Chapter 4
Thermochemical Conversion and Valorization of Woody Lignocellulosic Biomass in Hydrothermal Media

V. Chitra Devi, S. Mothil, R. Sathish Raam and K. Senthilkumar

Abstract Biomass conversion can provide the sustainable and promising alternative solution for the future energy demands and fuel supply. It can also be a major contributor to the chemical demand by acting as primary source for biofuel and value added chemicals. Thermochemical conversion can be a faster solution for this problem. Lignocellulosic biomass is the more preferred to other biomasses as it has uniform composition and well established models for degradation of its constituents such as Cellulose, Hemicellulose and Lignin. This process of thermochemical conversion of biomass is usually performed in the presence of hydrothermal media like water or acetone at high temperature and high pressure. The woody lignocellulosic biomass has a complex sterochemical structure compared to agricultural residues and energy crops. It is depolymerised into small compounds in sub critical and supercritical conditions to form three distinct phases such as: bio-oil, bio-gas and bio-carbon, which has their own significant role in the biorefinery. Based on the process conditions (temperature, pressure, media) the yield of the phases varies accordingly. According to the physicochemical properties of media, the process can be classified as hydrothermal carbonization, hydrothermal liquefaction and hydrothermal gasification. For the past two decades, significant researches is being reported for thermochemical conversion of various lignocellulosic biomass (hardwood/softwood), agricultural residues, fruit shells, cellulose wastes, industrial co-products, etc. in both wet and dry conditions. Also it was found that the wet biomass conversion results in high yield of various chemicals like alkanes, alkenes ketones, aldehydes, acids, alcohols, phenols, esters, ethers and other aromatic compounds with some amount of polymeric impurities. In this chapter more emphasis is given on the thermochemical conversion of woody biomass, its pre-treatment, hydro processing and refining of the products synthesised. It also focuses on the valorization of the end products obtained from the hydrothermal processing into value added chemicals in the presence of homogeneous and heterogeneous catalysts.

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4.1 Introduction

Biomass is carbon neutral and is the fourth major energy resource after petroleum, coal, and natural gas, delivering around 14% of the global energy demand. United Nations Conference on Environment and Development (UNCED) conducted an analysis on the future energy demand where this was projected to fulfill 50% by 2050 (Ramage and Scurlock 1996; Demirbas 2000). Biomass being renewable, sustainable and relatively environmentally friendly source is used to meet world's variety of energy requirements, including electric power, heat source for domestic and industrial needs, fuel and feedstock for chemicals (Balat 2006). Biomass is distinctive from all the renewable resources as it efficiently stores the solar energy from the sun in its cells through photosynthesis. This carbon stored in the plant cells can be transformed and used back as solid, liquid and gaseous fuels by various conversion methods (Demirbaş 2001; Saxena et al. 2009). The yield of biomass of one country varies from another due to the change in prevailing climatic conditions. Higher is the yield in sub tropics and tropics, and medium in temperate countries. From the 1992 statistics, the average carbon stored in tropical forests of Asia was calculated to be 255, 144 and 148 Mg ha^{-1} as potential, actual and biomass stored under the soil; corresponding to total carbon evaluated as 74, 42, and 43 Pg (1 Pg $= 10^{15}$ g), respectively (Brown et al. 1993). According to the 1993 calculations from species-wise volume records for all forest cover in various states of India, the mean above-ground biomass densities was 67.4 Mg ha^{-1}, equating to 34 Mg C ha^{-1} (Haripriya 2000). Compared to other energy resources, biomass fuels have a very smaller amount of sulphur and, thus contributing very negligible SO_2 releases that causes acid rain. Biomass on combustion produces relatively a lesser amount of ash than coal; in return it also can be mixed with the soil to enrich its fertility. Biomass is a potential and sustainable source to mitigate climate change as its contribution in atmospheric CO_2 level can be controlled (Owusu and Asumadu-Sarkodie 2016). With the better utilization of biomass, the lifetime of non-renewable crude oil that is used for the manufacture of petrochemicals and other value added substances would be extended. Biomass as a domestic resource is not subjected to the supply uncertainties, unlike the imported fuels that change according to the world market price. Thus it secures the future generation with clean, safe, renewable energy source that could drive the country's economy and environment to high standards (Demirbas et al. 2009).

Table 4.1 Classification of biomass according to the source

Supply sector	Type	Example
Forestry	Forest by-products	Wood blocks; logs and branches from thinning; wood chips; bark
Agricultural residue	Lignocellulosic agricultural residue	Straw and husk (rice, wheat, maize, barley, cereal, rye, sunflower, rapeseed); cobs (corn); shells (almond, olive, walnut, palm pit, hazelnut); stalk (flax, hemp, cotton, kenaf), leaves, seed pods and root
	Shrubs/herbaceous crop residue	Indian shrub, hay, switchgrass, Miscanthus, reed canary grass, and costal Bermuda grass
	Livestock waste	Manure from chicken, cattle, pigs, sheep
	Others	Weeds, aquatic plants, and algae
Industry	Wood/lumber industry residues	Waste wood residue from saw mills and timber mills (wood chips, off-cuts, bark, sawdust);
	Food industry residues	Bagasse (sugar cane); starch residue (potato, sugar beet, sweet sorghum, cassava, tapioka); fruit peels and residues
	Meat processing industry waste	Wastes from poultry houses, slaughterhouses, fisheries and dairies
	Others	Ethanol, paper pulp, black liquor, cellulosic sludge
Domestic	Organic waste	Waste food materials, kitchen vegetable waste; used cooking oil; municipal waste; sewage sludge

4.2 Classification of Biomass

There are various classifications of biomass. But in crude point of view classification based on the source is given in Table 4.1.

4.3 Lignocellulosic Biomass

The plant cell walls are primary made of lignocellulose. A plant cell wall constitutes layers of cellulose microfibrils, hemicellulose, pectin, and lignin in a uniform arrangement (Koppejan and Van Loo 2012). It also contains proteins, extractives

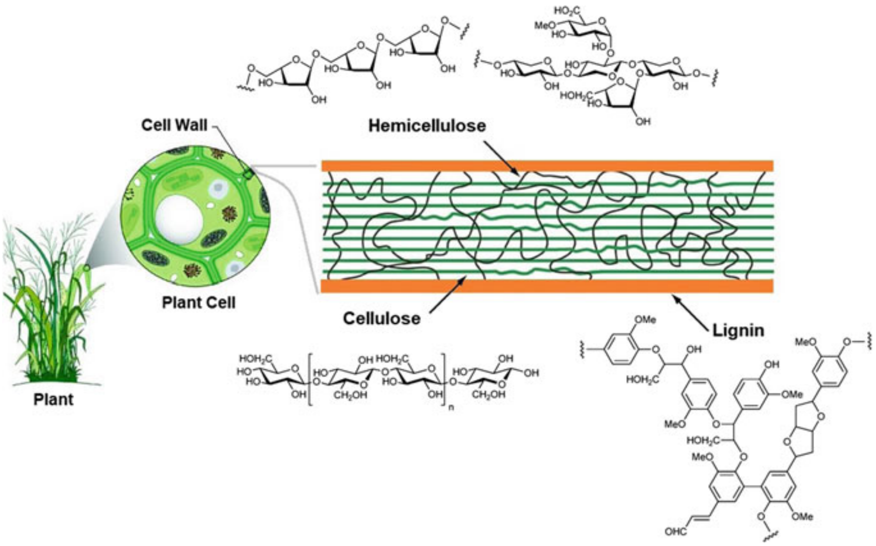

Fig. 4.1 Structure of Lignocellulosic Biomass

in smaller amounts which are soluble and assimilates such as sugars, nitrogenous materials, waxes, chlorophyll and ash (Sticklen 2008). The lignocellulosic biomass structure of a plant is given in the Fig. 4.1.

Cellulose is a linear polymer made of D-glucose subunits connected to each other by α-(1,4)-glycosidic linkage which constitutes to its organized fibrous structure. Cellobiose is the repeating unit that is established throughout this linkage. These long polymeric chains are held together, packed into microfibrils by hydrogen bonding and van der Waals forces. Hemicelluloses and lignin cover the microfibrils, thereby adding additional strength for the plant. The cellulose in biomass is predominantly crystalline with a small proportion of amorphous cellulose due to unorganized chains forms. The main feature of hemicellulose is its short lateral chains and branches which are mostly different sugars. These sugars include xylose, rhamnose, arabinose, glucose, mannose, galactose, and uronic acids like 4-omethyl glucuronic, D-glucuronic, and D-galactouronic acids (Zhou et al. 2017). Hemicellulose consists of either a homo or heteropolymeric chain with short monosaccaride branches majorly by α-(1,4)-glycosidic linkage like cellulose and intermittently by α-(1,3)-glycosidic linkages. Lignin is a complex cross-linked polymer with large molecular structure containing three phenyl propionic alcohols namely: coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol as monomers. These phenolic monomers are linked together by alkyl-aryl, alkyl-alkyl, and aryl-aryl ether bonds (Bajpai 2016). Extractives include a variety of organic compounds such as simple sugars, starches, proteins, and fats, simple to complex phenolics, alkaloids, glycosides, saponins, pectins, terpenes, mucilages, gums, waxes, resins and essential oils. Many of these are tree metabolites and intermediates act as energy alternatives, or used to defend the tree from insects and microbes. These compounds also contribute to wood's color, odor, durability and resistance to decay against moisture and other environmental conditions. Ash is the solid residue that remains after complete combustion composed of mostly metal carbonates and oxides. Wood from temperate zones have 1% ash and slightly higher in species from tropical climatic conditions (Pettersen 1984).

The chemical composition of one plant species varies from another. It is evident that woody species have higher amounts of cellulose, and hemicellulose, whereas grassy species like straw, husk and leaves have more extractives and ash (Table 4.2). In addition, these constituents vary from plant as a whole and within based on age, stage of growth, climatic conditions etc. *Eculalyptus globulus* species from Portugal is taken as an example to explain the above phenomena in Table 4.3.

This chapter covers mainly on woody biomass which has several advantages on the others. Also with little CO_2 emissions, less heavy metals and sulphur in the meager ash produced, the possibility of utilization of wood as low cost alternative fuel is studied. The energy intensification and thermal conversion of wood are also compared to other herbaceous and agricultural residues.

Table 4.2 Chemical composition of various lignocellulosic biomass types

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	Ash (%)	References
Hard wood						
Alder	45.5	20.6	23.2	9.8	0.7	Taherzadeh et al. (1997)
Aspen	52.7	21.7	19.5	5.7	0.3	
Willow	41.7	16.7	29.3	9.7	2.5	
Softwood						
Pine	46.9	20.3	27.3	5.1	0.3	Rabemanolontsoa and Saka (2013)
Spruce	45.6	20.0	28.2	5.9	0.3	
Japanese cedar	45	22	30	2.6	0.5	
Agricultural/herbaceous crop residue						
Rice straw	37	16.5	13.6	13.1	19.8	Rabemanolontsoa and Saka (2013)
Rice husk	37	23.4	24.8	3.2	17.3	
Corn cob	34.6	15.2	18.2	10.6	3.5	
Corn leaves	26.9	13.3	15.2	22	10.9	
Miscanthus	34.3	25.2	22.8	11.9	5.5	

Table 4.3 Chemical composition of *Eculalyptus globulus* wood at different conditions

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	Ash (%)	References
Age						
2 years	50.0	18.6	26.9	4.2	0.8	Miranda and Pereira (2007)
3 years	40.2	18.0	28.6	7.9	1.7	
6 years	43.8	18.9	27.3	4.2	0.6	
Height/position of sampling						
Bole wood	53.7	20.82	22.2	2.9	0.38	Pereira (1988)
Bole bark	51.5	19.89	20.2	6.3	2.11	
Top wood	52.3	19.34	24.8	2.8	0.76	
Branches (<1 cm)	41.2	18.77	21.8	16.7	1.53	
Climatic conditions (composition of Bole wood)						
Altitude (m): 500–550 rainfall (mm): 1273.0 Air Temp (°C): 13	53.7	20.82	22.2	2.9	0.38	
Altitude (m): 300 Rainfall (mm): 710.7 Air Temp (°C): 15.6	50.1	19.25	22.3	8.0	0.35	Pereira (1988)
Altitude (m): 150 Rainfall (mm): 882.9 Air Temp (°C): 15.2	58.2	10.81	24.9	5.6	0.49	

4.4 Biomass Conversion

Over 50% of all wood in the world is used as firewood especially. In developing countries, wood is the primary energy source and it makes up about 80% of the energy utilized for day to day purpose. Hence a fast, cost effective and economic energy intensification and conversion of biomass is needed. The two pathways by which biomass can be transformed into useful product are thermochemical and biochemical processes.

4.5 Thermochemical Conversion Techniques

4.5.1 Combustion

Combustion is the chemical process by which biomass is burned directly in the presence of air to transform the stored chemical energy into heat, mechanical, or electric power with evolution of hot gases (CO, CO_2, NO_x, SO_x) at a temperature range 800–1000 °C. Combustion can be experienced in domestic stoves for cooking; furnaces for metallurgical applications; boilers, steam turbines, and turbo-generators for energy production. The moisture content plays a significant role during combustion of biomass and it must not exceed 50% for the process to be feasible (McKendry 2002). Normally biomass do not arise in an acceptable form of combustion; hence it requires some simple operations like chopping, drying, grinding, etc., that contribute to some additional costs increasing the total energy expenditure.

Inorganic constituents such as alkali chlorides, sulphates, carbonates and silicates in the biomass react among each other and contribute to most of the problems such as fouling and slagging. The exact chemistry and mechanism behind fouling and ash slagging is yet to be fully developed. Some combustion studies showed an increase in the fusion temperature of the ash by elimination of alkali and other elements in the biomass using pre-treatment techniques (Jenkins et al. 1998). There are many power plants that operate mixed biomass and coal feedstock, which tends to reduce net CO_2 emissions. Few studies have also been done successfully on using the oxygenated compounds from combustion of lignocellulosic biomass and use it to run a compression ignition engine (Baumgardner et al. 2015).

4.5.2 Gasification

Gasification is the conversion of biomass into a mixture of low calorific value combustible gases of energy 4–6 MJ/Nm^3 by means of partial oxidation process at high temperatures from 800 to 900 °C. It is carried out at with limited oxygen supply and the gas produced can be burnt directly, or be used as a fuel for gas compression ignition engines and gas turbines. It is a most favorable route to generate producer gas with specified composition to produce fine chemicals like methanol.

There are four types of gas-solid gasifiers namely: Fixed bed, Moving bed, Fluidized bed and Entrained-flow bed. They were established primarily for coal gasification, but with advancement it is also used for gasification of lignocellulosic biomass with slight modifications (Zhou et al. 2009). The choice of gasifier is determined by various factors including the energy density, chemical composition, and other attributes of biomass feedstock, thus to attain desired form of the energy. The fixed and moving bed gasifiers generate huge volumes of tar and char, which is owing to the improper heat and mass transfer between solid biomass and the gasifying agent.

This is overcome in fluidized bed gasifier with enhanced reaction rate by using effective heat transfer medium and good quality catalysts (Alauddin et al. 2010). In the future, small gasifier plants may evolve into large scale units co-gasifying biomass with coal or with any other solid fuel to meet the growing energy demand.

4.5.3 Pyrolysis

Biomass pyrolysis is well-defined phenomenon involving thermal decomposition of the biomass into liquid bio-oil, solid biochar, and non-condensable gas products in the absence of oxygen. It can be classified into three main subcategories namely: slow, fast and flash pyrolysis depending on the heating rate and residence time (Mohan et al. 2006). Slow pyrolysis involves heating of biomass relatively at low temperatures from 300 to 700 °C for long residence time that ranges from hours to days. This type of pyrolysis has been conventionally applied in production of low grade fuel like charcoal. Fast pyrolysis involves a higher heating rate of 140–200 °C/s with typically very short residence time of 0.5 to 10 s (Demirbas and Arin 2002). The flash pyrolysis is characterized by a higher heating rate of 103–104 °C/s but with short residence time of 0–0.5 s (Amutio et al. 2012). Fast pyrolysis results in biooil yield of 50–70 wt% while flash pyrolysis can achieve biooil yield as high as 75–80 wt%.

4.5.4 Carbonization

The process of heating biomass under an inert or low-oxygen atmosphere to drive out the moisture and volatile matter present in it is called carbonization. This leads to a final product with increased relative carbon percentage and calorific value to that of the raw biomass. It is a very slow process which could take weeks for the whole carbonization process to end. Under these conditions with appropriate residence time, a normal dry wood would result in a charcoal with roughly double the calorific value with 75% weight loss (Meyer et al. 2011).

4.5.5 Hydrothermal Conversion

Hydrothermal Conversion involves thermal depolymerisation of biomass in the presence of subcritical or supercritical water at high temperatures and pressures. Water breaks the macromolecules by acting as a catalyst and as an excellent reaction environment (hydrothermal media) with higher ionic products favoring reactions that are typically by acid catalyzed or base catalyzed in subcritical conditions (Kruse et al. 2013). In general, hydrothermal conversion processes are categorized into three distinct processes namely: (i) Hydrothermal Carbonization, (ii) Hydrothermal Liquefaction and (iii) Hydrothermal Gasification depending on the severity of the process conditions.

Hydrothermal carbonization of biomass takes place at temperatures below 247 °C in subcritical water. This process overtakes the natural coalification process, where peat is formed in several hundred years, coal in million years, while biochar that has properties equivalent to brown coal in maximum 12 h (Ramke et al. 2009). The main product is biochar which is also called hydro char and it has similar properties to that of a low rank coal. Hydrothermal liquefaction is characterized by hydrolysis followed by de-polymerization of macromolecules at an intermediate temperature ranges between 247 and 374 °C, resulting in smaller molecules. Dehydration or decarboxylation induced by subcritical water reduces a significant part of the oxygen as alcohols and esters. The produced liquid product (biocrude or biooil) consists of small unstable reactive molecules and in most of the cases they re-polymerize resulting in larger tar like compounds. The chemical composition and properties of biooil purely depend on the composition of the biomass substrate (Toor et al. 2011). By increasing the temperature above 374 °C induces gasification reactions and this result in the synthesis of a higher fuel gas mixtures and low biooil. Even wet biomass and organic wastes can be efficiently transformed into hydrogen rich fuel gas under suitable hydrothermal conditions (Schmieder et al. 2000).

4.6 Valorization of Woody Lignocellulosic Biomass in Hydrothermal Media

Woody lignocellulosic biomass has a large potential and acts a permanent source for the value added chemicals through hydrothermal conversion technique. Among the three, hydrothermal liquefaction produces comparatively large quantity of biooil, which is the starting point of the value addition chain. The process parameters that have a significant influence on conversion of biomass to biooil are feedstock composition, temperature, heating rate, pressure, solvent, residence time, and catalyst. This chapter enlightens the readers on the woody biomass conversion and all the major factors that affect the production of the biooil.

4.6.1 Effect of Feedstock

Lignocellulosic biomasses are majorly composed of constituents such as cellulose, hemicellulose and lignin that influence the yield and quality of the oil formed during the hydrothermal conversion process. Due to different structure and properties each one acts different in the hydrothermal environment and depolymerizes in a specific manner.

Conversion of Cellulose. Hydrothermal conversion of cellulose happens along numerous reaction pathways during thermal depolymerisation process. It involved hydrolysis followed by Lorby de Bruyn-Alberda van Ekenstein transformation to break bulk molecules into small fractions. The interaction of molecules in the hydrothermal treatment were different during alkaline and acidic environments, where the alkaline environment led to further retro aldol transformation, rearrangement of aldehydes, hydration, dehydration to form simpler acid and alcohols, and acidic environment resulted in major portion of 5-(Hydroxy methyl) furfural (5-HMF) and its acid derivatives (Yin and Tan 2012). Baccile et al. (2009) study confirmed using ^{13}C solid-state CP-MAS NMR, even when cellulose were taken from various sources like starch, sucrose, maltose and glucose, the 65% of the solid hydrothermal carbon materials resulted in formation of HMF ring structure. The yield of biooil in acidic environment was 3 times higher than in the alkaline environment. Under neutral conditions, some of the short chain acid and aldehyde components also decomposed into gases and HMF polymerized into residual solids reducing the bio-oil yields significantly (Chuntanapum et al. 2008).

Conversion of hemicellulose. Hemicelluloses constitute to 20–40% of plant biomass. Hemicellulose with its simple structure and abundant side-groups are easily soluble and hydrolyzed both in acidic and alkaline subcritical conditions at 180 °C (Delmer and Amor 1995; Bobleter 1994). Mok and Antal (1992) investigated on various woody and herbaceous biomass materials and found that the entire hemicellulose was hydrolyzed in 2 min at 230 °C and 34.5 MPa. During rapid heating of the biomass at these conditions, hemicellulose is selectively decomposed as saccharides, following similar pathway as cellulose in the same environment. Sasaki et al. (2003) experiments on subcritical and supercritical water extraction of D-xylose resulted in glycolaldehyde, glyceraldehyde and dihydroxyacetone thorough retro-aldol condensation and dehydration at 360–420 °C, 25–40 MPa and 0.02–1 s.

Conversion of lignin. Lignin has a complex structure constituting primary building blocks as p-hydroxy phenyl propanoids namely coumaryl alcohol, coniferyl alcohol and sinapyl alcohol that are held together by C–C or C–O–C bonds. Compared to cellulose and hemicellulose, it is relatively more resistant to both chemical and enzymatic degradation and yet, during hydrothermal degradation under alkaline conditions, hydrolysis of C–O–C bonds result in various phenols and methoxy phenols, leaving the benzene ring. During the lignin hydrolysis and degradation, there is a significant production of solid residue due to the condensation of the phenolic products. Thus the feedstock must be selected in such a way that the balanced lignin content is carefully maintained. The hydrothermal breakdown of pure lignin at temperatures more than 350 °C was examined by Kanetake et al. (2007) resulting in products: catechols, phenols, and cresols, confirming the occurrence of 2° hydrolysis of methoxy groups. Similar results were obtained for Kraft pine with major products: phenol, 4-ethylguaiacol and methyl dehydroabietate (Zhang et al. 2007). The hydrothermal degradation yielded 58–78% of liquid products not as an oil-phase, but in the water phase as dissolved organics. Karagöz et al. (Karagöz et al. 2005) investigated on commercial lignin at 280 °C and also obtained phenolic compounds 2-methoxy-phenol, 1,2-benzenediol, 4-methyl-1,2-benzenediol, 3-methyl-1,2-benzenediol and phenol.

Liu et al. (2006) studied on hydrothermal conversion of walnut shell that contains about 53.5% lignin at reaction temperatures of 200–300 °C in both acid and alkaline conditions. During hydrothermal degradation in alkaline conditions, several phenol derivatives were obtained which confirms the hydrolysis of both the lignin and the resulting methoxy groups. The biooil yield varies with respect to the percentage of these three constituents in the biomass as shown in Table 4.4.

4.6.2 *Effect of Temperature*

Temperature plays a key role in the operation of hydrothermal processing of all biomasses. The temperature that ranges between 250–320 °C generally supports the conversion depending on the type of feed stock (Table 4.4). Under such elevated temperatures, hydrothermal conversion shows symbiotic effect in the yield of value-added products from organic feedstock. The increased temperature depolymerizes complex organic molecule present in the feed stocks which intern produces the fine chemicals. Such conditions not only upsurge the reaction rate but also create variations in reaction mechanisms. From literatures it is understood that when operating temperature is elevated beyond the activation energy, depolymerization reaction occurs which results in dissociation of complex bonds (Kruse et al. 2013; Dimitriadis and Bezergianni 2017; Sudasinghe et al. 2014). C. Zhong et al. explained the effect of temperature and impact of lignin composition had placed a remarkable on the yield of bio-oil under non catalytic condition on wood varieties like *Cunnighamia lanceolate*, *F. mandshurica, P. tomentosa Carr*. and *P. massoniana Lamb* (Zhong and Wei 2004). Tar that is formed during the process is the impact of temperature under subcritical condition and it extremely stifled under supercritical condition. The two reasons are possible for the stifled change, (1) truncated dielectric constant which leads to free-radical reactions leaving away gaseous products, (2) under supercritical region tarry material behaves like a solvent (Promdej et al. 2010). The hydrothermal liquefaction performed on Spruce wood at temperatures from 250 to 300 °C, the yield of bio-oil increases slightly from 3.9 wt% to 6.6 wt%. But beyond 300–350 °C, the yield progressively decreases to 4.9 wt% because of bio-oil vaporization at these temperature ranges. Thus it is clear that high temperatures favors the radical formation that occurs generally in sub-critical water while the lower temperature induces the ionic reactions (Watanabe et al. 2004).

4.6.3 *Effect of Hydrothermal Media*

The hydrothermal media in general called as solvents enhance the stability and solubility of the depolymerized macromolecules. They enhance the fragmentation of the complex structures in the biomass. The mass ratio of solvent to feed has to be maintained in such a way that it should not promote gasification of all residual material in the reactor. Some studies show that when a portion of water replaced with compounds like ethanol, methanol, acetone, 2-propanol, they act as a tarry material enhancing the ionic product of the mixture yielding higher biooil as shown in Table 4.4.

Table 4.4 Reaction parameters and their biooil yield of different wood species

Feed stock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Temperature range (°C)	Hydrothermal media	Yield without catalyst (%)	Catalyst	Yield in the presence of catalyst (%)	References
Oak wood	38.1	23	32	260–320	Water	27% bio-oil yield at 320 °C	Fe	29.35% bio-oil yield (water as solvent) at 280 °C	de Caprariis et al. (2019)
Common reed	43.3	29.6	27.1	250–290	EtOH, MeOH	53.6 and 38.7% bio-liquid yield at 290 °C	10 wt% NaOH	57.6 and 44.2% bio-liquid yield at 290 °C	Küçük and Ağırtaş (1999)
Pine sawdust	45.3	22.5	26.8	180–280	Water	Maximum total oil yield of 8.5% at 280 °C	K_2CO_3	Maximum total oil yield of 33.7% at 280 °C	Karagöz et al. (2006)
Pine sawdust	45.3	22.5	26.8	200–350	50% aqueous EtOH, MeOH	65% bio-oil yield	–	–	Cheng et al. (2010)
Rice straw	41.1	23.8	19.5	260–300	EtOH-water, 2-propanol-water	38.35% and 39.7% bio-liquid yield at 300 °C	–	–	Yuan et al. (2007)

(continued)

Table 4.4 (continued)

Feed stock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Temperature range (°C)	Hydrothermal media	Yield without catalyst (%)	Catalyst	Yield in the presence of catalyst (%)	References
Beech wood	47.7	21.4	25.5	300	Water	14% bio-oil yield	6 wt% NaOH	28% bio-oil yield	Haarlemmer et al. (2016)
Spruce wood	45.6	20	28.2	250–300	Water	6.6% bio-oil yield at 300 °C (water)	KF/Al_2O_3	13.9% bio-oil yield at 300 °C	Alper et al. (2019)
Corncob	38.8	33	13.1	300–360	Water, EtOH	38.6% and 38.8% bio-liquid yield at 340 °C	NaOH, KOH	56.4% and 57.5% at 10% alkali to sample ratio at 340 °C respectively.	Khampuang et al. (2015)
Grape seeds	32.7	37.6	24.9	300	Water, supercritical EtOH	18.7% and 46.33% bio-oil yield at 300 °C	$MgCl_2$, $TiCl_4$	17.47% and 50.69% bio-oil yield at 300 °C	Hao et al. (2019)
Cotton cocoon shell	32.6	10.2	48.7	235–300	Acetone, water	35.6 and 69.1% bio-liquid yield at 235 °C	NaOH, Na_2CO_3, KOH, K_2CO_3	80.2, 66.5, 86.2, 68.7% at 100% alkali to sample ratio at 300 °C respectively	Çağlar and Demirbaş (2001)

4.6.4 Effect of Catalyst

Although water as a catalyst during the sub critical or super critical hydrothermal processes, the products formed are mostly oxygenated. Thus to reduce this it requires addition of one more catalyst into the system. In hydrothermal processes, addition of catalyst improvise the gasification efficiency, reduces tar and char by suppressing the repolymerization reactions of unstable molecules. Alkali hydroxides and salts have been frequently used as homogeneous catalysts, whereas Ni, Mn, Fe, Ti were used as heterogeneous catalysts but less frequently utilized in biomass liquefaction process. Heterogeneous catalysts are meant to promote low-temperature water gasification in biomass.

Homogeneous catalysts. Mostly alkali salts have a positive effect on deconstruction of macromolecules of woody biomass. Homogeneous catalyst improves gasification by speeding up the water gas shift reaction and also resulting in increases yield of liquid products. Addition of these catalysts raises the pH making the mixture more alkaline, thereby inhibiting dehydration of the cellulose, hemicellulose and lignin present in the biomass. Alkali has a high ability to suppress char and tar during the process. It also prevents a high degree oxidation of the biooil instead of decarboxylation that might be leading to the formation of unstable unsaturated compounds and in turn polymerize into char or tar.

Küçük and Ağırtaş (1999) conducted the hydrothermal liquefaction of common reed (Prangmites australis) with and without catalyst in sub critical water environment. It was concluded that with 10 wt% of NaOH the biooil yield by 4% at 290 °C. In another study, Haarlemmer et al. (2016) investigated the addition of 6 wt% of NaOH and the liquefaction of beech wood found to have increased the biooil yield from 14 to 28% at 300 °C. Similarly, hydrothermal treatment on pinewood biomass in the presence of alkali especially potassium as K_2CO_3 at 280 °C for 15 min showed a progressive effect on yield of biooil (Karagöz et al. 2006).

The percentage addition of alkali varies from one feedstock to other depending upon the constituents present in it. In another study, it was observed that hydroxides and carbonates of potassium were more effective than that of sodium. The catalytic effect according the chemical activity of alkaline homogeneous catalysts was ranked in the order as follows: $KOH > NaOH > K_2CO_3 > Na_2CO_3$ (Khampuang et al. 2015; Çağlar and Demirbaş 2001). The alkali catalysts have the tendency to promote water gas shift reaction during hydrothermal liquefaction, thus favoring H_2 and CO_2 formation from CO. The hydrogen gas produced during the process in turn acts as the reducing agent improving quality of the biooil and its heating value (HHV).

Heterogeneous catalysts. They have been typically used in hydrothermal gasification processes and low temperature applications in enhancing the quality of biooil obtained. There are few cases where it was used for hydrothermal liquefaction. Gasification is also crucial to a certain extent during liquefaction process for deoxygenation, when the biooil had higher percentages of oxygenated compounds. de Caprariis et al. (2019) investigated on addition of Fe as a catalyst for hydrothermal liquefaction of oak wood and revealed that it acted as a sacrificial catalyst by oxidation into Fe_2O_3, thereby reducing the acids and aldehydes from macromolecules and enhancing the quality and quantity of biooil. In another study, by doping oxides like Al_2O_3 with active substance KF and using it as a catalyst, the yield of the biooil increased from 6.6 to 13.9% at 300 °C (Alper et al. 2019). However, extensive gasification has a negative impact on the yield of bio-oil. Other heterogeneous catalysts that have been reported to be used hydrothermal processing include Ni and Ru doped over Al_2O_3, TiO_2 and ZrO_2 (Grilc et al. 2016).

4.7 Essential Chemicals Obtained from Hydrothermal Conversion

The prime objective of the hydrothermal processing of biomass is to derive value added chemicals out of cheap raw materials and residues. Many researchers, through Gas Chromatography and Mass spectrometry have confirmed the presence of various fine chemicals in the biooil obtained from hydrothermal processing. Some of the chemicals identified in biooil resulting from the hydrothermal liquefaction of cellulose, barley straw and walnut shell and their commercial significance are listed in the Table 4.5.

4.8 Conclusion

The hydrothermal processing of lignocellulosic biomass is simple compared to other biomass feedstock owing to their complexities in structure and absence of predefined reaction mechanisms. This chapter discussed briefly about the future technologies that need to be adapted for generation of fine chemicals. In the event of complete depletion of the fossil fuels, the hydrothermal technologies would be a promising alternate solution as it does not need large modification of industrial infrastructure. At present studies are being carried out and more emphasis is given in production of selective value added chemicals that have a high commercial significance. In energy sector, the biooil or the biocrude can be mixed with the natural crude, so that no need of retrofitting the entire refinery. Thus lignocellulosic biomass has a huge potential in the field of bio refinery and is yet to be tapped at a larger extent.

Table 4.5 Essential Chemicals

S. no.	Compounds	Significance
1.	Phosphonic acid	Manufacturing of phosphate salts
2.	L-Methyltartronic acid	Production of mesoialic acid and hydroxy dicarboxylic acid
3.	4-Penten-2-ol, 2-methyl	Paper industries as an additive
4.	2-Cyclopenten-1-one, 2,3-dimethyl	Anti-constipation agent and treating gastrointestinal disorder
5.	3-Pentanol; 1-Pentanone,1-(2-furanyl)-	Alternate to gasoline
6.	3,4-Dimethyl-5-hexen-3-ol	Curing agent for epoxy resin
7.	2-Cyclopenten-1-one, 2,3,4-trimethyl-	Drug delivery agent, cosmetics, treatment of ion Exchange resins
8.	3-Pentanol, 3-ethyl-	Solvent for coating CD’s and DVD’s
9.	Phenol, 2-methoxy-	Household cleaners and mouthwashes
10.	Benzene, 1,2-dimethoxy-	Making resins, rugs, rubber lubricants, etc.
11.	1,2-Benzenediol	Oxidant in electroplating bath
12.	4-Ethylcatechol	Antibiotics, manufacture of protein kinase inhibitors
13.	Vanillin	Food flavoring, fragrances in beverages, ice-creams etc.
14.	Acetophenone, 4’-hydroxy-	Perfumes
15.	Ethanone, 1-(2,3-dihydroxy-4-methoxyphenyl)-	Odors reagents, enzyme modeling in inflammatory mediators produced by immune cells
16.	Ethanone, 1-(4-dihydroxy-3,5-dimethoxyphenyl)-	Odors reagents
17.	Eicosanoic acid	Hair care products
18.	Octadecanoic acids	Soaps, softening plastics
19.	Glycol	Antifreeze in automobile radiators
20.	Lactic acid	Food preservations ingredients
21.	Phenol	Disinfectant in cleaner liquids
22.	o-Cresol	Produce pesticide, MCPA phenoxy herbicide, etc.
23.	p-Cresol	Make phenol-formaldehyde resins
24.	Butanoic acid, 2-hydroxy-	Food and perfume
25.	Glycerol	Humectant, solvent and sweetener
26.	Catechol	Precursor to fine chemicals
27.	3,5-dihydroxytolune	Production of dye, as reagent in chemical tests.

(continued)

Table 4.5 (continued)

S. no.	Compounds	Significance
28.	Dodecanoic acid	Medicinal field for treating HIV, yeast infection, chlamydia and ringworm
29.	2-heptadecanone	Flavouring agent
30.	11-cis-Octadecenoic acid	Drug delivery, vitamin formulations
31.	9-Oleic acid	Agent to damage lung artificially in animals for testing in laboratories
32.	Fluorene	Dyes, pesticides, plastics, etc.
33.	Acetic acid	Disinfectant, preservation of pickles, etc.
34.	Homovanillyl alcohol	Treat diarrhoea
35.	1,2-Benzendiol, 3-methoxy-	Oxidant in electroplating bath and rubber lubricant
36.	Pentenoic acid, 4-oxo-	Vaccine to inhibit fatty acid oxidation in rat heart mitochondria

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