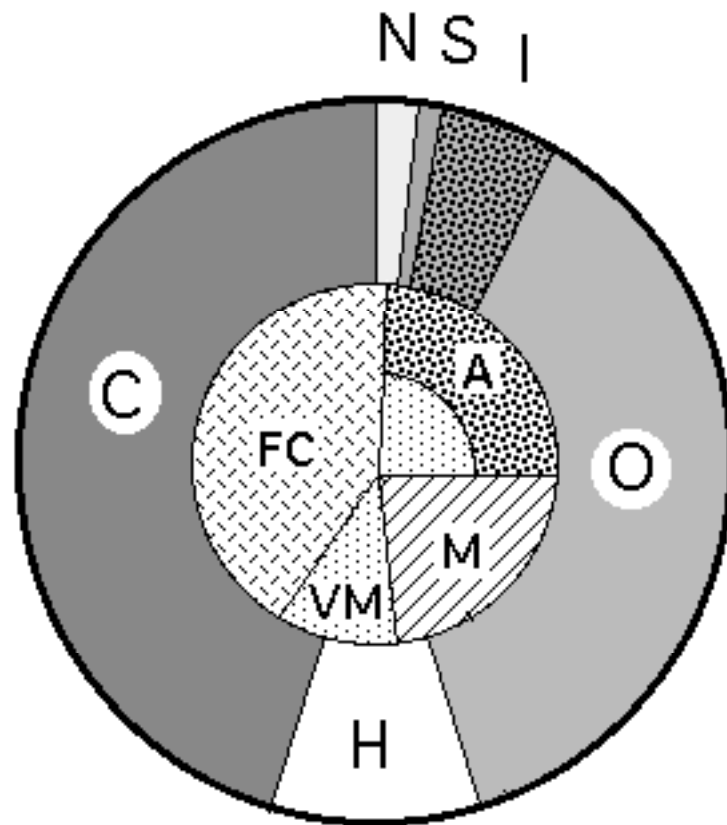


Figure 1. Qualitative correspondence between descriptors of ultimate (main elements C,O,H,N,S and others as I) and proximate analysis, fixed carbon (FC), volatile matter (VM), moisture (M) and ash (A).

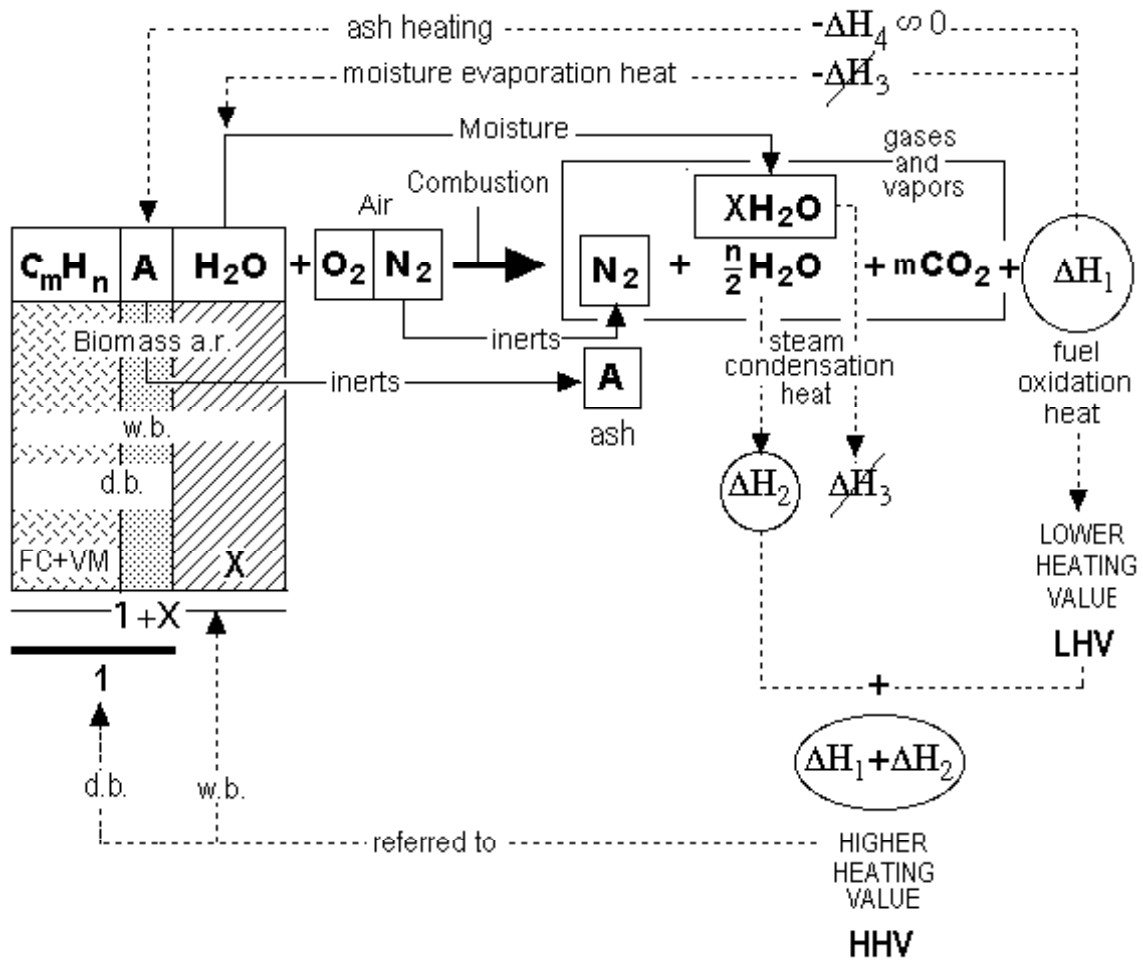


Figure 2. Definitions of HHV and LHV referring to dry (d.b.) or wet base (w.b.)

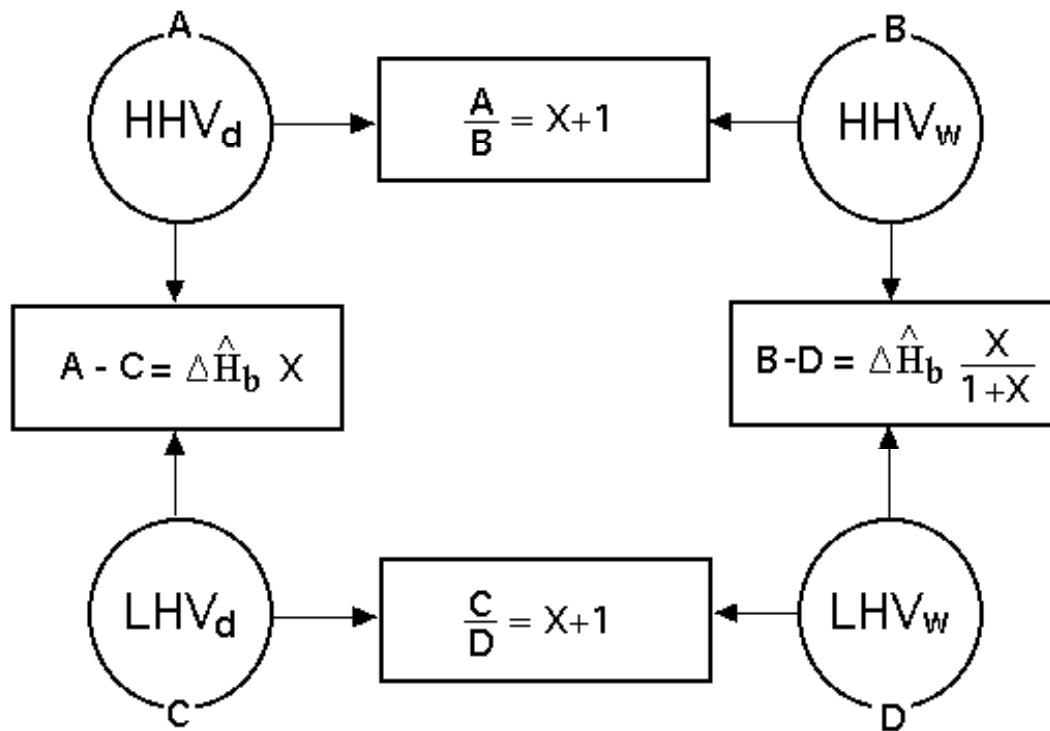


Figure 3. Reciprocal relations between heating values referring different bases

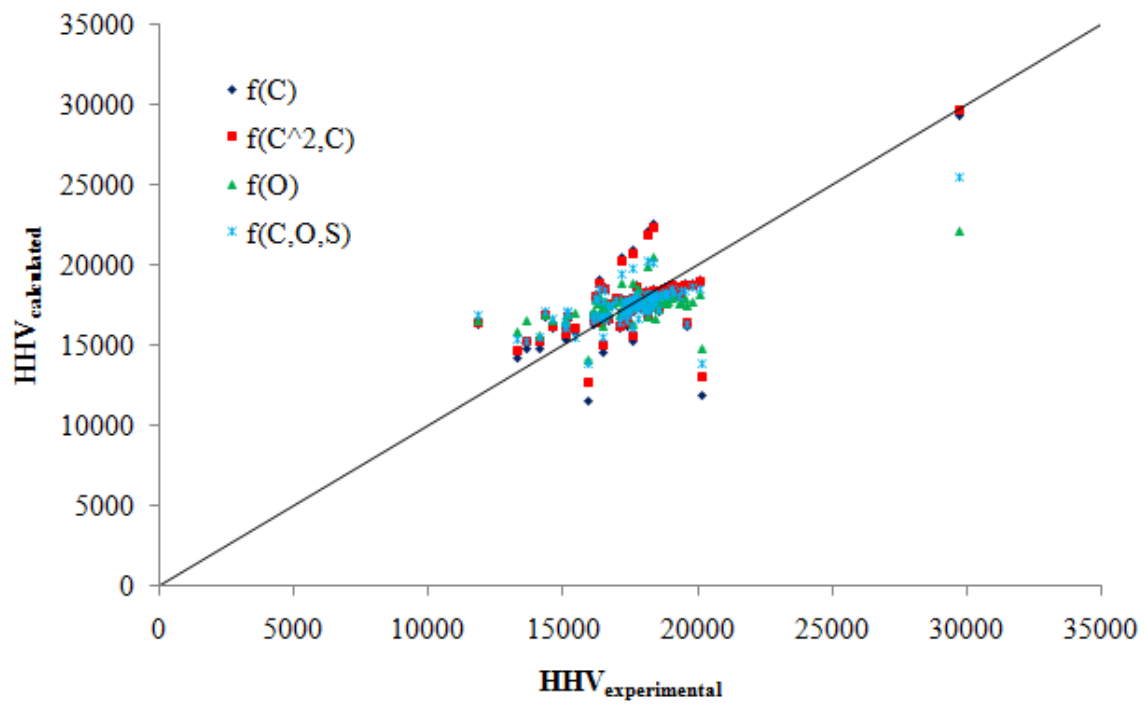


Figure 4. Experimental HHV versus calculated HHV for the proposed equations.

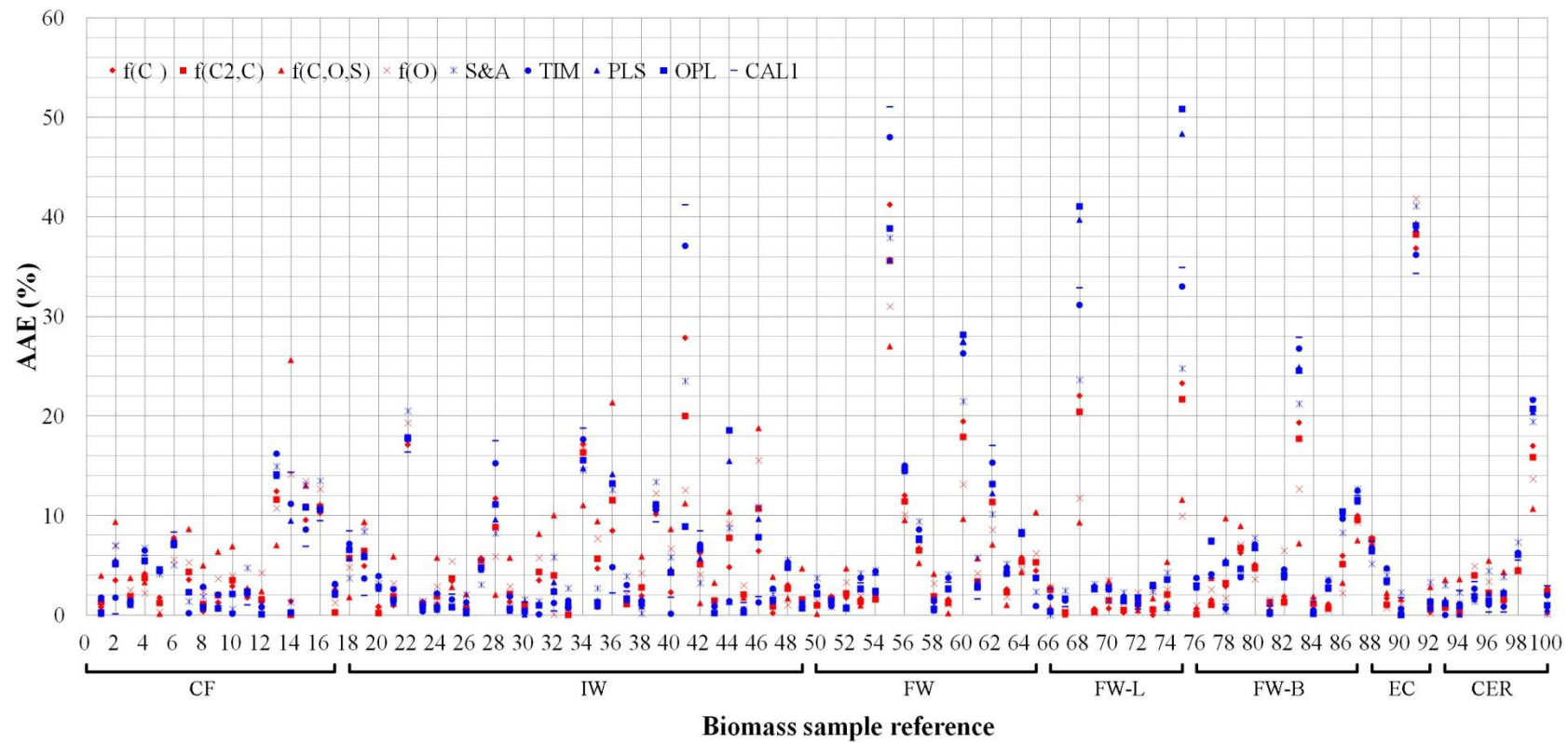


Figure 5. Percentage AAE errors corresponding to the application of the proposed equations to the potential solid fuel biomasses (numerical references taken from tables 1.1 and 1.2)

Fig1

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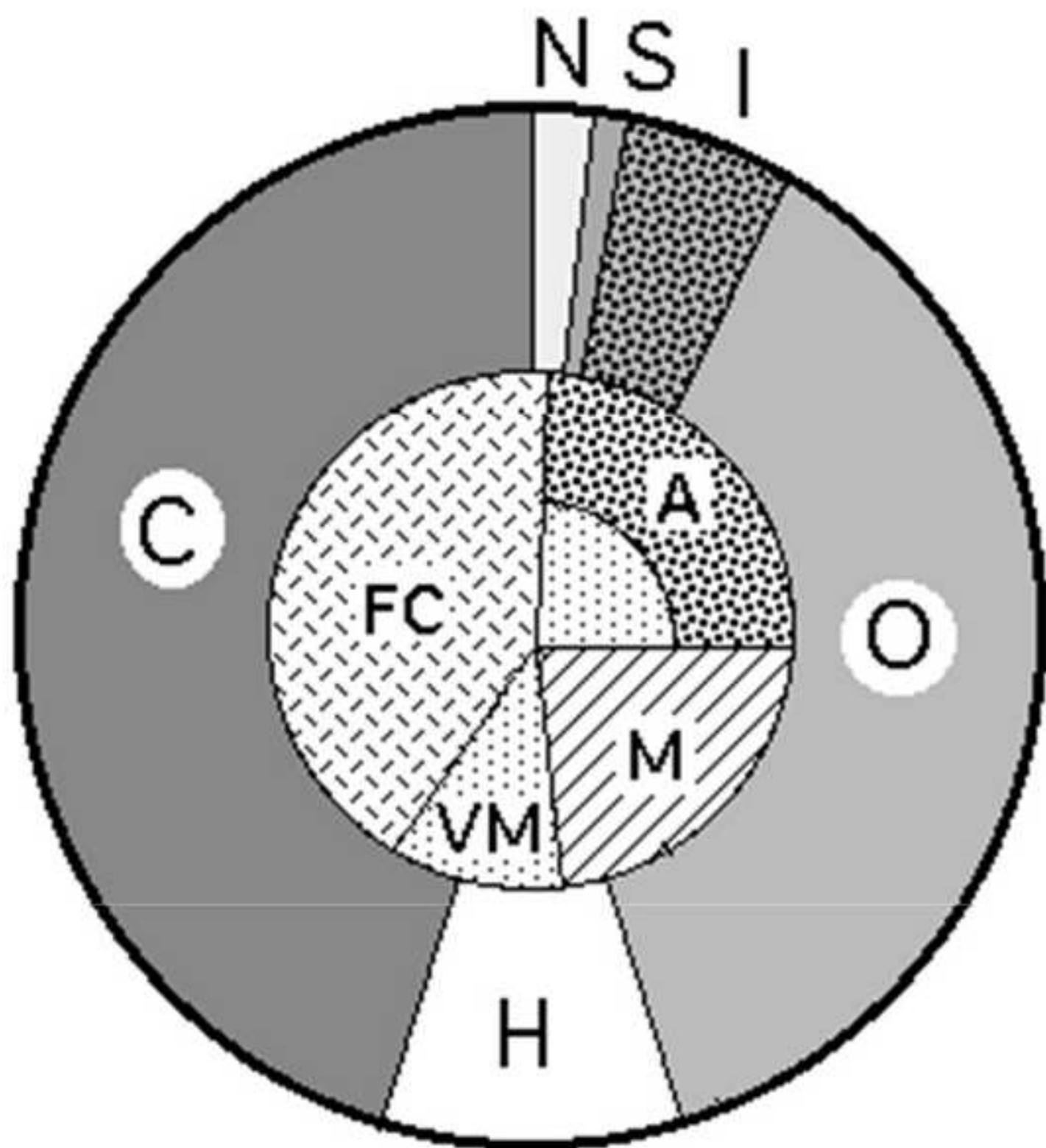


Fig2

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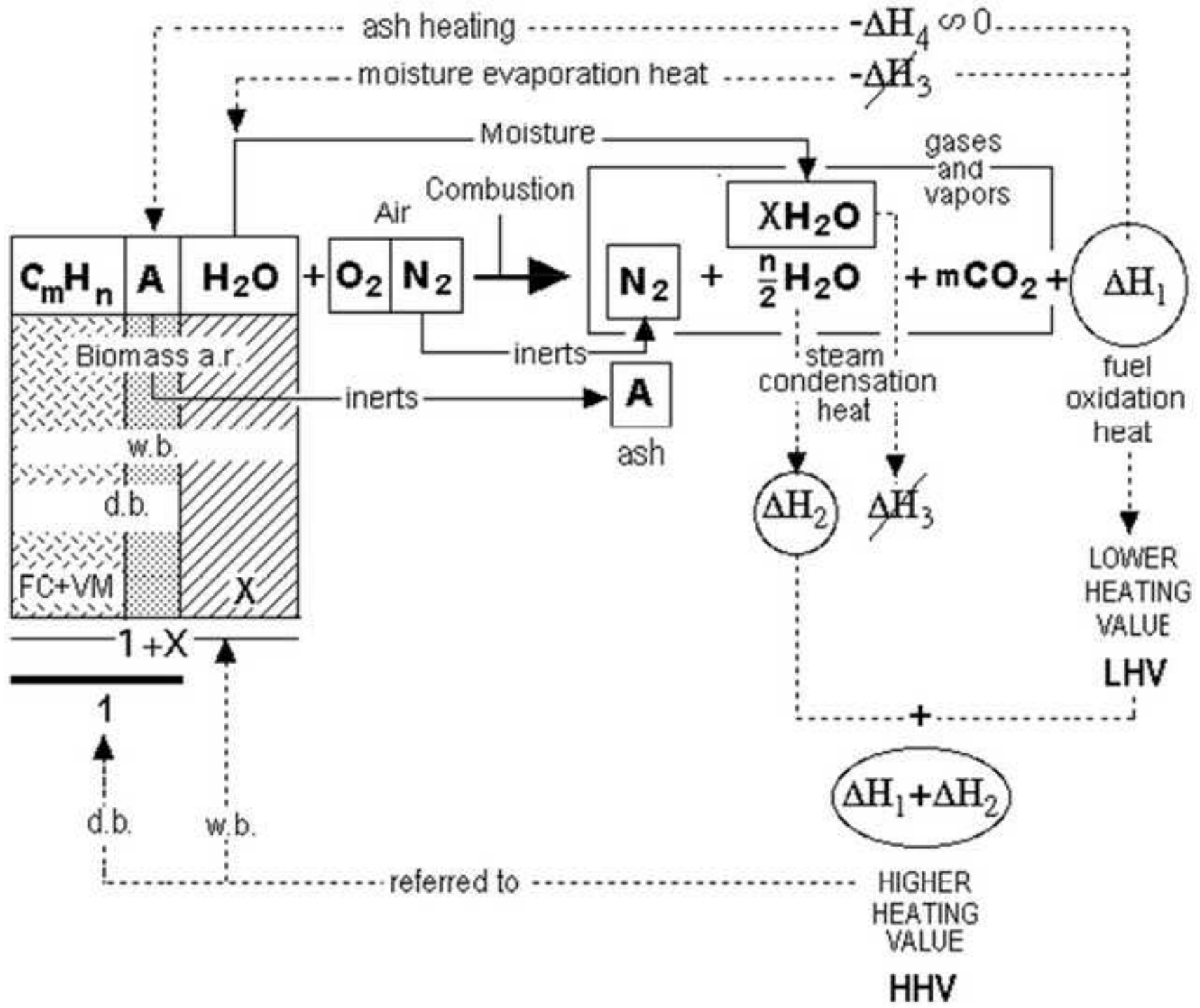


Fig3

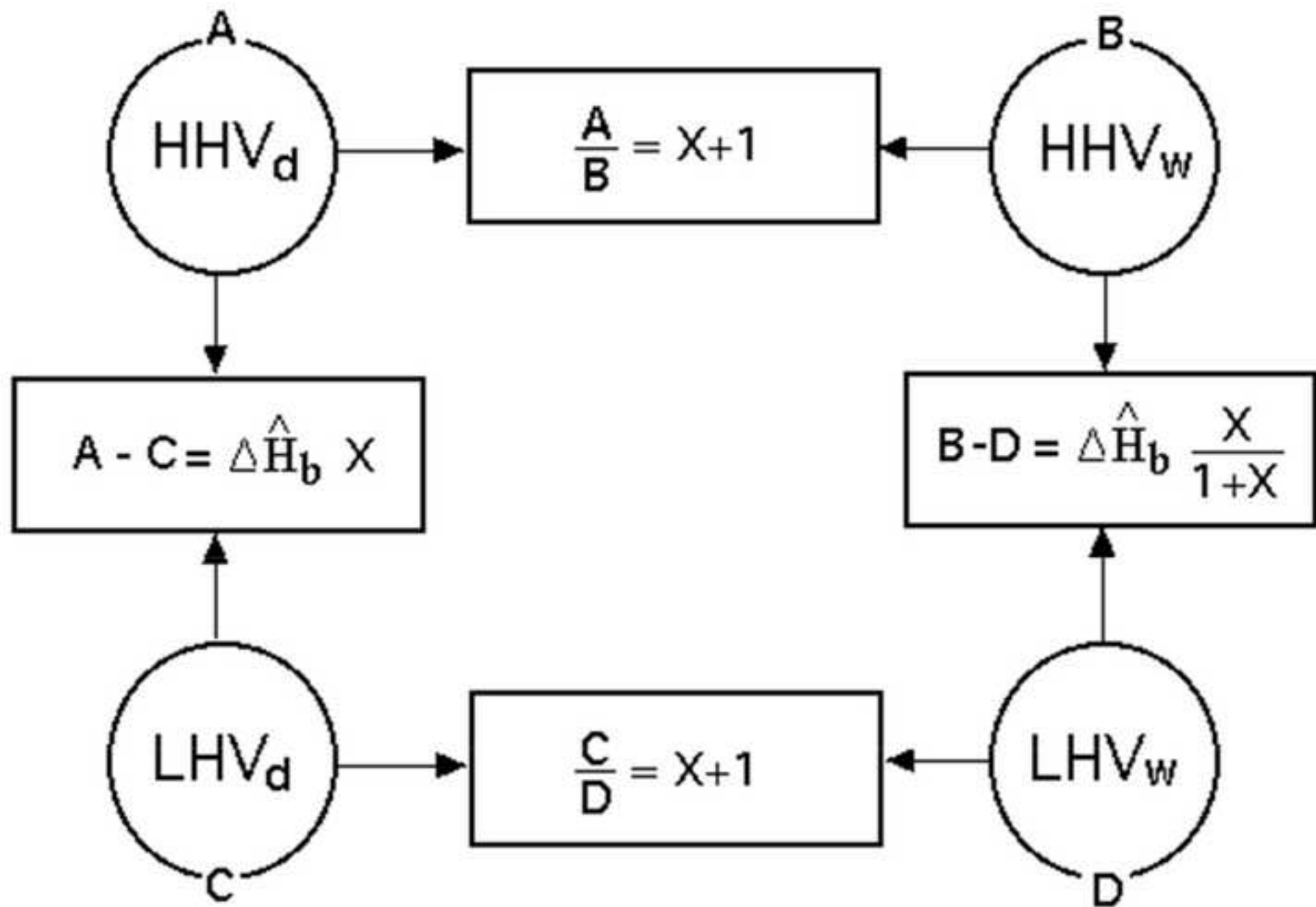
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Fig4

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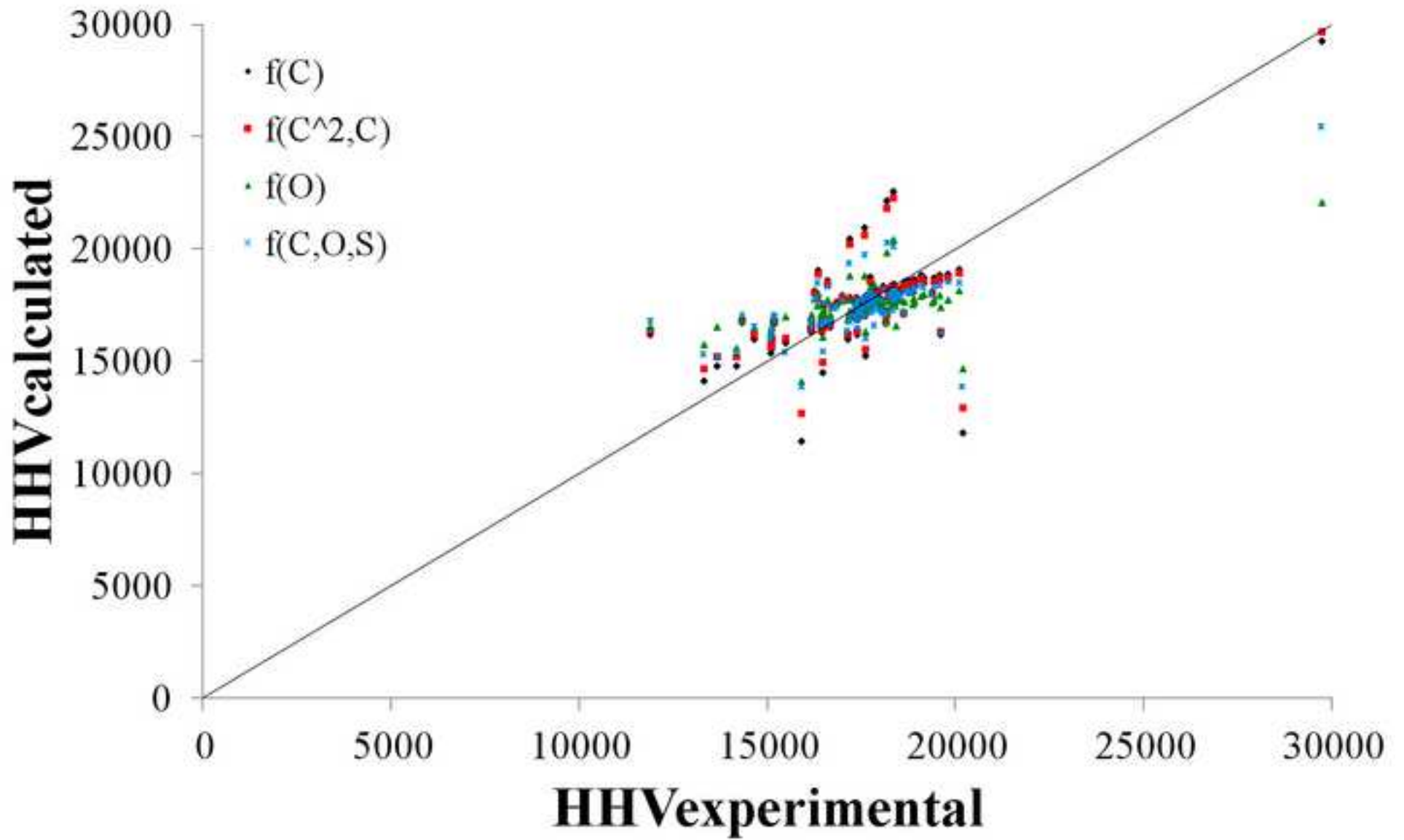


Fig5

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