# Prediction models for higher heating value based on the structural analysis of the biomass of plant remains from the greenhouses of Almería (Spain)

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ABSTRACT

Within the realm of renewable energies, biomass will play a fundamental role in the coming years, especially due to the rise in the prices of fossil fuels, the doubtful safety of nuclear energy, and the need to reduce $CO_2$ emissions.

In Almería (SE Spain), a million tonnes of plant wastes are generated per year from greenhouse crops such as *Cucurbita pepo* L., *Cucumis sativus* L., *Solanum melongena* L., *Solanum lycopersicum* L., *Phaseolus vulgaris* L., *Capsicum annuum* L., *Citrillus vulgaris* Schrad, and *Cucumis melo* L., which have an energy potential of around a million MW h year$^{-1}$. The aim of the present work is to conduct structural analyses (lignin, cellulose, hemicellulose, and extractives) together with new HHV prediction models based on these parameters. For the analyses, internationally recognised methods and norms were used. Also, in the 15 univariate and multivariate prediction equations formulated, $R^2$ and adjusted $R^2$ proved higher in all cases (0.748 and 0.717), respectively, with the mean absolute percentage error varying between 0.119 and 0.623. Finally, only 10 equations were validated.

## 1. Introduction

Renewable energies will play a crucial role in the coming years in the European Union due fundamentally to the serious doubts about the safety of nuclear energy, the constant rise in the price of fossil fuels (depletable) and the steadily greater restrictions on emissions of carbon dioxide ($CO_2$), methane ($CH_4$), and nitrose oxide ($N_2O$). From this perspective, the urgency of alternative renewable, environmentally friendly energy sources reflects the importance of hydraulic, wind, geothermal, solar, and biomass energy (renewable sources) [1–3]. This latter source could be defined as non-fossilized organic matter arising from an unprovoked spontaneous biological process, usable as an energy source apart from other industrial applications [4]. In addition, biomass is expected to take a leading role in agricultural, forestry, and marine systems.

In each of these systems, humans obtain products for food or raw materials for industrial transformation (wood, paper, fabrics, chemical substances, fruits, vegetables, etc.) while generally producing some type of biomass waste. This biomass (from the above systems) can be used for energy but need to be studied from the logistical–environmental standpoint [5–13], analysed from the physical–chemical perspective [14–16], and submitted to different transformations (physical or chemical), to produce so-called biofuels [17–22].

The use of biomass as a biofuel requires, among other parameters, the prior knowledge of proximal analysis (ash, volatile components, and fixed carbon), an element analysis (C, H, N, S, and O), chloride quantity, ash composition, ash fusibility, organic anal-ysis (lignin, cellulose, hemicellulose, and extractives) and higher heating value (HHV). The calculation of the HHV is usually costly,

**Table 1**
Recent models based on structural composition (updated [23]).

| Researcher | Correlation (HHV, MJ kg$^{-1}$ dry basis) | Biomass types | Publication year | References | Comments |
|---|---|---|---|---|---|
| Shafizadeh and degroot | HHV = 0.17389[Ce] + 0.26629[L] + 0.32187[E] | Lignocellulosic materials | 1976 | [24] | References with errors |
| Tillman | HHV = 0.17389[Ce] + 0.26629(100−[Ce*]) | Wood | 1978 | [25] | References with errors |
| White | HHV = 17.9017 + 0.07444[L*] + 0.0661[E][a] | Unextracted wood | 1984 | [26] | Not $R^2_{\text{ajusted}}$, Not SE |
|  | HHV = 17.6132 + 0.0853[L*][a] | Extractive-free wood |  |  | Not $R^2_{\text{ajusted}}$, Not SE |
|  | HHV = 17.4458 + 0.0907[L*][a] | Extractive-free softwood |  |  | Not $R^2_{\text{ajusted}}$, Not SE |
|  | HHV = 18.0831 + 0.0637[L*][a] | Extractive-free hardwood |  |  | Not $R^2_{\text{ajusted}}$, Not SE |
|  | HHV = 17.7481 + 0.0800[L*](100−[E])/100 + 0.0886[E][a] | Unextracted wood |  |  | Not $R^2_{\text{ajusted}}$, Not SE |
| Jiménez and González | HHV=(1−[Ash]/ ([Ce] + [L] + [E]))(0.17389[Ce] + 0.26629[L] + 0.32187[E]) | Wheat straw, olive twigs, olive Wood, vine shoots, sunflower talks, cotton plant stalks, sunflower seed husk, olive stones, olive marc, holm oak residues, eucalyptus residues | 1991 | [27] | Not $R^2_{\text{ajusted}}$, Not SE |
| Demirbaş | HHV**=0.0889[L**] + 16.8218 HHV**=0.0893[L**] + 16.9742 | Wood and non-wood Wood: beech wood, hardwood, Ailanthus wood, softwood, spruce wood, wood bark | 2001 | [28] | Not SE Not SE |
|  | HHV**=0.0877[L**] + 16.4951 | Non-wood: tobacco leaf, corncob, corn straw, wheat straw, waste material, tobacco stalk, hazelnut shell, olive cake | |  | Not SE References with errors |
| Demirbaş | ΔHHV = 0.00639[E]$^2$ + 0.223[E] + 0.691 | Spruce trunkwood, spruce trunk bark, beech trunk wood, beech trunk bark, Ailanthus trunk wood, sunflower shell, almond Shell, hazelnut shell, olive husk, hazelnut kernel husk, walnut shell | 2002 | [29] | Not SE References with errors |
| Demirbaş | HHV**=0.0864[L**] + 16.6922 | Sunflower shell, almond shell, hazelnut shell, wood bark, olive husk, hazelnut kernel husk, walnut shell | 2003 | [30] | Not SE |
| Demirbaş | ΔHHV = 0.383[E]−0.0387 | Hazelnut shell, wheat straw, olive husk, beech wood, spruce wood, corncob, tea waste, walnut shell, almond shell, sunflower shell | 2004 | [31] | Not $R^2$, Not SE |
| Acar et al. | HHV = 0.0979[L] + 16.292 | Corn stover, corncob, sunflower shell, beech wood, ailanthus wood, hazelnut shell, wood bark, olive husk, walnut shell | 2012 | [32] | Not SE |

Ce: cellulose (cellulose and hemicelluloses) (% by mass on dry basis); L: lignin (% by mass on dry basis); E: extractive matter (% by mass on dry basis); *Indicates composition in % by mass on dry, and extractive-free basis; **Indicates composition in % by mass on dry, ash free and extractive-free basis; Not SE: not study of errors.

[a] Correlations converted to MJ kg$^{-1}$ with the following conversion factor: 1 Btu·lb$^{-1}$ = 2.3261 × 10$^{-3}$ MJ kg$^{-1}$.

especially in time (of analysis) and money (of equipment), and therefore, mathematical models are usually used to predict the HHV based on other biomass properties or components (C, H, N, S, O, ash, volatile components, fixed carbon, lignin, cellulose, hemicellulose, extractives, etc.). The literature offers a high number of correlations and prediction models to calculate the HHV of biomass from the results of proximal and element analyses [23], and to a lesser degree from structural analyses. An update accord-ing to Vargas-Moreno et al. [23] appears in Table 1.

The main biomass-analysis methods, following the American Standard Testing Methods (ASTM) and the European Normalisation Committee (ENC) are presented in Table 2. On the other hand, the ENC provides no specifications for the structural analysis, while in the ASTM the regulations described are either outdated or refer only to the content in lignin and extractives. Therefore, in Table 2 other methods are added to analyse lignin, cellulose, and hemicellulose.

In addition, with these methods, other authors also analyse the physical and chemical properties of the biomass [23]. As the name itself indicates, these analyses are based on the physical and chemical properties (density, viscosity, etc.) of the vegetable oil obtained from the biomass [23,61–68].

In the agricultural system of the present research in Almería, SE Spain (Fig. 1), the potential energy of the greenhouse-crop wastes were computed (1,003,497.97 MW h year$^{-1}$) from the direct HHV calculation (differentiating by species) and performing linear uni-variate and multivariate mathematical models of HHV prediction based on proximal and element analyses, in addition to determin-ing the content in ash and its fusibility [14,15]. When this research was finished, the samples of the material analysed were preserved for later structural analysis of the biomass (Fig. 2). Thus, this study has two aims: first, to determine the content in lignin, cellulose, hemicellulose, and extractives of the greenhouse waste, differenti-ating by species; and, second, to establish mathematical HHV pre-diction models based on the structural analysis of the biomass studied.

## 2. Materials and methods

The plant species studied were courgette (*Cucurbita pepo* L.), cucumber (*Cucumis sativus* L.), eggplant (*Solanum melongena* L.), to-mato (*Solanum lycopersicum* L.), greenbean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), watermelon (*Citrillus vulgaris*

**Table 2**
Biomass analysis methods.

| Property | | Analytical method | References |
|---|---|---|---|
| Standard test meted for analysis | | ASTM E870-82(2006) | [33] |
| *Proximate analysis* | | | |
| Moisture content | | UNE-EN 14774-1:2010 | [34] |
| | | ASTM E871-82 (2006) | [35] |
| | | UNE-EN 14775:2010 | [36] |
| Ash | | ASTM D1102-84(2007) | [37] |
| | | ASTM E830-87(2004) | [38] |
| | | UNE-EN 15148:2010 | [39] |
| Volatile compounds | | ASTM E872-82(2006) | [40] |
| | | ASTM E897-88(2004) | [41] |
| Fixed carbon | | By difference | |
| *Elemental analysis* | | | |
| Carbon (C) | | UNE-CEN/TS 15104:2008 EX | [42] |
| | | ASTM E777-08 | [43] |
| Hydrogen (H) | | UNE-CEN/TS 15104:2008 EX | [42] |
| | | ASTM E777-08 | [43] |
| Nitrogen (N) | | UNE-CEN/TS 15104:2008 EX | [42] |
| | | ASTM E778-08 | [44] |
| Sulphur | (S) | ASTM E775-87(2008)e1 | [45] |
| Oxygen | (O) | By difference | |
| Chlorine (Cl) | | ASTM E776-87(2009) | [46] |
| | | UNE 164001:2005 EX; UNE 164001:2005 EX ERRATUM:2008 | [47,48] |
| Higher heating value | | ASTM D5865-10ae1 | [49] |
| | | ASTM E711-87(2004) | [50] |
| Sample preparation | | UNE-CEN/TS 14780:2008 EX | [51] |
| *Structural analysis* | | | |
| Lignin | | ASTM D1106-96(2007), Efland method (1977), Van Soest et al. method (1991) | [52–54] |
| Cellulose | | Seifert method, ASTM D1103-60(1977), Van Soest et al. method (1991) | [54–56] |
| Hemicellulose | | Wise method, Pettersen [58], Van Soest et al. method (1991) | [54,57–58] |
| Extractive contents (ethanol–toluene) | | ASTM D1107-96(2006) | [59] |
| Extractive contents (alcohol–benzene) | | ASTM D1107-84(1984) | [60] |



**Fig. 1.** Location of the study area.



**Fig. 2.** Biomass in containers (red lid) by plant species. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Schrad), and melon (*Cucumis melo* L.). All these represent almost 100% of the greenhouse crops in Almería, SE Spain (Fig. 1).

Two adult plants per sample were collected at random in different areas just before the end of the plant's life cycle (Fig. 1). The samples were taken to the laboratory for analysis within 24 h. There, the roots were separated and all foreign elements were removed, analysing only the vegetative part. The analyses were performed with according to UNE-CEN/TS 14780:2008 EX [51] in the Higher Polytechnic School of the University of Almería and the parameters studied were lignin (L), cellulose (C), hemicellulose (H), and extractives (E). For the analyses, the method of Van Soest et al. (1991) was used [54], except for the extractives, which were

estimated using an alcohol–benzene mixture following ASTM D1107-84 [60]. The method of Van Soest et al. [54] was chosen to calculate the lignin, cellulose, and hemicellulose because their estimation has not been normalised at the international level and

**Table 3**
Data replicates for the regression models and average with standard deviation.

| Species studied | Lignin | | Cellulose | | Hemicellulose | | Extractives | | HHV | M ± SD |
|---|---|---|---|---|---|---|---|---|---|---|
| | L | M ± SD | C | M ± SD | H | M ± SD | E | M ± SD | HHV | |
| *Cucurbita pepo* L. | 3.95 | | 10.85 | | 11.97 | | 1.47 | | 12.85 | |
| | 3.72 | | 11.03 | | 12.46 | | 1.49 | | 12.88 | |
| | 4.22 | 3.86 ± 0.22 | 10.72 | 10.82 ± 0.14 | 15.85 | 13.29 ± 1.58 | 1.59 | 1.50 ± 0.06 | 12.90 | 12.85 ± 0.05 |
| | 3.73 | | 10.66 | | 12.42 | | 1.42 | | 12.82 | |
| | 3.70 | | 10.83 | | 13.72 | | 1.51 | | 12.79 | |
| *Cucumis sativus* L. | 3.20 | | 16.44 | | 12.40 | | 2.10 | | 12.54 | |
| | 3.05 | | 16.01 | | 17.07 | | 2.17 | | 12.61 | |
| | 2.78 | 3.04 ± 0.47 | 17.69 | 16.64 ± 0.62 | 17.26 | 15.36 ± 2.04 | 2.11 | 2.13 ± 0.03 | 12.60 | 12.60 ± 0.05 |
| | 2.44 | | 16.54 | | 15.79 | | 2.10 | | 12.56 | |
| | 3.71 | | 16.52 | | 14.26 | | 2.16 | | 12.67 | |
| *Solanum melongena* L. | 7.61 | | 30.28 | | 11.55 | | 1.89 | | 16.52 | |
| | 7.39 | | 31.44 | | 11.24 | | 1.77 | | 16.53 | |
| | 7.22 | 7.47 ± 0.21 | 30.79 | 30.69 ± 0.48 | 11.41 | 11.48 ± 0.20 | 1.61 | 1.73 ± 0.10 | 16.48 | 16.53 ± 0.03 |
| | 7.76 | | 30.70 | | 11.43 | | 1.69 | | 16.55 | |
| | 7.38 | | 30.26 | | 11.79 | | 1.71 | | 16.56 | |
| *Solanum lycopersicum* L. | 7.91 | | 20.03 | | 11.28 | | 1.92 | | 14.87 | |
| | 7.90 | | 21.31 | | 8.94 | | 1.99 | | 14.86 | |
| | 8.33 | 7.82 ± 0.47 | 21.11 | 20.92 ± 0.72 | 10.44 | 10.36 ± 0.97 | 2.20 | 2.01 ± 0.11 | 14.79 | 14.83 ± 0.05 |
| | 7.89 | | 20.33 | | 9.90 | | 1.98 | | 14.85 | |
| | 7.05 | | 21.79 | | 11.21 | | 1.98 | | 14.76 | |
| *Phaseoulus vulgaris* L. | 8.23 | | 15.75 | | 16.72 | | 2.39 | | 17.02 | |
| | 7.73 | | 16.66 | | 14.92 | | 2.21 | | 17.01 | |
| | 7.05 | 7.51 ± 0.52 | 17.35 | 16.88 ± 1.14 | 14.67 | 15.16 ± 1.27 | 2.32 | 2.34 ± 0.08 | 16.95 | 17.01 ± 0.04 |
| | 7.57 | | 16.05 | | 16.04 | | 2.40 | | 17.07 | |
| | 6.97 | | 18.60 | | 13.44 | | 2.39 | | 17.02 | |
| *Capsicum annuum* L. | 6.20 | | 13.67 | | 12.26 | | 2.12 | | 15.25 | |
| | 7.85 | | 15.60 | | 9.61 | | 2.19 | | 15.32 | |
| | 8.02 | 7.35 ± 0.72 | 16.84 | 16.54 ± 2.07 | 9.89 | 9.98 ± 2.56 | 2.26 | 2.17 ± 0.07 | 15.33 | 15.26 ± 0.06 |
| | 7.17 | | 17.38 | | 12.17 | | 2.09 | | 15.22 | |
| | 7.50 | | 19.22 | | 5.97 | | 2.20 | | 15.20 | |
| *Citrillus vulgaris* Schrad | 4.87 | | 17.42 | | 16.02 | | 2.38 | | 14.26 | |
| | 5.48 | | 16.46 | | 14.09 | | 2.27 | | 14.26 | |
| | 5.32 | 5.81 ± 0.83 | 16.10 | 15.29 ± 1.96 | 14.75 | 15.24 ± 0.80 | 2.29 | 2.30 ± 0.06 | 14.28 | 14.26 ± 0.04 |
| | 6.75 | | 12.84 | | 15.51 | | 2.33 | | 14.30 | |
| | 6.60 | | 13.63 | | 15.82 | | 2.23 | | 14.18 | |
| *Cucumis melo* L. | 3.29 | | 13.35 | | 15.98 | | | | 13.53 | |
| | 2.39 | | 14.94 | | 14.82 | | | | 13.46 | |
| | 2.76 | 3.30 ± 0.75 | 14.47 | 13.70 ± 0.97 | 15.74 | 15.14 ± 0.95 | Not data | | 13.51 | 13.50 ± 0.05 |
| | 3.82 | | 13.12 | | 15.55 | | | | 13.44 | |
| | 4.24 | | 12.60 | | 13.62 | | | | 13.56 | |

L: lignin (% by mass on dry basis); C: cellulose (% by mass on dry basis); H: Hemicellulose (% by mass on dry basis); E: alcohol/benzene (1/1, v/v) extractives (% by mass on dry basis) and HHV: higher heating value (MJ kg$^{-1}$ on dry basis). M: Mean and SD: Standard deviation.

the University of Almería has the equipment and reagents for the quick and easy application of the method. To estimate the extractives, the alcohol–benzene method [60] was chosen for being the approach used in the literature, ruling out ethanol–toluene [59] in order to compare the data with other biomass estimates.

For all the properties, five replicates (i.e. five independent samples) were made per plant species, except for the extractives of melon biomass (*C. melo* L.), which could not be estimated for lack of samples.

The HHV was calculated with a heat pump in the Higher School of Engineers of the University of Seville (Spain). The data proved similar to those found in the previous study [14].

The aim of making five analyses per species was to increase the sample size needed for the univariate and multivariate regression models, for lignin, cellulose, hemicellulose, and extractives.

Up to a maximum of four variables were considered for the mod-els. The selection criteria of the models were based on the regression coefficient ($R^2$), adjusted regression coefficient (adjusted $R^2$), sum of the squares of the errors (SSE), mean square of errors (MSE), root mean square of the errors (RMSE), mean absolute percentage error (MAPE), Akaike's AIC and Schwarz's SBC [69–71]. Of all the above parameters with Akaike's AIC coefficient it could be discerned that the model could be improved (in addition to $R^2$, adjusted $R^2$, MSE, RMSE, and MAPE). Its equation is:

**Table 4**
Correlation matrix with all the variables (Pearson's coefficient).

| | HHV | E | L | H | C |
|---|---|---|---|---|---|
| HHV | 1 | 0.285 | 0.854 | −0.220 | 0.582 |
| E | – | 1 | 0.270 | 0.272 | −0.110 |
| L | – | – | 1 | −0.484 | 0.504 |
| H | – | – | – | 1 | −0.382 |
| C | – | – | – | – | 1 |

L: lignin; C: cellulose; H: Hemicelluloses; E: alcohol/benzene (1/1, v/v) extractives and HHV: higher heating value.

$$AIC = \left[ W \cdot \ln \left( \frac{SSE}{W} \right) \right] + 2 \cdot (p + 1)$$

where $W$ is the number of observations, SSE is the sum of the squares of the errors for the model, and $p$ the number of components of the model.

The same occurred with Schwarz's SBC:

$$SBC = \left[ W \cdot \ln \left( \frac{SSE}{W} \right) \right] + [\ln(W)] \cdot (p + 1)$$

For each explicative variable (L, C, H), there are 40 data, except for the extractives (E), which presented 35 data. Also, 40 data are shown for the higher heating value (HHV) as a dependent variable.

**Table 5**
The 15 equations selected as predictive models.

| No | Equations | SSE | MSE | RMSE | MAPE | $R^2$ | Adjusted $R^2$ | Akaike AIC | Schwarz SBC |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $HHV = 10.955 + 0.629[L]$ | 18.220 | 0.607 | 0.779 | 4.333 | 0.748 | 0.739 | −14.022 | −11.091 |
| 2 | $HHV = 8.866 + 0.803[L] + 0.141[C]-0.013[LC]$ | 16.448 | 0.587 | 0.766 | 3.705 | 0.793 | 0.771 | −13.296 | −7.433 |
| 3 | $HHV = 8.211 + 0.767[L] + 0.150[H]$ | 17.410 | 0.600 | 0.775 | 3.997 | 0.766 | 0.750 | −13.478 | −9.081 |
| 4 | $HHV = 10.380 + 0.004[H^3]-0.00001[C^3] + 0.0008[L^4]-0.0002[H^4] + 0.000002[C^4]$ | 16.201 | 0.623 | 0.789 | 3.411 | 0.763 | 0.717 | −9.782 | −0.987 |
| 5 | $HHV = 7.405 + 0.682[L] + 0.163[H] + 0.065[C]$ | 13.627 | 0.487 | 0.698 | 3.487 | 0.822 | 0.803 | −19.318 | −13.455 |
| 6 | $HHV = 8.186 + 0.084[H + C] + 0.073[E] + 0.596[L]$ | 9.160 | 0.382 | 0.618 | 2.915 | 0.860 | 0.842 | −23.287 | −17.958 |
| 7 | $HHV = 6.575 + 0.004[E] + 0.759[L] + 0.183[H] + 0.064[C]$ | 13.488 | 0.586 | 0.766 | 3.757 | 0.807 | 0.774 | −10.451 | −3.789 |
| 8 | $HHV = 9.052 + 0.0002[L^2C]-0.0000002[L^2] + 0.046[L + C] + 0.481[L]$ | 13.739 | 0.509 | 0.713 | 3.685 | 0.815 | 0.788 | −17.056 | −9.728 |
| 9 | $HHV = -1.904-1.982[L + C]-2.598[E + L] + 0.077[LH] + 0.923[LE]-0.139[HE]$ | 8.346 | 0.363 | 0.602 | 2.530 | 0.888 | 0.864 | −24.121 | −15.917 |
| 10 | $HHV = -1.904-1.982[L + C] + 2.167[E + C] + 16.869[E^{-1}] + 0.051[LH] + 0.874[LE]-0.092[HE]$ | 6.517 | 0.310 | 0.557 | 2.232 | 0.911 | 0.886 | −26.820 | −17.495 |
| 11 | $HHV = 11.651 + 0.003[H^2C] + 0.131[L^2E]-0.019[H^2E]-0.005[C^2E]-0.024[L^3] + 0.000003[C^4]$ | 4.467 | 0.213 | 0.461 | 2.033 | 0.925 | 0.903 | −37.393 | −28.068 |
| 12 | $HHV = 12.836 + 0.010[L^2H] + 0.002[H^2C]-0.033[H^2E]-0.003[C^2E]-0.001[L^4] + 0.191[E^4] + 0.00006[H^4]$ | 4.752 | 0.226 | 0.476 | 2.482 | 0.939 | 0.919 | −36.456 | −25.518 |
| 13 | $HHV = 13.555 + 0.010[L^2H] + 0.003[H^2C]-0.040[H^2E]-0.0008[C^3]-0.001[L^4] + 0.00008[H^4] + 0.00002[C^4] + 0.220[E^4]$ | 3.107 | 0.164 | 0.404 | 1.983 | 0.959 | 0.941 | −43.559 | −31.570 |
| 14 | $HHV = 16.863 + 0.008[L^2H] + 0.009[L^2C] + 0.002[H^2C] + 0.117[L^3]-0.002[C^3]-0.034[H^2E]-0.008[L^4] + 0.226[E^4] + 0.00006[H^4]-0.628[L^2] + 0.00003[C^4]$ | 2.084 | 0.123 | 0.350 | 1.357 | 0.969 | 0.949 | −52.354 | −35.946 |
| 15 | $HHV = 20.327 + 0.043[L^2H] + 0.006[L^2C] + 0.002[H^2C]-0.014[H^2L]-0.035[H^2E]-0.194[L^2]-0.166[H^2] + 0.018[H^3]-0.001[C^3]-0.003[L^4]$ $-0.0004[H^4] + 0.00002[C^4] + 0.220[E^4]$ | 1.551 | 0.119 | 0.345 | 1.367 | 0.980 | 0.959 | −49.141 | −30.999 |

L: lignin (% by mass on dry basis); C: cellulose (% by mass on dry basis); H: hemicelluloses (% by mass on dry basis); E: alcohol/benzene (1/1, v/v) extractives (% by mass on dry basis) and HHV: higher heating value (MJ kg⁻¹ on dry basis). SSE: sum of the squares of the errors. MSE: mean square of the errors, RMSE: root mean square of the errors and MAPE: mean absolute percentage error. The 95% confidence level applied to all equations.

For the prediction models to be carried out, as a general rule, 32 data were used and 8 were left for the validation, following a random criterion in each equation proposed, except for Eqs. (6), (7), (10), (11), and (13), in which 28 data were used for the model and 7 for the validation. Also, in Eqs. (9), (12), and (14), (29) data were used for the model and 6 for the validation, as well as 27 data for the model and 8 for the validation in Eq. (15).

The statistical program used was XLSTAT 2009, even for the calculation of the significance of the variables of the mathematical prediction models by the beta coefficients and Student's *t*-test.

## 3. Results

All the results of the higher heating value (HHV) and the structural analysis are reflected in Table 3. Lignin reached its absolute maximum value of 8.33% in *S. lycopersicum* L. and absolute minimum value of 2.39% in *C. melo* L. The cellulose content registered an absolute maximum of 31.44% in *S. melongena* L. and absolute minimum of 10.66% in *C. pepo* L. Also, *C. sativus* L. reached its absolute maximum value of 17.26% of hemicellulose and in *C. annuum* L. the absolute minimum of 5.97%. In turn, the absolute maximum extractive content of 2.40% was found in *Phaseolus vulgaris* L., while the absolute minimum was 1.42% in *C. pepo* L. Finally, the absolute maximum HHV of 17.07 MJ kg⁻¹ was reached in *Phaseolus vulgaris* L. and the absolute minimum of 12.54 MJ kg⁻¹ in *C. sativus* L.

When the mean values of each species were taken into count, the values of lignin content from lowest to highest were: *C. sativus* L. (3.04%), *C. melo* L. (3.30%), *C. pepo* L. (3.86%), *C. vulgaris* Schrad (5.81%), *C. annuum* L. (7.35%), *S. melongena* L. (7.47%), *Phaseolus vulgaris* L. (7.51%), and *S. lycopersicum* L. (7.82%). Similarly, for cellulose, the series was: *C. pepo* L. (10.82%), *C. melo* L. (13.70%), *C. vulgaris* Schrad (15.29%), *C. annuum* L. (16.54%), *C. sativus* L. (16.64%), *Phaseolus vulgaris* L. (16.88%), *S. lycopersicum* L. (20.92%) y *S. melongena* L. (30.69%). In hemicellulose the order was: *C. annuum* L. (9.98%), *S. lycopersicum* L. (10.36%), *S. melongena* L. (11.48%), *C. pepo* L. (13.29%), *C. melo* L. (15.14%), *Phaseolus vulgaris* L. (15.16%), *C. vulgaris* Schrad (15.24%), and *C. sativus* L. (15.36%).

Also, the content in extractives per species (from lower to higher but without data for *C. melo* L.) followed the order: *C. pepo* L. (1.50%), *S. melongena* L. (1.73%), *S. lycopersicum* L. (2.01%), *C. sativus* L. (2.13%), *C. annuum* L. (2.17%), *C. vulgaris* Schrad (2.30%), and *Phaseolus vulgaris* L. (2.34%). Finally, with respect to HHV, the order was: *C. sativus* L. (12.60 MJ kg⁻¹), *C. pepo* L. (12.85 MJ kg⁻¹), *C. melo* L. (13.50 MJ kg⁻¹), *C. vulgaris* Schrad (14.26 MJ kg⁻¹), *S. lycopersicum* L. (14.83 MJ kg⁻¹), *C. annuum* L. (15.26 MJ kg⁻¹), *S. melongena* L. (16.53 MJ kg⁻¹), and *Phaseolus vulgaris* L.(17.01 MJ kg⁻¹).

Table 4 shows Pearson's correlation coefficients between all the variables studied by a similarity matrix, indicating that the highest correlation with HHV occurred with lignin (0.854), followed by cellulose (0.582), extractives (0.285) and hemicellulose (−0.220).

To predict the HHV in MJ kg⁻¹ from the structural analysis (Table 3), more than 50 mathematical models were formulated, of which 15 were selected. Those selected (Table 5) include linear models as well as linear models with transformations, from one variable to four with the following components: [L], [C], [H], and [E] as pure variables, in addition to [LC], [LH], [LE], [HE],[E⁻¹], [L²], [H²], [H³], [C³], [L³], [L⁴], [H⁴], [C⁴], [E⁴], [L²C], [L²H],[H²L], [C²E], [H²E], [L²E], [H²C], [H + C], [L + C], [E + L], and [E + C] as transformations.

When only the observations for the formulation of the models are taken into account (from 32 to 27 data, depending on the equation), all the equations presented an $R^2$ and an adjusted $R^2$
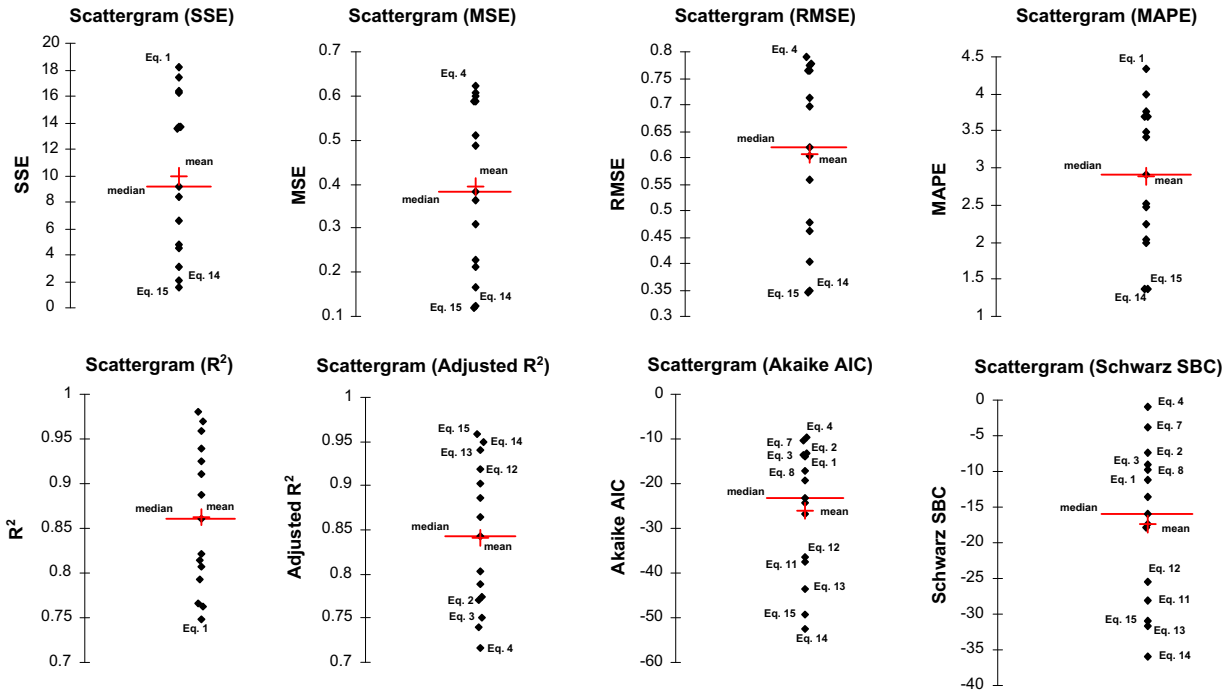
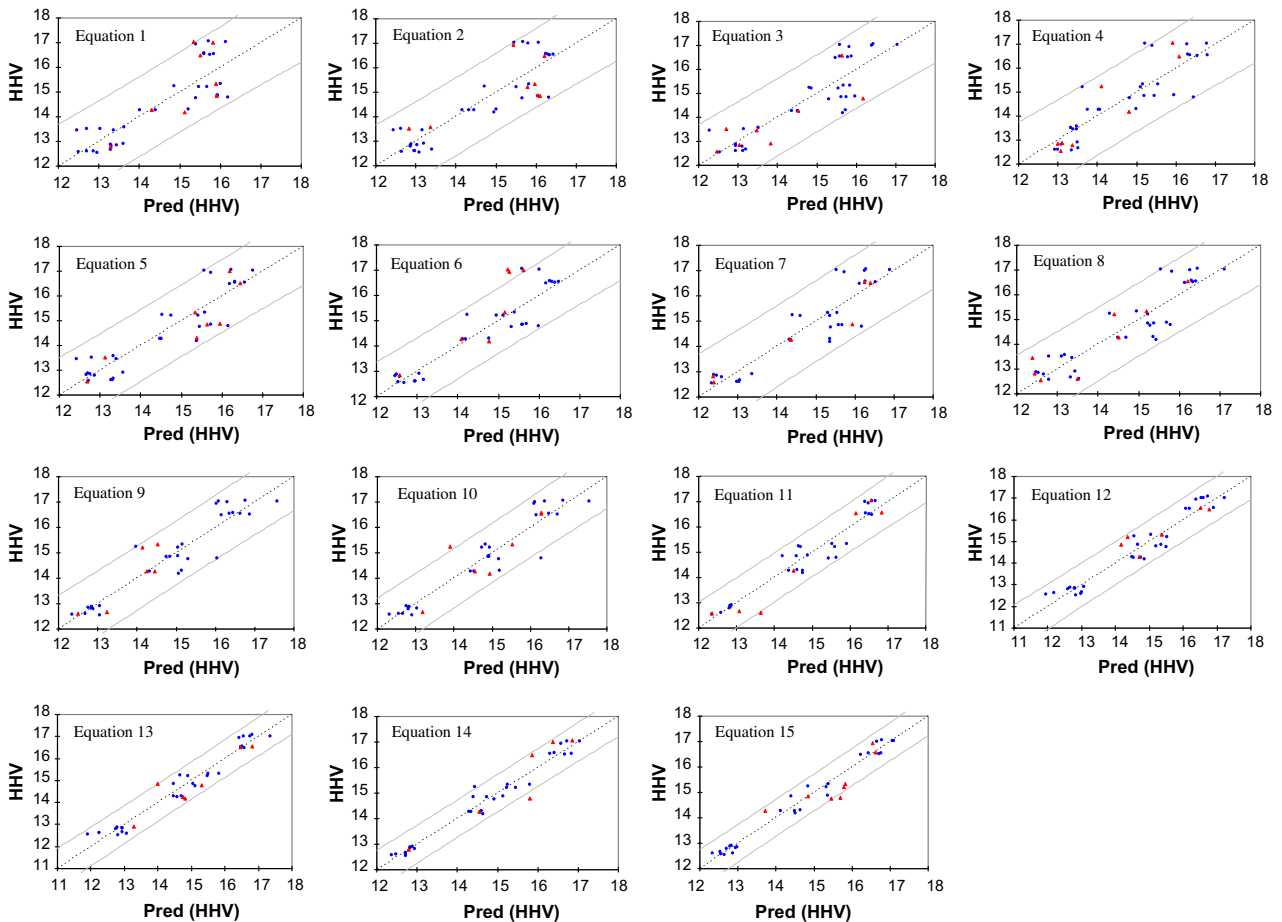**Fig. 3.** Scatter graphs for the variables used in the equations (see Table 5).



**Fig. 4.** Scatter graphs for the 15 equations showing their reliability as predictors of the higher heating value (Table 5; active in blue circle and validation in red triangle; Pred(HHV)/HHV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

higher than 0.7 (Table 5 and Fig. 3). Only one univariate equation was formulated (as a function of lignin) together with 14 multivariate ones.

Fig. 3 indicates that the median for the adjusted $R^2$ in all the multivariate models was 0.842. The minimum and maximum adjusted $R^2$ for the multivariate equations was 0.717 (Eq. (4)) and 0.959 (Eq. (15)), respectively. In all the equations (Table 5 and Fig. 3), the mean square of errors (MSE) fluctuated from 0.119 (Eq. (15)) to 0.623 (Eq. (4)). Also, the sum of the squares of the er-rors (SSE) ranged from 1.551 (Eq. (15)) to 18.220 (Eq. (1)). The median MSE was 0.382, while the mean of the MSE was 0.393. The root mean square of the errors (RMSE) varied from 0.345 (Eq. (15)) to 0.789 (Eq. (4)) while the median and mean of the RMSE were 0.618 and 0.607, respectively. The mean absolute per-centage error (MAPE) reached its minimum at 1.357 (Eq. (14)) and its maximum at 4.333 (Eq. (1)). The median and mean MAPE were 2.915 and 2.885, respectively.

Meanwhile, Akaike's AIC value varied from −52.354 (Eq. (14)) to −9.782 (Eq. (4)). The median and mean of Akaike's AIC were −23.287 and −26.036, respectively. Finally, Schwarz's SBC reached its minimum at −35.946 (Eq. (14)) and maximum at −0.987 (Eq. (4)). The median and mean of Schwarz's SBC were −15.917 and −17.269, respectively.

Fig. 4 lists the prediction values ($X$ axis) of all the models with respect to the values found experimentally ($Y$ axis), as well as the error limits. The active values for formulating the model appear as a blue circle and the values for the validation of the model are identified by a red triangle. All the graphs of equations in general presented good correlations between the observed and predicted data.

In Fig. 5, standardized coefficients (also called beta coefficients) are used to compare the relative weights of the variables. The higher the absolute value of a coefficient, the more important the weight of the corresponding variable. When the confidence inter-
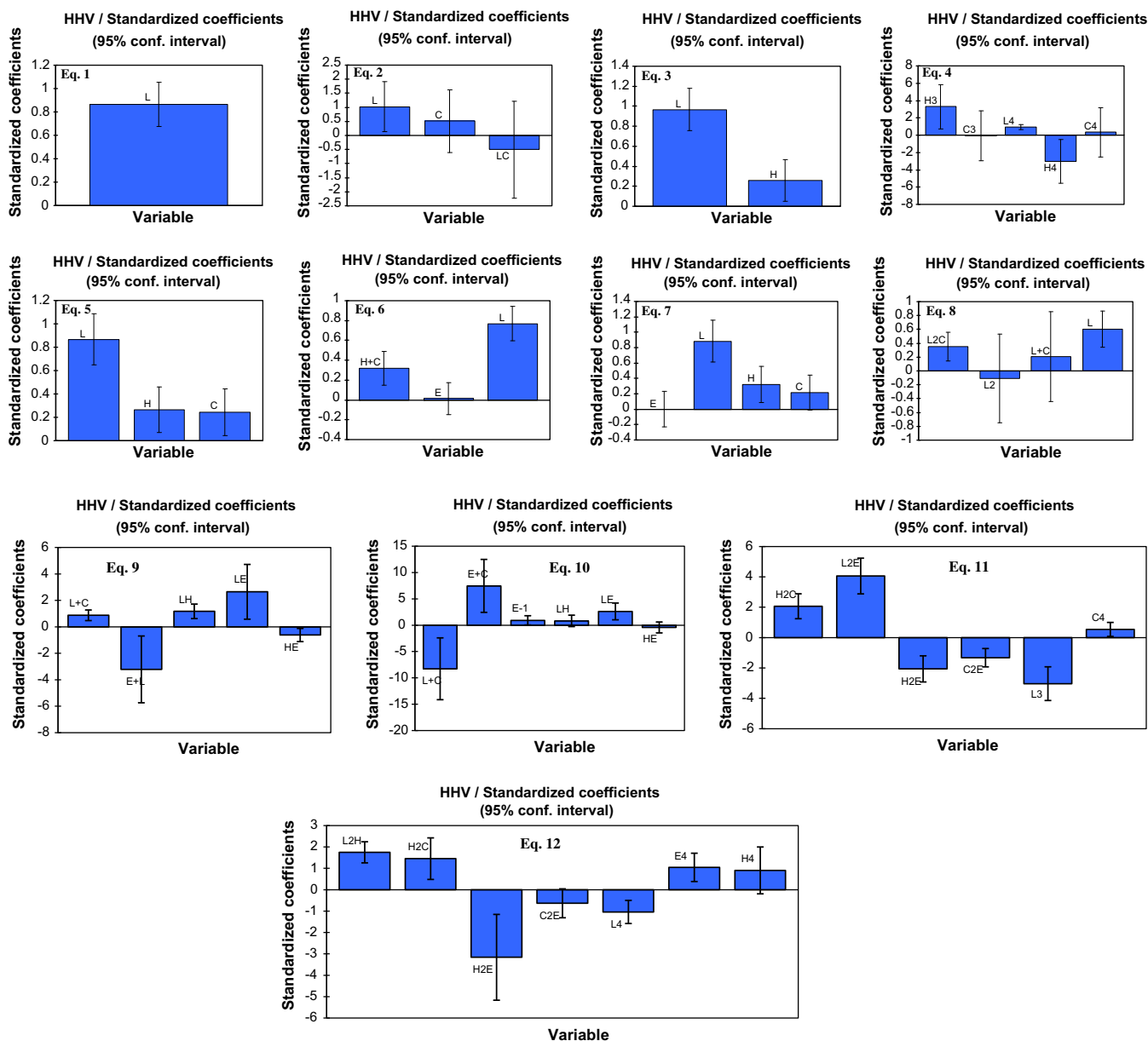


Fig. 5. Significance of the variables/components of each equation (see Table 5) by the standardized coefficient.
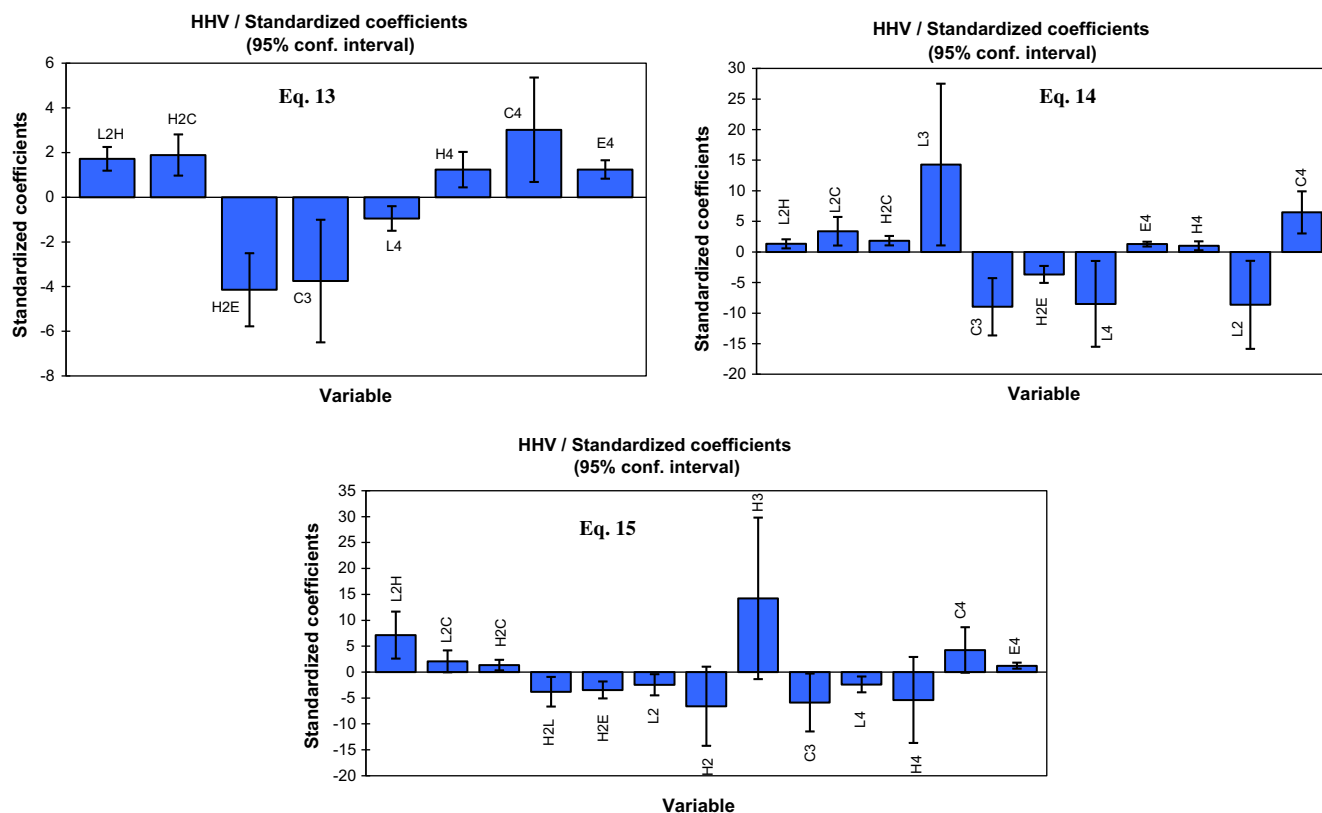
**Fig. 5** (*continued*)

val around standardized coefficients has value 0, the weight of a variable in the model is not significant.

Finally, it should be indicated that all the significance tests made for each variable using Student's *t*-test are shown in Table 6.

## 4. Discussion

The methods used to analyse the so-called "structural component" of the biomass (lignin, cellulose, hemicellulose) is not normalised at the international level because no European or American regulations have been established for this type of biomass analysis (Table 2), especially in terms of calculating cellulose and hemicellulose.

The lowest mean lignin content in the species studied was found in *C. sativus* L. (3.04%) and the highest in *S. lycopersicum* L. (7.82%). Nevertheless, an analysis by botanical families indicates that, curiously, the lower values corresponded to the Cucurbitaceae and the higher to Solanaceae and Leguminaceae (only *P. vulgaris* L.). This trend proved similar in the contents in carbon and volatile components reported by Callejón-Ferre et al. [14]. Therefore, as the percentage of carbon is related directly to the HHV, this being higher the more carbon content in the biomass [72–74], it would be expected that the greater the content in lignin, the higher the heating value the plant species (or family in this case) would have. This pattern is reflected in the data shown in Table 3. In addition, a higher correlation (0.854) was also found between the lignin content and the HHV in Table 4 and with all the mathematical prediction models of heating power based on lignin in Table 1. For this reason, the greater number of mathematical models of HHV prediction are based on the variable of lignin (L) analysis. Nonetheless, the absence of the study of errors in almost all the mathematical models de-scribed in Table 1 could lead to confusion. Certainly, the data of

the present study indicate, as stated above, that lignin is the biomass component with the highest correlation with HHV, but its combus-tion with other components such as cellulose, hemicellulose, and extractives provide mathematical HHV-prediction models that are more precise but more complex, as reflected in Table 5.

Meanwhile, the cellulose, hemicellulose, and extractive contents presented low correlations (Table 3), particularly in contents of extractives (0.285) and hemicellulose (−0.220), with no mathematical HHV-prediction models based one of these three variables proposed in Table 5 because of their low $R^2$ coefficients and high errors (SSE, MSE, RMSE, and MAPE). It is true that other authors (Table 1) have proposed models based on the content in extractives alone, but the difference in the type of biomass analysed in the present work suggests that the extractive content can vary between biomasses. In fact, this is true, given that in the plant material the extractives are fatty acids, resin acids, tannins, sugars, terpene oligomers, steroles, hydrocarbons, etc. and their contents depend on the species, the part of the plant analysed, the season of the year, and the state of growth, among other factors [75].

In relation to the prediction equations, it would be desirable to find the equation with the least number of independent variables that would explain the highest percentage of variance of the dependent variable – that is, the HHV. What it does not mean is that the equation with a higher mayor $R^2$ (for a single variable) or adjusted $R^2$ (for more than one variable) is the best. In short, it should be simple, interpretable, and reliable.

Taking into account the variables analysed (L, C, H, and E; Ta-ble 3) and the selection criteria (SSE, MSE, RMSE, MAPE, $R^2$, Ad-justed $R^2$, Akaike's AIC, Schwarz's SBC, and beta coefficients) for the 15 equations proposed (Table 5, Figs. 3–5), it appears that the best equation is number 14. This equation, though having the highest adjusted $R^2$, does present the lowest Akaike's AIC, the low-est Schwarz's SBC, and the lowest MAPE. Also, all its variables

**Table 6**

Components of each equation whose prediction is higher than the '*t*' of student and therefore not significant in the model equation.

| Components | 1 | | 2 | | 3 | | 4* | | 5 | | 6* | | 7* | | 8* | | 9 | | 10 | | 11 | | 12 | | 13 | | 14 | | 15 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ | $t_{pr}$ | $|t_{cal}|$ |
| L | X | 9.43 | 0.03 | 2.35 | X | 9.50 | | | X | 8.14 | X | 9.18 | X | 6.73 | X | 4.80 | | | | | | | | | | | | | | |
| C | | | 0.35 | 0.95 | | | | | 0.02 | 2.50 | | | 0.06 | 1.99 | | | | | | | | | | | | | | | | |
| H | | | | | 0.017 | 2.53 | | | 0.01 | 2.78 | | | 0.01 | 2.79 | | | | | | | | | | | | | | | | |
| $E$* | | | | | | | | | | | 0.87 | 0.17 | 1.00 | 0.01 | | | | | | | | | | | | | | | | |
| LC | | | 0.56 | 0.60 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| LH | | | | | | | | | | | | | | | | | 0.00 | 4.42 | 0.13 | 1.56 | | | | | | | | | | |
| LE | | | | | | | | | | | | | | | | | 0.01 | 2.65 | 0.00 | 3.41 | | | | | | | | | | |
| HE | | | | | | | | | | | | | | | | | 0.02 | 2.58 | 0.39 | 0.87 | | | | | | | | | | |
| $E^{-1}$ | | | | | | | | | | | | | | | | | | | 0.04 | 2.17 | | | | | | | | | | |
| $L^{2}$* | | | | | | | | | | | | | | | 0.73 | 0.35 | | | | | | | | | | | 0.02 | 2.54 | 0.02 | 2.62 |
| $H^{2}$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.08 | 1.87 |
| $H^{3}$ | | | | | | | 0.001 | 2.26 | | | | | | | | | | | | | | | | | | | | | 0.07 | 1.97 |
| $C^{3}$* | | | | | | | 0.96 | 0.05 | | | | | | | | | | | | | | | | | 0.01 | 2.87 | 0.00 | 4.04 | 0.04 | 2.28 |
| $L^{3}$ | | | | | | | | | | | | | | | | | | | | | X | 5.68 | | | | | 0.04 | 2.28 | | |
| $L^{4}$ | | | | | | | X | 6.39 | | | | | | | | | | | | | | | 0.00 | 4.01 | 0.00 | 3.63 | 0.02 | 2.55 | 0.01 | 3.40 |
| $H^{4}$ | | | | | | | 0.02 | 2.49 | | | | | | | | | | | | | | | 0.10 | 1.71 | 0.00 | 3.25 | 0.01 | 2.90 | 0.18 | 1.41 |
| $C^{4}$* | | | | | | | 0.81 | 0.24 | | | | | | | | | | | | | | | 0.02 | 2.44 | 0.01 | 2.70 | 0.00 | 3.96 | 0.06 | 2.09 |
| $E^{4}$ | | | | | | | | | | | | | | | | | | | | | | | 0.00 | 3.28 | X | 6.28 | X | 6.90 | 0.00 | 4.51 |
| $L^{2}C$ | | | | | | | | | | | | | | | 0.00 | 3.51 | | | | | | | | | | | 0.01 | 3.06 | 0.06 | 2.09 |
| $L^{2}H$ | | | | | | | | | | | | | | | | | | | | | | | X | 7.36 | X | 6.77 | 0.00 | 3.77 | 0.01 | 3.39 |
| $H^{2}L$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | 0.01 | 2.88 |
| $C^{2}E$ | | | | | | | | | | | | | | | | | | | | | 0.00 | 4.56 | 0.06 | 1.99 | | | | | | |
| $H^{2}E$ | | | | | | | | | | | | | | | | | | | | | X | 4.98 | 0.00 | 3.28 | X | 5.30 | X | 5.59 | 0.00 | 4.59 |
| $L^{2}E$ | | | | | | | | | | | | | | | | | | | | | X | 7.17 | | | | | | | | |
| $H^{2}C$ | | | | | | | | | | | | | | | | | | | | | X | 5.23 | 0.01 | 3.11 | 0.00 | 4.28 | 0.00 | 5.04 | 0.02 | 2.82 |
| H + C | | | | | | | | | 0.00 | 3.84 | | | | | | | | | | | | | | | | | | | | |
| L + C | | | | | | | | | | | | | | | | | 0.52 | 0.66 | 0.00 | 4.50 | 0.01 | 2.94 | | | | | | | | |
| E + L | | | | | | | | | | | | | | | | | 0.02 | 2.64 | | | | | | | | | | | | |
| E + C | | | | | | | | | | | | | | | | | | | | | 0.01 | 3.08 | | | | | | | | |
| Intercept* | X | 27.74 | 0.001 | 3.92 | X | 7.45 | X | 8.87 | X | 6.57 | X | 7.47 | X | 4.73 | X | 7.56 | X | 5.53 | 0.77 | 0.29 | X | 36.42 | X | 22.64 | X | 31.96 | X | 11.46 | X | 6.66 |

X: <0.0001; If '$t_{prediction} > t_{calculated}$' the variable is not significant into equation.

* Not significant.

(components) are significant in the equation (see Fig. 5). Eq. (15) would not be a bad selection, either, as it presents similar values. However, both equations are complex with four variables and 11 and 13 components, respectively. These facts imply the need to analyse lignin, cellulose, hemicellulose, and extractives (all variables). The same is true of Eqs. (14), (13), (12), (11), (10), (9), (7), and (6) (with four variables and components that vary from 4 to 12) (Table 5). Eqs. (4), (5), and (8) are slightly less complex, with only three variables, but with components 4 to 6 (Table 5). In turn, Eqs. (2) and (3) have 3 or 4 components with two variables each (Table 5). Finally, Eq. (1) is the only univariate one with two com-ponents (Table 5) and with less reliability by presenting a greater error (Table 5 and Figs. 3 and 4).

Fig. 5 shows that in all the variables of the equations the beta coefficient is greater than zero, even the variable "$E$" of Eq. (7), with a value of 0.00069. This indicates that all the variables of the equations are more or less significant in their corresponding model. The almost null value of "$E$" could be explained by the lack of five data in the plant waste of melon (Table 3). Nevertheless, the prediction value of Student's $t$-test (0.995) is higher than the $t$-test calculated (0.006) for the variable "$E$" of Eq. (7) (Table 6), indicating its non-significance. From this perspective, this variable could be removed from Eq. (7) and recalculated with the other 3, which would bring us to Eq. (5), which does present all its significant variables and with similar beta coefficient values for H, C, and L. Something similar occurs with the variable "$E$" of Eq. (6) ($t_{prediction} > [t_{calculated}]$; 0.865 > 0.172), with the variable $L^2$ of Eq. (8) (0.727 > 0.353), with the variables $C^3$ and $C^4$ of Eq. (4) (0.959 > 0.052), and with the independent component of Eq. (10) (0.865 > 0.172). Therefore, these anomalies would have to be discarded from Eqs. (4), (6)–(8), and (10).

In general, the rest of the models studied offer acceptable prediction behaviour as a function of the variables and of the analyses on which they depend (Fig. 4), and therefore no equation could be dismissed until knowing the laboratory means available to calculate one or more of the variables of this type of biomass in order to predict its HHV. The red triangles of Fig. 4 are almost 100% within the limits of the error of the models proposed, Eqs. (2), (3), (5), (9), and (12) being notable for their prediction and validation.

Clearly, these types of biomasses studied by the mathematical models based on proximal and element analysis, in presenting better $R^2$, MAPE, MSE, RMSE, and adjusted $R^2$ [14], are better than the models based on structural analysis.

## 5. Conclusions

Of the botanical families studied, Solanaceae (tomato, pepper, and eggplant) together with the Leguminaceae (greenbean) have higher lignin contents than do the Cucurbitaceae (watermelon, melon, and zucchini), all the species presenting a good correlation with HHV values.

The mathematical HHV-prediction models (Eqs. (1)–(3), (5), (9), (11)–(15)) based on structural analysis (contents in lignin, cellulose, hemicellulose, and extractives) of the biomass of zucchini, cucumber, eggplant, tomato, greenbean, pepper, watermelon, and melon studied are less reliable than the mathematical models of the same species based on proximal and element analysis. Nevertheless, their use cannot be ruled out, depending on the equipment available in the laboratory for analysing biomass.

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