Chapter 2

Review of Literature
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Wood one of the oldest source of energy has been used by men for over 500000 years [1]. Even much before the dawn of human civilization mankind relied on wood as the primary source of energy. However, with the advent of petroleum and modernization of human society a rapid decline in fuelwood usage was evident. This long-term decline in the diminishing importance of biomass energy was reversed following the 1973 OPEC oil embargo. With rapid decline in petro fuel reservoirs and frequent fluctuations in petroleum prices the importance of fuelwood is increasing dramatically. Biomass electrical power generation and cogeneration plants in Maine, New Hampshire, Vermont, Michigan, Wisconsin, and California have become significant new users of wood boiler fuel [2]. In developing nations, biomass in its traditional solid form (fuelwood and agricultural residues) represents a considerable and often insufficiently recognized proportion of the total energy supply. Fuelwood collected from forests, either by lopping branches, fallen wood or cutting down of dry and diseased trees, is the most common source of domestic energy in the rural areas [3]. In India, rural households depend primarily on locally available biomass sources collected from forests and nearby sites to meet their domestic energy needs [4]. Bhatt and Sachan [5] reported that fuelwood is the main source of energy in rural India. About 80% of the Indian population lives in villages where wood is the main source of primary energy. But however owing to the depletion of wood the rural poor are forced to use other forms of energy such as crop residues and dung [6].

Felling of trees for firewood accounts for the largest share of wood usage in developing nations, however this may lead to rapid deforestation [7]. In order to avert this situation, the prime requirement is large-scale energy plantations on unused and degraded lands. Although all kinds of trees and shrubs can be used as fuelwood for energy plantation, a systematic approach is necessary to identify locally available indigenous tree species, which can thrive best in the local climate. Local user’s knowledge is crucial for selecting proper fuelwood species as they have an intimate knowledge of the local environment [8]. Deka [9] emphasized the need for studying the fuelwood characteristics of different tree and shrubs species of a locality along
with their combustion performance, growth and biomass productivity in different agro
climatic conditions as vital criteria to select fuelwood species for energy plantation.
Time and again various researchers have identified plant constituents that correlate
with the fuelwood quality. The Technology Innovation Board on Science and
Technology for International Development Commission on International Relations,
National Academy of Sciences, Washington, has listed a large number of promising
firewood species of Humid Tropics, Arid and Semiarid Region and Tropical Highlands
[10].

Before utilizing wood as a source of energy a brief description about wood and
its properties have been presented below.

2.1 Wood and properties of wood

In general wood refers to the hard and fibrous structural tissues found in stems
and roots of trees [11]. Botanically, wood is defined as a hard and fibrous material
formed by the accumulation of secondary xylem, which is the principal strengthening
tissue, produced by the vascular cambium and found in the stems and roots of trees
and shrubs [12].

Wood, a natural, cellular, composite material of botanical origin possesses
unique structure and chemical characteristics that renders desirability for numerous
end uses [13-14]. An understanding of the anatomical and physico-chemical properties
of wood is a prerequisite for end applications. Anatomical properties identify the
macroscopic structures of soft and hardwood. Physical properties deal with the
relationship between specific gravity and moisture content. Chemical properties refer
to carbohydrate and lignin structures and their contents as related to fuel reactivity and
heating value [15].
2.1.1 Softwood and Hardwood structures

Generally wood is divided into two broad classes: hardwood and softwood. Botanically, hardwood is angiosperm and softwood is gymnosperm. Angiosperms are characterized by production of seeds, enclosed in the ovary of the flower whereas gymnosperms produce seeds that are naked [16-17]. This classification cannot be used universally to refer to the actual physical hardness of woods because some softwoods are quite hard (e.g. Dougla-fir and Southern yellow pines) and some hardwood are soft (e.g. Cotton wood.). Hardwoods are typically broadleaf, deciduous trees whereas softwoods are generally needle-leaved evergreen trees [18-19].

![Figure 2.1: Cross section of hardwood and softwood structure showing pores of vessel element of hardwood and tracheid of softwood, compiled from [20-23]](image)

Softwood and hardwood are quite different in terms of their cell components. Hardwood contain vessels, a structure composed of vessel elements which are joined
end-wise to tubes or vessels along the stem, branch or root and are seen as pores on the wood cross section. They serve as pathway for fluid conduction in hardwood. This type of cells are absent in softwood. On the other hand, long cells known as longitudinal tracheid comprise 90 – 95 percent of the volume of softwood and provide both conductive and mechanical functions to softwood [17-20]. The cross section of softwood and hardwood structure showing pores of vessel elements of hardwood and tracheid of softwood are presented in Figure 2.1. As physico-chemical composition of soft and hardwood are different, their chemical nature and resultant reactivity at the cellular level potentially influence their use for various end applications.

2.1.2 Physical properties of wood

2.1.2.1 Moisture content

Wood is a hygroscopic material because of the hydrophilic nature of the cell wall constituent polymers viz., hemicelluloses, cellulose, and to a lesser extent lignin. The hygroscopic character of wood is attributed primarily to the presence of hydroxyl (-OH) groups in the polymer constituents comprising the cell wall. Carbohydrate fraction (hemicelluloses and cellulose) of the cell wall is mainly responsible for wood’s hygroscopicity. Moreover, it is mainly the hemicelluloses that dictate hygroscopicity, due to their short, branched, open structures, and their location on the surface of microfibrils, which results in availability for water sorption. Cellulose, though abundant in -OH group, is less hygroscopic due to intra- and inter- molecular bonding within cellulose microfibrils. With changes in the chemical composition or chemical structure of these cell wall polymers, the water sorption capacity of wood changes and consequently the moisture content [24-25].

Water in wood is present in two forms: bound water which is held within the cell wall by intermolecular hydrogen bonding to the cell wall polymer constituents and free water which is located in the cell lumens. As the wood begins to dry, when exposed to ambient air, free water first leaves the wood from lumens while bound
water content remains unaffected. The moisture content level corresponds to the lumens containing no free water (only water vapour), while no bound water desorbed from cell wall material, is known as fiber saturation point (FSP). The fiber saturation point differs between tree species and is usually in the range of 20-25% (wet basis) [26-27]. FSP is important in drying of wood. More energy is required to drive off a given amount of water below the FSP because the bound water is being removed and therefore, the attractive forces between the wood and water must be overcome. The total amount of water, that wood can hold is dependent upon the actual amount of cell wall substance and the amount of void space (cell cavities) in a given volume of wood [28].

Moisture content is an important determinant of fuelwood preference as it affects the weight of wood on transportation, fire temperatures and ignition times [29]. It is also an important characteristic which is responsible for the ease of combustion of a fuelwood, the amount of smoke it emits, and its usable heat content [30]. As reported [31] moisture content does not contribute to the heating value but reduces the heat available from the fuel by lowering the initial gross calorific value of wood. The moisture content varies from species to species and also from one tree part to another. It is often lowest in the stem and increases towards the roots and the crown. Seasons are also known to effect moisture content [32]. Moisture content of wood is generally expressed in percentage of green moisture content, air dry and/or oven dry moisture content [33].

2.1.2.2 Density and Specific gravity

Density (D) is the mass or weight per unit volume of a material and is usually expressed in kilograms per cubic meter (kg m\(^{-3}\)) or grams per cubic centimeter (g cm\(^{-3}\)). On the other hand specific gravity (SG) is the ratio of the density of a material to the density of water. Both the term bears the same characteristic and they are different only in the fundamental sense that specific gravity is a pure number and density is not.
Wood density provides a simple measure of the total amount of solid-wood substance in a piece of wood. For this reason, wood density provides an excellent means of predicting end-use characteristics of wood such as strength, stiffness, hardness, heating value, machinability, pulp yield and paper making quality [34]. Density depends on the chemical nature and/or anatomical structure of wood, and these characteristics differ among species and environments [35-36]. Density or specific gravity of a wood species is greatly influenced by the moisture content. Weight of wood species varies with the moisture content and its volume changes with change in moisture content below the Fiber Saturation Point (FSP). Therefore, it is essential to specify the moisture condition during the determination of wood density or specific gravity [37]. When the weight of the wood is considered as oven dried weight (moisture free) and volume is taken at or above FSP (green volume), the density of wood is known as basic density [38].

2.1.3 Chemical properties of wood

The basic elements responsible for the formation of wood components are carbon, hydrogen, oxygen and nitrogen. A negligible amount of sulfur is also present in it along with ash forming inorganic minerals [37]. In chemical term, wood is defined as a three-dimensional biopolymer composite composed of an interconnected network of cellulose, hemicelluloses and lignin with minor amount of extractive and ash. The major chemical component of a living tree is water, but on a dry weight basis, all wood cell walls consist mainly of sugar-based polymers (carbohydrates) that are combined with lignin [39]. The Chemical composition of wood varies within the tree parts (root, stem, or branch), type of wood, geographic location, climate and soil conditions [40]. The chemical components present in wood is depicted in the general scheme shown in Figure 2.2.
2.1.3.1 Carbohydrates

The major carbohydrate portion of wood is composed of cellulose and hemicellulose polymers with minor amounts of other sugar polymers such as starch and pectin. The combination of cellulose and the hemicellulose is called holocellulose and usually accounts for 65–70 percent of the wood dry weight. These polymers are made up of simple sugars [39].

2.1.3.1.1 Cellulose

Cellulose is the most abundant constituent of the cell wall and constitutes 40–50% of dry weight of wood. Cellulose is a linear polysaccharide composed of β-D glucopyranose units linked together by (1→4) glucosidic bonds. The linear long chain polysaccharide, cellulose can be represented as \((\text{C}_6\text{H}_{10}\text{O}_5)_n\), where \(n\) is the degree of polymerization (DP) [42]. Goring and Timell [43] reported that the degree of polymerization (DP) is normally from 9000 to 10000, but possibly as high as 15000. Cellulose molecules are completely linear and have a strong tendency to form intra and
intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. Microfibrils build up fibrils and finally cellulose fibers. As a consequence of its fibrous structure and strong hydrogen bonding, cellulose has a high tensile strength [17, 39, 42]. Figure 2.3 shows a partial molecular structure of cellulose.

2.1.3.1.2 Hemicelluloses

Hemicelluloses are abundant components of the plant cell wall and constitute 20-35% of dry weight of wood. They are found in the matrix between cellulose fibrils in the cell wall. The main monomers of wood hemicelluloses are hexoses (D-glucose, D-mannose and D-galactose); pentoses (D-xylose and L-arabinose); uronic acids (4-O-methyl-D-glucoronic acid, D-galacturonic acid and D-glucuronic acid) and deoxyhexoses (L-rhamnose and L-fucose) in small quantity [44]. There are various types of wood hemicelluloses depending upon the types of monomers which undergo polymerization. Most of the hemicelluloses have a degree of polymerization of only 200 [17]. Generally, hemicelluloses are of much lower molecular weight than cellulose, having side groups and being branched in some cases [40]. Hardwood and softwood differ in structure and composition of hemicelluloses (Table 2.1). The representative structural formula of major hemicelluloses found in hardwood and softwood are represented in Figure 2.4 (a, b, c, d).
Table 2.1: Prime hemicelluloses found in softwood and hardwood [44]

<table>
<thead>
<tr>
<th>Wood</th>
<th>Hemicellulose type</th>
<th>Amount (% dry basis)</th>
<th>Units linkage</th>
<th>Molar ratio (App. values)</th>
<th>Linkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>Glactoglucomannan</td>
<td>5-8</td>
<td>β-D-Manp</td>
<td>3-4</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β-D-Glcp</td>
<td>1</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-D-Galp</td>
<td>1</td>
<td>1→6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O-Acetyl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Softwood</td>
<td>Glucomannan</td>
<td>10-15</td>
<td>β-D-Manp</td>
<td>3-4</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β-D-Glcp</td>
<td>1</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-D-Galp</td>
<td>0.1</td>
<td>1→6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O-Acetyl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Softwood</td>
<td>Arabinoglucuronoxylan</td>
<td>7-15</td>
<td>β-D-Xylp</td>
<td>10</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-O-Me-α-D-GlupA</td>
<td>2</td>
<td>1→2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α-L-Araf</td>
<td>1.3</td>
<td>1→3</td>
</tr>
<tr>
<td>Larch wood</td>
<td>Arabinogalactan</td>
<td>3-35</td>
<td>β-D-Galp</td>
<td>6</td>
<td>1→3, 1→6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L-Araf</td>
<td>2/3</td>
<td>1→6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β-D-Arap</td>
<td>1/3</td>
<td>1→3</td>
</tr>
<tr>
<td>Hardwood</td>
<td>Glucuronoxylan</td>
<td>15-35</td>
<td>β-D-Xylp</td>
<td>10</td>
<td>1→4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-O-Me-α-D-GlupA</td>
<td>1</td>
<td>1→2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O-Acetyl</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Hardwood</td>
<td>Glucomannan</td>
<td>2-5</td>
<td>β-D-Manp</td>
<td>1-2</td>
<td>1→4</td>
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<td></td>
<td>β-D-Glcp</td>
<td>1</td>
<td>1→4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>O-Acetyl</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.3: Partial molecular structure of cellulose [40]
Figure 2.4 (a): Representative structural formula for softwood galactoglucomannan

Figure 2.4(b): Representative structural formula for softwood arabinoglucuronoxylan
2.1.3.1.3 Lignin

Lignin is one of the important and abundant chemical constituents of wood. Lignin constitutes 23% to 33% of the wood substance in softwoods and 16% to 25% in hardwoods [19]. Lignin is complex polyphenolic material arising from enzymic dehydrogenative polymerization of the phenylpropane units. The precursors involved in lignin biosynthesis are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

![Figure 2.4(c): Representative structural formula for hardwood glucuronoxylan](image1)

![Figure 2.4 (d): Representative structural formula for hardwood glucomannan](image2)

Figure 2.4 (a-d): Structures of abundant hemicelluloses found in hardwood and softwood [44]
[39, 45] whose chemical structures are presented in Figure 2.5. Lignin precursors are linked together through ether (C-O-C) and carbon-carbon (C-C) bonds via β-O-4, 5-5, β-1, β-5, α-O-4, β-β, 4-O-5 linkages and the variation of the lignin structure are due to changes in frequency of these linkages. Lignin can be classified mainly into three categories on the basis of types of lignin precursors involved in its biosynthesis [46]. Softwood lignin or guaiacyl lignin consists almost exclusively of coniferyl alcohol and may contain small amounts of p-coumaryl alcohol (mainly in the compression wood), but no or only traces of sinapyl alcohol. Hardwood lignin or syringyl-guaiacyl lignin contains both coniferyl and sinapyl alcohol with proportions from approximately equal amounts, to three times higher levels of sinapyl alcohol. Some hardwood lignin may also contain small amount of p-coumaryl alcohol [47].

Lignin is an important constituent of wood from the point of biological function. It provides stiffness to the cell walls and acts as adhesive keeping different cells together in woody tissues. Lignin makes the cell wall hydrophobic and also protects wood against microbial degradation [47].

![Chemical structures of the lignin precursors](image)

**Figure 2.5: Chemical structures of the lignin**

### 2.1.3.2 Extractives

Extractives are non-structural and low molecular weight compounds present in wood. They include fats, waxes, alkaloids, proteins, simple and complex phenolics,
simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils [17, 48]. Extractive constitutes 4-10% of the dry weight of normal wood species that grow in temperate climates and may be as much as 20% for tropical species [49]. Some of them are soluble in water while others are soluble in neutral solvents (dichloromethane, ethanol-benzene and ethanol-toluene etc.). Softwoods contain higher extractive percentage than hardwoods [39]. They function as intermediates in tree metabolism, as energy reserves and protect trees from microbial attack. Besides, they contribute to wood properties such as color, odor, and decay resistance [17, 50].

2.1.4 Ash

Ash content in wood is defined as the inorganic residue remaining after combustion at a temperature of 575 ± 25 °C in the presence of abundant oxygen. Wood ash comprises of a variety of major (Ca, K, Mg, Na, P, Si, Al, Fe, Cl, and Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, and Zn) inorganic elements. The elements that are responsible for the bulk make up of ash in wood are Ca, Mg and K [51]. These elements probably exist in wood as oxalates, carbonates, and sulfates, or are bound to carboxyl groups in pectic materials [39, 52]. The ash percentage may vary within different parts of a tree (roots, bark, trunk, and leaves) and among different tree species [53]. Hardwoods contain higher ash content than softwoods [54]. These variations in ash content can be attributed to different soil and climatic conditions in which the tree grows [55].

2.1.5 Energy value of wood fuel

Calorific value indicates the heating potential of fuelwood and is a measure of its energy content [56]. This value in wood is mainly related to the physicochemical composition of plant species like percentage of carbon, hydrogen, moisture and ash [36, 57-58 44]. In general, the percentage of carbon and hydrogen mainly contributes to the heating value in wood. [59].
Three different conventions are commonly used in deriving the heating value of biomass fuels: (1) gross calorific value, (2) net calorific value and (3) usable heat content [60].

2.1.5.1 Gross Calorific Value and Net Calorific Value

If the products of combustion are condensed to ambient temperature, the latent heat of condensation of steam is also included in the measured heat. The total value calculated is known as higher or gross calorific value (HCV/GCV) and is defined as the total amount of heat liberated when one unit of the fuel is burnt completely and the combustion products are cooled to ambient temperature [61].

In actual practice, during combustion of a fuel the water vapors escape as such along with hot combustion gases and thus are not condensed. Hence a lesser amount of heat is liberated. This is called lower or net calorific value (LCV/NCV) and is defined as the amount of heat liberated when one unit of fuel is burnt completely and the combustion products are allowed to escape [61].

In standard test procedure, wood samples are usually oven-dried before calorimetric analysis. Values thus derived are termed as gross anhydrous calorific values (CV). Reported anhydrous CVs for wood range from 18.0 MJ/kg to 24.0 MJ/kg. But CV may vary according to tree species and its components. CV is higher for resinous conifers (typically 20.0 - 23.0 MJ/Kg) than for hardwood species (typically 18.5-20.0 MJ/Kg) [60].

2.1.5.2 Usable heat content

Gross and net calorific values are useful measures of energy content in fuels. But on the contrary, they do not represent the usable heat energy which can finally be recovered by burning a fuel in a combustion chamber. In calculating the net calorific value, it is assumed that the gaseous products of combustion are discharged at ambient temperature (25°C), so that no heat is lost except the latent heat of water vapor
(typically $200^\circ$C in an efficient furnace), and energy is lost in (1) superheated water vapor; (2) dry flue gases and (3) any excess air. These losses must be accounted for determining the usable heat content (recoverable heat energy) of wood as fuel [60].

2.1.6 Combustion quality of wood species

Heat of combustion is the most fundamental property with regard to fuel quality and is usually the best means to compare one fuel with another. Combustion is an oxidation reaction where the amount of heat liberated is related to the reduction state of the fuel i.e. the heat of combustion is dependent upon the chemical makeup of the fuel both at the molecular and atomic levels. For the various components in wood, the reduction state is in the following order: resins > lignin > cellulose and hemicelluloses. Normally, substances rich in reduced components give a high heat of combustion value. Thus, the heating value of woody material is generally modified to some extent by the amount of resinous extractives [62-63]. Combustion quality of fuelwood is also dependent on its moisture content. Presence of moisture in fuel does not change its higher heating value, but the usable heat per unit mass does change (i.e. reduce) for the following reasons: firstly, there is simply less combustible substance per unit weight of the fuel; secondly fuel moisture also causes heat loss during combustion, because some energy must be consumed to vaporize water [62-63]. The ash in fuelwood adversely affects the heat of combustion by reducing the heating value per unit weight of the fuel. Wood ash is not problematic for domestic use of fuelwoods. But, it may create problems in industrial fuelwoods where boiler furnaces achieve high temperatures, producing slag and clinkers from melting and fusion of ash [63]. Thus, tree species having high ash content are less desirable for industrial fuelwood [63-64]. In addition, wood species having high moisture show poor combustion quality and are less desirable for use as fuelwood [55].

Along with these physico-chemical properties, combustion quality of fuelwood is also related to some of its combustion characteristics. The important combustion characteristics which affect fuelwood properties are ignition temperature, peak
temperature, maximum combustion rate, mean combustion rate, burnout temperature etc.

2.2 Investigating fuelwood species in abroad

Anderson et al. [65] reported that chemical composition, specific gravity, fuel value and size are the most useful indices of woody biomass quality that influence its suitability for efficient conversion with respect to energy. According to Davidson [66], tree species with high wood calorific value, high specific gravity and capacity for rapid growth on a wide range of sites are suitable for bio-energy plantation. Recently, Moya and Tenorio [67] investigated 10 fast-growing species for plantation in Costa Rica with respect to the fuel characteristics such as calorific value and Fuel Value Index (FVI). They observed large variation in FVI among the fuelwood species. The calorific value of heart wood was significantly influenced by the amount of extractives (extracts in dichloromethane), carbon, nitrogen, lignin content and ash content. On the other hand, the calorific value in sapwood was affected by the amount of extractives (extracts in ethanol- toluene) and the amount of ash content. FVI was affected by the quantity of carbon, lignin, the extractives in sodium hydroxide and dichloromethane.

In an another study, Hindi et al. [68] determined wood properties such as gross heat of combustion, specific gravity, void volume, ash content, total extractives, lignin and holocellulose of 6 Saudi tree species and reported the relationship of the above properties with wood heating value. Khider and Elsak [69] investigated 4 hardwood species (Acacia mellifera, Acacia senegal, Eucalyptus tereticornis and Moringa oleifera) from Blue Nile state, South East Sudan for energy production purposes. They determined heat values of the species with the help of a regression model derived from chemical components of the wood. In a similar study, Cuvilas et al. [70] investigated 8 hardwood species from three provinces (Cabo Delgado, Nampula in northern Mozambique, and Sofala in the central part) of Mozambique. They determined fuelwood properties, such as higher heating value, density, ash, lignin, carbohydrates, volatile matter, extractives, elemental composition (C, H, N, O, S, and Cl), heavy
metals for the wood species and also calculated FVI (based on higher heating value, density and ash). They reported that tree species with higher FVI exhibited good fuelwood qualities. Mainoo and Ulzen-Appiah [71] investigated 3 tree species from the semi deciduous rainforest ecological zone of Ghana and correlated fuelwood properties including growth, wood yield, specific gravity, calorific value, moisture, chemical composition and FVI with wood biomass productivity and energy potentials of the species for use as fuelwood. Ramos et al. [72] carried out a study in a rural community in NE Brazil to scrutinize resemblance between local preferences for fuelwoods and their physical characteristics. They observed a significant relationship between plants with the highest FVIs and the most preferred fuelwood plants in the region. Lamers and Khamzina [73] investigated 3 tree species suitable for photo-remediation of marginal land in the Aral Sea Basin, Uzbekistan. They quantitatively determined fuelwood properties, such as such as calorific value, wood density, ash, moisture, C and N content and also calculated FVI (based on calorific value, density and ash content). Similar study was also reported by Munalula and Meincken [74] investigating 5 wood species (Acacia cyclops, Acacia erioloba, Eucalyptus cladocalyx, Pinus patula and Vitis vinifera) from Western Cape of South Africa with regards to their calorific values and environmental impacts when burned. In the Investigation of fuelwood properties of 31 species from Papua New Guinea, Jonathan et al. [75] reported that calorific value and ash content are the two important fuelwood properties for identifying new and reinforcing the traditionally used fuelwood species as quality fuelwood.

2.3 Investigating fuelwood in India

Studies on fuelwood characteristics of tree species available in different parts of India are also reported by several researchers. Singh and Khanduja [76] investigated 13 firewood shrub species in northern India. The authors determined calorific value, density, ash, moisture, silica, carbon, nitrogen and biomass/ash ratio for the species. The study revealed that Tamarix dioca, Carissa spinarum, Acacia calycina, Adhatoda
vasica and Dedonia viscosa could be used for intensive cultivation as firewood biomass in short rotations forestry. In a similar study, Bhatt and Todaria [77] investigated 33 high altitude vegetation, mountain trees and shrub confined to Garhwal Himalayas towards fuelwood characterization. Their findings suggested that temperate species offered better candidature as fuelwood species owing to high wood density, low ash content and low nitrogen percentage. They concluded that Premna barbata, Daphniphyllum himalense, Pyracantha crenulata, Lyonia ovalifolia and Cotinus coggygria possessed high FVI (correlated to high energy content, high wood density, low ash and water content) and may possibly be the most favorable species. Jain [78] investigated 26 perennial species grown in their natural habitat in Central India and 16 indigenous and exotic Pinus species from the Himalayan region at Kalika based on fuelwood properties like calorific value, density, ash, silica, moisture, nitrogen, volatile matter and FVI. In an another study, Jain [79] investigated 22 tree species grown in the natural habitat in Indian forests based upon fuelwood properties viz. calorific value, ash, density, silica, moisture, carbon, nitrogen, volatile matter and the FVI. The study revealed that Osmanthus fragrans, Quercus incana, Machilus odoratissma, Loger tromenia indica and Punica granatum exhibited the best fuelwood qualities among the species examined. Negi and Todaria [80] investigated quantitative fuel characteristics of 33 trees and shrubs of Garhwal Himalaya. In their study, FVI was considered as a standard parameter to identify suitable tree species for fuelwood production. They reported that Murraya exotica, Schlichera trijuga, Vlmus wallichiana, Flacour tia ramontchi, Rubus niveus, Callicarpa macrophylla, and Eleadendron glaucum were the most suitable tree species for fuelwood production. In a similar study, Puri et al. [81] determined fuelwood properties (calorific value, ash, density, water content, nitrogen content) of 6 indigenous (Acacia nilotica, Azadirachta indica, Casuarina equisetifolia, Dalbergia sissoo, Prosopis cineraria and Zizyphus mautitiana) and 4 exotic (Acacia auriculiformis, Acacia tortilis, Eucalyptus camaldulensis and Eucalyptus tereticomti) tree species (for tree parts such as stump, main stem, tree top, branches, foliage and bark) from Hisar region. They reported
that indigenous tree species were best suited due to their high density, low ash content and low nitrogen content. On the basis of FVI, they reported that *Acacia nilotica*, *Casuarina equisetifolia* and *Zizyphus mauritiana* were the most suitable fuelwood species among ten species studied. Goel and Bhel [82] investigated the fuelwood quality of 5 tree species suitable for plantation in alkaline soil sites of Banthra, Lucknow in relation to tree age for establishing harvest rotation cycles. They reported that *Prosopis juliflora* and *Acacia nilotica* were the most suitable species for short rotation fuelwood forestry programmes due to their high wood density, high biomass yield, low ash, low moisture content, and high heat of combustion at the juvenile stage. Jain and Singh [83] analysed 33 indigenous tree species grown in their natural habitat in subtropical forest of central India on the basis of fuelwood properties such as moisture, silica, ash, density, carbon, nitrogen, volatile matter and calorific value. FVI was also calculated to screen suitable species for potential production of fuelwood in these areas. They reported that *Acer oblongurn*, *Betula alonoides*, *Grevillea robusta*, *Limonia acidissima*, *Lyonia ovalifolia*, *Madhuca indica*, *Melia azedarch*, *Motinda tinctona*, *Myica sapida*, *Ptunus comuta*, *Pyrus pashia*, *Quercus langtnosa*, *Rhamnus triqueter* and *Stereospennum xylocarpum* exhibited better fuelwood qualities. Goel *et al.* [84] investigated the performance of 3, even-aged leguminous tree species (*Acacia nilotica*, *Acacia auriculiformis* and *Pithecellobium dulce*) on sodic soil sites at Banthra, Lucknow. In the study, they observed that *Acacia nilotica* has highest average girth at breast height (60.5 cm) and stand biomass (161 Mg ha\(^{-1}\)) despite its lowest plants survival after 15 years of growth. *A. nilotica* also showed superiority in respect to energy content in woody biomass (2467 GJ ha\(^{-1}\)) and fuel value index (1694) as compared to the other two species. The study concluded that species like *Acacia nilotica* could be selected as a promising species for afforestation of degraded soil sites, such as sodic soils, because of its higher biomass production potential, greater energy harvest, and efficiency to restore the soil quality suitable for climate-based productivity. Nirmal Kumar *et al.* [57] investigated 7 wood species (*Acacia nilotica*, *Cassia fistula*, *Acacia leucophloea*, *Prosopis cineraria*, *Tectona grandis*, *Butea
Fuelwood Characteristics of Some Indigenous Tree Species of Arunachal Pradesh

monosperma and Sterculia urens) from dry tropical forest, Udaipur and Bhilwara district of Rajasthan. In the study, fuelwood properties, such as density, ash content, and elemental composition (C, N, P, S, Pb, Al, As and Cd) of wood species were determined and correlated with the calorific value and evaluated in relation to their properties and environmental impact when burned. Their findings revealed that the wood with the highest calorific value does not necessarily constitute the best option as fuelwood, if elemental composition is taken into account. On the basis of overall determined properties they reported that all the species under study were preferable as fuelwood and their preference order were as Acacia nilotica > Acacia leucophloea > Prosopis cineraria > Tectona grandis > Butea monosperma > Sterculia urens. In another study, Nirmal Kumar et al. [85] investigated the fuelwood characteristics of 26 trees including shrub species from the dry deciduous forest in Aravally region, Rajasthan. On basis of FVI (based on calorific value, wood density and ash) they recommended A. nilotica, T. grandis, B. monosperma, P. cineraria and Albizia lebbek for inclusion in the energy plantation programme in this region. Chauhan and Soni [86] investigated about the biomass production, calorific value and chemical composition of different short rotation tree species and reported that short rotation tree species such as Gmelina arborea, Eucalyptus tereticornis, Pongamia pinnata, Terminalia arjuna, Toona ciliata exhibited better fuelwood properties and could be considered for inclusion in the energy plantation programme to minimize pressure on the traditional forests. Saravanan et al. [87] investigated Melia dubia wood species from different age groups (one, two, three, four and five year old) for assessing the fuel wood properties. Among the various tested age gradations of Melia dubia 5-year age old wood recorded the highest calorific value (3820 Kcal Kg\(^{-1}\)) and FVI (4125.60). From a comprehensive viewpoint, the study identified the prospects of 5-year Melia dubia with regard to energy properties and consequently its acquiescence for prospective energy utilities.

A large numbers of trees and shrubs grow well in natural habitats in the North Eastern region of India. But very little is known about their fuelwood characteristics.
Kataki and Konwer [88] investigated four indigenous perennial tree species namely *Albizia lucida*, *Syzygium fruticosum*, *Pterospermum lanceaeolium* and *Premna bengalensis* grown in their natural habitat of north-east India. They reported that *Albizia lucida*, *Syzygium fruticosum* and *Pterospermum lanceaeolium* exhibited better fuelwood properties and could be considered for inclusion in the energy plantation programme of north-east India. They further investigated fuelwood characteristics of 35 indigenous tree species grown in their natural habitat in north-eastern region of India [89]. They reported that *Acacia nilotica*, *Acacia auriculiformis*, *Albizia lebbeck*, *Albizia procera*, *Pinus kesiya* and *Elaeognus umbellata* were best suited as fuelwood and could be considered for inclusion in energy plantation programme in this region. Bhatt and Tomar [90] quantitatively analyzed 26 indigenous mountain fuelwood species of north-eastern Himalaya region. In the study, FVI was calculated by considering calorific value and density as positive criteria whereas ash content as negative criterion. They reported that tree species *Betula nitida*, *Machilus bombycina*, *Itea macrophylla*, *Cryptomeria japonica*, *Gmelina arborea*, *Simingtonia populnea*, *Macaranga denticulata* and *Schima wallichii* were prospective for fuelwood production. In a similar study, Bhatt et al. [30] investigated 25 indigenous trees and shrubs of the north-eastern Himalayan (NEH) region. On the basis of FVI, they reported that *Gaultheria fragrantissima*, *Litsea citrata*, *Myrica esculenta*, *Aesculus assamica*, *Daphniphyllum himalense*, *Mesua ferrea* and *Wendlandia tinctoria* were the most promising firewood species. In a similar study, Deka et al. [91] investigated 10 indigenous tree species of Assam, India preferred by its local people as fuelwood. In the study, fuelwood species were ranked on the basis of pair-wise comparison technique and FVI. The study revealed that the ranking order of the indigenous fuelwood species by pair-wise comparison technique used by the rural people of the sample areas of Assam has sufficient resemblance with those obtained from FVI. Bhatt et al. [92] quantitatively analysed 19 indigenous fuelwood species of eastern Himalaya, India to identify trees with potential for firewood production. FVI (calorific value X density/ash content) was calculated for fuelwood species. Over-all rank sum
index (ORSI) for firewood species was also determined with the help of firewood characteristics (FVI), fuelwood production potentiality, and availability in the region. On the basis of ORSI, they reported that *Castanopsis indica*, *Phoebe attenuata*, *Macropanax undulatum*, *Ixionanthes khasiana*, *Morus laevigata*, *Caryota urens*, *Lithocarpus elegans*, and *Litsea laeta* were the most preferred firewood species.

### 2.4 Study on fuelwood properties and their influence on heating value

The selection of a particular tree species for various end uses is based mainly on its physical and chemical properties.

Specific gravity is one of the most important physical characteristics of wood because of its positive association with fuel value and cellulose content and negative association with moisture content [93-95]. Wood with higher specific gravity is generally less susceptible to decay. The specific gravity of the cell walls of all wood species is approximately 1.5. However, because of the porous nature of wood, specific gravity (based on oven dry weight and green volume) ranges from 0.29 to 0.54 for most of the softwood and from 0.31 to 0.80 for most of the hardwood [96]. Kumar et al. [97] reported an average density range of 0.55-0.58 g/cm$^3$ for lower age (2-6 years) and 0.73 g/cm$^3$ for a matured (20 years) Eucalyptus hybrid. A positive correlation between gross calorific value and density of wood and bark samples of 45 multipurpose tree species from the homegardens of Kerala, India was observed by Shanavas & Kumar [98]. Variations in wood density are directly associated with structural differences at the molecular, cellular and organ levels [99]. It differs among tree species [9], age group [97, 100], tree parts [99], height of the tree [101] and also influenced by environmental factors [35].

Moisture content is the most commonly used fuelwood property in relations to its utilization as a source of energy. A living tree obtains its moisture through water uptake from the soil where it is found as bound water in cell walls and free water in cell lumens [102]. Moisture content is an important characteristic in defining the ease of combustion of a fuelwood, the amount of smoke it produces, and its caloric energy
Higher moisture content makes the fuelwood less efficient since it reduces the net calorific value as well as usable heat content in it [60]. Lyons et al. [60] and Demirbas [104] reported a negative relationship between heating value and moisture content of different fuelwood species. On the other hand, Romas et al [72] observed a significant inverse correlation between moisture content and density in fuelwood species. According to Demirbas [103] moisture percentage in wood species varied between 41.27 to 70.20%. Chettri and Sharma [105] reported that the moisture content among 16 tree species from west Sikkim, north-east India, varied between 25.3±0.9 (Rhododendron arboreum) to 76.3±0.33% (Symlocos ramosissima). However, moisture content in wood species depends on many factors; the moisture sorption capacity of wood changes with the chemical composition of its cell wall constituents (cellulose, hemicelluloses and lignin) [24-25]. Apart from physiological differences that might cause variation in moisture content in different tree parts, seasonal changes, local climate, and geographic location also influence towards the difference in moisture content among different species [32, 106]. According to Nurm [102], moisture content varies from one tree part to another. It is often the lowest in the stem and increases towards the roots and the crown.

The heating values of biomass fuel can be determined experimentally and can be calculated from the ultimate and/or proximate analysis data [107]. Demirbus [108] reported that calculation of HHVs from their ultimate and proximate analysis data show mean differences from measured values ranging from 0.1% to 4.0%. Glove et al. [109] reported the relationship between heating value and chemical composition of selected agricultural and forest biomass. He found that regression model with the ultimate elemental composition as independent variable gave better correlation to measure gross heating value than those based on the proximate chemical composition.

C, H, N, O and S are the elements which make up the various components of wood (cellulose, hemicelluloses, lignin etc.). Generally, in wood, the elemental compositions of C, O, H and N are 45-50%, 40-45%, 4.5-6% and 0.3-3.5%
respectively on dry weight basis whereas the percentage of S is negligible (less than ~0.1%) [37,110]. C and H are the main heat producing elements and directly contribute to the heating value of fuelwood [37]. Obernberger [51], Sheng and Azevedo [111] reported that HHV of fuelwood increases with the increase of C and H contents. Tilmann [112] also observed a positive correlation between HHV and C content. On the other hand, Saidur [113] reported a negative relationship between HHV of fuelwood and O content while no relationship was observed between HHV and O content by Sheng & Azevedo [111]. N and S contents in fuelwood pollute the environment by producing oxides of N and S (NOx and SOx) during combustion [114].

Volatile matter (VM) in wood is the fraction released when it is heated at a high temperature without considering moisture while fixed carbon (FC) is the mass left after the release of volatiles, excluding ash. The share of VM is typically high in wood than that of FC. About eighty percent of wood energy actually originates from the combustion of VM or gases and twenty percent from the combustion of FC (glowing embers) [37]. Saidur et al. [113] reported that high FC and VM increase the heating value of fuelwood. On the other hand, Sheng and Azevedo [111] observed only a trend between the higher heating value and the volatile matte while no correlation is found between higher heating value and fixed carbon. According to Haykiri-Acma and Yaman [115] holocellulose (sum of hemicelluloses and cellulose) portion in wood mainly contribute to the formation of volatiles. Grønli et al. [116] reported that the FC is directly related to the lignin content. In another study, Gominho et al. [117] observed an inverse relationship between VM and FC. Telmo et al. [118] observed the variation of VM in 17 wood species between 74.75-86.3% and FC variation between 13.3-22.5%. Mitchual et al. [114] reported that among the 6 tropical hardwood species (*Triplochiton scleroxylon, Ceiba pentandra, Aningeria robusta, Terminalia superba, Celtis mildbream and Piptadenia africana*) VM varied from 75.23% (*Aningeria robusta*) to 83.70% (*Celtis mildbream*). Senelwa and Sims [31] observed higher percentage of VM in wood in comparison to its bark. They also reported that VM
variations result from differences in volumetric percentage of the vessels in the different species and components.

Inorganic minerals remain in the oxidized form as ash after complete combustion of the fuelwood [119]. A high ash percentage reduces heating value of fuelwood, because a considerable amount of the fuelwood cannot be contributed towards energy [57,120-121]. Khider and Elsaki [69] reported that ash content in fuelwood is negatively correlated with heating value and holocellulose having correlation coefficients of -0.756 and -0.676 respectively. Nasser et al. [122] also observed a significant inverse correlation between ash content and heating value in fuelwood. According to Kumar et al. [97] higher ash amount is found in lower age trees. Werkelin et al. [123] observed that the ash amount varies within the tree parts and highest ash concentration is found in tree foliage (shoots and leaves). Demirbas [124] found significant variation in ash content (0.86 to 9.21%) among six indigenous fuelwood species: Picea orientalis, Fagus orientalis, Prunus laurocerasus, Quersus pedunculata, Carpinus betulus, and Carpinus orientalis that grow under similar agro-climatic conditions. In another study, Rai et al. [125] reported that among 66 tree species (from Sikkim, northeast India) ash content varied between 0.23-3.72%.

Woody biomass is composed of biopolymers that consist of various types of cells and the cell walls are built of cellulose, hemicelluloses and lignin [103]. The percentages of these polymeric constituents for softwood and hardwood, as reported by McKendry [126] are listed in Table 2.1

<table>
<thead>
<tr>
<th>Type of wood</th>
<th>Cellulose (%)</th>
<th>Hemicelluloses (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwoods</td>
<td>35–40</td>
<td>25–30</td>
<td>27–30</td>
</tr>
<tr>
<td>Hardwoods</td>
<td>45–50</td>
<td>20–25</td>
<td>20–25</td>
</tr>
</tbody>
</table>
Heating value of wood depend on the relative proportion of these biochemical constituents namely cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses which are composed entirely of sugar units have relatively low heat content due to their high level of oxidation while lignin have a lower degree of oxidation and a considerably higher heat of combustion [88, 127-128]. In other words, Lignin is richer in carbon and hydrogen, the main heat producing elements in wood and hence lignin has a higher heating value than carbohydrates [110, 49]. Typically, holocellulose (cellulose + hemicelluloses) have a higher heating value of ~18.60 kJg⁻¹, whereas lignin has a higher heating value of 23.26-26.58 kJg⁻¹. In general, the HHV of fuelwood increase with increase of their lignin content [129]. Demirbas [103], Telmo and Lousada [49], Vargas-Moreno et al. [130] observed a significant positive correlation between higher heating value of fuelwood and lignin. On the other hand, Demirbas [131] found no relationship between HHV and holocellulose of fuelwood. In a related study, Kataki and Konwer [88], Shanavas & Mohan [98] reported that density of wood species increase with increase of lignin content.

The heat of combustion of wood depends upon its chemical composition. Softwood of Pinus species contains a high amount of resin, waxes and lignin, which give a high heat of combustion [132-136]. Chandler et al. [137] reported the greater higher heating value of softwood than hardwood, as softwood contains more resins or extractive content. According to Kollman and Cote [138], extractives are more abundant in the heartwood than in the sapwood. Demirbas [103] reported that the higher heating values of the extractive-free tee parts are lower than those of non-extracted parts, which is the indication of positive relation between extractives and higher heating value. Demirbas [104] and White [58] also reported the positive relationship between extractives and higher heating value. According to Kumar et al. [127] the higher heat of combustion of extractives is due to its lower degree of oxidation in comparison with cellulose and hemicellulose. Nasser and Aref [139] reported that the extractive contents in six Acacia species varied from 9.94% (*Acacia ehrenbergiana*) to 13.82% (*Acacia tortilis*) where they found a significant correlation
between extractives and heating value of fuelwood species. In another study, Nasser et al. [122] observed highly significant correlations between the heating value and ethanol-benzene extractives whereas no significant correlation was found between heating value and total extractives as well as between water extractives and heating value. Howard [135] also observed a positive correlation between the alcohol/benzene extractives and heating value of loblolly pine. According to White [58], there are many different types of extractives and their higher heating values probably vary widely. He reported that terpenes and resin as the two classes of extractives that significantly affect the heating value of wood fuels. Howard [135] determined the higher heating value of resin portion of the extractives and found 34.89-37.21 MJ/kg.

### 2.5 Study on thermal degradation of wood/biomass

Analysis of the thermal degradation of biomass fuels is decisive in combustion and fire research for both fundamental and practical investigation. Wongsiriamnuay and Tippayawong [140] investigated the thermal degradation of giant sensitive plants (*Mimosa pigra* L.) or Mimosa under oxidative environment in different heating rates (10, 30 and 40°C) by using thermogravimetric method. The results indicated that there were three degradation steps in the TG/DTG curve: first one due to dehydration between the temperature range of 30-150°C, second one due to volatilization & oxidative degradation between the temperature range of 200-3700°C and third one due to char combustion between the temperature range of 375-500°C. They reported that mass loss and mass loss rates were strongly affected by heating rate. They further reported that average devolatilisation and combustion rates were increased with increasing heating rates whereas, activation energy showed minor increase with increasing heating rates. Brostow et al. [141] studied 6 wood species by using combined thermogravimetric and differential thermal analysis (TG/ DTA) to evaluate their combustion properties in terms of the amount of energy released, ignition temperature, and the cleanliness of burning. They observed that *Quercus rubra* burned to the hottest temperature among all the samples and also left the least amount of ash.
behind. They also observed that there was no correlation between the wood density and the parameters characterizing the burning process. In a similar study, the relation of the TG/DTG parameters with chemical properties, extractives and moisture content of 10 fast growing tree species was reported [142]. They observed little influence of extractives and chemical properties on combustion process, but moisture content influenced greatly on thermal stability and combustion process. Investigation on ignition behaviour and combustion characteristics (maximum combustion rate, burnout temperature, ignition index and combustion index) of various biomass fuels was also reported by many researchers [143-145]. Jiricek et al. [146] investigated the ignition and combustion behavior of biomass and biomass blends in various additive weight ratios. In the study, non-isothermal thermogravimetry was applied to determine the combustion characteristic of 6 samples, namely wheat straw, rape straw, flax straw (leftover after scutching), pulp-mill lignin, garden peat, and hardwood charcoal. According to the authors, the addition of a suitable additive could increase the combustion efficiency; since the additive contains a catalyst which is a carrier of oxygen. The results indicated that the Combustion Characteristic Factor (CCF) for all the biomass fuels chosen in this study were near to or greater than 2 with an exception for pulp mill lignin and peat while for the blends the CCF was between the original values. However for the additive, CCF values were highest indicating that blending biomass with the additives could lead to better combustion. The study revealed that the addition of oxygen to the primary air and the particle size of the samples influence the combustion process. It was also observed that the volatilization rate and the heat release were affected on addition of additive to biomass and the combustion residue was reduced at the same final combustion temperature.

Knowledge of the composition and specialization of inorganic elements in fuel is of vital importance for studies of combustion related topics, such as ash and deposit formation as well as sulphur and chlorine retention in ash.

The disposal of wood ash is a growing problem as environmental regulations become more stringent and landfill sites become less available and more expensive
Wood ash has been used in a variety of agricultural applications as it is an excellent source of potassium, lime and other plant nutrients [147-150]. Wood ash has also been used as a binding agent, a glazing base for ceramics, a road base, an additive in cement manufacturing and an alkaline material for the neutralization of different types of acidic wastes [151].

Etiegni and Campbell [152] made a study to evaluate the temperature dependence of wood ash yield and chemical components. They reported that wood ash decreased by approximately 45% as the combustion temperature increased from 538 to 1093°C. They also observed that potassium, sodium, zinc and carbonate content decreased with increase of temperature whereas other metal ions remained constant or increased. Wood ash leachate was found to contain 92% hydroxide and 8% carbonate. It was also reported that total dissolved solids of the ash increased by 500% as the pH decreased from 13 to 5.

The ash from biomass fuels contains only trace amount of heavy metals, which makes it fairly easy to dispose of. Some of the heavy metals are found to be good fertilizers [148-149, 153-155] and can be used as mineral nutrient for forest and agricultural soils. From a study on the characteristics of ashes from wood and straw, Olanders et al. [156] concluded that Potassium content was 3 times higher in straw ash than in wood ash or bark ash. They also observed that ash from wood or bark had higher percentage of carbonate content. CaCO₃ and SiO₂ were identified as the major crystalline compound in the wood or bark ash, while the straw ash was dominated by CaCO₃, KCl, K₂SO₄ and SiO₂. The higher percentage of ash content in bark and leaves were reported as 2.6-5.7% and 3.6-11.2%, respectively as compared to 0.4-1.2% in wood. According to Senelwa and Sims [31], higher ash content in bark and leaves was due to the concentration of potassium in the actively metabolizing portions of the tree crown and leaf area where nutrients from the soil are fixed prior to relocation to other parts of the plant. Shafizadeh [157] also observed that bark produced more ash than wood. He indicated that silica and other insoluble inorganic compounds in plant act as a heat sink, while the other soluble ionic compounds could have a catalytic effect on
the gasification and combustion of biomass fuels. Wood ash is dominated by calcium, silicon, aluminum, potassium and magnesium \[148, 152]\.

Many ash-forming inorganic species are associated with organic compounds in biomass fuels. During combustion the organic structures are decomposed and the ash formers are released. Alkaline earth metals leave the combustion zone as solid particles while the alkali metals are transported in vapour form as chlorides, hydroxides or oxides \[158]\). These compounds can react with \(SO_2\) in the combustion gas and form sticky sulphate particles, which adhere to heat exchange surface and form hard deposits \[158]\.
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