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Estimation of the Higher Heating Value of Lignocellulosic Materials

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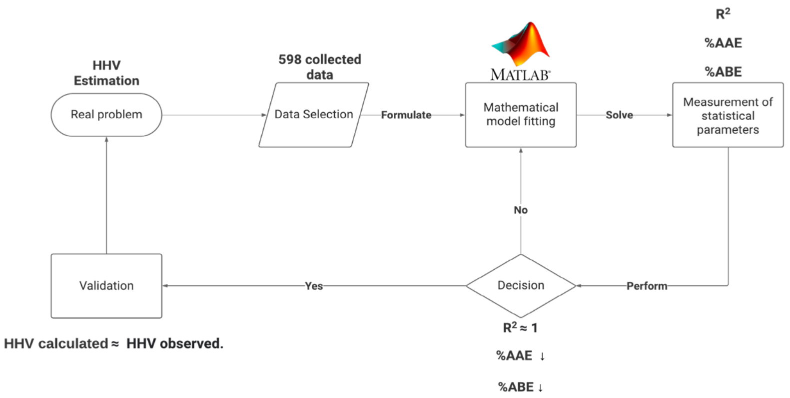
In the world of renewable energies, biomass will play a fundamental role in the coming years, this is how the interest in taking advantage of biomass from lignocellulosic materials is increasing. The objective of the present investigation was to develop a mathematical model for the prediction of the higher heating value (HHV) of lignocellulosic materials. Based on the proximate analysis of the raw materials, 598 data were collected from which possible correlations were established that allowed the development and validation of five statistical models; the best model proposed in the present study considers fixed carbon and ash content as variables, this model presents an average absolute error of 7.03% and an average bias error of 0.91%, in addition to presenting an R^2 of 0.801. Being the equation that provides the smallest error in relation to the higher heating value observed.

Graphical abstract



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1. Introduction

Economic growth, industrial and technological development depend mainly on the energy supply [1]. World demand is increasing, and the current concern is how to meet future energy demand, for years, fossil fuels have been used as primary energy sources (oil, gas and coal) [2]. However, their availability is limited, and greenhouse gas emissions greatly affect the environment [3].

Nuclear energy came to be considered as an alternative to avoid the problem of fossil fuel depletion, but the concern related to the storage of nuclear waste led to the search for renewable sources of energy [4]. For this reason, emphasis was given to second generation fuels produced from lignocellulosic raw materials [5] or also called lignocellulosic biomass, since it has the ability to become a supplier of clean and efficient energy for the production of heat [6], without the addition of large volumes of carbon dioxide to the atmosphere, as well as other harmful gases, unlike fossil fuels, [7]. In this context, biomass is considered a carbon neutral fuel and a renewable source for the generation of bioenergies [8].

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Lignocellulosic biomass is employed in several ways for the production of solid biofuels and subsequent energy generation. Studies indicate that the higher heating values (HHV) of agricultural residues such as corn stubble (17.80 MJ / kg) [9], African palm kernel (15.49 MJ / kg) and palm mesocarp fiber (16. 94 MJ / kg) [10], among others, present energy values comparable to those of fossil fuels (45.2 MJ / kg for diesel at 15 ° C and 101.3 kPa) [11].

According to Toscano and Foppa [12], the experimental determination of the heating value of lignocellulosic biomass requires the use of calorimetric pumps, this is a tedious process and it has a high economic cost that additionally presents a complicated measurement. Another methodology used results at the time to evaluate its elemental composition, which, requires expensive equipment and the presence of highly qualified analysts [13]. Therefore, several authors [9, 10, 14] propose the use of mathematical models based on the proximate composition of the biofuel; it is a simple and fast execution analysis, which makes this more affordable compared to elemental analysis [15], however, the literature does not reach a consensus regarding the expressions because these differ depending on the evaluated material [13].

Kucukbayrak et al. [16], Cordero et al. [14], Demirbas [9], Jiménez and González [17], Ahmaruzzaman [18] developed mathematical models based on proximate analysis of solid fuels targeting only a specific type of fuel or group. Sheng and Azevedo [19] analyze the negative effect of ash on HHV. Nhuchhen and Abdul Salam [20] proposed linear models based on non-volatile, volatile, and non-organic ratios from various groups of lignocellulosic biomasses on a dry basis and their non-linear effect on the selected linear correlation. Patel et al. [21], Mesroghli et al. [22], Uzun et al. [23], Estiati et al. [24] established models for the estimation of HHV from biomass using structures based on the artificial neural network (ANN). Some models include the four parameters of the proximate analysis (fixed carbon, volatile matter, ash and moisture) as shown by the study carried out by Akkaya [25]. However, the mathematical models proposed by these authors are not designed for a wide range of lignocellulosic biomasses and especially with large differences in the proximate composition.

Furthermore, each study shown by these authors do not suggest the reason for the variables present in their equations but rather their approach is to show a new model (linear, non-linear or both) that is developed by a new adjustment method and that considers the presence of one, two, three or up to four variables of the proximate analysis of groups of selected biomass, so that the replacement of models proposed by previous studies is achieved.

On the other hand, lignocellulosic materials are currently being evaluated for the elaboration of densified biomass (pellets) due to their handling advantages [26], however, the physical, chemical and structural properties have a significant influence on their energy value and therefore in solid biofuels made with these raw materials [27]. However, the mathematical models developed by various authors do not widely consider these products (pellets), for the approach of mathematical models that allow predicting energy behavior, which generates a disadvantage when using these models.

Due to the current need to use alternative materials for energy production, and to the need for more efficient and economical strategies that allow estimating with a low level of error the energy capacity that lignocellulosic materials can reach for use as biofuels, the objective of this work was to develop a mathematical model for the prediction of the higher heating value (HHV) of a large group of lignocellulosic biomasses, based on the meta-analysis of published data from proximate tests.

2. Results and Discussion

2.1 Data analysis

Table 1. Linear correlation coefficients for each variable of the proximate analysis as a function of the groups of lignocellulosic material.

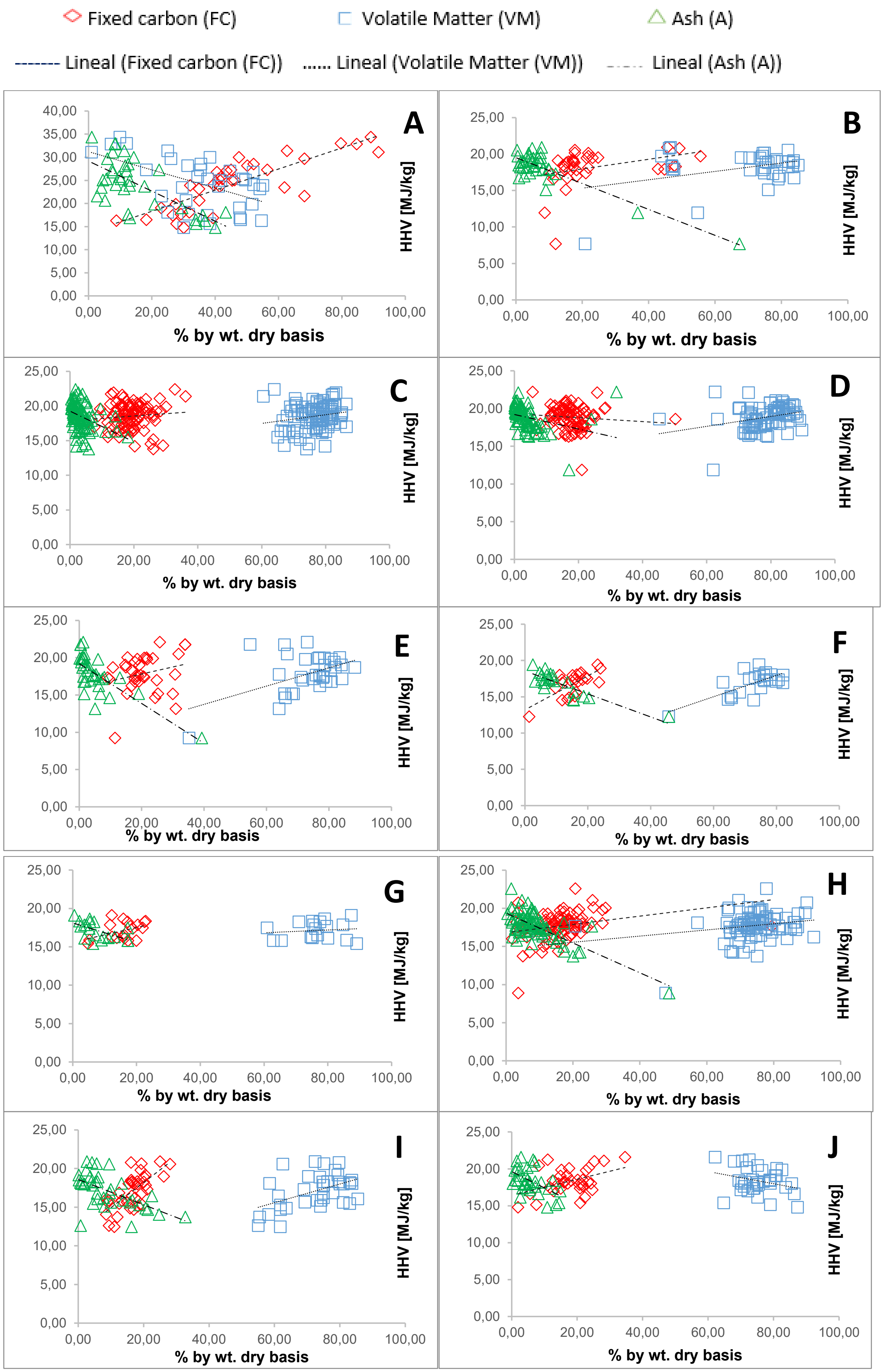
Group	rFC	rVM	rA	rM
A	0.8247	-0.5142	-0.6901	-0.6361
B	0.3494	0.3684	-0.8640	-0.4291
C	0.0916	0.1806	-0.3876	-0.2891
D	-0.0950	0.2989	-0.3035	-0.0329
E	0.2452	0.4707	-0.7455	-0.5525
F	0.7006	0.7093	-0.8614	0.4438
G	0.4254	0.1198	-0.5864	N/A
H	0.2806	0.2589	-0.7277	-0.2922
I	0.6974	0.4823	-0.5928	-0.4642
J	0.3950	-0.2333	-0.5308	-0.0256
K	0.4927	0.7683	-0.8584	-0.1805
L	0.8551	-0.4915	-0.6872	N/A

FC, Fixed Carbon; **VM**, Volatile Matter; **A**, Ash; **M**, Moisture **N/A**: Not analyzed

Table 1 shows the linear correlation coefficient values with respect to each group and each parameter of the proximate analysis related to the HHV values. For fixed carbon it is observed that groups A, F, I and L present a strong linear association; of these, only group D shows a negative slope, an inversely proportional correlation. However, it is known that the higher the amount of fixed carbon, the energy content is higher, as shown by Ozyuguran [28]. This discrepancy can be given since in some studies they suggest that the fixed carbon arises from the given difference between the unit, the content of volatile matter, ash and moisture (FC = 1- VM-M-ASH) [15, 29], while other studies analyze it without moisture content, that is, assuming a percentage on a dry basis [30].

Regarding the analysis of the volatile matter, groups F and K show a strong positive linear correlation, while a negative correlation can be evidenced in groups A, J and L. In the case of the study of ash content, only the groups C and D show a moderate correlation, the rest of the categories show a strong correlation, however, all report a negative slope (Figure 1), which reveals that, the lower the ash concentration in the lignocellulosic material, it contributes to the HHV is higher [19].

With these results, it is possible to define that the relevant parameters within the proximate composition of the lignocellulosic materials for the entire analyzed database are the fixed carbon and the ash content, which present a very strong correlation (table 1), therefore, it is possible to use only these two parameters as main variables to predict the HHV of lignocellulosic biomass for energy purposes.


Fixed carbon (FC)
Volatile Matter (VM)
Ash (A)
Lineal (Fixed carbon (FC))
Lineal (Volatile Matter (VM))
Lineal (Ash (A))
A
B
C
D
E
F
G
H
I
J
HHV [MJ/kg]
% by wt. dry basis

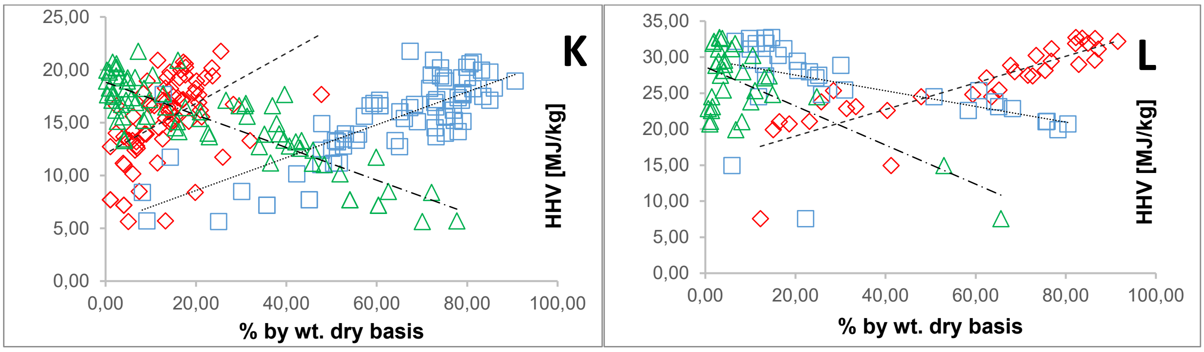


Fig. 1. Linear correlation for each variable of the proximate analysis in relation to HHV.

2.2 Analysis of mathematical models for prediction of HHV

For the analysis of the mathematical models, three measures were used: the coefficient of determination R^2, average absolute error (% AAE) and average bias error (% ABE). These parameters were calculated from the data points which stand in the supplementary material (Table S2).

Table 2 demonstrate that the M6 model presents a higher determination coefficient with regard to the others, this indicates that there is a great relationship with the variables of fixed carbon, volatile matter and ash, it also shows a better adjustment by presenting lower % AAE and % ABE. For its part, the M3 model is the one with the lowest adjustment and an R^2 that establishes little or no relationship with the values of the variables.

With this, it can be defined that those models that analyze more than 3 different categories of biomass destined to be used as fuels tend to present a lower percentage of error in relation to the correlations predicted for a single type of fuel, as occurs with the M1 models. M4 and M6.

As happened with the model proposed by Pons [31] whose correlation is directed only to the calculation of the HHV of sugarcane bagasse, which shows a lower adjustment, likewise, for the model proposed by Kücükbayrak [16] whose model was predicted only from lignite samples. On the other hand, the correlation calculated for M5 presented a low adjustment (R^2 = 0.1599), despite the fact that it was developed from several categories of lignocellulosic materials ranging from coke, wood, manufactured fuel and other lignocellulosic residues, which indicates that the model proposed by the author is unreliable.

Table 2. Comparative analysis of the mathematical models collected for the prediction of HHV.

Code	R^2	%AAE	%ABE	Reference
M1	0.7474	8.21	-1.19	[13]
M2	0.7127	10.3	6.95	[14]
M3	0.0028	25.2	-22.7	[31]
M4	0.7362	9.31	-6.21	[9]
M5	0.1599	11.76	-0.11	[20]
M6	0.7838	7.32	1.78	[32]
M7	0.6066	8.24	2.57	[33]
M8	0.5237	16.3	6.48	[16]

2.3 Adjusting the models.

A multiple linear regression was performed to obtain the first two models, while the last three models were treated by adjusting polynomials of degree three, four and five, as shown in Table 3.

Table 3. Comparative analysis of the mathematical models proposed for the prediction of HHV.

Model coefficients	Model				
	E1	E2	E3	E4	E5
a	11.9621	18.4189	-7.206	16.28	35.62
b	0.217181	0.14035	0.3714	0.3535	-0.268
c	0.0392564	-0.0292004	0.6997	0.3287	-0.3898
d	-0.0392564	-0.0667876	0.004705	-0.01271	-0.00689
e	-	-0.0704451	-0.0004388	-0.08365	0.04372
f	-	-	-0.01004	-0.02345	0.01313
g	-	-	-0.00007791	0.0001918	0.0001687
h	-	-	-0.00001072	0.003104	-0.000844
i	-	-	0.00005891	0.003286	-0.0005859
j	-	-	-	0.0005124	0.0003327
k	-	-	-	$-0.8x10^{-6}$	$0.9024x10^{-6}$
l	-	-	-	-0.00003198	$0.3945x10^{-5}$
m	-	-	-	-0.00007891	$0.8906x10^{-5}$
n	-	-	-	-0.00004563	$0.46x10^{-6}$
o	-	-	-	$-0.5656x10^{-5}$	$-0.2003x10^{-5}$
p	-	-	-	$0.874x10^{-7}$	-
q	-	-	-	$0.4064x10^{-6}$	-
r	-	-		$0.5312x10^{-6}$	-
s	-	-	-	$0.22x10^{-6}$	-
t	-	-	-	$0.235x10^{-7}$	-
R^2	0.7572	0.4667	0.7959	0.8006	0.7764
%AAE	7.97	9.32	7.34	7.03	7.39
%ABE	1.11	1.48	1.01	0.91	1.08

In accordance with the above, the correlation that presented the best adjustment was the E4 model whose variables are only the content of fixed carbon and ash, followed by the E3 model where it also presents two variables for the calculation of HHV, these are fixed carbon and volatile matter. Thus, these models establish two of these properties as the only measured variables, which would involve less time for the analyst and would translate into lower cost of analysis.

These equations can be widely used as they present a strong linear correlation and relatively lower error percentages in relation to the rest of the proposed models.

The E2 model, which contains the moisture percentage among its variables, presented a lower adjustment (R^2 = 0.4667) and higher error percentages than those reached by the other equations developed in this study (% AAE = 9.32% ABE = 1.48). It can be concluded that the moisture content in the biomass is a critical parameter. A high moisture content can affect the combustion process and therefore the efficiency of the biofuel. This is why any material that is destined for energy purposes, must be subjected to strict drying processes until the adequate percentage is achieved [34, 35], that is, this property can be modified so that it does not influence the HHV calculation.

Therefore, parameters such as fixed carbon, volatile matter and ash, for being inherent properties of the material to be burned have a great influence on the HHV calculation.

The E1 model clearly defines the relationship between HHV and these parameters. The coefficient b that accompanies the variable FC turns out to be positive, so that, if the content of fixed carbon is high, the higher heating value will be high too, because it acts as a main heat generator during combustion [28], consequently, it has a positive effect on the energy potential of biofuel. The same happens with the coefficient C for volatile matter (VM); but it contradicts what was stated in the E2 model by showing a negative coefficient for this parameter, although if it is true, the VM increases when the heating rate and the temperature also increase [9], a high volatile matter content does not always guarantee a high HHV, because some of the ingredients of volatile matter are formed from non-combustible gases such as CO_2 and H_2O [28].

However, the coefficient D that accompanies variable A is negative in both correlations (E1 and E2). This parameter, being relatively lower, contributes to the higher heating value will be higher, therefore, a high ash content present in a matter makes it an unfavorable option to be considered as fuel [36].

2.4 Validation and comparison.

To validate the mathematical models, data were used that were not considered for the adjustment of the models, this, with the aim of reaffirming that the models proposed in this research can be used to evaluate the HHV of different types of lignocellulosic biomass. For this validation 98 data from proximate analysis results of lignocellulosic materials were used.

In the case of the Pons equation [31] used as a reference, and equation 2 proposed in this study, only 47 data were used, due to the particularity that these mathematical models consider the moisture percentage as a variable. The information on the data used for validation is found in the supplementary material (Table S3 and Table S5 respectively).

To compare and validate the developed models in this research with the HHV models obtained from the literature, R^2, average bias error and average absolute error were determined as shown in Table 4. Which established that the E4 model proposed a better fit compared to the rest of models. Verifying the results obtained by the correlation coefficient (Table 1), where the fixed carbon and the ash content directly influence the calculation of the HHV, so that the best adjustment of the model could be evaluated in various categories must presenting both parameters among its variables (E4 model). This analysis is not reflected in additional references [9, 19, 37, 38] where the developed models assume a linear function of HHV in relation to the content of fixed carbon and volatile matter.

Table 4. Comparison of the correlations between the published models and those proposed in this study.

Code	R^2	%AAE	%ABE	Reference
E1	0.5919	8.90	1.28	P.S
E2	0.6057	7.59	-0.53	P.S
E3	0.5819	8.96	0.93	P.S
E4	0.7518	7.13	0.63	P.S
E5	0.5940	8.32	1.59	P.S
M1	0.5366	10.5	-1.00	[13]
M2	0.5558	11.6	7.31	[14]
M3	0.1697	29.3	-24.2	[31]
M4	0.5173	11.4	-6.33	[9]
M5	0.2280	11.2	-0.16	[20]
M6	0.6202	8.23	1.70	[32]
M7	0.5366	9.56	2.07	[33]
M8	0.3477	19.0	9.86	[16]

Thus, the E4 model proposed in this study turn out to be a simple, fast and inexpensive way to obtain good estimates of the HHV of lignocellulosic biomass and other solid organic materials, intended for being used as second-generation biofuels. It is worth mentioning that the meta-analysis carried out in this study included the use of materials, ranging from coke, wood, biomass residues to biochars, for which the model in question can also be applied to manufactured biofuels or solid waste that are subjected to some treatment (gasification, pyrolysis), or densification as in the case of pellets.

In Addition, proposed models were derived from a wide interval in terms of the content (%) of fixed carbon [1.00-91.50], volatile matter [0.92-91.98] and ash [0.10-77.70]. Therefore, the efficiency of the selected model (E4) encompasses various types of lignocellulosic materials with very different proximate characteristics, with which an alternative solution can be provided to that stated by various authors such as Meraz et al. [39], which raises the importance of the influence of high variations in biomass components in the calculation of HHV. However, in the case of lignocellulosic materials, it is complex to propose a universal mathematical expression, which allows describing the behavior of HHV for any condition and type of material, so it is necessary to indicate that the applicability of the mathematical model E4 (better adjustment) and the other models proposed in this research, is limited to the categories mentioned in Table 5.

3. Material and Methods

In this research, a meta-analysis was carried out for the validation and comparative evaluation of expressions given for the prediction of HHV of lignocellulosic materials. A series of data points from the proximate analysis of samples obtained from the published literature is presented, allowing to verify the developed models.

3.1 Data selection

598 data were used from the proximate analysis of lignocellulosic materials, from studies carried out from 1962 to 2020, which are annexed in the Suplementary Material (Table S1). The data were grouped into twelve categories depending on their nature, as established by Parikh et al [13]. Table 5 presents the relevant information of the categories. The complete information of each material is presented in the supplementary material that is attached.

For the analysis of the data, the verification of its linearity was considered. The linearity coefficient r was evaluated for each type of material. The determination was carried out by means of the CORREL function in Excel.

Table 5. Summary of data taken from the literature for the adjustment and validation of the models.

N°	Raw Material	Number of data points	Proximate analysis Range % by wt. Dry basis				Reference
			FC	VM	ASH	M	
A	*Coals Coke.*	35	8.73-91.47	0.92-55.02	1.02-43.29	1.15-29.29	[13,16,20,40-44]
B	*Manufactured fuel*	36	8.60-55.59	20.80-85.00	0.33-67.30	5.20-12.50	[13, 20, 40, 44-47]
C	*Pit Shells Seeds Cobs.*	101	7.60-36.10	60.50-86.50	0.35-18.10	2.28-65.20	[9, 10, 14, 20, 28, 32, 40, 43, 48-52]
D	*Wood Energy crops*	86	5.64-50.17	45.20-89.69	0.10-31.79	2.50-43.00	[9, 13, 14, 17, 20, 32, 40, 42, 43, 52, 53]
E	*Barks Prunings*	35	9.00-33.90	35.10-88.25	0.10-39.20	7.60-33.00	[9, 13, 17, 20, 40, 41, 43, 54]
F	*Straws*	23	1.33-24.00	45.68-82.12	2.50-45.76	6.56-9.80	[9, 13, 14, 20, 40, 43, 48, 53]
G	*Stalks*	19	4.67-22.80	60.90-89.01	0.50-17.30	8.21-8.90	[9,13,17, 20, 28, 55]
H	*Fibrous material Leaves Grass*	84	1.80-79.37	9.57-91.98	0.40-48.70	6.27-19.50	[9, 10, 13, 20, 40-42, 48]
I	*Hull Husk Dust*	37	8.48-28.06	55.03-85.44	0.15-32.70	7.00-34.93	[9, 13, 14, 17, 20, 28, 40, 41, 48, 56]
J	*Others*	35	1.90-34.60	62.10-87.30	0.30-14.79	6.67-14.90	[13, 20, 28, 48, 53, 55]
K	*Waste material*	74	1.00-47.70	8.10-90.60	0.20-77.70	1.50-78.10	[9, 13, 17, 20, 28, 32, 40, 41, 43, 52, 53, 57, 58]
L	*Biomass chars*	33	12.20-91.50	5.90-80.43	0.60-65.60	N/A	[6, 13, 14, 42]

N/A: Not analyzed.

3.2 Mathematical models for the prediction of HHV.

For the selection of the base models, eight mathematical expressions raised in the specialized bibliography were used to calculate the HHV of lignocellulosic materials based on its proximate analysis. The applicability of each expression is determined by the type of lignocellulosic material that was analyzed in the different investigations. Table 6 presents these mathematical expressions.

3.2.1. Proposed mathematical models

The adjustment of mathematical models based on the characteristics of the correlations of approximately 500 data is proposed (Table S2). These data were chosen for its extensive analysis to be used as an alternative to the use of fossil fuels. The mathematical models proposed in this research consider similar mathematical structures to those of Parikh [13], Cordero [14], Pons [31] and Dermibas [9].

The table below (Table 7) shows the proposed models, which were developed using the statistical programs *Statgraphics Centurion XVI* for linear models (model E1 and E2), and *the Curve Fitting Tool* of Matlab R2015a for the models polynomial (E3-E5).

For the approach of the E2 model, only 240 data were used (Table S4), since in addition to the content of fixed carbon, volatile matter and ash, said model considers the moisture percentage.

3.2.2 Validation of the models

For the validation of the mathematical models proposed in this research, as well as of the base models established in the specialized literature, 98 data from proximate analysis of lignocellulosic materials were used, with different characteristics from those used in the approach to the models.

The Microsoft Excel program was used, which obtained the values of the coefficients of determination R^2 in each mathematical model. On the other hand, the average absolute error (% AAE) and average bias error (% ABE) were also evaluated, for which the equations proposed by Parikh et al. [13].

$$Average\ Absolute\ Error\ (AAE) = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{HHVc - HHV}{HHV}\right| 100\% \quad (eq. 1)$$

$$Average\ Bias\ Error\ (ABE) = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{HHVc - HHV}{HHV}\right] 100\% \quad (eq. 2)$$

Table 6. Base mathematical expressions for the calculation of HHV from the proximate analysis.

N°	Equation	Reference
M1	$HHV = 0.3536FC + 0.1559VM - 0.0078A$	[13]
M2	$HHV = 35430 - 183.5VM - 354.3A$	[14]
M3	$HHV = 19522.6 - 51.29S - 194.1M$; where $S = 100 - M - A$	[31]
M4	$HHV = 0.312FC + 0.1534VM$	[9]
M5	$HHV = 19.288 - 0.2135(VM/FC) - 1.9584(A/VM) + 0.0234(FC/A)$	[20]
M6	$HHV = -0.0038(-19.9812FC^{1.2259} - 1.0298 \times 10^{-13} VM^{8.0664} + 0.1026A^{2.4231} - 1.2065 \times 10^{-7} (FC \times A^{4.6653}) + 0.0228(FC \times VM \times A) - 0.2511(VM/A)) - 0.0478(FC/VM) + 15.7199$	[32]
M7	$HHV = 0.365FC + 0.131VM + 1.397/FC + (328.568 \times VM)/(10283.138 + 0.531FC^3 \times A - 6.863FC^2 \times A)$	[33]
M8	$HHV = 76.56 - 1.30(VM + A) + 7.03 \times 10^{-3}(VM + A)^2$	[16]

HHV, [MJ / kg]; M, Moisture [%]; S, Soluble Solids [%]; FC, Fixed Carbon [%]; VM, Volatile Matter [%]; A, Ash [%].

Table 7. Mathematical expressions proposed for the calculation of HHV from the proximate analysis.

N°	Proposed equation
E1	$HHV = a + bFC + cVM + dA$
E2	$HHV = a + bFC + cVM + dA + eM$
E3	$HHV = a + bCF + cVM + dCF^2 + e(CF \times VM) + fVM^2 + gFC^3 + h(FC^2 \times VM) + i(FC \times VM^2) + jVM^3$
E4	$HHV = a + bFC + cA + dFC^2 + e(FC \times A) + fA^2 + gFC^3 + h(FC^2 \times A) + i(FC \times A^2) + jA^3 + kFC^4 + l(FC^3 \times A) + m(FC^2 \times A^2) + n(FC \times A^3) + oA^4 + p(FC^4 \times A) + q(FC^3 \times A^2) + r(FC^2 \times A^3) + s(FC \times A^4) + tA^5$
E5	$HHV = a + bVM + cA + dVM^2 + e(VM \times A) + fA^2 + gVM^3 + h(VM^2 \times A) + i(VM \times A^2) + jA^3 + kVM^4 + l(VM^3 \times A) + m(VM^2 \times A^2) + n(VM \times A^3) + oA^4$

HHV, [MJ / kg]; M, Moisture [%]; S, Soluble Solids [%]; FC, Fixed Carbon [%]; VM, Volatile Matter [%]; A, Ash [%].

4. Conclusions

Five mathematical models were proposed that allow estimating the higher heating value (HHV) on a dry basis, of various types of lignocellulosic biomass of highly variable proximate composition. The mathematical models proposed can estimate HHV of raw biomass or from some treatment or processing (such as pellets) and coke. One of the five proposed models was selected (model E4), because it considers among its variables the content of fixed carbon and ash as the most influential parameters in the calculation of HHV. This model provides results in an easy, fast and economical way in comparison with the other empirical models published in the specialized literature and other analytical application techniques (elemental and structural analysis and calorimetric pumps). The E4 model presented an average absolute error (% AAE) of 7.03% and an average bias error (% ABE) of 0.91%, values lower than those determined for the other base mathematical models and raised in the research. The model (E4) can predict the higher heating value of lignocellulosic materials having a fixed carbon content between 1.0 to 91.5% and an ash content between 0.1 and 77.7%; with a coefficient of determination (R^2) of 0.801 in all cases.

Supporting Information

Supplementary material is found in the supporting information file.

Author Contributions

Carolina Beltrón and Holger Palacios contributed equally to this paper in the investigation, methodology, writing of the original draft, review and editing prior to publication. Ricardo Baquerizo contributed to the writing, critical review of the manuscript and editing. Carlos Moreira contributed to the validation of the manuscript, verifying the experimental results and data analysis with other authors. Ernesto Rosero contributed to the supervision, project administration and writing-revision and editing prior to publication. All authors evaluated and approved the manuscript.

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