# CHAPTER 2

# THEORIES

## 2.1 Biomass

Biomass is a biological material derived from living organism and can be burnt as fuel. It excludes organic materials such as fossil fuels which have been transformed by geological processes into substances such as coal and petroleum. Biomass material has quite low volumetric density in comparison to that of coal. It typically contains more than 70% air and void space. This low volumetric energy density makes it difficult to collect, transport, store and utilize [22]. Biomass can be used for fuels, power production, and products that would otherwise be made from fossil fuels. The use of biomass energy greatly reduces greenhouse gas emission and enhances energy security by reducing dependence on foreign fuels.

## 2.2 Components of biomass

Generally, biomass contains absorbed and condensed moisture, some inorganic materials, and various types of organic compounds. Lignocellulose is another word for biomass that originated from plants. It generalizes the structure of plants to the three main sugar-based polymeric structures which are cellulose, hemicelluloses, and lignin. These three polymeric structures are mainly considered for the understanding of decomposition mechanisms of woody and herbaceous biomass. These components vary greatly according to the part and species of the plant [23].

### 2.2.1 Moisture content

Moisture is presented by both water which is contained in the cavity within the dead cell and also by some absorbed water. The water contained in the cavity within the dead cell can be removed by drying while the absorbed water equilibrates with the ambient relative humidity. The moisture content is normally expressed on a wet basis which refers to the weight of water as a percentage of the total wet fuel weight [23]. The moisture content of biomass has a significant effect on its conversion efficiency and heating value. The heating of water and its conversion to steam requires heat which is generated from biomass combustion.

This leads to longer heating time. Apart from loss of combustion efficiency, the high moisture content biomass has more of a tendency to decompose, resulting in energy loss during storage. Transportation of high moisture biomass is also costly, due to the larger space required and higher loaded weight [24].

### 2.2.2 Ash content

Ash content represents the inorganic materials which are non-combustible. The ash content can be expressed on a wet, dry, or dry ash-free basis. In general, the ash content is expressed on a dry basis. Ash is deposited within the biomass during plant growth which is varied according to the species, locality, and soil contamination. The composition of the ash affects its behavior under the high temperature application such as combustion, pyrolysis, and gasification. For example, molten ash may cause problems in combustion reactors [25].

### 2.2.3 Chemical compositions

In chemical terms, biomass is defined as a three dimensional biopolymer composite. It is composed of an interconnected network of cellulose, hemicelluloses, lignin, minor amounts of extractives and inorganic matter.

**Cellulose** is the most abundant organic chemical in many biomass species. It is polysaccharide having the generic formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000 to 500,000. Cellulose is a glucan polymer of D-glucopyranose units, which are linked together by β-(1→ 4)-glucosidic bonds. The building block for cellulose is actually cellobiose, the repeating unit of a two-sugar unit as in Figure 2.1. Cellulose is insoluble in water, forms the skeletal structure of most terrestrial biomass, and constitutes approximately 50 % of the cell wall material [26].

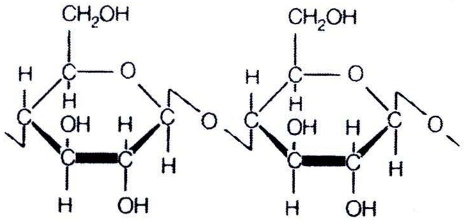

**Figure 2.1** Chemical structure of cellobiose [25]

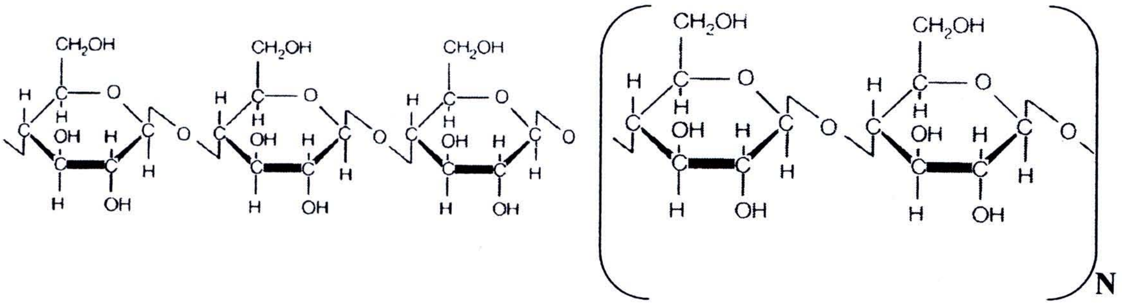

**Figure 2.2** Partial structure of cellulose [26]

**Hemicelluloses** are group of polysaccharide polymers which mainly are the sugar D-xylose, D-glucose, D-galactose, L-arabinose, and D-mannose, and D-glucuronic. The main hemicelluloses are shown in Figure 2.3. The structure of hemicelluloses can be understood by first considering the conformation of the monomer units. Hemicelluloses usually consist of 50 to 200 monomeric units and a few simple sugar residues. They are soluble in dilute alkali and consist of branched structures which vary significantly among different woody and herbaceous biomass species [26].

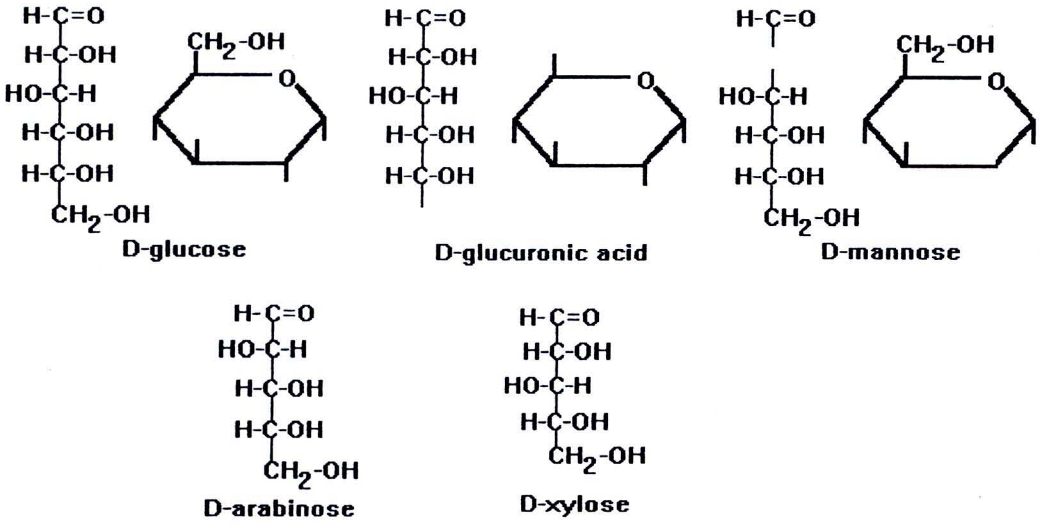

**Figure 2.3** Sugar monomer components of wood hemicelluloses [27]

**Lignin** is amorphous and highly complex. It mainly consists of aromatic polymers of phenylpropane units that are considered to be an encrusting substance. The linkages in the polymers occur directly between the rings, between the propane units, and through ether linkages via the hydroxyl groups. Lignin is generally found in the cell walls of certain biomass, especially woody species. Apart from cell wall, it is often bound to adjacent cellulose fibers to form what has been called lignocellulosic complexes. Lignin can be classified in several ways, but they are usually divided according to their structural elements [26, 28]. All wood lignin consist mainly of three basic blocks of guaiacyl, syringyl, and *p*-hydroxyphenyl moieties. Lignin can be isolated from wood in several ways. So-called Klason lignin is obtained after hydrolyzing the polysaccharides with 72% sulfuric acid. It is highly condensed and does not truly represent the lignin in its native state in the wood.

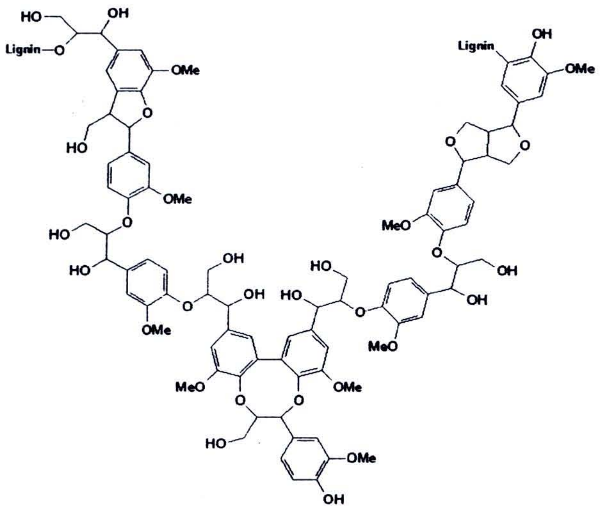

**Figure 2.4** Small piece of lignin structure [28]

**Extractives** are chemicals in the wood that can be extracted by solvents. In some cases, the extractives are classified by the solvent used to extract them. The extractives are a group of cell wall chemicals mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds. These chemicals exist as monomers, dimmers, and polymers. In general, softwoods have higher extractives content than hardwoods. Most of the extractives in both softwoods and hardwoods are located in the heartwood, and some are responsible for the color, smell, and durability of the wood [28].

## 2.3 The fundamental of pyrolysis process

Pyrolysis has been widely used for converting biomasses into liquids and solids among the thermo-chemical technologies [29]. Pyrolysis is generally described as the thermal decomposition of the organic components in biomass in the absence of oxygen at mediate temperature. When biomass is heated to elevated temperature, it is pyrolysed and divided into a hydrogen-rich fraction and a carbon-rich solid residue (char). The hydrogen-rich fraction consists of gases and tar (volatile matter). Volatile matter is a mixture of low molecular weight compounds (hydrogen, oxides of carbon, methane, etc.) and higher molecular weight hydrocarbons, such as light oils and tars. The solid residue is a composite of the non-volatile or fixed carbon mixed with the inorganic mineral matter which will form ash upon oxidation. Pyrolysis is usually completed before significant gasification or combustion has occurred [30].

### 2.3.1 Conventional pyrolysis or slow pyrolysis

In conventional pyrolysis or slow pyrolysis, cellulose and hemicelluloses are decomposed to volatile products and chars involving a series of highly complex reactions. These reactions may be classified in the following categories;

1) At temperatures below 300°C, pyrolysis of cellulose in inert atmosphere proceeds through a series of reactions. The reactions include free radical initiation, elimination (of water), depolymerization, formation of carbonyl and carboxyl groups and evolution of CO and $CO_2$. The reactions in this temperature range produce mainly a char residue.

2) At the temperature range of 300-450°C, the glycosidic linkage of the polysaccharide is broken by substitution involving one of the free hydroxyl groups to provide a mixture of levoglucosan, other derivatives of the glucose unit, and oligosaccharides.

3) At higher temperatures, dehydration, rearrangement, and fission of sugar units provide a variety of carbonyl compounds. The produced compounds such as acetaldehyde, glyoxal and acrolein readily evaporate. Condensation of the unsaturated products and cleavage of the side chains through a free radical mechanism leaves a highly reactive carbonaceous residue containing tapped free radicals.

Heating of the cellulosic material above 500°C provides a mixture of all of these products. Addition of an acidic catalyst or slow heating promotes the dehydration and charring reactions [23].

### 2.3.2 Fast pyrolysis

Fast pyrolysis is performed under rather high heating rate over 1,000 °C $s^{-1}$. Figure 2.5 shows a schematic of how fast pyrolysis of coal proceeds. Fast pyrolysis consists of two sets of reactions: primary devolatilisation reactions and subsequent secondary gas phase reactions.

The former are very rapid reactions that consist of many reactions as follow;

- Radical formation reactions
- Polymerization-condensation reactions
- Radical recombination reactions
- Hydrogen addition reactions, etc.
- The latter reactions are decomposition reaction of the volatile products produced through the primary reactions.

Fast pyrolysis can be used as a method to produce liquid products. It is known to increase the total of the volatile matter of the proximate analysis [30].

### 2.3.3 Pyrolysis at low temperature and torrefaction

Pyrolysis at low temperature and torrefaction are not totally the same process. The word torrefaction refers to the pyrolysis at more narrow range of reaction temperature (200-300°C) while the temperature of pyrolysis at low temperature can be higher than the maximum temperature of torrefaction. The link of torrefaction to pyrolysis is easy to make as torrefaction covers part of the initial decomposition reactions of pyrolysis.

Pyrolysis at low temperature is a thermochemical treatment method carried out under atmospheric conditions with absence of oxygen. Its main product is in the solid phase, which is referred as the char. In the field of torrefaction, the solid product is also frequently called torrefied wood or torrefied biomass. Similar to pyrolysis, the chemical structure of biomass is altered during torrefaction. This leads to the formation of a variety of volatile products for both liquid and vapor phase at room temperature. Other important reaction products apart from char are carbon dioxide, carbon monoxide, water, acetic acid and methanol. All these non-solid reaction products contain relatively more oxygen compared to the untreated biomass. Hence the O/C ratio of torrefied biomass is lower than untreated biomass, resulting in an increase of the calorific value of the solid product [31].

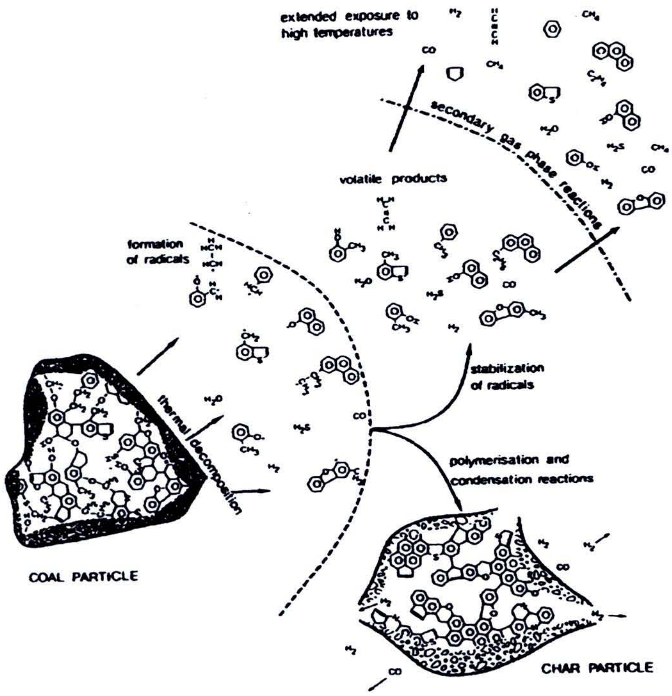

**Figure 2.5** Reactions and processes which occur upon flash pyrolysis of coal [30]

### 2.3.4 Decomposition mechanisms during torrefaction

From the three main polymeric components of biomass, cellulose has received most attention considering the thermal decomposition of biomass. Therefore, in pyrolysis research cellulose decomposition is very important. But cellulose decomposition is not the most relevant component in the temperature range of torrefaction (200 – 300°C) as shown in Figure 2.6. During torrefaction, mass loss will predominantly come from the decomposition of hemicellulose and some of lignin. Xylan-based hemicellulose generally has its peak rate in decomposition around 250 to 280°C. Lignin decomposition proceeds slower, but shows a gradual increase of decomposition rate starting from temperatures of about 200°C or even lower. However, the thermal decomposition behavior of the individual polymers of biomass may be different from their strongly interacted structure in biomass itself. As can be seen in Figure 2.6, wood starts to be decomposed at a temperature higher than 200°C on mass basis.

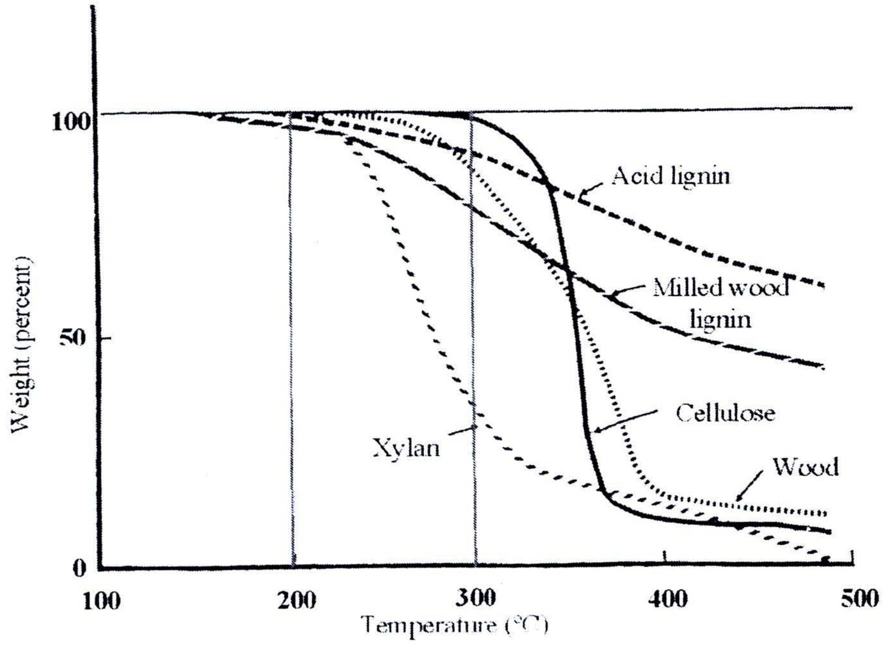

**Figure 2.6** Thermogravimetry of cotton wood and its components. The green lines are added to indicate the torrefaction temperature regime [15]

Hemicellulose decomposition can be well described by a two-step mechanism. The first reactions usually take place below 250°C. These first steps are depolymerisation reactions which lead to altered and rearranged polysugar structures. The decomposition of these oligosaccharides and monosaccharides at higher temperatures (250-300 °C) result in the formation of chars, CO, $CO_2$ and water. The formation of light volatiles like carbonyl compounds result from the fragmentation of the carbon skeleton [19].

Up to 250 °C, thermal decomposition of cellulose is hardly accompanied with a serious mass loss. The most important mechanism occurring is depolymerisation. Depolymerisation of cellulose has been observed at 70 °C [33]. It is known that depolymerisation of wood is already occurring at significant rates at 150 °C. At 190 °C, the rate of depolymerisation is already seriously fast. Cellulose decomposition involving mass loss starts at 250°C. A variety of permanent gases, condensable liquids and char are formed during this step [19].

The thermal degradation of lignin takes place over a wide temperature range. At temperatures below 200°C, some thermal softening has been observed resulting in a small weight loss of a small percent. Char formation and the release of volatiles result from a devolatilisation process in the temperature region of 240-600°C.

## 2.4 Fundamentals of analytical instruments

### 2.4.1 Thermo-gravimetric Analyzer (TGA)

The analysis is performed involving the continuous measurement of a physical or chemical change in a sample. This technique is widely used for chemical analysis and to simulate pyrolysis and combustion. In the experiment, a small quantity of powdered sample is heated on a highly sensitive microbalance in a given atmosphere. The experiment can be performed in an isothermal mode or in a non-isothermal mode. The change in weight of the sample is measured and plotted as a function of furnace temperature or time. The Thermo-gravimetric Analyzer apparatus used in this study was Perkin-Elmer, Pyris1 TGA.

### 2.4.2 Automatic Organic Elemental Analyzers (CHONS analyzers)

Analyses of organic compounds in which the common elements are carbon, hydrogen, oxygen, sulfur, and nitrogen are generally conducted in several experiments. The principle of analyses is based upon high-temperature decomposition of the organic compounds, which converts the sample to gaseous molecules. The gases are then separated by a chromatographic column or are based upon specific absorbents in some instruments. However, in most instruments, the thermal conductivity detection (TCD) is used as the detector for the final determinations [32]. The Automatic Organic Elemental Analyzer used in this study was Thermo Finnigan, Flash EA1112 Series.

### 2.4.3 Gas Chromatography (GC)

Basically chromatography involves adsorbing the sample onto some material called the stationary phase. While another phase, the mobile phase is allowed to move across the stationary phase. Depending on the properties of the two phases and the components of the mixture, the mixture is separated into its components according to the rate at which each is removed from the stationary phase by the mobile phase.

In gas chromatography, the stationary phase consists of beads of an inert solid support coated with a high-boiling liquid, and the mobile phase is a gas, usually helium. The sample is injected by syringe onto a heated block where a stream of helium carries it onto a column packed with the stationary phase. The components of the mixture move through the column at different rates. Gas chromatography is also referred as gas-liquid partition chromatography, because the technique depends on how different substances partition themselves between the gas phase (dispersed in the helium carrier gas) and the liquid phase (dissolved in the coating on the beads of solid support). After the components of a mixture are separated using gas chromatography, they must be detected at the exit of the GC column. The thermal-conductivity (TCD) and flame-ionization (FID) detectors are the two most common detectors on commercial gas chromatographs. Gas chromatography can also be used to identify the components of a mixture by comparing their retention times with those of authentic samples [33]. This study used Shimadzu, GC-14B for pyrolysis gas products analysis.

### 2.4.4 Mass Spectrometry

Mass spectrometry is widely used because it provides the information about (i) the qualitative and quantitative composition of both inorganic and organic analysts in complex mixture (ii) the structures of wide variety of complex molecular species (iii) isotopic ratios of atoms in samples and (iv) the structure and composition of solid surface [32].

The concept that mass spectrometry examines is that an organic molecule is bombarded with high-energy electrons. From this bombardment, the energy is transferred as a result of dislodgement on of the molecule's electrons.

$$\underset{\text{Molecule}}{A:B} \quad + \quad \underset{\text{Electron}}{e^-} \quad \longrightarrow \quad \underset{\text{Cation radical}}{A^{+\cdot}B} \quad + \quad \underset{\text{Two electrons}}{2e^-}$$

From above model, the molecule AB has been ionized by electron impact and the result is shown as the molecular ion, which is positively charged and has an odd number of electrons (cation radical). This molecular ion has the same mass as their original molecular form. At the same time, the excess used energy from the bombardment also further breaks the chemical bonds of molecular ions into smaller fragments. As a result, the cation radical is dissociation which produces a neutral fragment and a positively charged fragment.

$$\underset{\text{Cation radical}}{A^{+}\cdot B} \quad \longrightarrow \quad \underset{\text{Cation}}{A^+} \quad + \quad \underset{\text{Radical}}{B\cdot}$$

Considering the mass spectrometer, a very small amount of sample is introduced and converted to gaseous ions by the volatilization. Then the sample is bombarded with high-energy electrons resulting in the stream of positive charged ions which are then accelerated into an analyzer tube surrounded by a magnet. This magnet deflects the ions from their original trajectory, causing them to adopt a circular path, the radius of which depends on their mass-to-charge ratio (*m/z*). Ions of small *m/z* are deflected more than those of larger *m/z*. By varying the magnetic field strength, ions of a particular *m/z* can be selectively focused through a narrow slit onto a detector. Scanning all *m/z* values at a detector gives the distribution of positive ions which is also called a mass spectrum and considered as the characteristic of a particular compound [32]. The TG-MS used in this study was Perkin Elmer Clarus 500.