

Review

Influence of Chemical Composition on Heating Value of Biomass: A Review and Bibliometric Analysis

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Abstract: Biomass has become an increasingly important resource for energy generation. The influence of the chemical composition on the heating value of biomass has not been a thoroughly studied subject, as shown by a bibliometric analysis. 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 HHVs over 30 MJ/kg, depending on their oxidation levels. Therefore, the proportions of the chemical components in biomass determine its HHV. Softwoods generally have higher HHVs than hardwoods due to their higher contents of lignin and lipophilic resin. Ashes are incombustible, and a high ash content leads to a lower HHV in biomass. Several models have been proposed to correlate the heating values and chemical compounds of biomass, but the most accurate models are based on the lignin from extracted samples, while good correlations between lignin and extractives have also been reported. No good correlations have been obtained with polysaccharide compounds.

Keywords: heating value; lignin; cellulose; extractive models



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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.

This work provides a review of the chemical composition of biomass as well as the methods for determining HHVs and also presents a bibliometric analysis to understand how the subject of the chemical components of biomass and HHVs has been studied over the years. A state-of-the-art review shows the influence of each chemical compound on the HHV of biomass, and several models correlating lignin, cellulose, hemicelluloses, extractives, ash, and the HHV of biomass materials are presented and discussed.

2. Bibliometric Analysis

The bibliometric analysis used Web of Science (WoS) data from Clarivate Analytics between the years 1990 and 2022. Different search terms were used based on the most relevant articles on the subject of this review: “calorific power” or “heating value” or “calorific value” and “chemical composition” or “structural composition”. The search was made in the topic field, which searched titles, abstracts, author keywords, and keywords plus.

Figure 1 shows the annual number of publications between 1995 and 2022. Until 2000, there were practically no publications on this subject, while in the following 10 years (2001–2010) a few publications were made, with an average of six per year. The number of publications increased steadily year by year from 2011, with 25 published articles, to a maximum in 2021, with 90 publications.

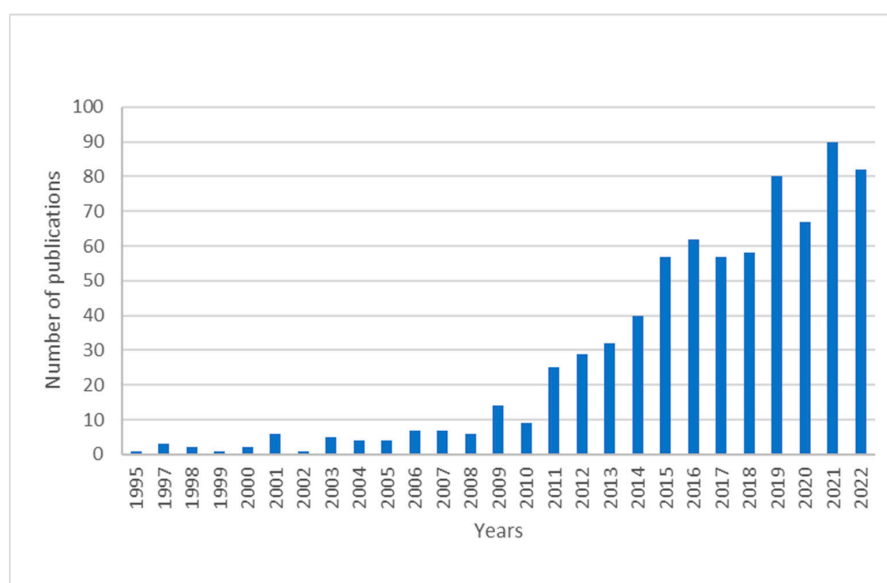


Figure 1. Number of publications in WoS on chemical composition and heating value by year of publication from 1995 to 2022.

The publications belong to a wide range of web of science categories. However, most refer to energy fuels (25% of the total publications), chemical engineering (12%),

environmental sciences (8%), and agricultural engineering (5%). Categories with less than 1% of the total publications represent 23% of the total, showing the high dispersion of the publications by category. Table 1 presents the 15 journals with the most publications, representing 35% of the total publications. *Fuel* leads the list with 37 publications, and *Energies* has 36 publications, while *Biomass and Bioenergy* and *Energy Fuels* both have 27 publications. An analysis of the journals where most publications have been made showed that they concentrate on energy and fuel issues as well as on biomass production and conversion.

Table 1. Journals that have published the most publications on the searched topic.

	Journals	Record Count
1	<i>Fuel</i>	37
2	<i>Energies</i>	36
3	<i>Biomass and bioenergy</i>	27
4	<i>Energy fuels</i>	27
5	<i>Bioresource technology</i>	19
6	<i>Biomass conversion and biorefinery</i>	17
7	<i>Bioresources</i>	16
8	<i>Energy</i>	16
9	<i>Journal of analytical and applied pyrolysis</i>	16
10	<i>Industrial crops and products</i>	14
11	<i>Energy sources part a. Recovery utilization and environmental effects</i>	13
12	<i>Waste management</i>	12
13	<i>Forests</i>	9
14	<i>Fuel processing technology</i>	9
15	<i>Journal of the energy institute</i>	9

The concept map in Figure 2 has been divided into four different clusters. In the first one, the main word is wood, followed by hemicellulose, lignin content, holocellulose, briquette, and pellets, which means that this cluster is essentially based on the structural composition of wood. The second cluster, connected by the hemicellulose term, mainly has words such as crop, year, energy crop, and cultivation as well as fatty acid. The third cluster is ruled by terms such as pyrolysis, bio-oil, reactor, and viscosity. The final one, which interconnects all the remaining clusters, has terms such as gasification, boiler, syngas, and calorific value. This concept map reveals that there is a wide variety of articles with the search terms used in this research.

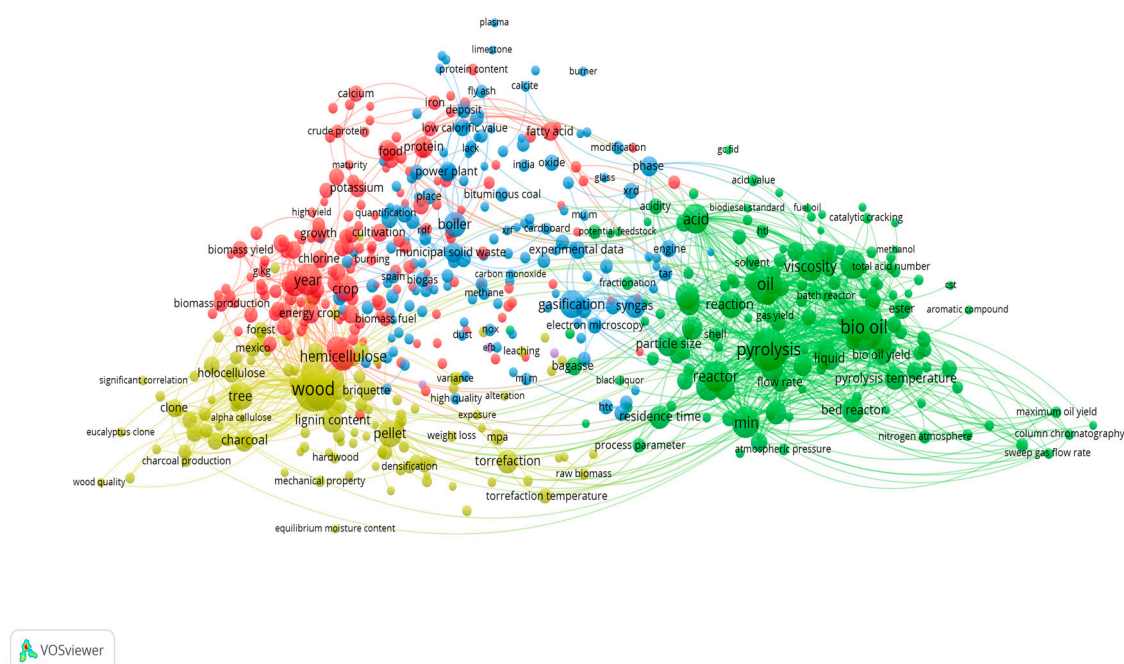


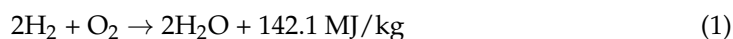
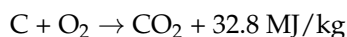
Figure 2. Concept map of the chosen publications with common terms (five appearances), obtained using Vosviewer software version 1.6.19.

3. 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:

$$\text{LHV} = \text{HHV} - h_{\text{fg}} \times m_{\text{w}}$$

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:



However, in reality, the burning is never complete; therefore, there are always some unburned hydrocarbons and the partial oxidation of carbon (CO and C_xH_y) [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.

4. 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 $\beta(1\rightarrow4)$ 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 guayacyl–sinapyl lignin (G-S), while monocotyledons usually have more p-coumaryl alcohol, leading to H lignin [16–18].

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 α,ω -alcanoic diacids, ω -hydroxyalcanoic acids and alcanoic 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].

5. 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.

5.1. Lignin

The HHV of lignin depends on the type of lignin as well as the isolation technique that is used [28]. In fact, isolated lignins, also called technical lignins, differ from native lignin owing to the chemical modifications caused by the extraction method [29]. Technical lignins are also different from each other due to the raw material used and the extraction method; for instance, 25 different types of technical lignins were described [30].

Estimating the HHVs of native lignins can be performed using their carbon, hydrogen, and oxygen ratio. For example, the lignin in beech wood is approximately $C_{5.026}H_{6.31}O_{2.83}$, leading to 24.07 MJ/kg, while in spruce wood ($C_{5.539}H_{6.16}O_{1.707}$) a higher amount of carbon and lower oxidation levels lead to a higher HHV of 26.85 MJ/kg [31]. Since hardwoods generally have higher oxygen contents, their lignins have lower HHVs [32]. The lignin contents of woody and non-woody plants and their heating values were determined, showing that the HHVs were different according to the type of lignin: lignin from walnut shells had the highest HHV, followed by spruce and beech lignins, reportedly due to the higher aromaticity of walnut shell lignin (2.37) and spruce wood (1.64) compared to beech wood [32].

Although the HHVs of technical lignins differ from those of native lignins, the knowledge of their HHVs is important for industrial purposes. For instance, the determination of the HHVs of lignins from several softwoods, hardwoods, and herbaceous materials using a sulfur-based isolation method showed that the values were higher for softwoods, at 26.73 MJ/kg for spruce and 27.00 MJ/kg for pine, while for poplar (hardwood) the value was lower (25.45 MJ/kg), similar to herbaceous materials such as bagasse (25.21 MJ/kg), switchgrass (25.27 MJ/kg), straw (25.16 MJ/kg), and corn stalks (25.20 MJ/kg) [33]. The value obtained for spruce was not far from the value previously estimated for native lignin (26.85 MJ/kg) [31].

Lignins from black liquors from the pulping industry are very different, the most common being kraft lignin, which has high levels of sulfur and ash, organosolv lignins that contain more hydroxyl and carbonyl groups due to the alcohols used in the delignification process, sulfite lignin, and soda lignin [29]. The HHVs of these five lignins were studied using commercial samples (DA30 (a lignosulfonate lignin), UPM BioPiva™ 100 and UPM BioPiva™ 300 kraft lignins, BLN alkali lignin, and an EHL or enzymatic hydrolysis lignin), and very different values were reported: the lowest value was obtained for DA30, at 17.6 MJ/kg, followed by EHL (24.9 MJ/kg), BLN (26.5 MJ/kg), UPM₁₀₀ (26.9 MJ/kg), and UPM₃₀₀ (27.1 MJ/kg).

Several other research works determined the HHVs of lignins isolated from several species, obtaining values around 25 MJ/kg, such as lignin extracted from *Eucalyptus urograndis* using the kraft process, with an HHV of 24.97 MJ/kg [34]; lignin isolated from *Gmelina arborea*, with an HHV of 25.4 MJ/kg [35]; and kraft lignin (Sigma-Aldrich, CAS# 8068-05-1), with an HHV of 26.85 MJ/kg [36].

Some recent extraction methods have been studied for lignin isolation. For example, the HHVs of lignins isolated from rice husks, sugar cane, corn stover, and coffee chaff using deep eutectic solvents were determined and compared with alkaline lignins and black liquor, with the corn stover, bagasse, and rice husks showing higher HHVs compared to the reference black liquor and alkaline lignins [37].

5.2. Cellulose and Hemicelluloses

The HHV of cellulose has been reported to be the same regardless of the species since the values obtained by several authors with different kinds of cellulose are in a close range [28], e.g., from 17.22 MJ/kg [38] to 17.56 MJ/kg [33], which on average are within the error range and are similar to the value of 17.36 MJ/kg reported for starch, which is also a homopolymer of D-glucose [32]. The studies conducted over the years used filter paper [39], cotton pulp [33], amorphous cellulose [38], I β [33,36,38,40], II [38], III [38], and microcrystalline cellulose [41].

Although cellulose is different from hemicelluloses and there are different kinds of hemicelluloses, their heating values are not very different due to their similar chemical structures. The reason why there have been many studies on the HHV of cellulose and no studies on the heating values of hemicelluloses is probably the difficulty in isolating hemicelluloses in their native states.

5.3. Suberin

No studies were found on the HHV of suberin, probably due to its complex nature and difficulty to isolate. Nevertheless, several studies confirmed that suberin is composed of a complex mixture of long aliphatic chains that also have polar groups (mainly OH and carboxylates) and unsaturations [42]. These long chains with low oxygen contents allow us to infer that suberin has a high HHV. Although no values were found for the HHV of suberin, there have been some studies reporting the HHV of cork-rich barks such as the HHV of cork from *Quercus variabilis*, which was reported to be 27.86 MJ/kg [43], and *Q. suber* cork, at 18.9 MJ/kg [44]. The HHV of the cork-rich fractions from *Quercus cerris* bark varied between 20 and 22 MJ/kg [45].

The extraction of *Quercus suber* cork with water and organic solvents led to extracts with HHVs of 20.29 MJ/kg for water and 37.91 MJ/kg for the organic extract. In the same study, liquefied cork was reported to have an HHV of 34.1 MJ/kg [46].

5.4. Extractives

Extractives are also important for the final HHVs of materials, depending on their amounts and compositions [47]. A report citing some old research [48] stated that extractives have the highest gross calorific values when compared with macromolecular compounds with values such as 32.3 MJ/kg [49], 34.9/37.2 MJ/kg [50], 38.9 MJ/kg [51], or 36.9/39.4 MJ/kg [52]. Nevertheless, the calorific values of extractives are certainly dependent on the species and the chemical type of the extractives.

A study that tested twelve different species (*Eucalyptus globulus*, *E. nitens*, *E. saligna*, *E. ovata*, *Salix kinuyanagi*, *S. matsudana* × *alba*, *S. matsudana* × *alba*, *Populus eridiano*, *Acacia dealbata*, *Paulownia tomentosa*, *Alnus glutinosa*, and *Pinus radiata*) reported that the different HHVs of extractives are due to the different oxidation levels, as combustion is an oxidation reaction, and therefore the compounds with only carbon and hydrogen generate more energy than those with oxygen [53]. For instance, some extractives containing terpenoid hydrocarbons and lipids have lower oxidation levels, while those containing phenolic compounds have higher oxidation levels and therefore produce less energy. The same happens with hydrophilic compounds such as saccharides, which have lower HHVs than the remaining extractives [25,53]. The leaves of *Gmelina arborea* presented a higher HHV than that of the wood, which was attributed to the high presence of lipids and terpenoids in the leaves, which have greater heating values since they are mainly constituted of carbon and hydrogen and therefore produce more energy than phenolic compounds, which contain more oxygen [35,54].

Since the heating values of extractives are usually higher than those of macromolecular compounds, the removal of extractives generally decreases the HHV of biomass. For example, the heating values of extractive-free woody and non-woody biomass samples were found to be significantly lower than those of unextracted samples. Heating values decreased by 1–17%, with the exception of coffee husks and rice husks [55]. Nevertheless, in some cases, the removal of extractives increases the heating value, as reported for several parts of *Albizia lucida*, *Syzygium fruticosum*, *Pterospermum lanceaefolium*, and *Premna bengalensis* [56]. Similarly, a study on the influence of extractives from different wood species on their calorific values concluded that the influence depended on the species since the removal of the dichloromethane extractives of *E. urophylla*, *P. oocarpa*, and *C. citriodora* reduced their HHVs, but it did not alter the HHV of *E. paniculate*, probably due to their low concentration [57]. On the other hand, the removal of extractives in cold water did not decrease the gross calorific value of the wood, most likely because most compounds removed by water are small sugar compounds with low HHVs. Several other studies were conducted on the influence of removing extractives on HHVs. For instance, for the influence of water extractives on the heating values of jatoba (*Hymenaea courbaril*), tornillo (*Cedrelinga catenaeformis*), ipe (*Tabebuia* sp.), and Brazilwood (*Paubrasilia echinata*) wood sawdust, it was concluded that it depended on the species, with decreases in heating values observed for jatoba and tornillo and an increase in ipe similar to Brazilwood [46,58]. Another study on the effect of the removal of extractives in several types of woody and non-woody biomass such as arecanut husks, bagasse, coffee husks, cotton stalks, groundnut shells, rice husks, wheat husks, *P. juliflora*, and *L. camara* found that the removal of extractives only led to an increase in the HHV of coffee husks [55]. Similarly the removal of extractives from yellow birch wood decreased the HHV, but it seemed to have no influence on the HHV of sugar maple wood, and this difference was associated with the type of extractive, since yellow birch generally has large amounts of triterpenes, while sugar maple has more small sugar compounds [59]. The removal of extractives mostly depends on the type of extractive rather than the species. For example, the removal of ethanol–benzene

extractives from four softwoods and four hardwoods increased the HHV of the wood for all of the species [60].

A study that determined the HHVs of the extractives from several tropical woods concluded that ethanol extractives had higher heating values of around 26.08 MJ/kg for a mixture of 20 hardwoods, 28.39 MJ/kg for beech, 31.07 MJ/kg for spruce, and 34.92 MJ/kg for maritime pine [61]. The correlations between the contents of benzene–ethanol extractives and the heating values of several parts of *Quercus variabilis* trees of six ages (from 16 to 55 years) showed that these extractives could be positively correlated with HHVs [62].

However, estimating HHVs from elemental composition is not the objective of this review. The elemental composition can be used to estimate the HHVs of individual compounds present in the extracts of different solvents. For example, the HHVs of some fatty acids from vegetable oils ranged from 24.29 to 41.20 MJ/kg, as estimated based on the ratios of carbon, hydrogen, and oxygen given by their chemical formulas [63].

Table 2 presents estimations of the most common wood extractives, as calculated using the formula developed by Demirbas et al. [63], which estimates the HHV based on the wt% of carbon, hydrogen, and oxygen as follows:

$$\text{HHV (MJ/kg)} = 0.305 (\text{C}) + 1.423 (\text{H}) - 0.154 (\text{O}) \quad (2)$$

Based on these results, sterols and triterpenes are among the extractives with the highest HHVs, reaching more than 40 MJ/kg, followed by saturated fatty acids, unsaturated fatty acids, and resin acids. The phenolic compounds, due to their greater oxidation levels, have much lower HHVs. For example, the estimated HHV for pinosylvin, a common stilbene is 29.95 MJ/kg. Catechin, a flavonol, has an HHV of 20.76 MJ/kg, and the lignan pinoresinol has an HHV of 25.12 MJ/kg. Gallic Acid, a precursor of tannins, has the lowest HHV, which is estimated to be 12.89 MJ/kg. In accordance with Demirbas [63], the differences between the experimental values and the estimated values for the HHVs of the fatty acids have a mean difference of 0.30%, which is an acceptable difference. The experimental values for the most common fatty acids determined by Sadrameli et al. [64], who used physical properties to estimate the HHVs of fatty acids, are higher than those obtained by Demirbas; however, Levine et al. [65] obtained similar values.

The heating values are the same for most of the oils (39–40 MJ/kg), except for castor oil, which has the lowest value (37.274 MJ/kg) [5].

HHVs have been measured for three classes of fatty esters and two classes of triglycerides (TGs), and the authors concluded that the higher heating value of a triglyceride increases with increases in its carbon number and molecular weight [66].

In a previous study, an ethanol–benzene mixture followed by 95% ethanol extracted volatile oils, resins, fatty acids, and pigments, while water extraction removed inorganic salts, some organic acids, and carbohydrates such as starch and simple sugars [53], which according to the estimated values of the most common extractives, showed that extractives with high HHVs are mainly removed by less polar solvents. This is the reason why the removal of ethanol–benzene extractives decreasing the HHV of wood has been reported before [60,62], while the removal of water extracts increases or has no effect on the HHV of extracted wood [57].

Table 2. Estimated values of the HHVs of the most common extractives.

	HHV (MJ/kg)
Common saturated fatty acids	
Lauric acid	36.67
Mystic	37.88
Palmitic	38.83
Stearic	39.6
Anteisoheptadecanoic	39.23
Arachinic	40.22
Behenic	40.74
Lignoceric	41.19
Cerotic	41.57
Common unsaturated fatty acids	
Palmitoleic acid	38.01
Oleic acid	38.86
Linoleic acid	38.12
Linolenic acid	37.37
Pinolenic acid	37.37
Common resin acids	
Abietic acid	36.82
Dehydroabietic acid	36.11
Pimaric acid	36.82
Levopimaric acid	36.82
Common sterols and triterpenes	
Sitosterol	42.31
Campesterol	42.17
Squalene	44.22
Betulinol	39.91
Other compounds	
Pinosylvlin	29.95
Catechin	20.76
Pinoresinol	25.12
Gallic Acid	12.89

5.5. Inorganics

The amounts of inorganic materials (ash) in biomass can range from around 0.5% in wood to about 12% in straws and cereals [59]. Ashes are noncombustible materials, and their presence has been associated with lower HHVs, as can be seen in the models presented in the next section, where the HHV is reduced by a factor depending on the ash amount. Increasing the ash content not only lowers the heating value but also implies a risk of sintering and negatively affects milling and pelleting equipment [67].

6. 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 [68]. 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) [28].

Table 3 presents an update of the models reported over the years related to the prediction of higher heating values using lignin, cellulose, extractives, ash, or a mixture of these chemical compounds. 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 [50]. Shafizadeh and Degroot [39] 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 [61] 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 [69] 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 [60] 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 engelmannii*), 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 [70] 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 [9,24,32,71,72] 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 [48] obtained a good correlation ($R^2 = 0.89$) for the HHV and the extractive content of spruce wood using a quadratic function (Equation (3)):

$$\text{HHV} = 20.314 + 0.134 [E] + 0.004 [E]^2 \quad (3)$$

In more recent years, several models were proposed, most of them using lignin or extractives as the main estimators for pine wood [73]; corn stover, corn cobs, sunflower shells, beech wood, Ailanthus wood, hazelnut shells, wood bark, olive husks, and walnut shells [74]; different wood species [3]; greenhouse crops [75]; or biomass samples from agro-forestry waste and industrial waste [76]. Callejón-Ferre et al. [75] reported a good correlation model using hemicellulose, cellulose, and lignin ($R^2 = 0.80$) 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. [47] 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 (4)) was obtained for lignin:

$$\text{HHV} = 16.531 + 0.113 [L] \quad (4)$$

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. [77] ($R^2 = 0.88$) for rice straw and wheat straw (Equation (5)):

$$\text{HHV} = 18.96016 - 0.22527 [\text{Ash}] \quad (5)$$

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 [5,78] 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.

Table 3. Models for the estimation of HHV in MJ/kg from cellulose (C), hemicelluloses (He), holocellulose (Ho), lignin (L), extractives (E), and ash (Ash).

Model	R ²	Biomass	Year	Name	Reference
$\text{HHV} = 19.307 + 0.118 [\text{E}]$	0.54	Pine biomass	1973	Howard	[28]
$\text{HHV} = 0.17389 [\text{C}] + 0.26629 [\text{L}] + 0.32187 [\text{E}]$	n.a	Lignocellulose materials	1976	Shafizadeh and Degroot	[68]
$\text{HHV}^* = 17.354 + 0.082 [\text{L} + \text{E}_{\text{E-B}}]$ $\text{HHV}^* = 20.800 - 0.147 [\text{A}] + 0.055 [\text{E}_{\text{E-B}}] - 0.096 [\text{Ew}] + 0.047 [\text{L}] - 0.031 [\text{Ho}]$	0.69 0.74	Tropical wood	1977	Doat	[61]
$\text{HHV} = 0.17389 [\text{Ho}] + 0.26629(100 - [\text{Ho}])$	±0.81	Extractive-free wood	1978	Tillman	[69]
$\text{HHV} = 19.246 - 0.196 [\text{Ash}]$ $\text{HHV} = 19.830 - 0.277 [\text{Ash}]$ $\text{HHV} = 21.043 - 0.282 [\text{Ash}]$ $\text{HHV} = 20.353 - 0.234 [\text{Ash}]$ $\text{HHV} = 20.179 - 0.365 [\text{Ash}]$ $\text{HHV} = 19.610 - 0.242 [\text{Ash}]$ $\text{HHV} = 20.060 - 0.352 [\text{Ash}]$ $\text{HHV} = 20.067 - 2.196 [\text{Ash}]$	n.a.	Field crops Vineyard prunings Food and fiber processing wastes Hulls and shells Forest residues Energy crops Wood All biomass	1985	Ebelin and Jenkins	[79,80]
$\text{HHV}^{**} = 17.9017 + 0.07444 [\text{L}] + 0.0661 [\text{E}]$ $\text{HHV}^{**} = 17.7481 + 0.0800 [\text{L}^*](100 - [\text{E}])/100 + 0.0886 [\text{E}]$	0.76 0.76	Unextracted wood. Four softwoods (Engelmann spruce, western redcedar, southern pine, and redwood) and four hardwoods (hard maple, yellow-poplar, red oak, and basswood).	1987	White	[60]
$\text{HHV}^* = 17.6132 + 0.0853 [\text{L}]_a$	0.97	Extractive-free wood			
$\text{HHV}^* = 17.4458 + 0.0907 [\text{L}]_a$	0.96	Extractive-free softwood (Engelmann spruce, western redcedar, southern pine, and redwood)			
$\text{HHV}^* = 18.0831 + 0.0637 [\text{L}]_a$	0.7	Extractive-free hardwood (hard maple, yellow-poplar, red oak, and basswood)			
$\text{HHV} = (1 - [\text{A}]/([\text{C}] + [\text{L}] + [\text{E}]))(0.17389 [\text{C}] + 0.26629 [\text{L}] + 0.32187 [\text{E}])$	±0.1	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	1991	Jiménez and González	[70]
$\text{HHV}^{**} = 0.0889 [\text{L}] + 16.8218$	0.95	Extractive-free wood and non-wood			
$\text{HHV}^{**} = 0.0893 [\text{L}] + 16.9742$	0.97	Extractive-free lignocellulosic materials			
$\text{HHV}^{**} = 0.0877 [\text{L}] + 16.4951$	0.93	Extractive-free non-wood: tobacco leaves, corn cobs, corn straw, wheat straw, waste material, tobacco stalks, hazelnut shells, and olive cake	2001	Demirbas	[24]
$\Delta\text{HHV} = 0.00639 [\text{E}]^2 + 0.223 [\text{E}] + 0.691$		Spruce trunk wood, spruce trunk bark, beech trunk wood, beech trunk bark, Ailanthus trunk wood, sunflower shells, almond shells, hazelnut shells, olive husks, hazelnut kernel husks, and walnut shells	2002	Demirbas	[9]

Table 3. Cont.

Model	R ²	Biomass	Year	Name	Reference
HHV ** = 0.0864 [L] + 16.6922	0.97	Extractive-free sunflower shells, almond shells, hazelnut shells, wood bark, olive husks, hazelnut kernel husks, and walnut shells	2003	Demirbas	[71]
Δ HHV = 0.383 [E] – 0.0387	-	Hazelnut shells, wheat straw, olive husks, beech wood, spruce wood, corn cobs, tea waste, walnut shells, almond shells, and sunflower shells	2004	Demirbas	[72]
HHV = 20.004 + 0.020 [L] + 0.050 [E] HHV = 20.015 + 0.020 [L] + (100 [E]) + 1001 + 0.053 [E] HHV = 20.137 + 0.008 [L] + 0.131 [E] + 0.004 [E] ² HHV = 20.083 + 0.003 [L] + 0.151 [E] + 0.003 [E] ² HHV = 20.314 + 0.134 [E] + 0.004 [E] ² HHV = 20.029 + 0.148 [E] + 0.003 [E] ²	0.67 0.67 0.89 0.81 0.89 0.81	Wood <i>Picea abies</i>	2004	Rhén	[48]
HHV = 19.914 – 0.2324 [Ash]	0.63	Several types of biomass	2005	Sheng and Azevedo	[5]
HHV = 18.96016 – 0.22527 [Ash]	0.88	Rice straw and wheat straw	2008	Huang et al.	[77]
HHV = 20.12 + 0.17 [E]	0.94	Pine wood	2010	So and Eberhardt	[73]
HHV = 0.0979 [L] + 16.292	0.93	Corn stover, corn cobs, sunflower shells, beech wood, Ailanthus wood, hazelnut shells, wood bark, olive husks, and walnut shells	2012	Acar et al.	[74]
HHV = 20.086 – 0.261 [Ash]	n.a.	Greenhouse crops	2011	Callejon-Ferre et al.	[81]
HHV = 14.338 + 0.123 [L] + 0.135 [E]	0.92	Wood	2011	Telmo and Lousada	[3]
HHV = 10.955 + 0.629 [L] d 0.74 HHV = 8.211 + 0.150 [He] + 0.767 [L] HHV = 7.405 + 0.163 [He] + 0.065 [C] + 0.682 [L]	0.74 0.75 0.80	Greenhouse crops	2014	Callejon-Ferre et al.	[75]
HHV = 16.1964 + 0.0555 [L] HHV = 17.0704 – 0.0202 [He] + 0.0449 [L]	- -	Twenty biomass samples belonging to agro-forestry wastes and industrial wastes	2015	Alvarez et al.	[76]
HHV = 18.0980 – 0.0705 [Ash] HHV = 17.7722 + 0.00547 [E] HHV = 16.5477 + 0.0479 [L] HHV = 17.8816 – 0.124 [Ash] + 0.0185 [E] HHV = 16.7467 – 0.0400 [Ash] + 0.0451 [L] HHV = 16.5365 + 0.000864 [E] + 0.0476 [L]	0.09 0.02 0.44 0.23 0.47 0.44	Five semi-arid Mexican tree species (<i>Helietta parvifolia</i> (Gray) Benth., <i>Ebenopsis ebano</i> (Berl.) Barneby, <i>Acacia berlandieri</i> (Benth.), <i>Havardia pallens</i> (Benth.) Britton and Rose, and <i>Acacia wrightii</i> (Benth.))	2016	Ngangyo-Heya et al.	[82]
HHV = 15.605 + 0.074 [L] + 0.172 [E] HHV = 15.5988 + 0.0737 [L] + 0.1740 [E]	0.82 0.83	Non-wood	2018	Akdeniz et al.	[83]

Table 3. Cont.

Model	R ²	Biomass	Year	Name	Reference
HHV = 19.393 + 0.039 [E] HHV = 20.382 − 0.558 [Ash] HHV = 23.527 − 0.055 [C]	0.33 0.32 0.38	Tree Species from Oaxaca, Mexico: <i>Alnus acuminata</i> subsp. <i>arguta</i> (Schltdl.) Furlow, <i>Arbutus xalapensis</i> Kunth, <i>Myrsine juergensenii</i> (Mez) Ricketson and Pipoly, <i>Persea longipes</i> (Schltdl.) Meissner, and <i>Prunus serotina</i> Ehrh.	2019	Ruiz-Aquino et al.	[84]
HHV = 17.893 + 0.068 [L]	0.60.	Mixture of eight untreated and heat-treated woods	2020	Domingos et al.	[47]
HHV = 17.5188 + 0.0746 [L] HHV = 0.4982 [C] − 4.5813	0.21 0.73	Pine sawdust, alder dust, and rape straw stems	2021	Maksimuk et al.	[28]

* Converted from cal/g. ** Converted from Btu/lb. EE-B—ethanol–benzene extractives. Ew—water.

7. Conclusions

This research shows that the influence of the chemical composition on the heating value of biomass has not been a thoroughly studied subject. Nevertheless, the HHV of biomass is mainly influenced by the amounts of lignin and the lipophilic extractives that have the highest HHVs due to low oxidation levels. The estimated values showed that sterols and triterpenes have higher HHVs, followed by saturated fatty acids, unsaturated fatty acids, and resin acids. Good correlations have been achieved between chemical compounds and HHVs, and the most accurate models are based on the lignin from extracted samples. High ash contents have been associated with lower HHVs in biomass.

Several knowledge gaps were found:

1. There have been no studies on the higher heating value of suberin, which is important for cork-rich barks.
2. Studies are deficient or nonexistent on the HHVs of G, GS, and H lignins obtained using different isolation methods.
3. Data are scarce on the experimental values of the HHVs of different extractives.
4. Correlations based on hemicelluloses and extractives are insufficient.
5. Knowledge on the use of non-standard methods for the determination of chemical composition is insufficient.

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