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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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HIGHLIGHTS

- Structural analyses of plant remains from the greenhouses have been made.
- Prediction models for higher heating value based on the structural analysis have been made.
- Ten prediction models of higher heat value have been validated.

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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 analysis (lignin, cellulose, hemicellulose, and extractives) and higher heating value (HHV). The calculation of the HHV is usually costly,

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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 $R^2_{ajusted}$, Not SE
	HHV = 17.6132 + 0.0853[L*][a]	Extractive-free wood			Not $R^2_{ajusted}$, Not SE
	HHV = 17.4458 + 0.0907[L*][a]	Extractive-free softwood			Not $R^2_{ajusted}$, Not SE
	HHV = 18.0831 + 0.0637[L*][a]	Extractive-free hardwood			Not $R^2_{ajusted}$, Not SE
	HHV = 17.7481 + 0.0800[L*](100−[E])/100 + 0.0886[E][a]	Unextracted wood			Not $R^2_{ajusted}$, 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 $R^2_{ajusted}$, Not SE
Demirbaş	HHV**=0.0889[L**] + 16.8218	Wood and non-wood	2001	[28]	Not SE
	HHV**=0.0893[L**] + 16.9742	Wood: beech wood, hardwood, Ailanthus wood, softwood, spruce wood, wood bark			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 according 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 univariate and multivariate mathematical models of HHV prediction based on proximal and element analyses, in addition to determining 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, differentiating by species; and, second, to establish mathematical HHV prediction 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.), tomato (*Solanum lycopersicum* L.), greenbean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), watermelon (*Citrillus vulgaris*