# Chapter 8
# Biomass Quality

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## 8.1 Introduction

Biomass used for energy conversion ranges from wood, especially planted for energy purposes, over harvesting residues, other woody biomass, such as shrubs or bamboo to waste materials, such as sawdust or pulp residues. These types of biomass differ widely in their properties and furthermore there is a variation within each species or type of biomass, due to biological variation. An assessment of the biomass quality is therefore vital to decide on its feasibility for conversion, the most suitable type of conversion and the need for further processing.

Wood, for example, differs in density, moisture content (MC) and chemical composition within one tree in horizontal and vertical direction. The variation between different trees is even larger, as these properties depend on the quality of the site where the tree is grown (water availability, temperature etc.) and of course there is a difference between wood species as well, although the difference due to site may be larger than the differences due to species. Therefore, in order to characterise biomass, care has to be taken, to work with statistically meaningful values. This means that samples should be obtained at the very least from different positions of a tree, but rather also from different trees and that sufficient samples have to be measured in order to obtain a representative average value. Practically, biomass is collected on a much larger scale than just a few trees, so sampling for quality assessment is commonly done by mixing e.g. the wood chips of many trees thoroughly and taking a few randomly chosen chips for sampling.

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The obvious advantage of biomass compared to fossil fuels is its renewable character. Its disadvantages are low density, which makes it bulky and difficult to store, the inhomogeneous form, which could be a problem for industrial equipment, a fairly large content of inorganic substances, which remain as ash and generally a high MC, which leads to an energy loss, because energy is needed to evaporate the water. Due to these characteristics, biomass usually requires additional processing before it can be used as a biofuel. Preparations, such as chipping, dehydration, densification and removal of incombustible material might be necessary.

## 8.2 Drying and Storage

After harvesting, the biomass is commonly stored and air-dried before it is transported and further processed. The rate of drying depends strongly on environmental factors, such as temperature and humidity, the particle size and the stacking method. Whole logs lose their moisture slowly and reach a MC of about 30 % after drying anything between 4 weeks and 6 months. This time can be decreased, if the logs are sheltered and cut into smaller pieces. Chips of a few cm size can reach a MC of about 12 % after a few weeks in sunny, arid conditions (Sturos et al. 1983).

Good ventilation is vital to good drying results. This becomes especially a problem, when the biomass is first comminuted and then dried. If the chips are piled on top of each other, ventilation is inhibited and fungi and bacteria can attack the particles. Biological and chemical degradation caused by bacteria and other organisms lead to an increase of temperature, which can in some cases lead to self-ignition of the entire pile.

Air drying should ideally happen on a flat area without contact to moisture (e.g. on a concrete slab under shelter) and the pile should be turned over on a regular basis.

All these problems can be avoided by oven or kiln drying the biomass, which on the other hand increases the processing costs drastically and sets free carbon dioxide, which affects the energy balance negatively (see Chap. 10).

## 8.3 Particle Size

For many applications the particle size plays a vital role. Conversion reactors can only be optimized with regards to their processing parameters if the biofuel is evenly sized. Fixed bed gasifiers, for example, can be fed with chunks or pellets of a few centimetre diameter, while fluidized bed gasifiers require fuel of smaller particle size.

As most biomass is very heterogeneous in size and density, it needs to be comminuted (made smaller) and sometimes compressed into pellets or briquettes.

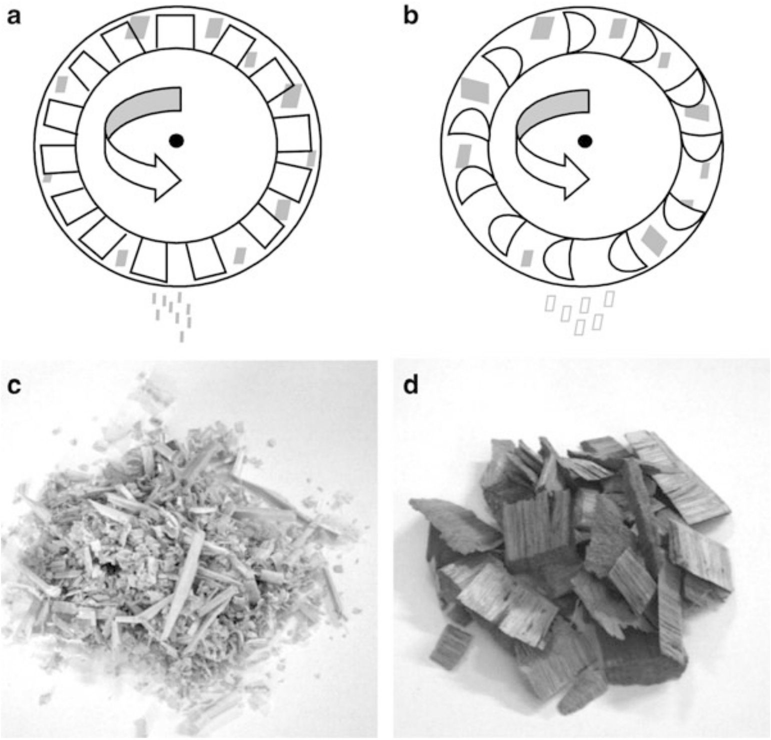

**Fig. 8.1** schematic drawing of a (**a**) hammermill and (**b**) chipper and the resulting (**c**) wood particles and (**d**) chips

Pellets are cylindrical particles with a diameter of 5–10 mm and about 1–3 cm length. Briquettes are larger, with a diameter of 5–10 cm and a length of about 15–20 cm.

After felling, trees are typically debarked and cut into logs and the remaining bark, branches, twigs and leaves form the harvest residue. The logs can be further comminuted into chunks or fire logs, with a length of about 30 cm and a diameter of about 10 cm. The harvest residue is too heterogeneous in size to be used directly and needs to be processed further.

### *8.3.1 Comminution*

Wood chunks or residues can be further comminuted with a hammermill (Fig. 8.1a) or a chipper (Fig. 8.1b). A hammermill breaks down particles with blunt metal hammers and the resulting particles have a fairly wide size distribution. The

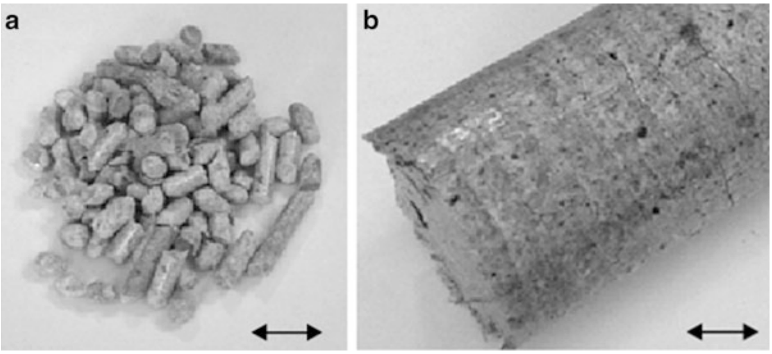

**Fig. 8.2** Pellets (**a**) and a briquette (**b**). The bar indicates 1 cm length

maximum particle size can be determined by a sieve through which the particles have to pass before they can leave the mill. In a disk- or drum-chipper the particles are cut along the grain with a knife, which results in fairly even sized chips of a few centimetre side lengths.

Further mechanical comminution of chips can be attained by grinding or milling (0.2–2 mm) with various mills. Ball mills, vibratory mills, hammer mills, knife mills, two-roll mills, colloid mills, attrition mills or extruders can be employed for this purpose. The choice of equipment is largely determined by the moisture content of the biomass (Kratky and Jirout 2011). While colloid mills and extruders are only appropriate for materials with a moisture content of 15–20 %, ball or vibratory ball mills can be employed for dry and wet materials. The energy requirements and hence subsequent costs of the comminution step are dictated by the type of mill, the original and target particle size, and the lignocellulose characteristics.

## *8.3.2 Compression*

If biomass needs to be compressed into pellets or briquettes, they need to be further comminuted into particles of a few millimetre lengths. This happens with refining mills that grind the biomass between serrated disks. These particles are then compressed in a pellet or briquette press to particles of uniform size and density. The heat produced during pressing degrades the lignin present in the biomass and allows it to flow freely between the particles. Lignin is a natural binder and as the particle leaves the press and cool it hardens resulting in a stable biomass particle (Fig. 8.2).

## 8.4 Moisture Content

The moisture content (MC) is the mass of moisture in biomass and can be either expressed as a percentage/fraction of the ovendry mass (mass with 0 % MC)

$$MC = \frac{m - m_0}{m_0} \times 100\% \tag{8.1}$$

$m = mass\ of\ wet\ wood$; $m_0 = ovendry\ mass$

or as a percentage/fraction of the wet mass

$$MC = \frac{m - m_0}{m} \times 100\% \tag{8.2}$$

$m = mass\ of\ wet\ wood$; $m_0 = ovendry\ mass$

The MC on dry basis is commonly used in the wood processing industry, while the MC on a wet basis is used in the Forestry and Pulp & Paper industry. The MC on wet basis has a maximum value of 100 %, while the MC on dry basis can be larger than 100 %. The MC on a wet basis is mostly used for practical reasons, as all transport costs are based on the weight of the wet biomass. The problem with the MC on wet basis is that it is not well defined, because in contrast to the MC on dry basis the weight of wood is very variable.

Typically, considerable MC variation can be found in all biomass, depending on location, age, season etc. In wood, for example, heartwood generally has a lower MC than sapwood and in softwoods it tends to be larger close to the bark and higher up. Softwoods generally have a larger MC than hardwoods. Care has to be taken therefore to determine a statistically significant average value that describes the entire biomass. Typical values are displayed in Table 8.1.

The MC is the most important property for biomass utilisation as fuel, because it affects the entire supply chain and the related costs, i.e. transport, storage, energy content, conversion methods and end use.

**Table 8.1** Typical MC values for different types of biomass

| Biomass | MC (%) |
|---|---|
| Freshly harvested trees | 80–180 |
| Trees, 6 month stored | 30–60 |
| Freshly chopped wood | 60–120 |
| Air-dried chopped wood | 15–30 |
| Bark, fresh | 60–120 |
| Wood chips, sawmill waste | 30–60 |
| Chips, biomass | 60–100 |
| Wood pellets/briquettes | 8–12 |

From Marutzky and Seeger (1999)

### *8.4.1 MC Determination*

The MC of partially dried wood can be measured with a resistance meter. In this method two pins are inserted into the wood and the measured resistance can be converted to a MC value. This technique works, however, only for MC values below fibre saturation point (around 30 % MC), on large enough samples and is generally not very accurate.

For bioenergy purposes the MC is typically determined with the ovendry method (ASTM D1762). For this a small sample is cut, weighed when wet, dried at 103 ± 2 °C for at least 24 h and weighed again when dry. MC can then be calculated according to Eqs. 8.1 or 8.2.

### *8.4.2 Dehydration*

Free water in excess of 65 % MC can be extracted by compressing the biomass with a press. In this way the MC can be reduced to about 20 %. To remove the remaining water, the biomass must either be air or oven dried. The drying time depends on the particle size and the composition of the biomass used. Typically wood chips reach a MC of 10–12 % after a few weeks of air drying in the Western Cape in South Africa and this process is faster for smaller particles (Sturos et al. 1983; Wondifraw 2010). Drying in a kiln or oven can remove the water entirely, depending on the time and temperature employed. Torrefaction (see Chap. 7) is an alternative to drying, resulting in products highly suited for thermochemical processing that can be stored for long periods of time.

Any moisture present in biomass reduces its calorific value. For combustion, gasification and pyrolysis the MC should therefore be as low as possible. Acceptable values for most reactor types are between 10 and 20 % (Schuck 2006; McKendry 2002). If too much moisture is present, much of the energy contained in the biomass is used to evaporate the water. Furthermore, biomass with a high MC cannot generate certain compounds when pyrolysed, which also affects the acidity and composition of liquid produced (Guillen and Ibargoitia 1999).

On the other hand, moisture is desirable for biochemical conversion, such as fermentation and anaerobic digestion (see Chap. 7) and the biomass is kept as wet as possible, typically with MC values between 80 and 90 %.

## 8.5 Density

Density is the mass (m) contained in a volume (V) of material.

$$r = \frac{m}{V} \quad \left[\frac{g}{cm^3}\right] \quad or \quad \left[\frac{kg}{m^3}\right]$$

**Table 8.2** Typical density values of South African biofuels as determined in house for various samples

| Species | Density (kg/$m^3$) |
|---|---|
| Eucalypts | 700–800 |
| Acacias | 600–900 |
| Pines | 400–550 |
| Other woody biomass (shrubs etc.) | 350–500 |
| Bark | 450–500 |

When looking at biomass, however, care has to be taken as to *which* mass and volume are regarded, as both parameters depend on the moisture content, wood structure (earlywood/latewood, etc.) and chemical composition.

The only reproducible density values are the "ovendry" density, which is

$$\mathrm{r}_0 = \frac{\mathit{Ovendry\ Weight}}{\mathit{Ovendry\ Volume}} \tag{8.3}$$

and the basic density, which is defined as

$$\mathrm{R} = \frac{\mathit{Ovendry\ Weight}}{\mathit{Fully\ saturated\ Volume}} \tag{8.4}$$

Typical average density ranges of woody biomass regarded in this book are given in Table 8.2.

As with the moisture content a large variation of density can be found within one tree. Generally juvenile wood has a lower density than mature wood, heartwood is denser than softwood (this is more pronounced in hardwoods) and in softwoods the density decreases with height (Tsoumis 2009).

For bioenergy purposes the bulk density of chips is determined via shock impact (BS EN 15103). A cylindrical vessel with known volume is filled to the rim with chips and shock exposed (dropped from a certain height) to compact the chips. The vessel is then either refilled to maximum level or the surplus material is removed. The basic bulk density of the wet chips is then given by:

$$\mathrm{BD_w} = (\mathrm{m}_2 - \mathrm{m}_1)/\mathrm{V} \tag{8.5}$$

*with* $m_1$: *weight of vessel*, $m_2$: *weight of vessel* + *biomass*, $V$ = *inner volume of vessel*

The bulk density of the dry chips can be calculated if the MC is known:

$$\mathrm{BD_d} = \mathrm{BD_w} * (100 - \mathrm{MC})/100 \tag{8.6}$$

The Diana Smith method (Smith 1959) is often used to determine the exact basic density of oddly shaped samples, such as wood chips. This method is more time consuming, but disposes of the volume in the equation. The samples are submerged

**Table 8.3** Typical distribution of cellulose, hemicelluloses and lignin in wood

| Wood type | Cellulose (%) | Hemicelluloses (%) | Lignin (%) |
|---|---|---|---|
| Hardwood[1] | 40–44 | 15–35 | 18–25 |
| Softwood[1] | 40–44 | 20–32 | 25–35 |
| Pine[2] | 26.4 | 44.7 | 18.6 |
| Eucalyptus[2] | 27.7–25.9 | 49.5–57.3 | 13.1–16.8 |
| Black Wattle[3] | 17.9–21.2 | 63.9 | 12.7 |

From: [1]Walker (2006), [2]Hamelick et al. (2005), [3]Kumar and Gupta (1992)

in water and cyclically exposed to pressure (to get water in) and under-pressure (to get air out). The basic density is then calculated according to:

$$R = \frac{1}{\frac{m_{sat}-m_0}{m_0} + \frac{1}{1.53}} \quad \left[\frac{g}{cm^3}\right] \tag{8.7}$$

$m_{sat} = saturated\ weight;\ m_0 = ovendry\ weight$

The volume to weight ratio of most biomass is generally rather unfavourable, which decreases the possible energy output. The solid content of wood chips is only around 0.4, which is a major reason for densification (e.g. pelletising). This decreases transport and storage costs and increases the energy density at the same time. The calorific value increases linear with density, because more material is available (Kataki and Konwer 2001; Munalula and Meincken 2009). For combustion and gasification the biomass should therefore have a density as high as possible, whereas for fermentation and digestion a low density is more desirable, because this is correlated to a looser wood structure, which can be degraded more easily (see Chap. 7).

## 8.6 Chemical Composition

Wood contains a significant amount of carbohydrates and consists of about 50 % Carbon, 6 % Hydrogen and 44 % Oxygen and other elements, often grouped together under the name “extractives”. Wood is primarily composed of macromolecular substances, which are mainly polysaccharides (cellulose and hemicelluloses) and lignin (Table 8.3).

### *8.6.1 Cellulose*

Cellulose is one of the most abundant, naturally-occurring organic compounds in the world. Approximately 40–45 % of dry substance in most wood species is cellulose, located mainly in the secondary cell wall. It is a linear homopolysaccharide composed exclusively of β-D-anhydro-glucopyranose units, which are linked together by β (1 → 4)-glycosidic bonds. It is the main structural component of plant cell walls. Because of its strong tendency for intra- and intermolecular hydrogen bonding, bundles of cellulose molecules aggregate into microfibrils, which form either highly ordered (crystalline) or less ordered (amorphous) regions. This highly ordered three-dimensional structure confers the mechanical strength of cellulose, and also results in its low susceptibility to chemical and enzymatic attack.

It is often assumed that wood of the same species is identical in all structural and physical characteristics. However, this is not true as different pieces of wood from the same tree are never identical but are similar only within broad limits. Therefore, structural components, such as cellulose, which determine the physical and chemical properties, are also never found in the same quantities throughout a tree or in different trees of the same species (Howard 1973). The cellulose content differs between the roots, stem, branches, normal wood versus reaction wood, juvenile wood versus mature wood, earlywood versus latewood and varies from the pith to the bark (Downes et al. 2000; Haygreen and Bowyer 2007).

Most studies on the variation of cellulose content have been carried out on softwoods, showing minimum values of cellulose of 40 % in earlywood and maximum values of 50 % in the latewood (Downes et al. 2000). The cellulose content in latewood is not only higher but the cellulose also has a higher degree of polymerisation, which is very important for most applications, which use cellulose as a raw material. The latewood cellulose also has a higher packing density and a higher degree of crystallinity than that in the earlywood.

The cellulose content increases from pith to bark correlated with the tracheid length, which increases from juvenile wood to mature wood. It has been found that the cellulose content decreases about 2 % vertically in *Pinus densiflora S* and in *Pinus radiata* (Panshin and De Zeeuw 1980).

Reaction wood also shows a considerable difference in cellulose content. The tracheids in compression wood are about 30 % shorter than in normal wood, leading to a decrease in cellulose content of about 10 %.

The different cellulose content in branches can be ascribed to a larger amount of bark, knots, as well as the presence of reaction wood. Branches also have narrower growth rings, resulting in overall lower cellulose content than in stem wood (Haygreen and Bowyer 2007).

### *8.6.2 Hemicelluloses*

Hemicelluloses are short chains of branched hetero-polysaccharides composed of both hexoses and pentoses. D-xylose and L-arabinose are the main constituents of pentosans (xylans), while D-glucose, D-galactose and D-mannose are the main constituents of the hexosans (mannans). The major hemicelluloses component of softwood is mannan-based whilst the hemicelluloses in hardwoods are xylan-based. Hemicelluloses comprise 20–25 % of the material in hardwood and 7–12 % in softwoods. The close association of hemicelluloses with cellulose and lignin in the fibre cell walls contributes both rigidity and flexibility. The type and amount of hemicelluloses vary widely, depending on plant material, tissue type, growth rate, growth conditions, storage and method of extraction. A study of *Pinus resinosa Ait* has shown that the xylose content in earlywood was about 1–2 % higher than in latewood and the ratios were reversed for mannose (Panshin and De Zeeuw 1980). No difference was found between early wood and late wood for galactose, arabinose, and glucose in young trees. Analysis of successive growth increments within the tree in *Pinus radiata* D. Don showed a 3 % reduction of hemicelluloses from pith to bark and from the top to the butt of a tree. A maximum hemicelluloses content of about 11 % was found near the pith and toward the top of the tree. Glucose and mannose were shown to increases with age and decrease upwards while arabinose, xylose and galactose were shown to decrease with age and increased with height. Compression wood contains about 8–9 % more hemicelluloses than normal wood (Haygreen and Bowyer 2007).

### *8.6.3 Lignin*

Lignin is the second most abundant organic compound after cellulose. It is an integral part of the wood cell wall. In wood, it carries the major part of the methoxyl content, is unhydrolysable by acids, readily oxidisable and is soluble in hot alkali and bisulphite (Schubert 1965). It has a network structure and lacks a defined primary structure (Herman 1987). According to Hatfield and Vermerris (2001), lignin can be described in two ways: either from a chemical point of view i.e. its functional groups and lignin-type sub-structure compositions, or from a functional point of view that stresses what lignin does within a plant. The lignin content and composition (syringyl/guaiacyl ratio) do not change significantly with tree height or diameter (Sykes et al. 2008).

Lignins contain up to 67 % carbon, depending on the method of isolation (Jakab et al. 1995). As such, lignin is a major energy-bearing compound in wood with a calorific value of about 23 MJ/kg (Blunk and Jenkins 2000). Softwoods in general have a higher energy content than hardwoods, due to the proportionally higher lignin content.

Lignin is a natural bonding agent for the cellulose fibres when combined with hemicelluloses and imparts rigidity to the cell wall, generating a composite structure that is outstandingly resistant towards impact, compression and bending. Lignin also protects the polysaccharides from microbial attack. This makes a high lignin content undesirable for anaerobic digestion or hydrolysis-fermentation.

Lignin, due to its structure and high molecular weight also serves as UV protection and flame retardant agent. The latter property is of benefit in forest fires where the lignin-carbohydrate complex is able to protect wood from the effects of fire (Wünning 2001).

**Table 8.4** Chemical composition throughout a tree in *Pinus elliottii* (Howard 1973)

| Tree part | Cellulose (%) | Hemicelluloses (%) | Lignin (%) | Extractives (%) | Ash (%) |
|---|---|---|---|---|---|
| Bark | 23.7 | 24.9 | 50.0 | 13.0 | 0.9 |
| Needles | 42.6 | 22.3 | 37.7 | 26.2 | 2.4 |
| Branches | 36.9 | 33.7 | 35.0 | 13.6 | 1.2 |
| Top | 41.5 | 31.2 | 32.5 | 11.0 | 0.8 |
| Roots | 44.6 | 25.6 | 31.3 | 11.7 | 1.6 |
| Stem | 51.1 | 26.8 | 27.8 | 9.1 | 0.3 |

### *8.6.4 Other Cell Wall Components*

In addition to cellulose, hemicelluloses and lignin, wood cells also contain extraneous substances. Many of these substances are extractable with neutral solvents and are generally referred to as extractives. Extractives (proteins, fats, fatty acids, terpenes, resins, phenols and alcohol, etc.) can represent between 4 and 10 % of lignocelluloses (Fengel and Wegener 2003). There is a considerable variation in the type, distribution and amount of extractives between tree species and even within species. Sugars and other sap-soluble constituents, such as starch are found in the cell lumens of parenchyma cells. Phenolic materials are deposited in the heartwood to protect the wood from insect, fungal or bacterial attack (Harju et al. 2003). Water repellent fats are found in the parenchyma cells, especially in the ray parenchyma, whereas resins are secreted by epithelial cells and tend to form resin ducts. Some extractives are utilized commercially such as vegetable tannins, turpentine and tall oil, fatty acids etc.

Resins have a high CV of >30 MJ/kg (Novaes et al. 2010), which explains why softwoods generally have a higher CV than hardwoods and also leads to a fairly high CV value of bark.

Variation in extractives within the stem is mostly between sap- and heartwood, except for resins. The resin content in softwoods is reported to be highest near the pith and at the butt of the tree, decreasing upward and towards the outside (Fengel and Wegener 2003). The resin content is significantly lower in the sapwood than in the heartwood and slightly lower in earlywood than latewood. Many heartwood extractives, on the other hand, increase from the pith to the outer heartwood boundary (Panshin and De Zeeuw 1980) (Table 8.4).

## 8.7 Elemental Composition

All biomass contains Carbon (C), Oxygen (O), Hydrogen (H), Nitrogen (N) and various other trace elements. On average wood contains about 49 % C, 6 % H and 44 % O with some variation between wood species (Fengel and Wegener 2003).

A high carbon content is directly related to a high density and therefore a high calorific value and desirable for combustion and gasification.

The major elements contained in any biomass, such as C, N, H, can be determined with elemental analysis and/or x-ray fluorescence (XRF) as described by Perkel (2012).

C, N and H can be determined by combustion in a pure oxygen atmosphere at high temperatures, which converts the sample elements into $CO_2$, $H_2O$ and $N_2$. The amount of the product gases is proportional to the amount of C, N and H in the sample.

In the XRF technique a material is exposed to high energy x-rays, which eject electrons from the sample atoms. The transition of outer electrons to the vacant spaces results in photo energy that is characteristic for the element and can be detected by a fluorescence detector.

## 8.8 Calorific Value

C, O and H can be broken down with the release of energy (heat) to form $CO_2$, $H_2O$ and other by-products. The calorific value or energy content is a measure for the heat that can be produced and is measured in MJ/kg. The two major breakdown processes are:

$$C + O \rightarrow CO_2 + 32.8\ \mathrm{MJ/kg}\ (C)$$

$$2H_2 + O_2 \rightarrow 2H_2O + 142.2\ \mathrm{MJ/kg}\ (H)$$

The amount of the released energy depends on the ratio of C, H and O in the biomass used and the MC, as part of the released energy will be consumed for the vaporization of present water. Commonly it is differentiated between gross and net calorific value or higher heating value (HHV) and lower heating value (LHV). The gross CV is the energy content of the sample without any moisture and therefore the maximum value, while the net value is measured in a moist sample, as it would be used for conversion.

Typical gross calorific values for different types of biomass that might be used for energy conversion are given in Table 8.5. It can be seen that the values do not differ much for woody biomass – they are generally between 19 and 20 MJ/kg. This suggests that other factors, such as ash content, are more important when deciding which biomass should be used for energy conversion.

The energy content is typically determined with a bomb calorimeter, which is a closed system in which small temperature increases after combustion in a pressurized oxygen atmosphere can be determined with high sensitivity. The calorific value is defined as the amount of thermal energy per weight unit produced by the total combustion of the sample in MJ/kg.

About 0.5 g of biomass are combusted in a pressurized oxygen atmosphere with a pressure of about 3,000 kPa. The measured temperature increase of the vessel is very small, requiring very sensitive temperature sensors in the calorimeter and good calibration before each measurement. Calibration is generally performed with benzoic acid.

## 8.9 Ash Content

Ash is the inorganic residue such as silica, potassium, calcium, sulphur and chlorine that remains after combustion at high temperatures and constitutes between 0.2 and 20 % of the biomass weight. In general most biomass contains similar levels of C, H and O, but the amounts of Si, Ca, Mg, K, P, S, Cl, Al, Fe and Mn, or heavy metals such as Cu, Zn, Co, Mo, As, Ni, Cr, Pb, Cd, V and Hg can differ widely (Obernberger et al. 1997).

The ash content of different types of biomass used in South Africa for energy conversion is given in Table 8.5.

### *8.9.1 Determination of the Ash Content*

To determine the ash content, ovendry samples are placed in a ceramic crucible and the weight of each crucible and the biomass is noted. The crucibles are then placed and in the furnace at a temperature of 575 °C for 3 h (EN 14775).

After cooling, the ash content is calculated according to Eq. 8.8:

$$Ash\ (\%) = \frac{m_A \times 100}{m_0} \tag{8.8}$$

$m_A = mass\ of\ ash,\ m_0 = mass\ of\ ovendry\ sample$

**Table 8.5** Calorific values and ash content of typical South African wood species (Munalula and Meincken 2009; Smit 2010)

| Biomass | Gross CV (MJ/kg) | Ash content (%) |
|---|---|---|
| *Acacia cyclops* (Rooikrans) | 19.4 | 2.79 |
| *Eucalyptus cladocalyx* (Blue Gum) | 19.3 | 2.38 |
| *Pinus patula* (Pine) | 19.0 | 0.45 |
| *Acacia eriloba* (Camelthorn) | 19.3 | 2.79 |
| *Vitis vinifera* (Vine stumps) | 19.2 | 0.34 |
| *Acacia saligna* (Port Jackson) | 19.1 | 2.47 |
| *Acacia mearnsii* (Black Wattle) | 19.2 | 1.64 |
| *Acacia longifolia* (Long Leaved Wattle) | 19.1 | 1.32 |
| *Casuarina cunninghamiana* (Beefwood) | 19.0 | 1.67 |
| *Pinus pinaster* (Cluster pine) | 19.6 | 0.78 |

## 8.10 Volatile Content

The volatile content is given by the mass loss (excluding moisture) due to thermal degradation when the biomass is heated. The degradation products are gaseous substances, such as CO, $CO_2$, $NO_x$ etc. The combustion of these volatile components results in the bright flame when wood is combusted and its colour and temperature depend on the chemical composition of the wood.

Because of its low C/H ratio, wood has a rather high volatile content – between 75 and 90 %. A high volatile content is directly proportional to a lower CV, resulting in the low energy density of biofuels compared to, e.g. coal.

To determine the volatile content, ovendry samples are placed in a ceramic crucible and the weight of each crucible and the biomass is noted. The crucibles are then placed and in the furnace at a temperature of 900 °C for 7 min (ASTM E872-82).

After cooling, the volatile content is calculated according to Eq. 8.9:

$$Volatiles\ (\%) = \frac{100 * (m2 - m3)}{m2 - m1} \tag{8.9}$$

*m1* = *mass of crucible*, *m2* = *mass of ovendry sample and crucible*, *m3* = *mass of contents and crucible after heating*

## 8.11 Biomass Requirements

The conversion techniques described in Chap. 7 have different requirements with regards to the biomass feedstock. The energy yield can be optimised, if the biomass is chosen and prepared correctly, as the pre-treatment of the initial feedstock has a big impact on the product yield and quality. These pre-treatments can be mechanical and/or chemical, such as sieving, water washing, solvent or acid-leaching. Table 8.6 lists some of the requirements for a selection of conversion techniques and reactor types (extracted from van Loo and Koppejan 2008; Stephen et al. 2010):

### *8.11.1 Thermochemical Conversion: Combustion, Torrefaction, Pyrolysis and Gasification*

Ideally the ash content of biomass should be as low as possible for thermochemical conversion, as it poses many practical problems in the conversion process, ranging from slagging to corrosion of the reactor. A high nitrogen content in the biomass will lead to increased $NO_x$ emissions during combustion. Particularly undesirable in ash are Silicon (Si), Chlorine (Cl), Potassium (K) and Sulphur (S), as they form silicates, sulphates and alkali chlorides. For example, high potassium and chlorine

**Table 8.6** Biomass requirements of various conversion techniques

| Conversion type | Reactor | Biomass | | | |
|---|---|---|---|---|---|
| | | Type/size | Density (kg/m$^3$) | MC (%) | Ash (%) |
| Combustion | Fixed grate | Chunks, briquettes<br>∅ < 50 mm | As high as possible | <20 | As low as possible |
| | Suspension boiler | Sawdust, small shavings<br>∅ < 10 mm | 150–200 | <15 | <5 |
| | FB or CFB boiler | Sawdust, small shavings, low alkali<br>∅ < 50 mm | 400–600 | <50 | <5 |
| Gasification | Fixed bed | Wood chunks, briquettes etc. not too small<br>∅ < 100 mm | 100–600 | <20 | <10 |
| | Moving bed | Chips, pellets<br>∅ < 50 mm | 200–300 | <15 | <20 |
| | CFB | Chips<br>∅ < 50 mm | 200–500 | <50 | <10 |
| Pyrolysis | Slow | Chips, pellets<br>∅ < 70 mm | 200–500 | <15 | <5 |
| | Fast | Chips, pellets<br>∅ < 5 mm | 200–500 | <10 | <20 |
| Alcoholic fermentation | Pretreatment-hydrolysis-fermentation | Wet chips; never dried material | | | As low as possible |
| Anaerobic digestion | Single stage | Chips, residues | Low | High<br>> 50 % | N/A |

contents can cause slagging and corrosion in the combustion unit (Skrifvars et al. 2004). For an efficient use of biomass for power generation, the amounts of K and Cl should thus be as low as possible. The ash content is typically also inversely related to the calorific value, making biomass with high ash content undesirable for combustion and gasification. For pyrolysis, solvent-leaching can be used as a de-ashing step for either the biomass feedstock or the char product, to increase the char adsorption properties (Carrier et al. 2012). These changes in char adsorption due to de-ashing are directly related to the pyrolysis rate and volatile yield (Raveendran and Ganesh 1998; Carrier et al. 2012).

Thermochemical conversion processes are well suited to uniform, densified feedstock, such as pyrolysis products or pellets (Stephen et al. 2010). Torrefaction is an example of such a pre-treatment step to decrease the MC of the biomass, while at the same time increasing the energy density and CV. Subsequent size reduction, such as grinding, before feeding the reactor is easier with torrefied biomass, as it is more brittle.

The Lignin content has a significant impact on the suitability of biomass for thermochemical conversion. Although the high CV of lignin makes it desirable for combustion and gasification, an increased lignin content also affects the rate of thermal degradation. As a result, biomass with a higher lignin content will pyrolyse more slowly, while wood with high cellulose content can be pyrolysed faster (Gani and Naruse 2007). The positive impact of lignin on the CV, however, generally outweighs the negative effects of reduced reaction rate.

In the case of vacuum pyrolysis of wood, extractives showed an inhibiting effect on the oil yield, as they inhibited the levoglucosan formation. Removal of extractives did modify the hemicelluloses composition significantly, as reflected by the similar acetic acid yield derived from wood and extractive-free wood material (Roy et al. 1990).

### 8.11.2 Biological Conversion: Anaerobic Digestion and Alcoholic Fermentation

Compared to agricultural biomass (i.e. wheat straw), woody biomass has a higher density, higher cellulose and lignin content and lower hemicelluloses content, which means it is more resistant to biological conversion. Enzymatic hydrolysis and digestibility of lignocellulose are the key steps in biological conversion and they depend strongly on the feedstock composition and structure, pre-processing of the material and dosage and efficiency of the enzymes used for hydrolysis.

Biological conversion of lignocellulose is enhanced by mechanical comminution that reduces the particle size as well as the degree of polymerization of the cellulose. For biochemical conversion the biomass should have a loose structure that can easily be penetrated by enzymes. Therefore additional pre-treatment is needed to improve accessibility of the cellulose and increase the digestibility to above 50 % for enzymatic hydrolysis (Vidal et al. 2011). High crystallinity of the cellulose and a high degree of polymerization limit enzymatic hydrolysis, mainly the initial hydrolysis rate.

For biochemical conversion feedstock with a high moisture content is preferred and drying reduces the accessibility of biomass to chemicals, steam and enzymes (Stephen et al. 2010; Liu et al. 2002). Special care must therefore be taken to avoid drying and the associated “hornification” phenomenon. Freshly harvested wood chips are the optimal woody feedstock for bioconversion of lignocellulose.

The disruption of the lignocellulose structure by pre-treatments can significantly reduce the recalcitrance of lignocellulose to biological degradation. Most of the pretreatments alter not only the chemical composition but also the physical structure of the biomass by increasing the accessible surface area and pore volume, thereby enhancing cellulase attack.

An increase in lignin content reduces the digestibility of biomass, thereby decreasing the rate and extent of enzymatic hydrolysis. Lignin with a high syringyl content (typical for hardwoods) can be easier degraded by pre-treatments (diluted acid, alkali, hydrogen peroxide, etc.). Apart from being a physical barrier to hydrolysis, lignin can adsorb irreversibly to the enzymes, thereby reducing the yield and increasing time required for effective conversion. The adsorption capacity of lignin depends on the type of lignin and pretreatment applied. Unlike in the pulping process, where the objective is to maintain the fiber integrity, these pretreatments aim for maximum digestibility by removing lignin and loosening the fibre structure.

The type of hemicelluloses also affects the choice of pre-treatment and the enzymes used for the fermentation process. For example, the acetyl content in hemicelluloses from hardwoods is involved in autohydrolysis reactions during thermochemical pretreatments, enhancing the cellulose accessibility. On the other hand, residual acetyl groups in pre-treated material constitute a steric hindrance for the enzymatic hydrolysis.

However, the pretreatment of lignocellulose to improve digestibility may also result in the production of sugar and lignin degradation compounds, which may lead to hydrolysis/fermentation inhibition.

Biomass with a low ash content is preferred for biological conversion, not only because it maximizes the availability of carbohydrates and lignin for the conversion process, but also because the buffering capacity of ash may increase the chemicals requirement in acid-catalysed pretreatments for biological conversion.

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