

Chapter 4

Hydrothermal Processing of Lignocellulosic Biomass to Biofuels



R. Divyabharathi  and P. Subramanian

4.1 Introduction

The demand for energy is constantly increasing due to the rapid industrialization and increasing human population. Industrialization increased the consumption of fossil fuels and its associated environmental pollution problems leading to the release of harmful greenhouse gases causing global warming. Global warming is mainly associated with the release of CO₂ in the atmosphere. Unless the released CO₂ is captured, the effects of climate change is going to be inevitable in future. Hence, efforts are needed to find alternate energy solutions for fossil fuel usage and carbon capture like the utilization of biomass as an energy source. Biomass is advantageous since it is renewable i.e., the plants can be regrown within a period of time and it is a clean source of energy (McKendry 2002). The CO₂ released in the atmosphere is taken by plants, utilized as an energy resource, and can be released into the atmosphere, thus making the cycle completely carbon neutral. Lot of research are currently progressing on the utilization of biomass to produce fuels.

Among the various biomass energy conversion technologies, hydrothermal processing has gained recent interest to thermally process biomass directly for energy conversion in the presence of water at high pressure and temperature. Biomass components gets solubilized in water as the dielectric constant of water decreases at elevated reaction conditions, making it a good solvent for non-polar compounds (Elliott 2011). As a result, biomass hydrothermally degrades to produce various solid, liquid and gaseous biofuels via processes called carbonization, liquefaction and gasification respectively. In addition, biomass generally have significant moisture content, which must be dried before use in case of non-hydrothermal processing. This adds further costs for industrial applications. Thus, the energy cost associated

R. Divyabharathi (✉) · P. Subramanian

Department of Renewable Energy Engineering, Tamil Nadu Agricultural University, Coimbatore 641003, India

with drying will be significantly reduced in hydrothermal methods, which marks its major importance for research.

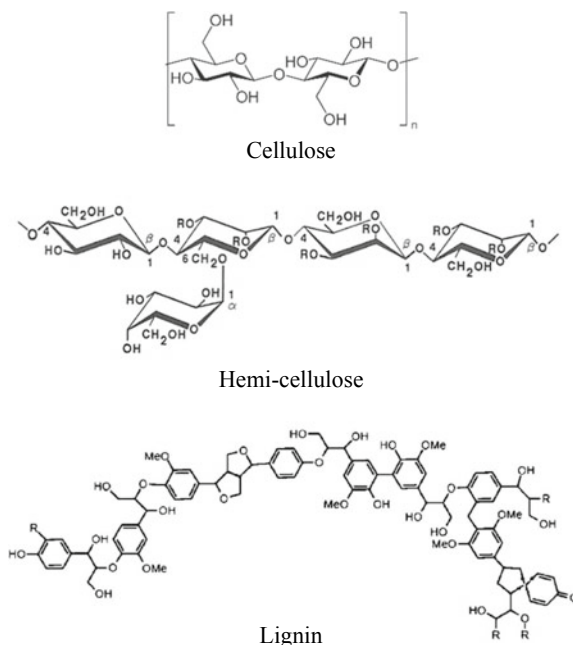
This chapter highlights the components of biomass, bioenergy conversion technologies, hydrothermal processing methods, separation and characterization of biofuels from hydrothermal treatment of lignocellulosic biomass.

4.2 Lignocellulosic Biomass as an Energy Source

Biomass are sun-derived organic substances produced by the process of photosynthesis having carbon, hydrogen, nitrogen, oxygen and sulphur as major elements (Vassilev et al. 2013). Among the alternate energy sources, biomass offers a great source of energy potential which constitutes about 50% of world's primary energy demand (Svetlana and Johan 2000). Its major sources include agricultural wastes, forestry residues, industrial wastes, animal-based wastes, algae, sewage etc. Biomass finds its major applications as a raw material for producing chemicals, fuels, thermal and electrical energy. However, it is under-utilized and releases less pollution compared to other sources of energy. Generally, biomass is selected based on its properties like moisture content, calorific value, cellulose, lignin, fixed carbon and volatile content. Based on these properties and type of energy conversion applied, the biofuel product formation varies significantly. The basic components of a lignocellulosic biomass include cellulose, hemi-cellulose, lignin and extractives, whereas algal biomass majorly contain lipids, proteins and carbohydrates. The composition of these organic substances depends on the biomass type, and growing conditions. Inorganic substances which constitute a minor portion in biomass are usually sulphur and nitrogen derived compounds producing ash. The cellulose, hemi-cellulose and lignin compounds help in building mechanical and structural stability of biomass which constitutes for the major chemistry behind biofuel production (Basu and Basu 2010).

The richest natural long chain polymer present in any biomass is the cellulose ($C_6H_{10}O_5$)_n which is formed by 1,4 β-glycosidic linkage units of D-glucopyranose (Cao et al. 2009). Generally cellulose constitutes about 50% in lignocellulosic biomass and is insoluble in most of the solvents including water at normal temperature of 25 °C, however they become hyperactive and fully soluble at higher sub-critical temperatures. This is due to its tight hydrogen bonding with a high degree of polymerization (Kumar and Gupta 2008; Liu et al. 2010). Hemi-cellulose is a hetero-polymer containing xylan and mannan units with less degree of polymerization (Ren et al. 2010). It constitutes about 35% of lignocellulosic biomass, which varies depending on the type of biomass like woody, herbaceous or agro biomass. Hemi-cellulose binds with cellulose and lignin components in biomass through hydrogen and covalent bonds respectively. When subjected to heat treatment, hemi-cellulose disintegrates easily due to its unstable nature compared to cellulose and lignin. Lignin on the other hand is a natural aromatic polymer composed mainly of phenyl units linked by ether bonds (Savage et al. 2010). It constitutes about 20% of lignocellulosic biomass

Fig. 4.1 Structure of cellulose, hemi-cellulose and lignin



representing the fibrous nature (Rowell et al. 2005). Lignin helps in strengthening the structure of biomass by storing energy in tightly bound fibers and is higher in woody biomass than herbaceous or agro biomass. Comparatively lignin has higher heating value due to its energy content and is more stable to biological degradation. Followed by cellulose, hemi-cellulose and lignin, there are few heterogeneous substances extracted from biomass composing of proteins, fats, lipids, resins, acids and sugars which vary depending on the type of biomass. Extractives constitutes only about 2–5% of biomass composition (Peng et al. 2010) but they contribute to significant plant characteristics like odor, color, taste etc. It is found more in herbaceous biomass like corns and sugars than in woody biomass. The structures of cellulose, hemi-cellulose and lignin are shown in Fig. 4.1. This lignocellulosic composition has a substantial impact on bioenergy conversion and product yield in terms of both quantity and quality.

4.3 Bioenergy Conversion Technologies

There are two significant pathways of bioenergy conversion to convert biomass to biofuels and valuable chemicals. They are biochemical conversion, which process biomass in the presence of microbes and enzymes and thermochemical conversion which process biomass using heat. Oxygen or air supply during these conversion plays a crucial role determining the end products. Based on the characterization of

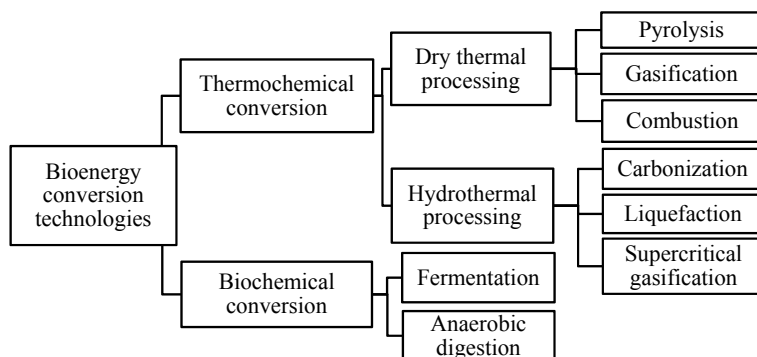


Fig. 4.2 Energy conversion technologies from biomass

biomass, suitable energy conversion technologies can be adopted. A very simple way to select the energy conversion route for a biomass depends on its moisture content. Usually, biomass with moisture content $>10\%$ finds it non-economical to process under thermochemical conversion, rather it will be suitable for biochemical conversion. This is because most of the heat supplied will be used for removing the moisture and the chemistry of products formation will be affected. The possible energy conversion routes from biomass are shown in Fig. 4.2.

Biochemical conversion is a natural process carried under aerobic or anaerobic environment. Enzymatic microbial fermentation and anaerobic digestion are the two major biochemical pathways performed by bacteria and enzymes in an anaerobic environment. In these processes, microbes use oxygen integrated in biomass for its chemical conversion producing alcohol, gases and other chemicals. Ethanol is the main product obtained from fermentation of sugars, starchy and lignocellulosic biomass by yeasts and biogas (CH_4 and CO_2) is the main product obtained from anaerobic digestion of wet biomass by hydrolytic, acetogenic and methanogenic bacteria. Usually, pretreatment methods are employed before fermentation for degradation of complex biopolymers like lignocellulose to sugars. This method is used commercially in most of the industries and it adds more to energy costs.

Thermochemical conversion is a heat treatment process carried on biomass with or without the supply of oxygen to produce fuels and chemicals. This conversion is performed from ancient ages where the biomass like wood is burnt for cooking and space heating. They are classified into dry thermal processing where dry biomass with moisture content of $5\text{--}10\%$ is used for biofuel production and hydrothermal processing where high moisture content biomass ($>10\%$) are used directly for fuel conversion (Elliott 2011). Dry thermal processing includes pyrolysis, gasification and combustion processes which differ in process and product formation based on the amount of oxygen supplied. Hydrothermal processing includes carbonization, liquefaction and supercritical gasification which differs based on the process conditions of

temperature and pressure. In general, dry thermal processing involves high temperature and low pressure, whereas hydrothermal processing involves low temperature and high pressure.

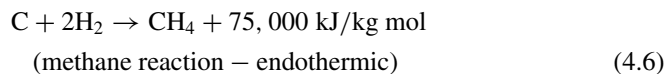
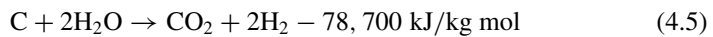
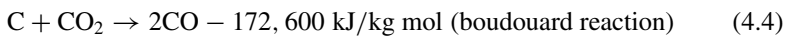
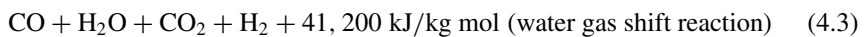
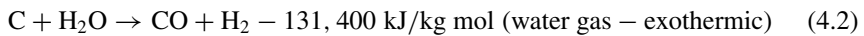
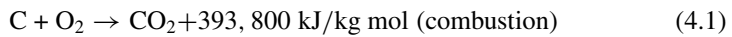
4.4 Dry Thermal Processing

4.4.1 *Pyrolysis*

Pyrolysis is the thermal disintegration of biomass in the absence of air, mostly in an inert atmosphere like nitrogen or argon. The oxygen/air entrapped between biomass pore spaces is removed by the inert gases ensuring a completely anaerobic environment. At this condition, when the biomass is heated, the cellulose and hemi-cellulose components react vigorously releasing volatiles and organics from biomass which is the major ingredient for bio-oil formation. Lignin on the other hand is responsible for the amount of charred biomass left after volatilization. As a result, pyrolysis yields solid (biochar) as an outcome of release of volatiles, liquid (bio-oil) as an outcome of condensation of volatiles and gas (syngas) which are non-condensable output having low molecular weight gaseous products. Based on the pyrolytic conditions of temperature and reaction time, it is classified into slow pyrolysis, intermediate pyrolysis and fast pyrolysis. Slow pyrolysis occurs at 250–400 °C with residence time between 6 and 24 h at a very slow heating rate of <10 °C/min yielding biochar (35%) as a major product (Frederik et al. 2013). Intermediate pyrolysis occurs at 350–450 °C with 30 min residence time at a heating rate of 1.5 °C/s yielding bio-oil (50%) and syngas (35%) as major products (Deodatus et al. 2021). Fast pyrolysis occurs at 500–900 °C with residence time of <5 s at a rapid heating rate of 1000 °C/s yielding bio-oil (75%) as major product (Czernik and Bridgwater 2004). Biochar has higher carbon content (60–90%) and heating value of 25–30 MJ/kg, hence can be used as a solid fuel or as precursor for activated carbon. It also has significant adsorptive qualities to be used in soil to enhance microbial biomass and soil biology. Bio-oil is a dark brown viscous liquid which can be marketed as liquid smoke, used as a substitute for fuel oil or as a blend with existing fossil fuels, if upgraded. Syngas contains hydrocarbons which can be potentially used for thermal and engine applications. The most commonly used pyrolytic reactors are bubbling fluidized bed pyrolyser, circulating fluidized bed pyrolyser, rotating plate pyrolysis reactor and rotating cone pyrolysis reactor. The yield of pyrolysis products varies depending on the composition of biomass feed, particle size of biomass, residence time, temperature, heating rate and reactor type.

4.4.2 Gasification

Gasification is the thermal decomposition of biomass with limited supply of air/oxygen to yield producer gas or syngas as major product. The process is also referred as partial oxidation, wherein the biomass components like C, H, O, N and S reacts with each other to give gaseous products like CO, CO₂, H₂, CH₄, H₂O and traces of sulphur compounds, which all together referred as producer gas (Antonio et al. 2016). The chemistry of gasification takes place in four zones viz. drying, pyrolysis, oxidation and reduction zones. In drying zone, the moisture content in biomass (10–15%) is evaporated into steam at 100–150 °C. In pyrolysis zone, the organic components are converted at 150–700 °C to charcoal, wood oil, tar and gas. In oxidation zone, the carbon and hydrogen components in biomass reacts with oxygen in the air-steam blast at 1400 °C, to yield CO₂ and H₂O respectively. In reduction zone, the CO₂ and steam coming from the oxidation zone are converted at 800–1000 °C to carbon monoxide and hydrogen, which are the main constituents in producer gas of about 30–60% and 25–30%, respectively (Pratik and Babu 2009). This makes the gas combustible with a calorific value of 950–1200 kcal/m³. There are two major designs of gasifiers viz. fixed bed gasifiers (updraft, downdraft and cross draft gasifiers) and fluidized bed gasifiers, which find their own applications for direct heating, running engines, chemicals production and power generation. On an average, 1 kg of biomass yields about 1.5–2 m³ of producer gas, which vary depending on biomass type and gasifier design. The chemistry behind gasification yielding producer gas is given by the following equations.



4.4.3 Combustion

Combustion is a thermochemical conversion that takes place in the presence of excess amount of air or oxygen to form CO_2 and H_2O as the ultimate products. The process is exothermic leaving heat as a result of interaction between the biomass components like carbon and hydrogen with oxygen. This process is age old and has been most commonly used for cooking, heating and power generation. The amount of heat released in the process depends on the calorific value of the biomass fuel burnt which in turn depends on the carbon, moisture and ash content (Daniel et al. 2013). Calorific value is directly proportional to the amount of carbon and indirectly proportional to the amount of ash and moisture in the biomass. Combusting the biomass with excessive moisture leads only to the wastage of heat in drawing out the water by evaporation. Hence for an efficient combustion to take place, the factors of temperature, biomass type, time and fuel-air mixing ratio are most influencing. General applications of combustion include fuel combustion in boilers and power plants for steam and power generation. Biomass nowadays is gaining more interest when co-fired with coal in power plants. The process is called co-combustion or co-firing. Co-combustion reduces the dependence on fossil fuels in power plants and produces clean renewable power at limited capital cost, thereby ensuring highest efficiency. The reactors commonly used for co-combustion involve fluidized bed combustor (atmospheric/pressurized), grate combustor and pulverized combustor where the biomass and coal will be directly co-fired, indirectly co-fired or parallel co-fired (Sahu et al. 2014). Using this technology, there will be a net reduction in the emission of NO_x and SO_x due to the distinct interactions between varying chemical composition in biomass and coal.

4.5 Hydrothermal Processing

Hydrothermal processing is a pressurized thermochemical conversion of wet biomass into valuable fuels and chemicals. It occurs at temperatures involving sub-critical and supercritical conditions between 200 and 374 °C at self-generated pressures between 5 and 22 MPa (Peterson et al. 2008). It involves three processes namely hydrothermal carbonization, liquefaction and gasification, which vary depending on the reaction conditions of temperature and pressure. The main advantage of hydrothermal processing of biomass is that it eliminates the need to pretreat the biomass by drying unlike conventional thermochemical processes. Thus, it can directly handle a variety of biomass with moisture content ranging from 20 to 90% like food waste, algae, industrial wastes, sewage sludge etc., which is difficult to process in conventional processes (Yokoyama and Matsumura 2008). Due to this, the energy costs associated with drying is saved and comparatively less energy is required for processing. Since, the processing takes place under pressure, there is an increased yield in terms of products like hydro-char, biocrude and syngas with aqueous phase as byproduct.

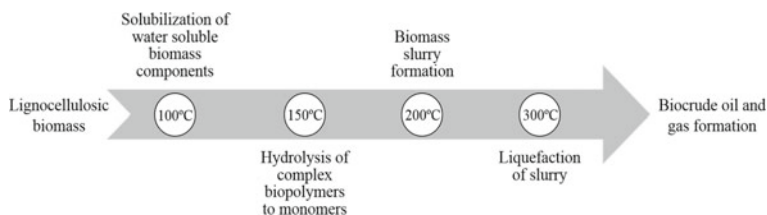


Fig. 4.3 Biomass hydrothermal degradation

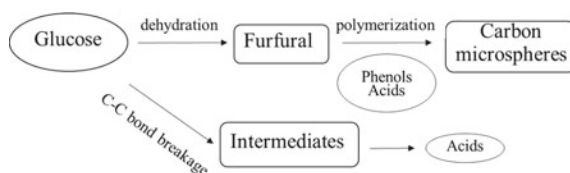
Besides these, there are few disadvantages like the need for expensive and high-capacity sturdy reactors, product extraction procedures and up-scaling to industrial level (Zhang et al. 2010a). Hence a lot of research is required on the downstream processing of products from hydrothermal conversion.

The hydrothermal conversion is based on two conditions of sub-critical and super-critical media, which is reliable on water's critical point at 374 °C and 22 MPa. Water behaves differently and has its own distinct characteristics in each condition. For example, water solubilizes the components of cellulose and lignin at high temperatures and pressure, which are insoluble at atmospheric conditions. Also at critical conditions, the complex polymers of biomass are broken easily to their monomers releasing gaseous compounds, which when condensed produce biocrude oil and remaining non-condensable low molecular weight compounds collect as syngas. The biomass decomposition pathway in hydrothermal process is shown in Fig. 4.3. The properties of water can be changed with respect to temperature and pressure. At sub-critical conditions (<374 °C and <2 MPa), the water medium favors acid and base catalyzed reactions due to the increase in ionic product of water and decrease in viscosity (Guo et al. 2010). At supercritical conditions (>374 °C and >22 MPa), water has high diffusion rates (Ogunsola and Berkowitz 1995) making it as a source of hydrogen and involve in hydrolysis reactions. In hydrothermal processing, liquefaction takes place at sub-critical conditions of 200–370 °C with pressures up to 20 MPa, whereas hydrothermal gasification or supercritical gasification takes place at 370–500 °C with pressures up to 30 MPa. Commercially supercritical gasification is used in industries for power generation and removal of toxins from bio-wastes.

4.5.1 Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is an aqueous slow pyrolysis process occurring at a medium temperature and pressure for longer residence time. HTC processes wet biomass at a rapid rate to release volatiles at temperatures from 150 to 250 °C and pressures from 1 to 5 MPa for a longer residence time up to 20 h (Titirici and Antonietti 2010) to yield hydro-char as major product. Biomass with moisture content of 70–90% is ideal for HTC requiring no pretreatment. Hydro-char is formed after complete volatilization of the wet biomass along with aqueous phase as byproduct.

Fig. 4.4 Chemistry of hydrothermal carbonization of glucose



The formation of hydro-char depends on the lignin and fixed carbon content in biomass. For example, if the biomass has high lignin content, it constitutes to the degradation of fibers to carbon monomers thereby increasing the carbon content of material. This results in more char formation after removal of volatiles by decarboxylation and dehydration reactions removing H_2 as H_2O and O_2 as CO_2 . Thus hydro-char has high calorific value and carbon content with less sulphur, nitrogen and ash. The carbon-rich hydro-char finds potential applications as fuel alternative for coal, alternative adsorbent or precursor for activated carbon and as an additive in soil for nutrient amendment (Xiao et al. 2012).

HTC process is advantageous over conventional slow pyrolysis by the factors of requirement of medium carbonization temperature, direct wet biomass processing, higher yield of char at less time and comparatively low energy requirement (Sevilla and Fuertes 2009). Several inexpensive and easily available biomass materials like sugars, cellulose and carbohydrate sources have been tested for HTC which has the major chemistry of fractionation to furfurals, polymerization to furans and intermolecular carbonization (Titirici and Antonietti 2010). The end hydrothermal carbon product derived has distinct characteristics of various polar functional groups which makes it to disperse easily in water and other solvents. The chemistry of hydrothermal carbonization of glucose is shown in Fig. 4.4.

4.5.2 Hydrothermal Liquefaction

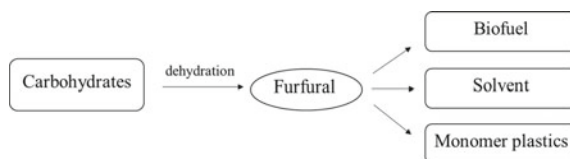
Hydrothermal liquefaction (HTL) also called hydrolysis takes place at sub-critical water temperatures $<370^\circ C$ and at high pressures up to 20 MPa to produce liquid biofuels (Toor et al. 2011). The phenomenon is related to the geological fossil fuel formation happening underground for thousands of years at high temperatures and pressures. Similarly, in HTL, organic liquid fuel is produced at high pressures within a specific period. The biocrude oil formed has comparable properties as that of the conventional crude oil in terms of color, odor, density, heating value etc. HTL technology is welcoming not only for the value of biocrude oil formation but also for a number of reasons like the use of an environment friendly water as solvent, use of wet biomass for thermal treatment without drying, thus increasing the energy efficiency and processing temperatures much lower than the conventional pyrolysis for bio-oil production (Savage et al. 2010).

The chemistry of hydrothermal liquefaction is complex due to the complexity of degradation of biomass components in sub-critical water conditions. The biomass components viz. cellulose, hemi-cellulose, lignin, lipids, fats, proteins etc. undergo hydrolysis, depolymerization, dehydration, decarboxylation and fragmentation reactions to ultimately yield a dark brown viscous liquid called biocrude (Toor et al. 2011). The chemical complexity involved in the hydrothermal liquefaction of lignocellulosic components is given by the following steps.

- Hydrolysis of macro molecules to water soluble oligomers
- Degradation of glycosidic linkages in cellulose to form glucose monomers
- Dissolution of sugar monomers of hemicellulose in water by hydrolysis
- Decomposition of glucose monomers to acids, aldehydes, and furfural derivatives
- Fragmentation of xylose monomers of hemicellulose to furfural
- Dissociation of open chain molecules to ketones, aldehyde, and acids
- Decomposition of lignin to low molecular weight compounds like phenol.

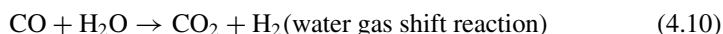
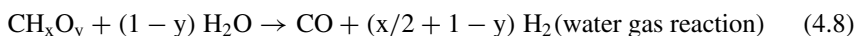
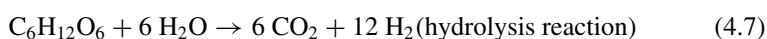
Most of the organic compounds are insoluble in water, however at sub-critical conditions between 200 and 350 °C, they tend to be soluble and water acts both as a reactant and solvent in chemical reactions. The aromatic compounds of ethers, nitriles, amides, and phenyls gain the ability to thermally react at temperatures up to 250 °C, however they dissociate and rapidly hydrolyze to alkenes, phenols and anilines at increased temperatures (Zhang et al. 2010b). This also depends on various factors such as pressure, catalyst, biomass composition, particle size, reaction time and medium. Overall, the chemistry favours an increase in formation of volatiles leading to biocrude oil production at 300–350 °C and gas yield >350 °C. The liquid biocrude formed has high calorific value and less oxygen content compared to the bio-oil obtained from conventional pyrolysis. However, it cannot be directly used as a transportation fuel to its high viscosity, oxygen, water and acid content, which affects its stability on storage. Hence for biocrude to be used as a blend or replacement with existing fossil fuels, it needs to be further upgraded by means of catalytic dehydration or decarboxylation reactions to remove oxygen and water such that the overall calorific value and C/H ratio of biocrude is increased. This improvement of obtaining high quality, stable and high energy biocrude can be made by down-streaming techniques like solvent extraction by using polar solvents namely dichloromethane, diethyl ether, acetone, toluene, hexane, chloroform etc. (Valdez et al. 2011) and by catalytic hydrodeoxygenation at 300–600 °C which combines oxygen in biocrude with hydrogen to form water and saturated hydrocarbons (Huber et al. 2006). Figure 4.5 shows the hydrothermal liquefaction of carbohydrates to valuable chemicals.

Fig. 4.5 HTL pathway of carbohydrates



4.5.3 Hydrothermal Gasification

Hydrothermal gasification (HTG) also called as supercritical gasification refers to the thermochemical conversion of biomass to biofuels under hot compressed water. In this environment, water is said to attain supercritical properties such as change in solubility and reactivity, since the temperature and pressure inside the reactor are at elevated levels of $>374\text{ }^{\circ}\text{C}$ and $>22\text{ MPa}$ respectively. Biomass molecules which are insoluble in water at normal conditions undergo rapid hydrolysis under supercritical conditions, making the fragments of biomass to dissolve, which in turn prevents the formation of hydro-char (Kruse 2009) and paves way for higher gas production. HTG is most commonly used for the production of H_2 and CH_4 rich syngas and it depends on the temperature and catalyst used. The process may produce hydrogen rich gas at temperatures $>500\text{ }^{\circ}\text{C}$ under non-catalytic or non-metallic catalytic conditions, or it may produce methane rich gas at temperatures between 374 and $500\text{ }^{\circ}\text{C}$ under metallic catalytic condition or it may produce a combined syngas product using heterogeneous catalysts at near critical condition (Kruse 2008). The chemistry of supercritical biomass degradation is complex such that there will be an occurrence of hydrolysis, fragmentation, methanation, water-gas and water gas shift reactions simultaneously. High temperatures and pressures fragment the bonds of complex biopolymers to produce syngas compounds of H_2 , CH_4 , CO_2 and CO . To further specialize the process and to enable a sole-rich gas, a catalyst addition is needed. Heterogeneous catalysts such as Ni, Pt, Rh and Rb or homogeneous alkaline catalysts such as Na_2CO_3 , K_2CO_3 , NaCl and KCl may be used at temperatures between 500 and $800\text{ }^{\circ}\text{C}$ to promote water-gas-shift reactions and other free radical reactions, generating hydrogen and methane rich gas products (Lee et al. 2002). This is also dependable on the biomass composition like carbon and hydrogen content and also on the reaction time of HTG. The Eqs. (4.7) to (4.10) shows the reaction network of hydrothermal gasification of glucose.



In the HTG study on glucose, the gasification reactions were favorable to H_2 formation and CO formation decreased at increased temperatures $>600\text{ }^{\circ}\text{C}$ under non-catalytic conditions, which was due to the rapid rate and dominance of water-gas-shift reaction (Xu et al. 1996). This rate was found to decrease when the concentration of glucose was increased. Hence to alter this, non-metallic catalyst like activated carbon can be added to completely convert glucose to hydrogen rich gas. The

remaining aqueous phase may have lignin dissolved which may break down to form phenolic compounds. Phenols on polymerization in hydrothermal media produces formaldehyde which in turn results in cross-linking to form hydro-char compounds (Yoshida and Matsumura 2001). Thus, cellulose and lignin-based biomass should be used with heterogeneous catalysts like Ru in supercritical gasification to completely gasify and form CH₄ and CO₂ (Osada et al. 2004). HTG is therefore advantageous in processing wet biomass to produce H₂ and CH₄ rich gases which can be potentially used in power generation, chemical synthesis and for fuel cell applications.

4.6 Extraction and Analysis of Hydrothermal Products

There are various procedures for extraction of each type of hydrothermal products. In general, after hydrothermal processing, the condensable vapors are collected as liquid products, non-condensable gaseous product is vented or sometimes collected in tedlar bags and the remaining solid product from reactor is filtered. The condensable liquid product has biocrude mixed with water which can be separated by solvent extraction techniques and the solvent can be removed by vacuum filtration (Alba et al. 2012). In cases where homogeneous alkaline catalysts are used, the quality of biocrude extraction can be enhanced by dual solvent extraction process using two typical polar and non-polar solvents (Karagoz et al. 2005). The reaction mixture containing solid product dissolved in water is filtered to get aqueous phase which may contain water soluble organics and the filtrate is obtained as solid hydro-char by drying in hot air oven at 103 ± 2 °C.

The biocrude obtained after solvent extraction is a viscous organic liquid that has high C/H ratio comparable to conventional crude. This can be verified by GC-MS and FT-IR analyses by detecting the functional groups present in the product. The aqueous phase is centrifuged and can be analyzed for total organic carbon (TOC) and for chemical composition by GC-MS. The solid hydro-char can be analyzed by FT-IR and SEM to identify the functional compounds and the formation of pore structures respectively. After the detection of chemical compounds in hydrothermal products by these analyses, the selective extraction of those chemicals is found to be challenging. This is due to the complexity of organics present in the products. However, certain liquid-liquid extraction techniques may selectively recover phenols and certain acids, which may be used for chemical substitution or for industrial applications (Hu et al. 2012). In case of alkaline catalyst usage in hydrothermal processing, it is difficult to separate liquids and solids. This is because catalysts retain in solid product which may in turn retain solids in liquid fraction. This can be rectified by the addition of acids like HCl during extraction (Miller et al. 1999). The separation and extraction of products post hydrothermal processing is shown in Fig. 4.6.

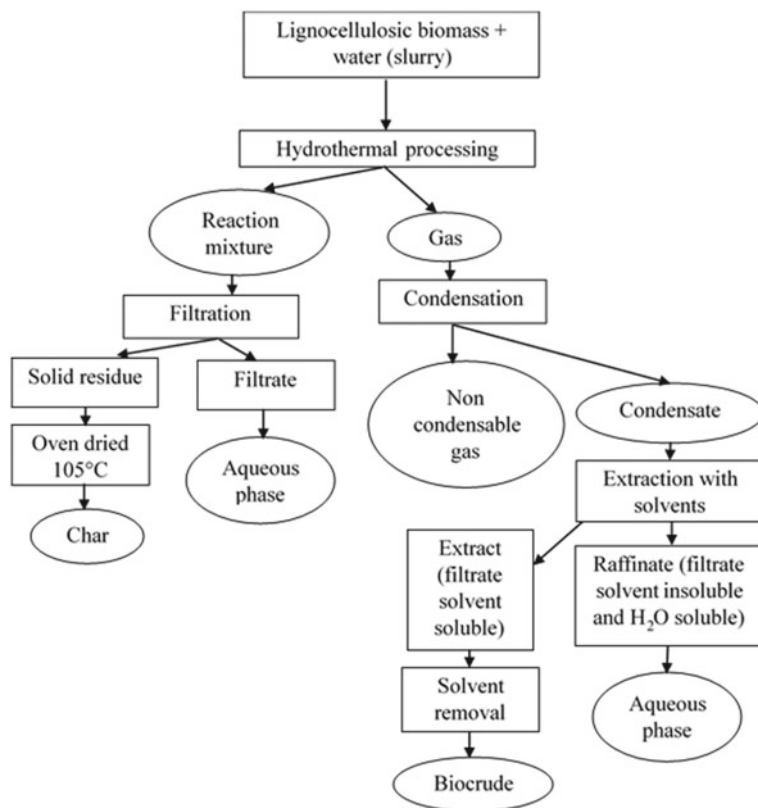


Fig. 4.6 Separation and extraction of hydrothermal products (Divyabharathi and Subramanian 2021a)

4.6.1 Gas Chromatography-Mass Spectroscopy

Gas Chromatography-Mass Spectroscopy (GC-MS) is a significant technique to detect and measure the unknown compounds present in the sample. There are various other chromatography techniques like Liquid chromatography-mass spectrometry (LC-MS), High performance liquid chromatography (HPLC), Tandem mass spectrometry (MS-MS) etc., amongst which the most suitable one for analysis of hydrothermal products is GC-MS. This works by the principle of ionization of gases and measurement of mass:charge (m/z) ratios. The organic samples must be diluted in a proper ratio with suitable solvents before injecting. GC-MS detects and quantifies most of the organics in the sample by comparing with internal standards. However, there will be certain limitations like choking of injector port or non-detection of volatiles in biocrude oils, carbon deposition inside the sampling port and few organics not formed as expected in hydrothermal processing, which solely depends on the biomass processing conditions. The primary compounds in the biocrude as detected

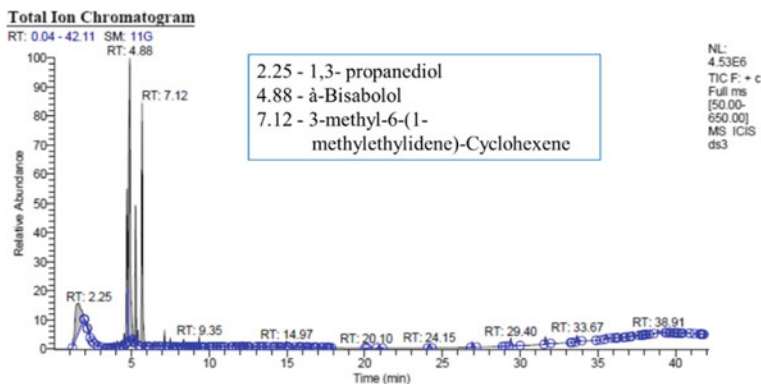


Fig. 4.7 GC-MS chromatogram of paddy straw biocrude at 275 °C (Divyabharathi and Subramanian 2021b)

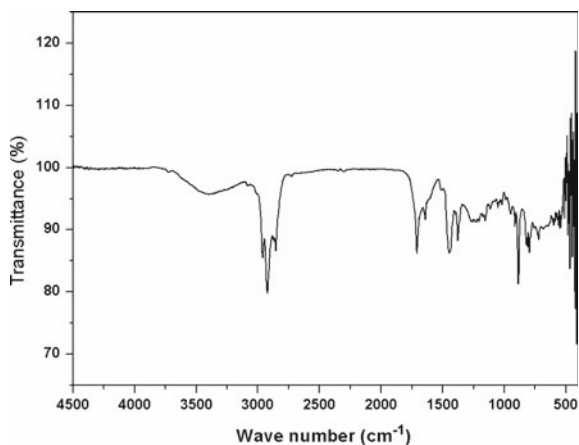
by GC-MS include phenols, acids, alcohols, alkanes, alkenes, ketones, furfurals etc. which mainly depends on the biomass composition. However, it is challenging to get high quantity of a specific compound when processing a mixed composition biomass. The GC-MS chromatogram obtained for biocrude produced from paddy straw (Divyabharathi and Subramanian 2021b) is shown in Fig. 4.7.

4.6.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy technique is used to detect the functional groups of compounds present in the sample. It is analyzed using a Fourier Transform Infrared Spectrophotometer which has zinc selenide attenuated total reflection (ATR) crystal mode and KBr beam splitting. Biomass, biocrude, hydro-char and aqueous phase byproducts may be analyzed in the range from 4800 to 400 cm^{-1} at 4 cm^{-1} resolution using origin software. Thin films of samples are applied to dry and the spectra will appear after smearing sample over the surface of crystal. In general, the major spectra shown by GC-MS, indicating typical organic compounds will be confirmed from the results of FTIR. The FTIR spectrum of transmittance plotted against wavelength obtained for biocrude produced from hydrothermal liquefaction of orange peel (Divyabharathi and Subramanian 2021a) is shown in Fig. 4.8.

The spectrum depicts that biocrude is a complex mixture of aliphatic and aromatic derivatives. It presented strong bands at 2875–3000 cm^{-1} , which illustrated the C-H stretching vibrations, which was due to the decomposition of cellulose to levoglucosan, saturated hydrocarbons and acids. The peaks at 1700 cm^{-1} were assigned to the C=O groups which represents the esters and carboxylic acids. Bands at 1300–1490 cm^{-1} were assigned to C=C benzene ring groups especially the phenol derivatives which occur as a result of polymerization. Lower peaks at

Fig. 4.8 FTIR spectrum of orange peel biocrude at 275 °C (Divyabharathi and Subramanian 2021a)



1100–1270 cm^{-1} were assigned to the C-O groups which represented the carbohydrate derivative compounds due to decarboxylation reactions (Divyabharathi and Subramanian 2021a).

4.6.3 Elemental Analysis

Elemental analysis also called ultimate analysis is used to find the composition of elements like carbon, hydrogen, nitrogen, oxygen and sulphur in the sample. This analysis is significant for finding the heating value of biomass and biofuels which is derived by Dulong's formula. It is also used to determine the C/H and O/H ratios which estimates the chemistry of product formation and the composition of hydrothermal products. In general, C/H ratio and O/H ratio determines the aromatic composition and rate of de-oxygenation reactions taking place during hydrothermal processing (Tekin et al. 2014). Table 4.1. shows the elemental composition and higher heating values of hydro-char obtained by hydrothermal processing of lignocellulosic biomass viz. orange peel, dairy manure and food waste at 250 °C. The obtained

Table 4.1 Elemental composition and heating values of hydro-char obtained from hydrothermal processing of lignocellulosic biomass

Biomass	Hydro-char composition					
	C (%)	H (%)	O (%)*	N (%)	S (%)	HHV (MJ/kg)
Orange peel	70.19	4.25	24.60	0.93	0.02	24.93
Dairy manure	63.41	5.58	30.03	0.92	0.06	24.68
Food waste	70.93	4.08	23.65	1.30	0.03	24.34

* Calculated by difference

hydro-char had high oxygen and low carbon content which was due to the incomplete biomass degradation expected due to the increase in the aqueous phase during hydrothermal processing (Caprariis et al. 2017). Hydro-char has higher heating value (25 MJ/kg) which proves that it can be potentially used as solid fuel or as a precursor for activated carbon production (Malins 2017).

4.7 Conclusion

This chapter reviewed the various hydrothermal processing methods viz. carbonization, liquefaction and gasification of biomass into biofuels like hydro-char, biocrude and syngas respectively in comparison with conventional thermochemical conversion processes. Depending upon the target product, suitable hydrothermal processing technology can be adopted. Water in hydrothermal conditions of sub-critical and super-critical media have different physico-chemical properties in terms of solubility and reactivity than at normal conditions, which makes the process and chemistry unique to obtain high-value fuels and chemicals from biomass. Though hydrothermal processing has few shortcomings like the use of high pressure and expensive reactors, difficulty in scaling up of process and upgrading of biofuels, it is a viable technology that can operate with a wide range of wet biomass at low to moderate temperatures and pressures. Separation and extraction of hydrothermal products plays a crucial role and if performed carefully, it is potentially feasible to upgrade and scale up hydrothermal processes in near future for biofuel usage to replace conventional fossil fuels.

References

- Alba LG, Torri C, Samori C, VanderSpek J, Fabbri D, Kersten SRA, Brilman DWF (2012) Hydrothermal treatment (HTT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept. *Energy Fuels* 26:642–657
- Antonio M, Simeone C, Dino M (2016) Biomass gasification technology: the state of the art overview. *J Energy Chem* 25(1):10–25
- Basu P (2010) Biomass characteristics. In: Basu P (ed) *Biomass gasification and pyrolysis*. Academic Press, Boston, pp 27–63
- Cao Y, Wu J, Zhang J, Li HQ, Zhang Y, He JS (2009) Room temperature ionic liquids (RTILs): a new and versatile platform for cellulose processing and derivatization. *Chem Eng J* 147:13–21
- Caprariis BD, Filippis PD, Petruolo A, Scarsella M (2017) Hydrothermal liquefaction of biomass: influence of temperature and biomass composition on the bio-oil production. *Fuel* 208:618–625
- Czernik S, Bridgwater AV (2004) Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 18(2):590–598
- Daniel M, Ana S, Javier R, Fernando S (2013) Assessment of CCHP systems based on biomass combustion for small-scale applications through a review of the technology and analysis of energy efficiency parameters. *Appl Energy* 102:1303–1313
- Deodatus K, Justin N, Godlisten K (2021) A review of intermediate pyrolysis as a technology of biomass conversion for coproduction of biooil and adsorption biochar. *J Renew Energy* 2021:1–10

- Divyabharathi R, Subramanian P (2021a) Biocrude production from orange (*Citrus reticulata*) peel by hydrothermal liquefaction and process optimization. *Biomass Convers Biorefinery*
- Divyabharathi R, Subramanian P (2021b) Hydrothermal liquefaction of paddy straw for biocrude production. *Mater Today Proc* 45:603–606
- Elliott DC (2011) Hydrothermal processing, thermochemical processing of biomass: conversion into fuels. In: Brown RC (eds) *Chemicals and power*. John Wiley & Sons, Ltd, Chichester, UK, pp 200–231
- Frederik R, Sven VH, Dane D, Wolter P (2013) Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *GCB Bioenergy* 5:104–115
- Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY (2010) Review of catalytic supercritical water gasification for hydrogen production from biomass. *Renew Sustain Energy Rev* 14:334–343
- Hu X, Mourant D, Gunawan R, Wu L, Wang Y, Lievens C, Li CZ (2012) Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid–liquid extraction. *RSC Adv* 2:9366–9370
- Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts and engineering. *Chem Rev* 106:4044–4098
- Karagoz S, Bhaskar T, Muto A, Sakata Y, Oshiki T, Kishimoto T (2005) Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. *Chem Eng J* 108:127–137
- Kruse A (2008) Supercritical water gasification. *Biofuels, Bioprod Biorefin* 2:415–437
- Kruse A (2009) Hydrothermal biomass gasification. *J Supercrit Fluids* 47:391–399
- Kumar S, Gupta RB (2008) Hydrolysis of microcrystalline cellulose in subcritical and supercritical water in a continuous flow reactor. *Ind Eng Chem Res* 47:9321–9329
- Lee I, Kim M, Ihm S (2002) Gasification of glucose in supercritical water. *Ind Eng Chem Res* 41:1182–1188
- Liu CF, Sun RC (2010) Cellulose. In: Sun RC (ed) *Cereal straw as a resource for sustainable biomaterials and biofuels*. Elsevier, Amsterdam, pp 131–167
- Malins K (2017) Production of bio-oil via hydrothermal liquefaction of birch sawdust. *Energy Convers Manage* 144:243–251
- McKendry P (2002) Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 83(1):37–46
- Miller JE, Evans L, Littlewolf A, Trudell DE (1999) Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Fuel* 78:1363–1366
- Ogunsola OM, Berkowitz N (1995) Removal of heterocyclic S and N from oil precursors by supercritical water. *Fuel* 74:1485–1490
- Osada M, Sato T, Watanabe M, Adschiri T, Arai K (2004) Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water. *Energy Fuels* 18:327–333
- Peng P, Bian J, Sun RC (2010) Extratives. In: Sun RC (ed) *Cereal straw as a resource for sustainable biomaterials and biofuels*. Elsevier, Amsterdam, pp 49–72
- Peterson AA, Vogel F, Lachance RP, Fröling M, Antal MJ, Tester JW (2008) Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy Environ Sci* 1:32–65
- Pratik NS, Babu BV (2009) Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier. *Biores Technol* 100(12):3127–3133
- Ren JL, Sun RC (2010) Hemicelluloses. In: Sun RC (ed) *Cereal straw as a resource for sustainable biomaterials and biofuels*. Elsevier, Amsterdam, pp 73–130
- Rowell RM, Petersen R, Han JS, Rowell JS, Tshabalala MA (2005) Cell wall chemistry. In: Rowell RM (ed) *Hand book of wood chemistry and wood composites*. Taylor & Francis Group, Boca Raton, pp 9–40
- Sahu SG, Chakraborty N, Sarkar P (2014) Coal–biomass co-combustion: an overview. *Renew Sustain Energy Rev* 39:575–586
- Savage PE, Levine RB, Huelsman CM (2010) Hydrothermal processing of biomass: thermochemical conversion of biomass to liquid. In: Crocker M (ed) *Fuels and chemicals*. RSC Publishing, Cambridge, pp 192–215

- Sevilla M, Fuertes AB (2009) Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. *Chem Eur J* 15:4195–4203
- Svetlana L, Johan V (2000) Global potential of sustainable biomass for energy. SLU report. Swedish University of Agricultural Sciences, Department of Energy and Technology
- Tekin K, Karagöz S, Bektaş S (2014) A review of hydrothermal biomass processing. *Renew Sustain Energy Rev* 40:673–687
- Titirici MM, Antonietti M (2010) Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem Soc Rev* 39:103–116
- Toor SS, Rosendahl L, Rudolf A (2011) Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy* 36:2328–2342
- Valdez PJ, Dickinson JG, Savage PE (2011) Characterization of product fractions from hydrothermal liquefaction of *Nanochloropsis* sp. and the influence of solvents. *Energy Fuels* 25:3235–3243
- Vassilev SV, Baxter D, Andersen LK, Vassileva CG (2013) An overview of the composition and application of biomass ash. Part1. Phase-mineral and chemical composition and classification. *Fuel* 105:40–76
- Xiao LP, Shi ZJ, Xu F, Sun RC (2012) Hydrothermal carbonization of lignocellulosic biomass. *Biores Technol* 118:619–623
- Xu X, Matsumura Y, Stenberg J, Antal MJ (1996) Carbon-catalyzed gasification of organic feedstocks in supercritical water. *Ind Eng Chem Res* 35:2522–2530
- Yokoyama S, Matsumura Y (2008) *The Asian biomass hand book*. The Japan Institute of Energy, Tokyo
- Yoshida T, Matsumura Y (2001) Gasification of cellulose, xylan, and lignin mixtures in supercritical water. *Ind Eng Chem Res* 40:5469–5474
- Zhang L, Xu C, Champagne P (2010a) Overview of recent advances in thermochemical conversion of biomass. *Energy Convers Manage* 51:969–982
- Zhang Y (2010b) Hydrothermal liquefaction to convert biomass into crude oil. In: Blaschek HP, Ezeji T, Scheffran J (eds) *Biofuels from agricultural wastes and byproducts*. Wiley-Blackwell, USA, pp 100–276