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Modelling higher heating value of different separated fractions from municipal and construction and demolition wastes

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Abstract:

Higher heating value (HHV) is an important property of biomass and wastes used to evaluate their potential conversion to useful thermal or electric energy. Because the measurement of this property requires expensive resources and is somewhat time-consuming, many works focused their attention on the determination of mathematic models relating the HHV with the composition of lignocellulosic biomass or other fuel materials, such as their ultimate and proximate analysis. These models can supply appropriate estimates of HHV but only for analogous materials, so they should not be used to compare samples with marked differences in composition or physical and chemical properties. In this work, 9 different separated fractions of municipal and construction and demolition wastes (wood, paper/card, plastics, sewage sludge and mixtures among them) were used to deduce a mathematical expression relating HHV with their contents of carbon, hydrogen, oxygen, nitrogen, sulphur and ash. For this purpose, HHV's, proximate and ultimate analysis were experimentally obtained and the results used to create three different expressions applying linear regression methods. The best expression was selected and validated by comparing deviations among the calculated results and those retrieved from the literature and from experimental measurements regarding different wastes. It was concluded that the best expression was HHV (MJ/kg db) = $0.3845\times C+0.8831\times H-29.1217\times S-0.0630\times O-1.0063\times N+0.3888\times ASH-0.2546$ (with C, H, S, O, N and ASH in wt% db, considering atomic ratios O/C and H/C within $0.0\leq O/C\leq 1.2$ and $0.1\leq H/C\leq 0.2$), giving an average absolute error of 8.5 % and an average bias error of -1.6 %. However, appreciable deviations may be found when estimating the HHV of polyurethane, paper/card, mixtures of paper/plastic and sewage sludge and thus the application of the expression for these materials is questionable.

Keywords:

Higher Heating Value, Modelling, Municipal Waste, Construction and Demolition Waste.

1. Introduction

Valorisation of wastes from municipal and construction and demolition wastes for energy generation constitute a promising alternative to replace fossil fuels that are scarce and contribute for the global warming, and at the same time reduce the negative impact for health and environment due to an incorrect management and disposal [1].

The composition of these wastes is rich in hydrocarbons that give them an interesting calorific potential that can be assessed through the higher heating value (HHV). This quantity measures the total heat released through the combustion of the material, including the energy needed to vaporize the existing moisture, and is important to project adequately an energy production system (thermal and/or electric) and for numerical simulation of thermal processes [2, 3]. Another similar property that may be determined is the lower heating value (LHV) which does not take into account the heat required to vaporize the present moisture.

The experimental determination of HHV may be carried out in a calorimetric bomb, but this is usually a time-consuming and expensive method, which requires specialized operators. Since HHV depends on the composition of the material, a lot of literature concerned their efforts in establishing equations that correlate HHV with the composition in an attempt to produce a more expeditious and economic procedure for the determination [1, 3, 4].

Existing correlations can be grouped according to the type of composition of the material: physical (based on mass fractions of constituents, viscosity or density), chemical (e.g. molecular weight and double bonds), proximate analysis (contents of fixed carbon, volatiles, ash and moisture) and ultimate analysis (contents of elemental carbon, hydrogen, oxygen, sulphur and nitrogen) [1, 4]. It can be seen that correlations based on the latter two compositions are the most frequent, although one of the drawbacks of their use is related with the representativeness of samples, that may be too small or too specific from the location where they were collected. Moreover, the majority are applicable to coals and lignocellulosic materials but a few were formulated for urban wastes like municipal solid wastes (MSW), refuse-derived fuels (RDF) and sewage sludges [1, 4, 5]. It must be pointed out that these correlations should be used for analogous materials in terms of composition and nature and not for different materials, since significant deviations of results may be obtained, as was already demonstrated in [3].

Deductions of HHV equations from the proximate and ultimate analysis of municipal wastes were made from a large set of experimental samples or data from literature, which may vary in the range of 25-225 samples [3, 5]. Table 1 exhibits some of these equations for the specific type of wastes they represent, as well as the average error levels that are associated with them. As can be seen, these error levels vary substantially among the equations but are less than 10 %.

Table 1. Some HHV correlations based on proximate and ultimate analysis reported in the literature.

Equation	Average error, %	Waste residue	Reference
$HHV=0.404207\times C+0.318857\times H$	3.9	RDF (on a daf basis)	[3]
$HHV=0.416638\times C-0.570017\times H +0.259031\times O+0.598955\times N-5.829078$	-0.59	MSW	[4]
$HHV=0.4302\times C-0.1867\times H-0.1274\times N +0.1786\times S+0.1842\times O-2.3799$	9.3	Sewage sludge with ash content ≤50 %.	[6]
$HHV=0.3491\times C+1.1783\times H+0.1005\times S -0.1034\times O-0.0151\times N-0.0211\times A$	1.45	Fossil fuels, vegetable biomass, MSW, RDF, chars*	[5]

* May be used if $0 \leq C \leq 92.25$, $0.43 \leq H \leq 25.15$, $0 \leq O \leq 50$, $0 \leq N \leq 5.6$, $0 \leq S \leq 94.08$ and $0 \leq A \leq 71.4$ (values in wt% db).

To extend the work done about the definition of HHV correlations for application to urban wastes, the present work aims to deduce a new correlation based on the ultimate analysis + ash retrieved from nine separated materials present in municipal wastes (MW) and construction and demolition wastes (CDW), and to compare the results with experimental data and with information available in the literature for a final validation. It was preferred to predict HHV rather than LHV of wastes since the former can be experimentally measured using a calorimetric bomb, and also because the majority of correlations found in the previous literature are used to calculate HHV, therefore simplifying the comparison and validation of results.

2. Materials and methods

The followed methodology was based on the work of [5] and is structured in five stages: (i) selection and characterization of experimental wastes, (ii) selection of general HHV correlations for testing, (iii) calculation of constants present in each correlation, (iv) definition and (v) validation of the best correlation. The next subchapters clarify the procedure used in each stage.

2.1. Selection and characterization of materials

For the derivation of correlations, nine different fractions of wastes (R1 through R9) were collected from MW and CDW received by a specialized company in waste management (Pragosa Ambiente,

S. A.), which are described in Table 2 along with the designation from the European list of waste (ELW). Also, a brief description of 10 additional wastes (R10 through R19) used for validation of the correlations and retrieved from the literature is exposed.

Table 2. Wastes used for the derivation and validation of correlations.

Code	ELW code	Material	Observations	Reference
R1	17 02 01	Wood (CDW)	-	This work
R2	20 01 38	Wood (MW)	-	
R3	20 01 01	Paper/card	-	
R4	15 01 02	Plastic packages	-	
R5	15 01 05	Composite packages	99.9 wt% paper + 0.1 wt% plastic	
R6	15 01 06	Mixture of packages	64.5 wt% paper + 35.5 wt% plastic	
R7	17 02 03	Plastics	-	
R8	17 06 04	Polymeric insulations	Mainly polyurethane and polystyrene	
R9	20 03 06	Sludges from sewage cleaning	-	
R10	-	Wood (CDW)	-	[9]
R11	-	Wood (MW)	-	[12]
R12	-	Paper	-	[12]
R13	-	Plastics	-	[10]
R14	-	Mixture paper+plastics	70 wt% paper + 30 wt% plastic	[9]
R15	-	Polyethylene	-	[11]
R16	-	Polypropylene	-	[11]
R17	-	Polyvinyl Chloride	-	[11]
R18	-	Polyurethane	-	[13]
R19	-	Sewage sludge	-	[6]

Pre-treatment of the first nine experimental wastes for characterization consisted in stages of crushing, milling and sieving at 425 µm, except in the case of some plastic materials (R4 and R6) where they were cut in pieces among 2-10 mm due to difficulties found in the preparation of fine particles. Since sludge presented originally high water contents, it was firstly dried at 105 ºC for several hours until all moisture evaporated before proceeding with the crushing and sieving operations.

After that, all samples were again dried at 105 ºC for 2 h and submitted for characterization in order to determine the HHV, ultimate analysis and ash content. HHV was measured in a calorimetric bomb (IKA C200), while ultimate analysis was carried out in an elemental analyser (ThermoFisher Scientific Flash 2000 CHNS-O) with oxygen contents determined by difference relative to 100 % - ash. Contents of ash for each waste were obtained according to ASTM E830-87.

2.2. Selection of general HHV correlations for testing

Three expressions for HHV determination from the ultimate analysis and ash content were chosen from [5]. Table 3 exposes a summary of these expressions.

Table 3. General HHV correlations selected for the study.

Brief description	Expression	Number
Direct proportionality among *HHV* and chemical elements in the waste	$HHV=a_1\times C+a_2\times H+a_3\times S+a_4\times O+a_5\times N+a_6\times A+a_7$	(1)
Dulong's criteria of available hydrogen	$HHV=a_1\times C+a_2\times(H-O/8)+a_3\times S$	(2)
Linear dependence on both element proportions and amount of air required for the complete combustion of the material	$HHV=[a_1\times C/(1-0.01\times A)+a_2\times H/(1-0.01\times A)+a_3\times(O+N)/(1-0.01\times \mathrm{A})+a_4\times S/(1-0.01\times \mathrm{A})+a_5]\times(C/3+H-O+S/8)$	(3)

2.3. Calculation of correlation coefficients

Coefficients a_i of the preceding expressions were calculated using a multiple linear regression method based on the minimization of least squares, as described in [7], where systems of equations were developed and solved using the numerical software Scilab. These systems were written in the matrix form $A\times X=B$, with A and B representing matrices determined by the regression method and X the column vector of coefficients a_i to be calculated. The matrix equations obtained for expressions (1), (2) and (3) are referred next in (4), (5) and (6), respectively.

$$\begin{bmatrix} 9 & \sum_{i=1}^{9} C_i & \sum_{i=1}^{9} H_i & \sum_{i=1}^{9} S_i & \sum_{i=1}^{9} O_i & \sum_{i=1}^{9} N_i & \sum_{i=1}^{9} A_i \\ \sum_{i=1}^{9} C_i & \sum_{i=1}^{9}(C_i)^2 & \sum_{i=1}^{9}(C_iH_i) & \sum_{i=1}^{9}(C_iS_i) & \sum_{i=1}^{9}(C_iO_i) & \sum_{i=1}^{9}(C_iN_i) & \sum_{i=1}^{9}(C_iA_i) \\ \sum_{i=1}^{9} H_i & \sum_{i=1}^{9}(H_iC_i) & \sum_{i=1}^{9}(H_i)^2 & \sum_{i=1}^{9}(H_iS_i) & \sum_{i=1}^{9}(H_iO_i) & \sum_{i=1}^{9}(H_iN_i) & \sum_{i=1}^{9}(H_iA_i) \\ \sum_{i=1}^{9} S_i & \sum_{i=1}^{9}(S_iC_i) & \sum_{i=1}^{9}(S_iH_i) & \sum_{i=1}^{9}(S_i)^2 & \sum_{i=1}^{9}(S_iO_i) & \sum_{i=1}^{9}(S_iN_i) & \sum_{i=1}^{9}(S_iA_i) \\ \sum_{i=1}^{9} O_i & \sum_{i=1}^{9}(O_iC_i) & \sum_{i=1}^{9}(O_iH_i) & \sum_{i=1}^{9}(O_iS_i) & \sum_{i=1}^{9}(O_i)^2 & \sum_{i=1}^{9}(O_iN_i) & \sum_{i=1}^{9}(O_iA_i) \\ \sum_{i=1}^{9} N_i & \sum_{i=1}^{9}(N_iC_i) & \sum_{i=1}^{9}(N_iH_i) & \sum_{i=1}^{9}(N_iS_i) & \sum_{i=1}^{9}(N_iO_i) & \sum_{i=1}^{9}(N_i)^2 & \sum_{i=1}^{9}(N_iA_i) \\ \sum_{i=1}^{9} A_i & \sum_{i=1}^{9}(A_iC_i) & \sum_{i=1}^{9}(A_iH_i) & \sum_{i=1}^{9}(A_iS_i) & \sum_{i=1}^{9}(A_iO_i) & \sum_{i=1}^{9}(A_iN_i) & \sum_{i=1}^{9}(A_i)^2 \end{bmatrix} \times \begin{bmatrix} a_7 \\ a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{9} HHV_i \\ \sum_{i=1}^{9}(C_iHHV_i) \\ \sum_{i=1}^{9}(H_iHHV_i) \\ \sum_{i=1}^{9}(S_iHHV_i) \\ \sum_{i=1}^{9}(O_iHHV_i) \\ \sum_{i=1}^{9}(N_iHHV_i) \\ \sum_{i=1}^{9}(A_iHHV_i) \end{bmatrix} \quad (4)$$

$$\begin{bmatrix} \sum_{i=1}^{9}(C_i)^2 & \sum_{i=1}^{9}\left(C_i\left(H_i-{O_i}/{8}\right)\right) & \sum_{i=1}^{9}(C_iS_i) \\ \sum_{i=1}^{9}\left(\left(H_i-{O_i}/{8}\right)C_i\right) & \sum_{i=1}^{9}\left(H_i-{O_i}/{8}\right)^2 & \sum_{i=1}^{9}\left(\left(H_i-{O_i}/{8}\right)S_i\right) \\ \sum_{i=1}^{9}(S_iC_i) & \sum_{i=1}^{9}\left(S_i\left(H_i-{O_i}/{8}\right)\right) & \sum_{i=1}^{9}(S_i)^2 \end{bmatrix} \times \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{9}(C_iHHV_i) \\ \sum_{i=1}^{9}\left(\left(H_i-{O_i}/{8}\right)HHV_i\right) \\ \sum_{i=1}^{9}(S_iHHV_i) \end{bmatrix} \quad (5)$$

$$\begin{bmatrix} \sum_{i=1}^{9}(C_ik_{1i})^2 & \sum_{i=1}^{9}(C_iH_ik_{1i}{}^2) & \sum_{i=1}^{9}(C_i(O_i+N_i)k_{1i}{}^2) & \sum_{i=1}^{9}(C_iS_ik_{1i}{}^2) & \sum_{i=1}^{9}(C_ik_{1i}k_{2i}) \\ \sum_{i=1}^{9}(H_iC_ik_{1i}{}^2) & \sum_{i=1}^{9}(H_ik_{1i})^2 & \sum_{i=1}^{9}(H_i(O_i+N_i)k_{1i}{}^2) & \sum_{i=1}^{9}(H_iS_ik_{1i}{}^2) & \sum_{i=1}^{9}(H_iK_{1i}k_{2i}) \\ \sum_{i=1}^{9}((O_i+N_i)C_ik_{1i}{}^2) & \sum_{i=1}^{9}((O_i+N_i)H_ik_{1i}{}^2) & \sum_{i=1}^{9}((O_i+N_i)k_{1i})^2 & \sum_{i=1}^{9}((O_i+N_i)S_ik_{1i}{}^2) & \sum_{i=1}^{9}((O_i+N_i)k_{1i}k_{2i}) \\ \sum_{i=1}^{9}(S_iC_ik_{1i}{}^2) & \sum_{i=1}^{9}(S_iH_ik_{1i}{}^2) & \sum_{i=1}^{9}(S_i(O_i+N_i)k_{1i}{}^2) & \sum_{i=1}^{9}(S_ik_{1i})^2 & \sum_{i=1}^{9}(S_iK_{1i}k_{2i}) \\ \sum_{i=1}^{9}(k_{2i}C_ik_{1i}) & \sum_{i=1}^{9}(k_{2i}H_ik_{1i}) & \sum_{i=1}^{9}(k_{2i}(O_i+N_i)k_{1i}) & \sum_{i=1}^{9}(k_{2i}S_ik_{1i}) & \sum_{i=1}^{9}(k_{2i})^2 \end{bmatrix} \times \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{9}(C_ik_{1i}HHV_i) \\ \sum_{i=1}^{9}(H_ik_{1i}HHV_i) \\ \sum_{i=1}^{9}((O_i+N_i)k_{1i}HHV_i) \\ \sum_{i=1}^{9}(S_ik_{1i}HHV_i) \\ \sum_{i=1}^{9}(k_{2i}HHV_i) \end{bmatrix} \quad (6)$$

Constants k_{1i} and k_{2i} present in (6) assume the values indicated in (7) and (8).

$$k_{1i} = \left(\frac{1}{1-0.01\times A_i}\right)\times\left(\frac{C_i}{3}+H_i-O_i+\frac{S_i}{8}\right) \tag{7}$$

$$k_{2i} = \frac{C_i}{3}+H_i-O_i+\frac{S_i}{8} \tag{8}$$

Values of C_i, H_i, N_i, O_i, N_i and A_i were replaced by the results from the ultimate analysis and determination of ash content for each experimental waste characterized in section 2.1.

2.4. Selection of the best correlation

The best correlation was selected based on the deviations found between the calculated HHV using each expression and the results determined during the experimental characterization of the previous nine wastes plus other 10 similar materials retrieved from the literature. Therefore, the correlation that presented the minimum absolute deviations was defined as the best that fitted the real results with the greatest accuracy. To accomplish this analysis, the average absolute error (*AAE*) and average bias error (*ABE*) were determined in order to estimate the accuracy provided by each expression and to evaluate if the calculated result was over- or underestimated relative to the real values, in average terms. The expressions for *AAE* and *ABE* (in %) are transcribed in (9) and (10) [3, 5].

$$AAE = \frac{100}{20}\times\sum_{i=1}^{20}\left|\frac{HHV_{calc\,\mathrm{i}}-HHV_{real\,\mathrm{i}}}{HHV_{real\,\mathrm{i}}}\right| \tag{9}$$

$$ABE = \frac{100}{20}\times\sum_{i=1}^{20}\left(\frac{HHV_{calc\,\mathrm{i}}-HHV_{real\,\mathrm{i}}}{HHV_{real\,\mathrm{i}}}\right) \tag{10}$$

In these expressions, $HHV_{calc\ i}$ and $HHV_{real\ i}$ refer, respectively, to the values of HHV calculated by the expressions and to the real ones obtained during the experimental measurements and from the literature regarding waste *i* (MJ/kg db). Whenever applicable, values of C_i, H_i, N_i, O_i, N_i, A_i and $HHV_{real\ i}$ collected from the literature were converted to db, as required by the three expressions under analysis.

2.5. Validation of the best correlation

This task was carried out by calculating and evaluating the absolute and bias errors (*AE* and *BE* in %, respectively) for each particular waste *i* and using the best correlation that was selected. These errors were obtained from (11) and (12).

$$AE_i = \left|\frac{HHV_{calc\,\mathrm{i}}-HHV_{real\,\mathrm{i}}}{HHV_{real\,\mathrm{i}}}\right| \tag{11}$$

$$BE_i = \frac{HHV_{calc\,\mathrm{i}}-HHV_{real\,\mathrm{i}}}{HHV_{real\,\mathrm{i}}} \tag{12}$$

Finally, results obtained from the best correlation were compared with those determined with the published expressions exhibited in Table 1 through an assessment of the *AAE* and *ABE* values calculated from (9) and (10).

3. Results and discussion

Table 4 presents the results for the ultimate analysis, ash contents and HHV determined for each of the experimental wastes (R1-R9) used to establish the correlations, and for the additional 10 wastes (R10-R19) employed for validation and which were collected from the literature.

Table 4. Results of the characterization of all wastes (experimental and from the literature) used for deduction of correlations and for final validation.

Waste	Ultimate analysis (wt%, db)					A (wt%, db)	HHV_{real} (MJ/kg db)
	N	C	H	S	O		
R1	2.0	45.8	5.8	0.0	43.7	2.7	18.886
R2	0.1	47.8	6.0	0.0	44.8	1.3	19.368
R3	0.3	38.6	5.2	0.1	37.5	18.3	14.903
R4	0.0	83.9	14.0	0.0	0.0	2.5	44.940
R5	0.2	40.2	5.4	0.1	48.0	6.1	17.039
R6	0.0	41.8	5.9	0.0	43.2	9.1	26.536
R7	0.3	50.9	6.6	0.1	31.2	10.9	25.013
R8	3.3	70.9	7.4	0.0	16.5	1.9	30.265
R9	0.1	33.4	4.6	0.4	11.7	49.8	24.562
R10	0.1	50.4	6.5	0.0	43.0	0.5	20.800
R11	1.7	54.9	6.8	0.2	43.3	6.8	19.460
R12	0.4	51.2	6.7	0.3	53.6	12.2	15.890
R13	0.2	80.1	13.2	0.1	4.5	2.0	42.690
R14	0.2	52.0	8.0	0.1	60.3	7.9	24.600
R15	0.1	85.9	14.2	0.1	0.1	0.3	42.900
R16	0.1	85.4	14.0	0.0	1.0	0.4	46.000
R17	0.1	62.4	4.4	0.1	33.2	0.2	23.090
R18	7.1	69.2	6.9	0.0	16.5	5.2	30.500
R19	2.3	18.0	2.9	0.8	16.7	61.8	9.400

The presence of plastic materials in wastes R4, R6, R7 and R8 increased their HHV's to values among 25-45 MJ/kg db, which is explained by the lower O/C ratios (0.00-0.61) which are near to those found in fossil fuels (<0.4 [8]). Sludge (R9) has also an interesting HHV (24.6 MJ/kg db) due to the same reason, although the ash content is relatively high (≈50 wt% db) which constitutes a disadvantage in combustion processes since a lot of parallel byproducts will be generated.

Appreciable differences in the composition among wastes can be found in Table 4, especially regarding the contents of C, O and ash that ranged between 33-84, 0-48 and 1-50 wt% db, respectively. As such, results of HHV varied substantially among materials (14.9-44.9 MJ/kg db), demonstrating the heterogeneous chemical nature of the materials. Within acceptable limits of variability, it can be said that experimental results agree to those found in the literature [6, 9-12]. The source of waste (MW or CDW) appears to not influence significantly the properties of woods (R1 and R2) but it does in the case of plastic materials (R4, R7, R8 and R9).

Table 5 reports the complete expressions for HHV determination after the application of the multiple regression method.

Table 5. Expressions of HHV deduced from the regression method.

Number	Expression
(1)	$HHV=0.3845\times C + 0.8831\times H - 29.1217\times S - 0.0630\times O - 1.0063\times N + 0.3888\times A - 0.2546$
(2)	$HHV=0.4191\times C+0.6523\times(H-O/8)+ 18.4007\times S$
(3)	$HHV= [0.0793\times C/(1-0.01\times A)-0.4055\times H/(1-0.01\times A)-0.0482\times(O+N)/(1-0.01\times \mathrm{A}) +5.0532\times S/(1-0.01\times \mathrm{A})+0.0516]\times(C/3+H-O+S/8)$

In all expressions S is associated with higher coefficient values in magnitude, indicating that HHV depends strongly on this parameter but the way that this influence occurs is not the same: while in (1) the HHV decreases with greater values of S due to the negative coefficient (-29.1217) the opposite case happens with (2) and (3) (+18.4007 and +5.0532, respectively). Furthermore, it seems that available hydrogen and air for combustion as modelled by (2) and (3) have minor contributions for HHV since the associated coefficients assume smaller absolute values (<0.7). Other parameters that have some influence are *C* and *H* (<0.8), although in a much lesser extent when compared to *S*.

By evaluating the coefficient signals of (1) one may state that HHV increases with *C*, *H* and *A* and decreases with *S*, *O* and *N*. According to the last formula introduced in Table 1, it was expected that HHV would be inversely proportional to *A* since this fraction does not have organic matter to be burned. The explanation around this paradox may be due to the high heterogeneity of materials in terms of composition and to the small number of replicated samples used for the deduction of expressions.

Table 6 reports the real and calculated values for HHV of each waste by using expressions (1), (2) and (3). Average error analysis between real and calculated results is illustrated in Fig. 1. It must be pointed out that some waste points (R7, R11, R12, R14, R15, R17 and R19) were not depicted in Fig. 1(c) because they fell out of the range of both axes.

Table 6. Results of real and calculated HHV's using the three correlations for all wastes.

Code	HHV_{real} (MJ/kg db)	HHV_{calc} (MJ/kg db)		
		Expression (1)	Expression (2)	Expression (3)
R1	18.886	18.762	19.415	20.295
R2	19.368	21.006	20.294	17.508
R3	14.903	20.717	18.352	7.657
R4	44.940	45.340	44.295	44.187
R5	17.039	16.204	18.297	23.975
R6	26.536	21.844	17.845	28.612
R7	25.013	24.202	24.933	-3.362
R8	30.265	29.920	33.196	25.451
R9	24.562	23.522	23.405	18.397
R10	20.800	22.249	21.856	13.168
R11	19.460	19.238	27.594	-9.476
R12	15.890	17.573	26.978	-10.241
R13	42.690	39.580	43.653	48.012
R14	24.600	22.962	23.935	56.308
R15	42.900	42.411	47.095	68.638
R16	46.000	44.937	44.842	45.530
R17	23.090	22.596	28.155	-16.934
R18	30.500	26.284	32.157	22.743
R19	9.400	6.583	22.794	-68.492

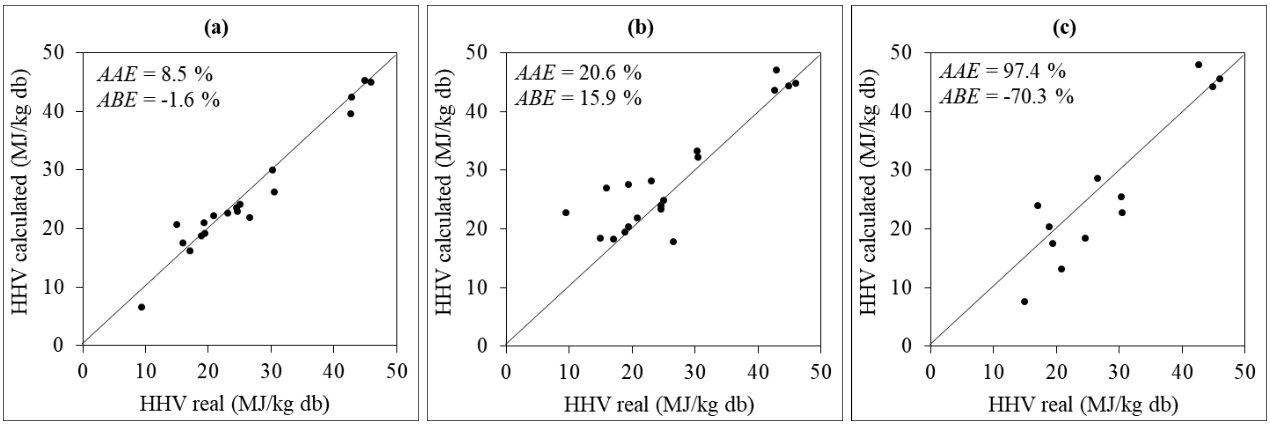

Fig. 1. Relative deviations and average error results among real and calculated HHV's obtained from (a) expression 1, (b) expression 2 and (c) expression 3.

From the figure it can be inferred that the correlation that fits better the real results is expression (1), producing the lowest errors in magnitude for *AAE* (8.5 %) and *ABE* (1.6 %). In fact, the majority of real HHV points are close to the reference diagonal line, meaning that HHV is best described if it is determined from the sum of terms where each one depend linearly from the proportion of each component present in the material. Since *ABE* is negative (-1.6 %), this correlation underestimates the HHV for a particular waste in average terms. Other correlations gave higher results for *AAE* and *ABE* in magnitude (>15 %) and therefore their validation is not confirmed for the type of wastes that were considered in this study, as compared with the results generated from expression (1).

Figure 2 presents the results of *AE* and *BE* found during HHV calculation for each particular waste, as determined through expression (1).

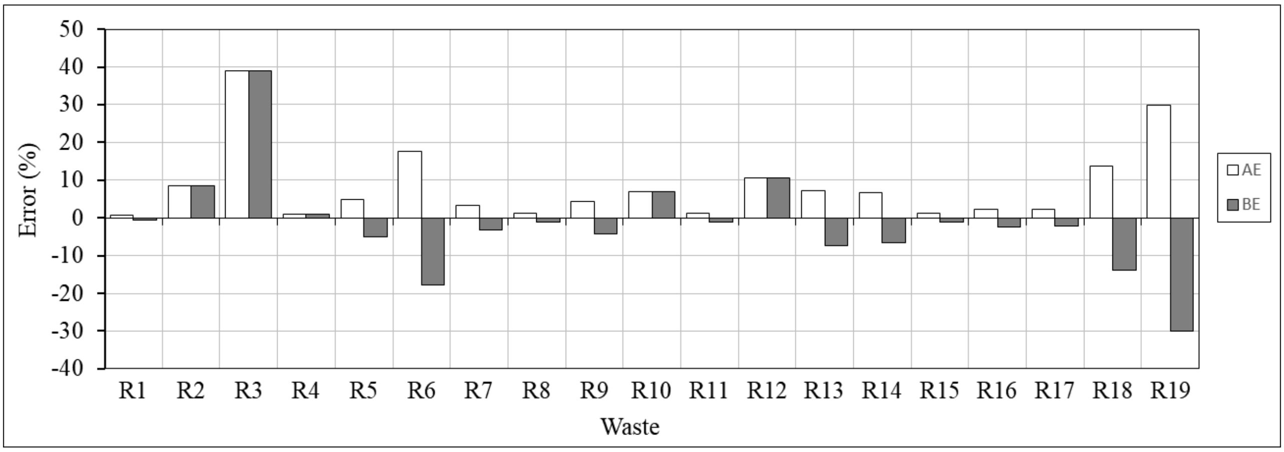

Fig. 2. Absolute and bias errors obtained during HHV determination from expression (1) and for each waste.

Supposing that *AE's* until around 10 % would be acceptable to use the correlation as was seen in Table 1, wastes that produced the highest values were R3 (paper/card from MW), R6 (mixture of paper and plastic), R18 (polyurethane) and R19 (sewage sludge). However, it was observed that the correlation gave good estimations of HHV for some similar materials as was the case of R14 (mixture of paper/plastic) and R9 (sludge). The greatest errors in magnitude were found for R3 (39 %). Reasons behind the high *AE*'s found for these four wastes may be generally explained by the significant deviations of contents of C, O and ash from the average values and by the higher contents of S and N present in R18 and R19, both associated to high coefficients inside expression (1). Therefore, the use of the expression for these types of wastes is questionable.

If one tries to remove these four wastes from the error analysis it may be verified that the *AAE* provided by the correlation reduced from 8.5 % to 4.1 %, which is a significantly better situation in terms of accuracy.

Comparison among the *AAE* produced by expression (1) and by the published correlations presented in Table 1 is summarized in Table 7. The correlation collected from [5] was not considered because levels of *O* present in some wastes were out of the limits reported for which that correlation is valid. In addition, ultimate analysis of all wastes were converted to daf basis in order to use the expression from [3], as indicated in the text.

Table 7. Results for AAE and ABE obtained from expression (1) and literature correlations mentioned in Table 1.

Equation	Reference	*AAE*, %	*ABE*, %
$HHV=0.3845\times C+0.8831\times H-29.1217\times S-0.0630\times O-1.0063\times N+0.3888\times A-0.2546$	This work	8.5	-1.6
$HHV=0.404207\times C+0.318857\times H$	[3]	15.5	3.6
$HHV=0.416638\times C-0.570017\times H+0.259031\times O+0.598955\times N-5.829078$	[4]	30.3	-9.7
$HHV=0.4302\times C-0.1867\times H-0.1274\times N+0.1786\times S+0.1842\times O-2.3799$	[6]	27.9	5.9

Analysis of these results indicates that expression (1) had the best accuracy in HHV estimation among all the studied expressions and for the set of wastes that were tested, since its *AAE* was the lowest (8.5 %). The over- or underestimation of results was not uniform because different signals of *ABE* were obtained for the different expressions. Regarding expression from [6] that was derived exclusively from samples of sewage sludge, the *AAE* was higher as expected (27.9 %). However, even this expression was not able to estimate conveniently the HHV of sludge samples employed in this work, namely R9 and R19, once appreciable *AE* were found for both (45.7 % and 17.6 %, respectively). The same situation happened with expression (1) for R19, as was already stated (30.0 %).

A polystyrene waste with a carbon concentration higher than 90 wt% was considered to validate expression (1) but the calculated HHV had a significant *AE* of around 67 %, so it was considered an outlier of the model. This suggests that materials with carbon contents higher than 90 wt% may not be well described by this model and should not be considered when applying this correlation.

In synthesis, expression (1) continues to be the most recommended for usage among all expressions retrieved from the literature when trying to estimate the HHV for the types of wastes analyzed in this work, preferably those for which error levels were lower. According to the obtained results and taking into account the list of wastes for which appreciable deviations were found, the deduced expression is valid when the atomic ratios O/C and H/C are within the ranges $0.0\leq O/C\leq 1.2$ and $0.1\leq H/C\leq 0.2$, respectively.

4. Conclusions

In this work, a new mathematical expression was deduced to estimate the HHV of separated fractions of MW and CDW from their ultimate analysis and ash contents. A multiple linear regression method was used to derive this expression from nine different materials collected from those wastes.

The best one achieved an absolute error of 8.5 % and underestimated the real value by 1.6 %, in average terms. Application of the expression for wastes like paper/card, mixtures of paper and plastic, polyurethane and sewage sludge is questionable due to the higher errors that were generated. Still, the expression that was deduced presented the highest average accuracy in the HHV prediction when compared with other expressions from the literature and for the set of wastes that were analyzed in this work.

The improvement of the accuracy of this expression may be carried out by increasing the number of samples used for the deduction in future works, but the high heterogeneity of materials may difficult this task. Even so, it is expected that the developed expression can be useful in HHV estimation instead of the experimental determination that is expensive and prolonged.

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Nomenclature

A	ash content, wt% dry basis
AE	absolute error, %
AAE	average absolute error, %
ABE	average bias error, %
a	coefficient in the correlation expression
BE	bias error, %
C	carbon content, wt% dry basis
daf	dry and ash-free
db	dry basis
ELW	European list of waste
H	hydrogen content, wt% dry basis
HHV	higher heating value, MJ/kg dry basis
LHV	lower heating value
k	general constant
N	nitrogen content, wt% dry basis
O	oxygen content, wt% dry basis
S	sulphur content, wt% dry basis

Subscripts

calc	calculated value
i	number of waste residue
real	real value

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