Chemical Composition on Heating Value of Biomass

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Biomass has become an increasingly important resource for energy generation. It is well known that the heating value of lignin is significantly higher (23.26–25.58 MJ/kg) than that of polysaccharides (18.6 MJ/kg), while extractives often have higher heating values (HHVs) over 30 MJ/kg, depending on their oxidation levels. Therefore, the proportions of the chemical components in biomass determine its HHV.

Keywords: heating value ; lignin ; cellulose ; extractive models

1. Introduction

Biomass is increasingly considered as a resource for materials, chemicals, and energy, given the current need to account for sustainability, the green economy, and minimal environmental impacts. The concept of biorefineries has therefore developed in the last decades, considering different types of biomass as feedstocks and different conversion platforms ^[1]. The thermochemical biomass platform is one of the most important, embracing conversion processes such as combustion, pyrolysis, gasification, and liquefaction, and has seen considerable research efforts as well as successful industrial outcomes targeted to energy products ^{[1][2]}.

The higher heating value (HHV) is the most important property of biomass when addressing its use as a fuel. Different types of biomass are potential fuel resources (e.g., wood; barks; forest waste products; and residues from the agriculture, forest, and food industries) that differ in their physical characteristics as well as in their chemical compositions. The higher heating values range between 17 MJ/kg and 21 MJ/kg for dry wood ^[3] and between 19 and 23 MJ/kg for bark ^[4]. These values are lower than those for charcoals (29-33 MJ/kg) [3][4]. Before coals, charcoals, or lignocellulosic biomass are to be used as fuels, it is important to determine their higher heating values. This task can be performed by measuring the calorific value of a fuel using a bomb calorimeter, which is a special and costly piece of equipment. Alternatively, higher heating values can be estimated using empirical correlations. The usual correlations include an ultimate analysis (elemental composition), a proximate analysis, and the chemical composition ^[5]. An ultimate analysis requires an elemental analyzer, and correlations based on an ultimate analysis generally result in a high level of accuracy. A proximate analysis can be performed using a high-temperature oven to calculate the moisture, ash, volatile matter, and fixed carbon of a fuel, but correlations based on proximate analyses were shown to have lower accuracy than those based on ultimate analyses ^[5]. Correlations based on chemical composition also have lower accuracy than ultimate analysis data based on the chemical composition of lignocellulosic biomass, which are usually available. The reported range of higher heating values is an important parameter for screening fuels. For instance, 1 ton of wood with an HHV of 17 MJ/kg provides 4709 kwh of energy, while the same amount of wood or bark with an HHV of 23 MJ/kg provides 6371 kwh of energy. The chemical composition is determined to establish the biomass energy value. Therefore, knowledge on the influence of the different chemical components on the HHV of biomass will allow us to infer the potential of several types of biomass to be used as fuel and can be used as a first screening and in process design.

2. Heating Value

The heating value, also called the heat value, the calorific value, or the heat of combustion, is the amount of heat released during the complete combustion of a material and is expressed in energy per a specified amount ^[6]. The SI unit is MJ/kg, but it can also be expressed in cal/kg or Btu/lb. The heating value can also be determined as the energy per unit of volume, such as kJ/m³, or the energy per molar unit, such as kJ/mol. The higher heating value (HHV), also called the gross calorific value, accounts for the latent heat of water vaporization. When the latent heat of water vaporization is not accounted for, the heating value is named the lower heating value (LHV) or the net calorific value ^[7]. The relationship between the gross calorific value and the net calorific value can be expressed by the following equation:

where h_{fg} is the latent heat of the evaporation of water at the reference temperature and m_w is the mass of water in the products of combustion per unit of mass of fuel ^[6]. If the combustion of biomass is complete, the generated heat is the sum of the heat released by the following equations:

 $C + O_2 \rightarrow CO_2 + 32.8 \text{ MJ/kg}$

 $2H_2 + O_2 \rightarrow 2H_2O + 142.1 \text{ MJ/kg}$ (1)

However, in reality, the burning is never complete; therefore, there are always some unburned hydrocarbons and the partial oxidation of carbon (CO and CxHy) ^[8]. The HHV of biomass is generally presented on a dry basis since the moisture content significantly affects the heating value ^[9].

The standard equipment used for the determination of the HHV is the oxygen bomb calorimeter ^[10]. Nevertheless, some other experimental techniques have been used, such as the ballistic bomb calorimeter, which was developed for food and is faster but less accurate ^{[6][11]}, and the oxygen consumption calorimeter ^{[6][12]} and carbon dioxide generation calorimeter ^{[6][13]}, which measure the "effective heat of combustion" ^{[6][14]}, which is the actual heat released in a combustion that is generally incomplete and therefore smaller than the heat of combustion. The value obtained for the HHV cannot be considered as a thermodynamic property of a material since it depends on the burning process and conditions, as stated before ^[6].

Several standards are used to determine the HHV. ASTM D5865 is the standard test method for the determination of the HHV of coal and coke, and it is performed using either an isoperibol, whose precision depends on the operator, or an adiabatic bomb calorimeter, which is the most used method. The technical specification CEN = TS 14918:2005 provides a method for the determination of the HHVs of solid biofuels at a constant volume and at the reference temperature of 25 °C in a bomb calorimeter calibrated by the combustion of certified benzoic acid. DIN 51900-2 specifies how to determine the HHVs of solid and liquid fuels using isoperibol or a static jacket calorimeter and the calculation of the net calorific value.

3. Chemical Components of Biomass

Biomass is chemically characterized as being of lignocellulosic nature, and wood, including softwoods and hardwoods, is usually considered the benchmark biomass material ^[15]. In general, the chemical composition of biomass may be characterized as including two groups of components that are differentiated by their molecular sizes and structural functions: the structural compounds (cellulose, hemicelluloses, and lignin) that play an important role in the cell wall structure and the nonstructural components (extractives and inorganic components) that can be removed without affecting the cell wall structure.

Cellulose is the most abundant natural compound in nature and the main chemical compound in hardwoods and softwoods. It is a homopolysaccharide with a polymerization degree of about 10,000 that is composed of β -d-glucopyranose units joined by $\beta(1 \rightarrow 4)$ linkages in a chair conformation, building a thermodynamically stable plane molecule. The proximity of cellulose molecules and the presence of OH groups in their structure favor the formation of hydrogen bonds between chains, which are only possible given the linearity of the molecules. These connections, together with the van der Waals forces between the various planes, allow the formation of a compact and orderly structure that constitutes the crystalline structure of cellulose. The crystalline zones, which alternate with amorphous zones, correspond to about two thirds of the cellulose present in wood.

Hemicelluloses are polysaccharide heteropolymers with smaller chains than cellulose and a branched linear structure. The monomeric constituents of hemicelluloses are mainly pentoses and hexoses, but they also contain hexuronic acids and deoxyhexoses. Hardwood and softwood hemicelluloses differ not only in percentage but also in chemical composition, with more xylans in hardwoods and more glucomannans in softwoods ^[4]

Lignin is a polydisperse phenolic polymer composed of phenylpropane units linked to hydroxyl and methoxy groups, forming a three-dimensional network. Numerous studies have confirmed that the lignin precursors are p-coumaryl, coniferyl, and sinapyl alcohols. In softwoods, the main precursor is coniferyl alcohol, which forms guayacyl lignin (G), and in hardwood it is coniferyl alcohol and sinapyl alcohol that form guaycyl–sinapyl lignin (G-S), while monocotyledons usually have more p-coumaryl alcohol, leading to H lignin ^{[16][17][18]}.

Suberin is also a cell wall structural component, although it is restricted to the cork component in barks, which may be substantial in some species ^[19]. Suberin is a glyceridic macromolecule with a polyester nature built by the esterification of glycerol and long-chain carboxylic acids and alcohols, mainly including a,w-alcanoic diacids, w-hydroxyalcanoic acids and

alkanoic acids with and without mid-chain functionalization ^[20]. In cork, suberin is a major structural cell wall component that, with lignin, imparts cork with its specific properties, while cellulose and hemicelluloses are present in a much lower proportion than in wood ^[21].

The extractives are small molecules, usually formed by metabolic processes, that can be removed from wood by solubilization with adequate solvents without affecting the mechanical properties since these compounds are not constituents of the wood cell wall. The primary metabolites that are usually detected in most extracts are generally simple sugars, fats, amino acids, and carboxylic acids, while the secondary metabolites include phytosterols, terpenes, aliphatics, and phenolic compounds. Extractives show broad chemical diversity, and their amounts and compositions vary between species, seasons, tree ages, parts of trees, etc.

Ash contents vary between 0.1 and 0.5% ^[22] or up to 1% ^[4] of wood in temperate zones and between 3 and 4% in tropical woods ^[22]. The main components of wood ash are calcium, potassium, and magnesium. The amount and composition of ash in wood depend on the growing conditions of trees, such as the soil type, environmental pollution, and the fertilizers that are used. Moreover, wood preservatives may alter the ash content and composition ^[22]. The ash content of barks is much higher, usually over 10%, and is typically dominated by the presence of calcium (82–95%) ^[22]. Regarding the proportions of the different chemical components in biomass, a substantial range has been found related to interspecies and within-species genetic diversity; the specific plant physiology phase, e.g., age; and environment-associated variation. It was reported that hardwoods and softwoods from the US contain 65–72% holocellulose and 23–29% Klason lignin, respectively ^[23].

4. HHVs of Chemical Compounds of Biomass

There have not been many studies on the influence of chemical composition on the heating value of biomass, as proven by the bibliometric analysis. Nevertheless, several studies mentioned that the HHVs of biomass materials reflect their chemical compositions, mainly the compositions of the macromolecular compounds that make up the majority of the biomass. The different structural components have different HHVs; for instance, polysaccharides have an HHV of around 18.60 MJ/kg, while lignin has an HHV of 23.26–25.58 MJ/kg ^[24]. The lower HHV of cellulose was reported to be due to its high oxidation levels, contrary to lignin ^[25].

A study that collected information about the HHVs of 402 wood species showed that they ranged from 15.6 to 23.7 MJ/kg for hardwoods and from 18.6 to 28.5 MJ/kg for softwoods ^{[26][27]}. The higher HHVs of softwoods compared to hardwoods have been associated with their higher lignin and resin contents.

When present in significant amounts, some types of extractives influence the heating value of biomass, with some increasing it, while others may even decrease it.

5. HHV Prediction Models

A review presented several models for the prediction of the HHVs of biomass materials based on ultimate, proximate, structural, and chemical analyses ^[28]. A structural analysis was considered to be based on cellulose, hemicelluloses, lignin, and extractives, while a chemical analysis was related to different values such as the mean numbers of carbon atoms and double bonds in fatty acids or other indexes such as saponification values and the iodine index. Models based on the amount of ash were reported as proximate analysis models. Another review presented the prediction of HHVs based on the structural composition of biomass (cellulose, hemicelluloses, lignin, and extractives) ^[29].

One of the first models estimated the HHV from the extractive content of pine biomass, but the determination coefficient was only 0.54, explaining only 54% of the variation ^[30]. Shafizadeh and Degroot ^[31] proposed a model based on the combination of cellulose, lignin, and the extractive content for lignocellulosic materials, but the coefficient of determination was not mentioned. Later on, in 1977, Doat ^[32] proposed two different correlations for the HHV of tropical wood, the first with lignin and ethanol–benzene extractives (R^2 = 0.69) and the second with ash, ethanol–benzene extractives, water extractives, and holocellulose, with a higher determination coefficient of 0.74. The Tillman model ^[33] was based on a negative correlation with holocellulose, and a high determination coefficient was reported (R^2 = 0.81). Several models were proposed by White ^[34] for the higher heating values (the gross heat of combustion) and the lignin and extractive contents of samples from four hardwoods and four softwoods. The softwoods were Engelmann spruce (*Picea engelnzanni*), western redcedar (*Thuja plicata*), southern pine (*Pinus* sp.), and redwood (*Sequoia sempervirens*), and the hardwoods were hard maple (*Acer* sp.), yellow-poplar (*Liriodendron tulipifera*), red oak (*Quercus* sp.), and basswood (*Tilia* sp.). The best model, with an R^2 of 0.97, only used the lignin content in extractive-free wood. Jiménez and González ^[35]

proposed a model with all the chemical compounds for wheat straw, olive twigs, olive wood, vine shoots, sunflower stalks, cotton plant stalks, sunflower seed husks, olive stones, olive marc, holm oak residues, and eucalyptus residues, but it had a very low determination coefficient of 0.1. Demirbas ^{[9][24][36][37][38]} has been one of the most active researchers of models to estimate the HHV of biomass. The best correlations were obtained for lignin; for instance, for extractive-free beech wood, Ailanthus wood, and spruce wood and bark and for extractive-free sunflower shells, almond shells, hazelnut shells, wood bark, olive husks, hazelnut kernel husks, and walnut shells, both models explained 97% of the variability.

From the models that have been reported over the years, those based on the lignin from extractive-free biomass seem to be the most accurate, which is probably due to the HHVs of extractives being highly dependent on their compositions and different extractives having very different HHVs. Rhén ^[39] obtained a good correlation ($R^2 = 0.89$) for the HHV and the extractive content of spruce wood using a quadratic function (Equation (2)):

HHV = $20.314 + 0.134 [E] + 0.004 [E]^{2} (2)$

In more recent years, several models were proposed, most of them using lignin or extractives as the main estimators for pine wood $^{[40]}$; corn stover, corn cobs, sunflower shells, beech wood, Ailanthus wood, hazelnut shells, wood bark, olive husks, and walnut shells $^{[41]}$; different wood species $^{[3]}$; greenhouse crops $^{[42]}$; or biomass samples from agro-forestry waste and industrial waste $^{[43]}$. Callejón-Ferre et al. $^{[42]}$ reported a good correlation model using hemicellulose, cellulose, and lignin (R² = 0.80) for greenhouse crops, while Ngangyo-Heya et al. $^{[25]}$ reported several models based on the ash, lignin, and extractives of five semi-arid Mexican tree species, with a maximum determination coefficient of 0.44. Domingos et al. $^{[44]}$ reported the correlation between each individual chemical compound and the HHV of wood. Although no models were mentioned, calculating them from the presented results showed that the best model (Equation (3)) was obtained for lignin:

HHV = 16.531 + 0.113 [L] (3)

All the models based on the ash content reinforce that higher amounts of ash lead to lower HHVs. The best correlation was obtained by Huang et al. [45] (R² = 0.88) for rice straw and wheat straw (Equation (4)):

Sheng and Azevedo ^[5] statistically evaluated some of the most used correlations based on proximate analyses, ultimate analyses, and chemical composition and concluded that those based on ultimate analyses were the most accurate, while the correlations based on proximate data had lower accuracy but were better than those based on chemical composition, which had very poor quality and were only suitable for the materials they were derived from. This was to be expected since only cellulose has a uniform chemical formula, while the chemical composition of hemicellulose depends on the biomass species ^{[5][46]} and lignin has several different chemical structures. Moreover, extractives are very different according to the biomass species and the extraction solvents used. Furthermore, the determination and isolation methods lead to different chemical compositions and heating values.

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