

# Hydrothermal Conversion of Biomass into Fuel and Fine Chemicals



Chitra Devi Venkatachalam, Mothil Sengottian,  
and Sathish Raam Ravichandran

## Contents

1	Introduction .....	202
2	Hydrothermal Conversion .....	205
2.1	Hydrothermal Carbonization .....	206
2.2	Hydrothermal Liquefaction .....	206
2.3	Hydrothermal Gasification .....	207
2.4	Conversion Chemistry .....	207
3	Hydrothermal Conversion Process Conditions .....	209
3.1	Effect of Temperature .....	210
3.2	Effect of Hydrothermal Media .....	213
3.3	Effect of Biomass to Solvent Ratio .....	213
3.4	Effect of Catalyst .....	215
4	Biomass to Fuel .....	216
5	Biomass to Fine Chemicals .....	221
6	Conclusion .....	221
	References .....	221

**Abstract** Hydrothermal conversion is an important thermochemical conversion technique that is used to convert waste biomass into valuable products or biofuel. The process is usually performed in the presence of water at high temperature and high pressures. The biomass is depolymerized to form three phases such as biocrude, biogas, and biocarbon into small components in water. Based on the process conditions (temperature, pressure, catalyst, and time), the yield of the phases varies accordingly. Comparing to other thermochemical conversion techniques like combustion, pyrolysis, and gasification, the hydrothermal conversion is highly appropriate for handling biomass with high moisture content. According to the physicochemical properties of water, the process can be classified as hydrothermal

---

C. D. Venkatachalam (✉), M. Sengottian, and S. R. Ravichandran  
Kongu Engineering College, Erode, Tamil Nadu, India  
e-mail: [erchitrasuresh@gmail.com](mailto:erchitrasuresh@gmail.com)

Manuel Jerold, Santhiagu Arockiasamy, and Velmurugan Sivasubramanian (eds.),  
*Bioprocess Engineering for Bioremediation: Valorization and Management  
Techniques*, Hdb Env Chem (2020) 104: 201–224, DOI 10.1007/698\_2020\_583,  
© Springer Nature Switzerland AG 2020, Published online: 8 July 2020

201

carbonization, hydrothermal liquefaction (at subcritical conditions  $T$ , 250–374°C, and  $P$ , 4–22 MPa), and hydrothermal gasification (at supercritical conditions  $T > 374^\circ\text{C}$  and  $P > 22$  MPa). There has been significant research reported on the hydrothermal conversion of lignocellulosic biomasses, algal biomasses, and also co-utilization of these two with other waste materials. The interaction of water with the biomass results in formation of various chemicals like acids, alcohols, cyclic ketones, phenols, and methoxyphenols and more condensed structures like naphthols and benzofurans. This chapter focuses on the influence of the process parameters and types of biomass utilized on the hydrothermal conversion of biomass. Additionally, the use of biomass as not only an energy source but also as a viable source for value-added chemicals is discussed.

**Keywords** Biocrude, Biomass, Fine chemicals, Hydrothermal conversion

## 1 Introduction

Energy Alternatives India (EAI) estimates 450–500 million tons of biomass is produced from various sources in that 31.2% of it is highly utilized for production of bioenergy [1]. Bioenergy is one of the key renewable resources taken from different sources that is awfully heterogeneous. Bioenergy is the most suitable form of alternate energy that is derived from biological substances rich in organic substance – biomasses. For each generation of feedstock, the compositions vary broadly and are tedious to classify as most biomasses are wastes of various biochemical processes and are heterogeneous. The first-generation feedstocks are edible crops like sugarcane, palm oil, and rapeseed that were used for thermochemical conversion [2], whereas second-generation feedstocks are nonedible crops of lignocellulosic biomass like wood, straw, etc., used to avoid the shortage of food compared to first-generation feedstock [3]. In both generations, the plants or crops fix carbon through photosynthesis in the form of carbohydrates. When processed, they leave out carbon dioxide ( $\text{CO}_2$ ), and thus the vent gas can be recycled by other plant. In the past few years, the third-generation feedstocks, i.e., algal biomasses, emerges loudly and attract the researchers than the first- and second-generation feedstocks [4]. They can be broadly classified into microalgae and macroalgae based on its size, and like plants, algae store energy in the form of carbon-rich lipids through photosynthesis.

In a crude point, the various classifications of biomass based on their primary source are given in Table 1.

The two major categories of biomass that are going to be discussed are lignocellulosic and algal biomass. The lignocellulosic plants belong to the division Spermatophyta of the subkingdom Phanerogame in the kingdom Plantae where the

**Table 1** Biomass classification based on the source

Source	Type	Example
Forest	Forestry plantations from natural forests and woodlands	Wooden blocks, logs and sticks
	Forestry by-products	Wood chips; tree branches from thinning; bark
Agricultural wastes	Plants and agricultural residue	Cane trash; stover, straw, hay from small grains; cobs (corn, maize); stalk (cotton, jute, hemp, flax, kenaf); shells (almond, pistachio, walnut, pecan, macadamia, Brazil nut, hazelnut, peanut, olive); pith(coconut, palm, date, peach, <i>Sabal</i> ); seed burs, pods, leaves, and roots
	Shrubs and herbaceous green residue	Garden wastes, shrubs, creepers, reeds, grasses (switch, canary, and Coastal Bermuda)
	Livestock waste	Animal waste (cattle, goat, sheep, pigs) and poultry
	Others	Weeds and aquatic plants
Algae	Fresh water and marine	Green algae (Chlorophyceae, Charophyceae, Micromonadophyceae, Pleurostrophyceae); brown algae (Phaeophyceae); dinoflagellates (Dinophyceae); diatoms (Cryptophyceae); red algae (Rhodellophyceae, Compsopogonophyceae); euglenoids (Euglenophyceae)
Industry	Wood and lumber industry residues	Waste wood residue from timber mills and saw mills (barks, chips, offcuts, and sawdust);
	Food industry residues	Sugarcane bagasse; starch residue (potatoes, yam, cassava, sugar beet, tapioca, sweet sorghum); fruit peels; residues such as husks, hulls, and shells (barley, cereal, rice, wheat, maize, rye, and oil seeds like cottonseed, linseed, sunflower, rape-seed, etc.)
	Meat processing industry waste	Poultry houses and slaughterhouse wastes, wastes from dairies and fisheries
	Others	Winery wastes, distillery ethanolic wastes, paper industry wastes such as pulp, black liquor, and cellulosic sludge
Domestic	Organic waste	Food waste materials, kitchen-generated vegetable wastes and used cooking oil; sewage sludge
	Municipal waste	Food waste, plastics, paper, rubber, leather, wood, cardboard, cloth rags, and inerts

algae belong to the division Thallophyta of the subkingdom Cryptogamae in the kingdom Plantae. There are major differences in the structure and composition of both biomasses. For a terrestrial lignocellulosic plant, the cell wall is made of uniformly arranged layers of cellulose, hemicellulose, lignin, and pectin [5]. It also contains smaller amounts of proteins, soluble extractives, sugars, nitrogenous amino compounds, resins, waxes, oils, chlorophyll, and ash [6]. While the main

composition of algae is proteins, carbohydrates, and lipids, their percentage might vary even in a single alga depending upon the conditions of growth and age of the culture, and there are some algal species like *Coleochaete thallus* which even contains lignin as well in smaller percentages [7].

Cellulose is a polymer of D-glucose subunits linked by  $\alpha$ -(1,4)-glycosidic bonds throughout its length that forms the organized fibrous linear structure. These long fibrous polymeric chains are packed into bundles of microfibrils by hydrogen bonds and weak van der Waals bonds. These microfibrils are concealed by hemicelluloses and lignin, thereby adding additional strength to the cell wall. The hemicellulose is a heteropolymer made of short lateral chains and branches of sugars and polysaccharides linked by  $\alpha$ -(1,4)-glycosidic bonds like cellulose and occasionally by  $\alpha$ -(1,3)-glycosidic bonds. Xylose is the major sugar component, and it also includes arabinose, rhamnose, glucose, galactose, mannose, and other uronic acids like 4-O-methylglucuronic and D-glucuronic, and D-galacturonic acids [8]. Lignin has a complex cross-linked polymeric structure with large molecular weight which mainly constitutes coniferyl alcohol, p-coumaryl alcohol, and sinapyl phenyl propionic alcohols as monomers which are linked together by alkyl-alkyl, alkyl-aryl, and aryl-aryl ether bonds [9]. Extractives include some organic compounds like alkaloids, phenolics, glycosides, saponins, terpenes, pectins, waxes, gums, mucilages, resins, and oils. They act as plant's energy storage units and also as a defense against insects and microbes that take plants as food. They also contribute to the wood properties such as color, odor, and decay resistance. Ash is the inorganic final residue that remains after complete combustion of the biomass at a high temperature [10]. Proteins are made of one or more peptide chains with various percentages of amino acids, namely, lysine, cysteine, methionine, and tyrosine folded together into a solid or fibrous form. They act as the means of nitrogen storage for the algal cells which decreases as it grows with age [11]. Carbohydrates consist of starches and sugars that are formed as a result of energy absorbed by the chloroplasts and reduction of carbon dioxide into 3-phosphoglycerate in the presence of ribulose-1,5-bisphosphate carboxylase/oxygenase. They act as the structural part of the algal cell wall and provide energy needed for metabolism under dark conditions [12]. Lipids are long carbon chain molecules with carbon numbers 16–24 that consist of polar and neutral constituents of fatty esters, fatty acids, hydrocarbons, and triglycerides. They are formed in the inter-thylakoidal space of the chloroplast and stored inside the cytoplasm which serves as a structural component of the cell membrane. The increased lipid content in algae decreases the specific gravity, making the cells buoyant [13].

The chemical composition of the biomass varies from one plant species to another. The lignocellulosic and algal biomass compositions with their constituents of some of the feedstock are given in Tables 2 and 3, respectively.

The chemical energy stored in the biomass can be converted into energy and useful products by numerous ways. The two frequently and majorly used pathways are (a) thermochemical processes and (b) biochemical processes. Thermal conversion processes include combustion, gasification, pyrolysis, carbonization, and hydrothermal conversion techniques, while biochemical processes include anaerobic digestion, fermentation, transesterification, and biohydrogen production. Though

**Table 2** Lignocellulosic biomass feedstock composition

Category	Feedstock	Constituents (wt% in dry basis)		
		Cellulose	Hemicellulose	Lignin
Woody biomass	Pine wood	45.3	22.5	26.8
	Oak wood	38.1	23	32
	Spruce wood	45.6	20	28.2
Agricultural residue	Rice straw	41.1	23.8	19.5
	Common reed	43.3	29.6	27.1
	Corn cob	38.8	33	13.1
	Cotton cocoon shell	32.6	10.2	48.7

**Table 3** Algal biomass feedstock composition

Category	Feedstock	Constituents (wt% in dry basis)			
		Protein	Carbohydrate	Lipids	Others (ash and fibers)
Macroalgae	<i>Caulerpa serrulata</i>	14.48	45.6	4.24	27.66
	<i>Daviesia divaricata</i>	8.89	14.6	10.51	38.99
	<i>Padina tetrastromatica</i>	3.87	15.54	3.92	34.58
	<i>Turbinaria triquetra</i>	4.13	16.3	1.62	53.19
	<i>Sargassum subrepandum</i>	4.22	17.21	3.83	39.73
Microalgae	<i>Chaetoceros calcitrans</i>	34	6.0	16	44
	<i>Nannochloropsis oculata</i>	35	7.8	18	39.2
	<i>Dunaliella tertiolecta</i>	20	12.2	15	52.8
	<i>Chroomonas salina</i>	29	9.1	12	49.9
	<i>Isochrysis galbana</i>	29	12.9	23	35.1

there are many methods available, this chapter focuses on one of the fastest and cost-effective conversion methods, which is hydrothermal conversion.

## 2 Hydrothermal Conversion

The biomass is converted into biochar, biocrude, and biogas in the presence of subcritical or supercritical water at high temperatures and pressures. The three phases of water and various points can be identified from the phase diagram as given in Fig. 1. Water at subcritical conditions breaks the long chain macromolecules of the biomass into smaller fragments by acting as a catalyst due to its higher ionic product that favors acids or base-catalyzed reactions [14]. In general, hydrothermal conversion is further divided into three separate processes: (1) hydrothermal carbonization, (2) hydrothermal liquefaction, and (3) hydrothermal gasification depending on the severity of its operating conditions.

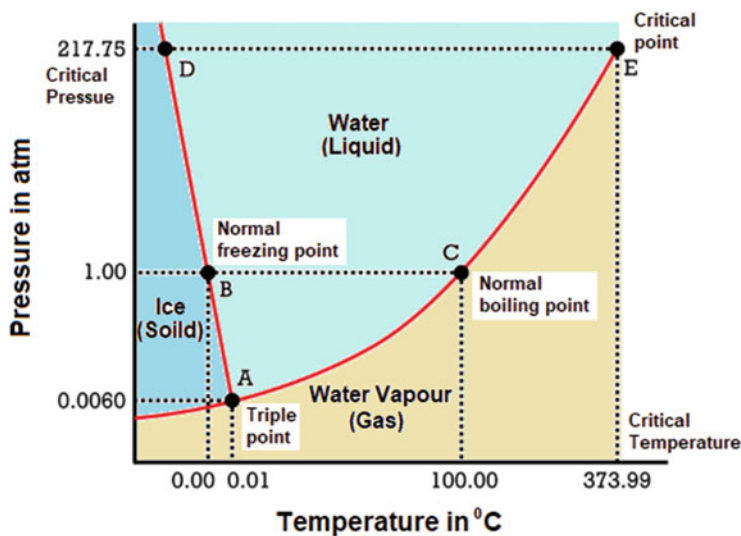


Fig. 1 Phase diagram for water

## 2.1 Hydrothermal Carbonization

This is a process in which the biomass is kept suspended in water at elevated operating temperature and pressure range of 180–350°C and 2–10 MPa, where high-potential solid chars of moderate calorific value are obtained. Generally, the process is exothermic since it utilizes the oxygen and hydrogen present in the raw material [15]. The reaction pressure is not actually controlled; rather presence of liquid in biomass helps to promote the pressure up to a maximum of 10 MPa [16]. Though the process is carried over at mild operating conditions, care should be taken in keeping the water under subcritical state. Sometimes the medium becomes alkaline due to the drop in pH, and this is because of the formation of by-products inside the reactor. The main advantage of HTC is handling of high moisture content feedstock; the solid char is highly sterilized (biologically) due to the thermal conversion, and energy incentive product is derived [17]. But still HTC was found to gain less interest among the researchers because of the datum that hydrochar possesses less energy-carrying space for solid products than liquefaction and gasification [18].

## 2.2 Hydrothermal Liquefaction

Biomass with higher percentage of moisture can be utilized for the liquefaction process. Unlike hydrothermal carbonization, liquefaction is carried out under lower temperature (250–450°C) and high pressure (4–20 MPa) in presence of water or

other organic solvents like hexane, methanol, acetic acid, acetone, etc. [19]. At this range the solvent behaves like a compressible fluid which generates high solvation environment, thus making the long chain hydrocarbons dissociate into the shorter chain [20]. A wide variety of raw feedstocks can be utilized for HTL conversion like lignocellulosic biomass, algal biomass, solid wastes that contain organic matters, etc. The primary product from HTL is the biocrude that should be further moved for upgradation. Along with the primary product, other by-products like hydrochar, aqueous, and biogas are produced. HTL finds its own place in attracting the research group because of its integrated characteristics of solvents like high ion product and low dielectric constant [21]. The major advantages of HTL than other thermochemical conversions are the following: effort for preconditioning of feed is not mandatory; it operates at moderate temperature; and heating rates can be slower than pyrolysis [22].

### ***2.3 Hydrothermal Gasification***

The other way of depolymerizing biomass is by hydrothermal gasification in which water reacts with biomass to produce gaseous hydrocarbon. Based on the operating conditions, they are classified into supercritical water gasification, near-critical water gasification, and low-temperature aqueous-phase reforming [23]. For low temperature HTG the sugar-like fructose or sugar alcohols like galactitol, sorbitol APR is considered as raw material. For high-temperature SCWG, raw materials like glucose, mannose, and fructose can be considered as good feedstocks [24]. To understand the background of HTG, the behaviors of solvents at high temperature and high pressure should be studied. The operating temperature for gasification ranges between 350 and 700°C which yields the gaseous products like H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> [25]. Unlike other hydrothermal conversions, HTG produces hydrocarbon gas that has high HHV and negligible percentage of tar that is considered as advantage over other hydrothermal processes.

### ***2.4 Conversion Chemistry***

It is necessary to understand the behavior and mechanism by which the lignocellulosic and algal biomass degrades in the subcritical and supercritical environment. In case of lignocellulosic biomass, the major constituents present are cellulose, hemicellulose, and lignin, which influence the yield and composition of the products formed. Likewise for algal biomass, the degradation of carbohydrates, proteins, and lipids is to be studied. Due to different structures and properties of the major constituents, the depolymerization reaction pathways are different in the hydrothermal environment as given in Fig. 2.

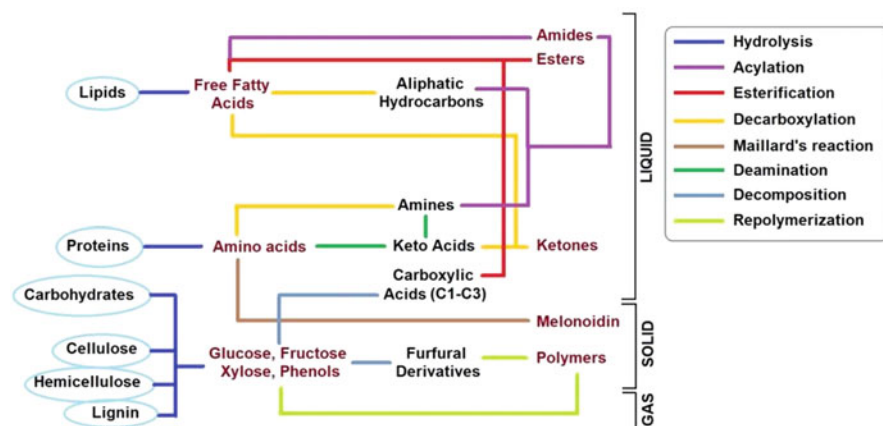


Fig. 2 Hydrothermal conversion reaction pathways

**Conversion of Cellulose** Hydrothermal depolymerization of cellulose involves several reaction pathways where linear bulk chain of molecules is fragmented into small fractions by hydrolysis and Lobry de Bruyn-Alberda van Ekenstein transformation. It was also observed that the molecular interaction was different in alkaline and acidic environments during the hydrothermal treatment. The alkaline environments led the products from hydrolysis to further degrade by retro-aldol transformation, followed by rearrangement of aldehydes, hydration, and dehydration into simpler acid and alcohols, while acidic environment resulted in the production of mostly 5-hydroxymethylfurfural (5-HMF) and its acid derivatives [26].

**Conversion of Hemicellulose** Hemicelluloses constitute about 20–40% of the total plant biomass, where during high pressure hot compressed water uncatalysed solvolysis on various wood and herbaceous biomass materials showed that 100% hemicellulose was hydrolyzed and selectively decomposed into saccharides at 230°C, 34.5 MPa at 200 reaction time of 2 min [27]. Sasaki et al. [28] experimented on D-xylose, which is a substitute compound for hemicellulose under subcritical and supercritical water extraction, which confirmed the same reaction pathway at lower temperatures. At higher temperatures and pressures of 360–420°C and 25–40 MPa with a time of 0.02–1 s, retro-aldol condensation and dehydration resulting in glycolaldehyde, glyceraldehyde, and dihydroxyacetone followed.

**Conversion of Lignin** Lignin consists of p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol units of p-hydroxy-phenylpropanoids held together by C-C or C-O-C bonds. Compared to cellulose and hemicellulose, lignin is relatively resistant to chemical or enzymatic degradation during hydrothermal conversion. In alkaline hydrolysis conditions of lignin, the C-O-C bonds result in phenols and methoxyphenols, where the condensation of these phenolic products resulted in significant amounts of solid residue.



Thus to reduce the solid residue and increase the yield of biocrude, the feedstock chosen must be in such a way that its lignin content is carefully balanced with cellulose and hemicellulose. The hydrothermal conversion of pure lignin at higher temperatures of 350°C, carried out by Wahyudiono et al. [29], resulted in products catechol, phenols, and cresols, which confirms the existence of secondary hydrolysis of methoxy groups. Similar results were found for hydrothermal conversion of Kraft pine resulting in major products as phenol, 4-ethylguaiaicol, and methyl dehydroabietate [30].

**Conversion of Carbohydrates** The carbohydrates in algae mainly constitute polysaccharides, celluloses, hemicelluloses, and starches. They are hydrolyzed to form simple sugars with glucose as the main product; the glucose is then rapidly converted to fructose which in turn degrades with fragmentation to form carbon-carbon double bond components like aldehydes and phenols which are intermediates, thus converting into gaseous products like H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, etc. [31].

**Conversion of Proteins** Proteins mostly consist of linear polymeric amino acids that are connected to carboxylic and amine group using C-N bond links. During the hydrothermal conversion process, these bonds get hydrolyzed to produce free amino acids which quickly undergo decarboxylation and deamination to produce hydrocarbons, amines, aldehydes, and acids [32].

**Conversion of Lipids** Lipids are mainly comprised of fatty acid triglycerides (TAG) which are nonpolar components with aliphatic characteristics. TAG is hydrolyzed to form fatty acids and glycerol, where glycerol readily gets converted into water-soluble components. Free fatty acids are pretty much stable but partially get converted into hydrocarbons via decarboxylation [33].

### 3 Hydrothermal Conversion Process Conditions

The hydrothermal conversion processes depend upon various parameters: temperature and heating rate, solvent or hydrothermal media, biomass to solvent loading, residence time, and catalysts. Once the reaction is over, the reaction products are taken out and filtered for the residual water. Then it is washed with extraction solvent to leach out the biocrude from the biochar, where the excess solvent is removed by vacuum evaporation. There are various methods by which the recovery of the products is calculated, and most widely used conventions are given below:

$$\text{Biocrude yield(wt\%)} = W_{es}/W_f \times 100 \quad (1)$$

$$\text{Biogas yield(wt\%)} = W_c - W_{rp}/W_c \times 100 \quad (2)$$

$$\text{Biochar yield(wt\%)} = W_r/W_f \times 100 \quad (3)$$

$$\text{Water Soluble Products yield(wt\%)} = 100 - (\text{Crude} + \text{Gas} + \text{Residue}) \quad (4)$$

where  $W_f$  is the weight of the biomass (dry basis);  $W_{es}$  is the weight of products soluble in extraction solvents (ether, acetone, acetone, dichloromethane, etc.);  $W_c$  is the charged weight (biomass + hydrothermal media);  $W_{rp}$  is the weight of reaction products; and  $W_r$  is the weight of solid residue, i.e., biochar.

Some of the woody and algal feedstock, their possible hydrothermal pathway, type of reactor and its specifications, hydrothermal media used, catalyst, and the extraction solvent used are listed Table 4.

### 3.1 Effect of Temperature

Temperature plays an important role in the hydrothermal processing irrespective of biomasses. The temperature for a typical hydrothermal conversion process ranges between 180 and 700°C, and it mainly depends on the type of feedstock and its constituent composition (Table 4). Under such given elevated temperatures, it shows symbiotic effect in the yield of resultant products (biocrude, and biochar) from the biomass. The increased temperature depolymerizes the long chain complex organic molecule of length 800–10,000 units into chemicals of  $C_{15+}$  to simple gases like  $H_2$ ,  $CH_4$ , and  $CO_2$ . Such conditions not only improved the reaction rate but also created variation in reaction mechanisms. Tungal and Shende [34] explained the effect of temperature on pine sawdust under carbonization and liquefaction conditions, where the biocrude yield increased from 24.04 to 30.5% at 1:10 biomass loading and 90 min reaction time [34]. The tar formed during the hydrothermal conversion process is due to the impact of temperature under the subcritical condition, and its formation is extremely lowered under supercritical conditions. The two reasons that controlled this reaction are (1) reduced dielectric constant which led to free-radical reactions to leaving away with gaseous products and (2) under supercritical region tarry material which behaves like a solvent [51]. From studies it is observed that when operating temperature is elevated beyond 500–600°C, the depolymerization reaction occurs resulting in dissociation of complex bonds into simpler gaseous molecules [35]. Figure 3 shows the effect of temperature (225–600°C) on the yield of different hydrothermal products. This effect was also confirmed by a recent study by Alper et.al [38] on hydrothermal liquefaction of spruce wood at 250–300°C; the yield of biocrude increased slightly from 3.9 to 6.6 wt%. But beyond 300–350°C, the yield progressively decreased to 4.9 wt% due to the vaporization of biocrude at this temperature range [38]. Similar phenomena was observed beyond the supercritical condition (>374°C, 219 bar) in the case of algal biomass *Posidonia oceanica* due to the stimulation of steam-reforming and methanation reactions reducing the liquid and solid residue while increasing the gaseous products [50].

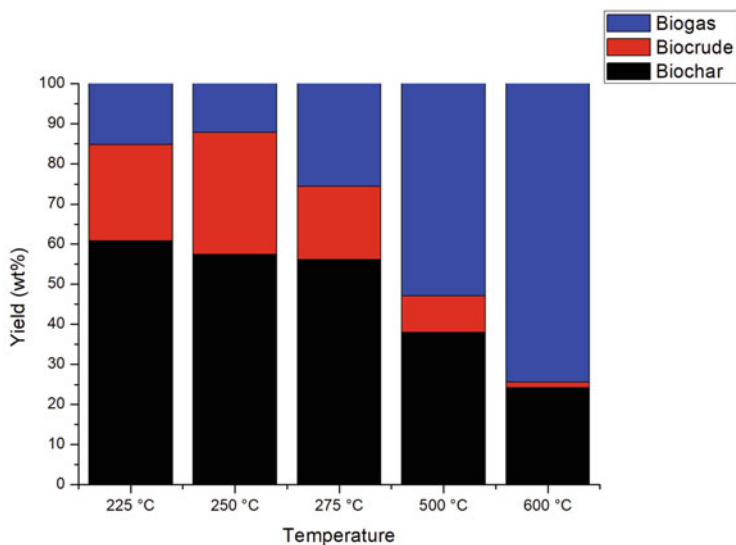
**Table 4** Reaction parameters of different woody and algal species

Feedstock (possible hydrothermal routes)	Reactor specifications	Temperature range (°C)	Hydrothermal media	Catalyst	Extraction solvent	Ref
Pine wood (HTC, HTL)	300 mL SS316 PARR reactor with heating rate 5 K/min	200–275	Water	5 wt% Ni(NO <sub>3</sub> ) <sub>2</sub>	Ethyl acetate, acetone	[34]
Pine wood (HTG)	100 mL SS 316 batch-type autoclave reactor with heating rate of 8–10 K/min	500–600	Water	10 wt% K <sub>2</sub> CO <sub>3</sub>	–	[35]
Pine wood (HTC, HTL)	600 mL stainless steel autoclave reactor with heating rate of 10 K/min	200–350	50% aqueous EtOH, MeOH	–	Acetone	[36]
Oak wood (HTL)	10 mL AISI 316 tubular microreactor with heating rate of 60 K/min	260–320	Water	Fe, Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> (0.05–0.3 g/g biomass)	Acetone	[37]
Spruce wood (HTL)	600 mL Parr 4,848 high-pressure reactor with heating rate of 5 K/min	250–300	Water	KF/Al <sub>2</sub> O <sub>3</sub>	Dichloromethane	[38]
Rice straw (HTC)	2 L stainless steel pressure reactor	180–300	Water	–	–	[39]
Rice straw (HTL)	1,000 mL GSHA-1 type autoclave with heating rate of 3 K/min	260–300	EtOH-water, 2-propanol-water	–	Tetrahydrofuran	[40]
Common reed (HTL)	250 mL SS316 autoclave reactor with heating rate of 3 K/min	250–290	EtOH, MeOH	10 wt% NaOH	Benzene, diethyl ether	[41]
Comcob (HTL)	250 mL Parr reactor with heating rate of 5 K/min	300–360	Water, EtOH	5–10% NaOH, KOH	Acetone	[42]
Cotton cocoon shell (HTL)	100 mL SS316 cylindrical autoclave reactor with heating rate 5 K/min	235–300	Acetone, water	NaOH, Na <sub>2</sub> CO <sub>3</sub> , KOH, K <sub>2</sub> CO <sub>3</sub>	Benzene, acetone	[43]
<i>Nannochloropsis</i> sp. (HTC, HTL)	500 mL SS316 batch reactor (MMJ500) with heating rate of 6 K/min	210–250	Water	5 wt% Nano-Ni/SiO <sub>2</sub> , synthesize zeolite, Na <sub>2</sub> CO <sub>3</sub>	Dichloromethane	[44]
<i>Enteromorpha prolifera</i> (HTL)	1,000 mL stainless steel autoclave	250–310	Water	0.02 M H <sub>2</sub> SO <sub>4</sub> , 0.2 M CH <sub>3</sub> COOH	Dichloromethane	[45]

(continued)

Table 4 (continued)

Feedstock (possible hydrothermal routes)	Reactor specifications	Temperature range (°C)	Hydrothermal media	Catalyst	Extraction solvent	Ref
<i>Chlorella pyrenoidosa</i> (HTL)	100 mL Parr 4,593 stainless steel reactor with heating rate of 6 K/min	240–280	Nanopure® water	Pd/C, Pd/Al <sub>2</sub> O <sub>3</sub> , Pt/C, Pt/Al <sub>2</sub> O <sub>3</sub> , Al=Ni, NaOH, Na <sub>2</sub> CO <sub>3</sub>	Toluene	[46]
<i>Nannochloropsis gaditana</i> , <i>Chlorella</i> sp. (HTC, HTL)	PARR 4593 stainless steel bench top reactor	180–330	Water	–	Dichloromethane	[47]
<i>Spirulina</i> (HTL)	100 mL 316 stainless steel batch reactor	230–290	Water	Ni/TiO <sub>2</sub>	Dichloromethane	[48]
<i>Tetraselmis</i> sp. (HTL)	7.5 mL micro-tubing reactor	250–350	Water	–	Dichloromethane, n-hexane	[49]
<i>Posidonia oceanica</i> (HTL, HTG)	100 mL batch-type reaction vessel	300–600	Water	–	–	[50]



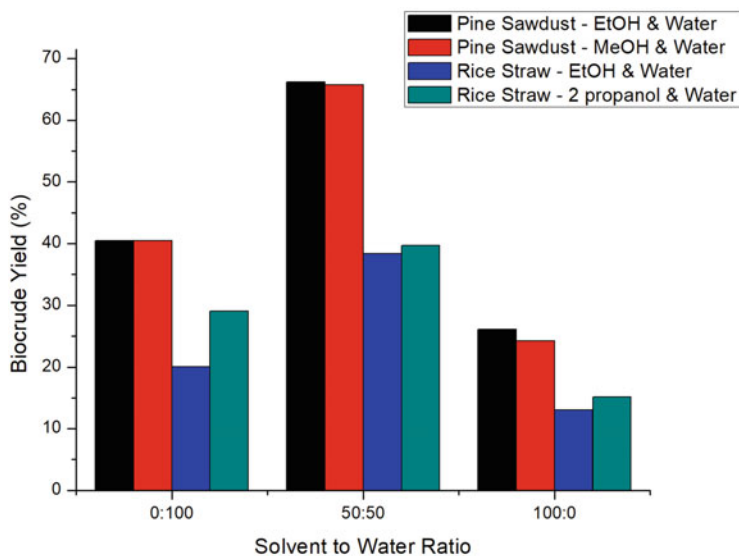
**Fig. 3** Effect of temperature on yield of hydrothermal products

### 3.2 *Effect of Hydrothermal Media*

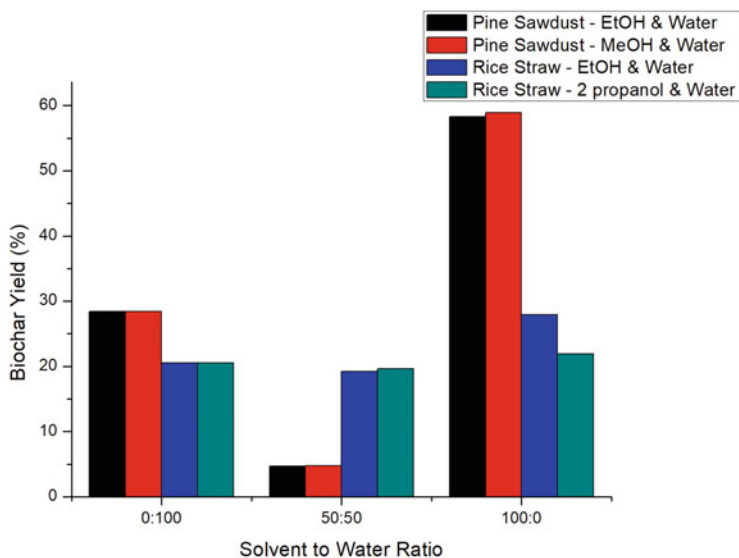
The hydrothermal media are generally called solvents, and they enhance the stability and solubility of the depolymerized macromolecules. Under subcritical conditions, these solvents act not as molecules but as radicals and induce the ionic reactions [52]. In most of the cases, deionized water is used as solvent, and sometimes Nanopure<sup>®</sup> water having ionic purity of 18.2 MΩ was used to eliminate any effects caused by the minerals present in tap water [46]. Few other studies [36, 40–43] revealed that replacing a portion of water with compounds like ethanol, methanol, acetone, and 2-propanol enhances the ionic product of the mixture yielding maximum biocrude and minimum biochar at 50:50 solvent to water ratio as shown in Figs. 4 and 5.

### 3.3 *Effect of Biomass to Solvent Ratio*

The amount of solvent/hydrothermal media present inside the reactor is very crucial for the process. If the quantity is very less, it enhances carbonization, and on excess it promotes gasification of all residual materials irrespective whether it is of lignocellulosic or algal origin. Hence the biomass to solvent ratio has to be maintained carefully. Tungal and Shende [34] explained the effect of biomass to solvent ratio on



**Fig. 4** Effect of hydrothermal media on biocrude yield



**Fig. 5** Effect of hydrothermal media on biochar yield

pine sawdust under liquefaction conditions of 250°C, where the biocrude yield increased from 22.14 to 33.1% with catalyst loading of 5 wt%  $\text{Ni}(\text{NO}_3)_2$  and 120 min reaction time [34]. This effect is shown in Fig. 6.

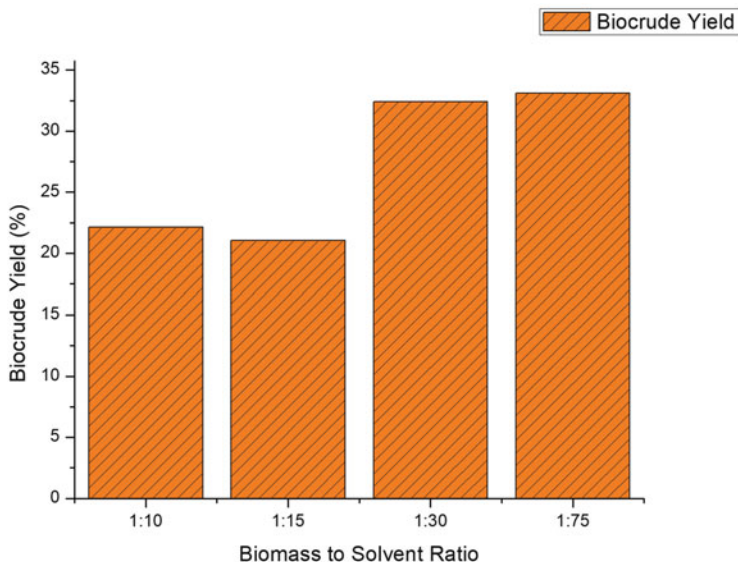


Fig. 6 Effect of hydrothermal media on biochar yield

### 3.4 Effect of Catalyst

Water acts itself as a catalyst during subcritical or supercritical hydrothermal conditions, and yet the products resulted with mostly oxygenated compounds with low high heating value (HHV). Thus to reduce the high O/H ratio in the resulting biocrude, it is required to add more catalysts into the reacting system. The addition of catalysts improves the gasification efficiency and reduces the solid residue (tar and char) by suppressing the condensation and repolymerization into stable macromolecules. Alkali salts and hydroxides have been frequently used as homogeneous catalysts, whereas Ni, Fe, Al, Pd, Pt, and Ti were used as heterogeneous catalysts, which were utilized to enhance the yield of biocrude.

**Homogeneous Catalysts** Homogeneous catalysts improve gasification by accelerating the water-gas shift reaction, thereby increasing the liquid product yields. They raise pH of the mixture to more alkaline, which in turn inhibits the dehydration of the cellulose, hemicellulose, and lignin; thereby increasing the H/C ratio in the biocrude and biochar. Alkali addition suppresses tar and biochar formation during the hydrothermal conversion process. It also prevents higher degree of oxygen removal in the biocrude, and instead of decarboxylation, it might result in the formation of unstable unsaturated compounds that can be easily polymerized into char and tar.

Küçük and Ağırtaş [41] investigated alkali-catalyzed hydrothermal liquefaction of common reed in subcritical water environment, where catalytic solvent (ethanol) + 10% NaOH resulted in high conversion of 57.6% at 290°C [41]. In another

study, Khampuang et al. [42] observed that liquefaction performed for 60 min at 340°C with a 1:1 (v/v) ethanol/water with addition of 10 wt% of NaOH resulted in oil yield of 50.2–57.2%; rather with no catalyst it was 49.0%. The oil yield with KOH addition (51.4–57.5%) was slightly higher than that with NaOH (50.5–56.4%) [42]. Similarly, alkali especially potassium in the form of  $K_2CO_3$  exhibited a progressive effect on yield of biocrude. The hydrothermal treatment of cotton cocoon shell showed a catalytic activity which is as follows:  $KOH > NaOH > K_2CO_3 > Na_2CO_3$  [43]. The alkali catalysts weaken the C-C bond, thereby decreasing the activation energy. It also triggers biomass swelling and increase in the surface area exposed, enhancing the retro-aldol cleavage. These alkali catalysts have the tendency to promote water-gas shift reaction during the hydrothermal conversion, thus favoring  $H_2$  and  $CO_2$  formation from CO. The resulting hydrogen gas in turn acts as a reducing agent, increasing the HHV and quality of the biocrude.

**Heterogeneous Catalysts** Heterogeneous catalysts have been mostly used in hydrothermal gasification process and low-temperature applications, where they enhance the quality of the biocrude obtained. de Caprariis et al. [37] investigated that HTL of oak wood with addition of Fe as a catalyst increases the quality and quantity of biocrude. Fe acts as a sacrificial catalyst, which in turn undergoes surface oxidation into  $Fe_2O_3$ , thereby reducing the acids and aldehydes formed during the process. Gasification is crucial to a certain extent for biocrudes containing higher percentages of oxygenated compounds. Few other studies show that by doping oxides like  $Al_2O_3$  with active substance like KF, Pd, and Pt and using it as a catalyst, the yield of the biocrude increased significantly [38, 46]. However, extensive gasification will reduce the biocrude yield. Some of the other heterogeneous catalysts reported for hydrothermal conversion of lignocellulosic and algal biomass include Ni doped over  $SiO_2$ ,  $TiO_2$ , and zeolite [44, 48].

## 4 Biomass to Fuel

The useful products obtained from the hydrothermal processing are biochar, biocrude, and biogas, which have their own significance. These products were always energy intensified compared to their feedstock. This was confirmed by elemental analysis of the feedstock and the resulting products. The biochar obtained is converted into pellets and used for various applications, whereas the biocrude and biogas are further purified to get fine chemicals. The main parameter that is to be noted for any fuel is its heating value. The energy density of products can be compared by calculating the HHV using the united formula by Channiwala and Parikh [59] that can be used for both feedstock and the resulting products [59]:



$$\text{HHV}(\text{MJ}/\text{kg}) = 0.3491(\text{C}) + 1.1783(\text{H}) + 0.1005(\text{S}) + 0.1034(\text{O}) + 0.0151(\text{N}) + 0.021(\text{A}) \quad (5)$$

$$\text{O} = 100 - (\text{C} + \text{H} + \text{N} + \text{S}) \quad (6)$$

$$\text{Energy Densification(ED)} = \text{HHV}_{(\text{Biochar or Biocrude})} / \text{HHV}_{\text{Biomass}} \quad (7)$$

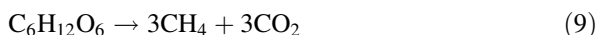
The elemental composition of the raw material, biochar, and biocrude obtained from the hydrothermal carbonization and liquefaction process is given in Table 5.

The high heating value (HHV) of the hydrothermal products compared to the feedstock is increased significantly due to the carbonization. It is observed from Table 5 that the hydrothermal products (biochar and biocrude) have a high energy densification ratio higher than 1, which proves the decarboxylation and deoxygenation reactions were involved during the hydrothermal carbonization and liquefaction. Table 6 shows the elemental composition of reference feedstock. Figure 7 depicts the van Krevelen plot, and it shows that the lignocellulosic feedstock is converted to products similar to that of lignite and liquefaction of algal biomass resulted in biocrude that resembles petroleum crude. The only disadvantage is the high nitrogen content in the biocrude.

Compared to other energy intensification processes, the hydrothermal processes have higher ratios and also low heat of reactions as the subcritical and supercritical water lowers the activation energy. Additionally, the mechanical dewatering or any other preheating is not required, as the feedstock of the process is moist biomass.

Hydrothermal coal is also called biocoal and has ash melting point similar to lignite, although in the case of algal biomass, the minerals in the solid product fuse together to form a sticky dense slurry-like material that changes the behavior of biochar entirely compared to lignocellulosic biochar. The algal biochar and solid residue are hygroscopic, and they are difficult to separate. Materials that are obtained from hydrothermal carbonization also have shown promising properties with varying functionalities, morphologies, and porosities [60]. They have important applications in a variety of modern fields such as electrode materials in superior performance supercapacitors, Na-based batteries, Li-ion batteries, and fuel cells [14].

At supercritical conditions, hydrogen and methane from biomass can also be manufactured from single-step hydrothermal gasification process without the formation of any solid residue:



Thus, Table 7 shows promising results that both lignocellulosic and algal biomass can be used for hydrogen gas production.

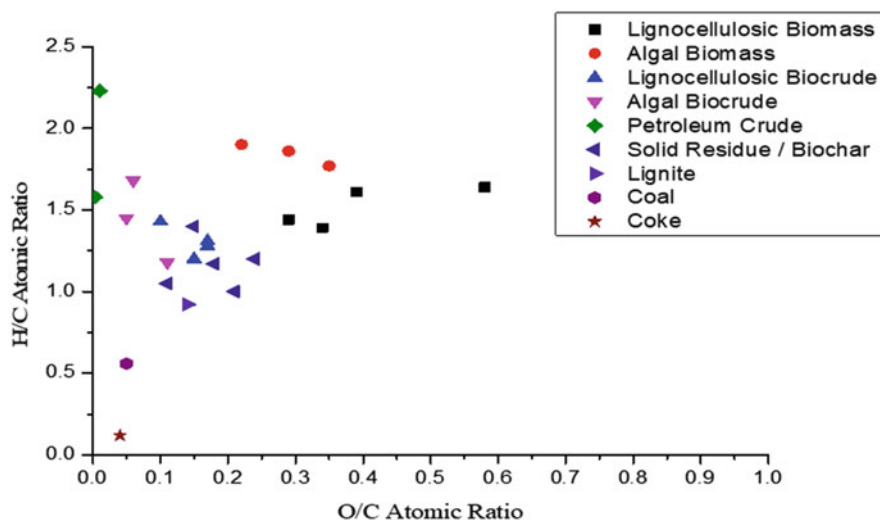
**Table 5** Energy intensification of woody and algal species

			Temp (°C)	C	H	N	S	O	H/C	O/C	HHV MJ/kg	ED	Ref
PS	Raw			52.5	6.32	0.10	0.05	40.6	1.44	0.29	29.98		
	Biochar	HTL	250	72.4	6.31	0.78	–	20.51	1.05	0.11	34.84	1.162	[34]
	Biocrude	HTL	250	63.5	6.78	0.65	–	29.07	1.28	0.17	33.17	1.107	
RS	Raw			36.81	5.025	1.059	0.416	56.69	1.64	0.58	24.69		
	Biochar	HTC	220	45.50	4.43	1.56	0.15	21.59	1.17	0.18	23.37	0.947	[53]
	Biocrude	HTL	300	71.34	8.509	1.451	0.211	18.489	1.43	0.10	36.89	1.494	[40]
BW	Raw			49.1	5.7	0.3	0.05	44.5	1.39	0.34	28.47		
	Biochar	HTC	210	56.9	5.7	0.3	0.2	36.9	1.20	0.24	30.42	1.069	[54]
	Biocrude	HTL	300	68.2	6.8	–	–	27.3	1.20	0.15	34.64	1.217	[55]
CC	Raw			43.1	5.8	0.23	0.12	44.6	1.61	0.39	26.51		
	Biochar	HTC	210	56.7	4.72	0.53	0.06	31.5	1.00	0.21	28.63	1.080	[56]
	Biocrude	HTL	280	63.0	6.87	0.42	1.31	28.82	1.31	0.17	33.21	1.253	[57]
NS	Raw			49.93	7.91	6.33	0.64	28.71	1.90	0.22	29.88		
	Biochar	HTC	210	54.89	6.42	5.98	0.50	21.79	1.40	0.15	29.12	0.975	[44]
	Biocrude	HTC	250	72.65	10.19	5.13	0.42	10.88	1.68	0.06	38.61	1.292	
EP	Raw			35.20	5.20	2.10	–	32.98	1.77	0.35	21.86		
	Biocrude	HTL	290	69.2	6.8	3.9	–	20.1	1.18	0.11	34.31	1.570	[45]
SP	Raw			46.16	7.14	10.56	0.74	35.44	1.86	0.29	28.43		
	Biocrude	HTL	350	73.73	8.90	6.30	0.90	10.17	1.45	0.05	37.46	1.318	[58]

PS pine sawdust, RS rice Straw, BW beech wood, CC Comcob, NS *Namochloropsis* sp., EP *Enteromorpha prolifera*, SP *Streptomyces platensis*

**Table 6** Elemental composition of reference feedstock

	C	H	N	S	O	H/C	O/C	HHV
Coke	87.91	0.88	1.19	0.66	9.36	0.12	0.04	32.78
Coal	83.02	3.89	1.59	1.03	10.47	0.56	0.047	34.78
Lignite	67.8	5.2	0.8	0.8	25.4	0.92	0.14	32.51
Petroleum crude 1	79.5	14.8	3.5	0.1	2.1	2.23	0.01	45.47
Petroleum crude 2	87.1	11.5	0.1	0.5	0.8	1.58	0.003	44.09

**Fig. 7** van Krevelen plot for biomass and hydrothermal products**Table 7** Gaseous product composition result of hydrothermal conversion from woody and algal biomass (yield moles/kg biomass)

Feedstock	Temperature (°C)	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
Pine sawdust	225	1.32	2.85	0.03	7.80
	275	12.26	6.03	0.44	8.36
	500	15.52	7.12	2.25	13.81
	600	26.15	8.90	2.41	23.32
<i>Enteromorpha prolifera</i>	300	0.15	0.6	–	8.9
	400	0.9	0.5	0.3	10.2
	500	3.2	–	2.4	8.4
	600	10.2	–	6.1	6.7

**Table 8** Essential chemicals from hydrothermal processing

Feedstock	Compounds	Relative area %	Significance
Beech wood	Guaiacol	26.4	Flavoring agent in baking industry
	2,6-Dimethoxyphenol (Syringol)	18.6	Food industry to artificially produce smoky aroma to food items
	2-Methyl-2-cyclopenten-1-one	7.89	Ketonic group added as ingredient in fragrance
	Acetic acid	4.41	Production of vinyl acetate monomer, as solvent in recrystallization to purify organic compounds
Pine wood	2-Furancarboxaldehyde/furfural	77.68	Herbicide, solvents in agricultural preparations
	1-Hydroxy-2-methoxybenzene	42.99	Herbicide and also in biomedical applications
	5-Methylidihydro-2 (3H)-furanone	8.85	Flavor and fragrance agents that give the caramel-like odor and brown-type flavor
	2-Oxo-3-cyclopentene-1-acetaldehyde	7.61	Solvent for extraction due to its high polarity
	Acetic acid, butyl ester	2.22	Solvents, flavoring agents
Corncob	p-Xylene	6.65	Polymer industry for production of polyethylene terephthalate
	Naphthalene, decahydro-	6.57	Solvent
	Ethylbenzene	3.60	Manufacturing products such as inks, insecticides, and paints
	Benzene, 1,3-dimethyl-	2.85	Smaller proportion in making resins, rugs, rubber lubricants, etc.
<i>Nannochloropsis</i> sp.	n-Hexadecanoic acid (C16:0)	23.45	Ingredient in soaps, cosmetics, etc.
	cis-9-Hexadecenoic acid (C16:1)	19.49	Disinfectants in water treatment
	Docosahexaenoic acid	8.50	Food industry as supplements
	Oleic acid (C18:1)	5.72	Manufacture of soaps as an emulsifying agent
	Tetradecanoic acid (C14:0)	5.68	Medicine preparation
	Pyrrolidine derivative	5.00	Pharma industry to produce tolmetin
<i>Enteromorpha prolifera</i>	1,4-Pentadiene	20.12	Paints, flavors, perfumes, varnishes as odor-causing agents
	3-Methyl-2-cyclopenten-1-one	10.26	Food additives, flavors, colorings, etc.
	Palmitic acid	9.78	Saponification of soaps

(continued)

**Table 8** (continued)

Feedstock	Compounds	Relative area %	Significance
	2,3-Dimethyl-2-cyclopenten-1-one	7.77	Solvent in many extraction process
	3-Methyl-1,2-cyclopentanedione	6.68	Ketonic group added as ingredient in fragrance

## 5 Biomass to Fine Chemicals

The primary objective of any hydrothermal processing is to derive value-added products (biochar, biocrude, and biogas) in which biocrude on further processing results in a significant amount of fine chemicals. All these years many researchers have confirmed the presence of various fine chemicals in the biocrude through GC-MS analysis. The chemicals identified in biocrude obtained from the hydrothermal conversion of few woody and algal biomass feedstock and its commercial significance are listed in Table 8.

## 6 Conclusion

The hydrothermal conversion of both lignocellulosic and algal biomasses was studied with the help of predefined reaction mechanisms of their respective constituents. This chapter briefly explained about the advanced technologies that are adapted in generation of energy-intensified fuels and value-added fine chemicals. The hydrothermal technologies with biorefinery would be a promising solution for sustainability as it can be implemented with minor modifications to the current industrial infrastructure. In the energy sector, the biocrude in addition to the natural crude can be used as such as the feed to existing refinery equipment, and there is no need for modification or retrofitting. Thus this technology is yet to be explored, and more value-added chemicals can be obtained from the hydrothermal conversion of lignocellulosic and algal biomass, thereby maximizing the yield of products with commercial significance.

## References

1. Bhaskar T, Pandey A (2015) Advances in thermochemical conversion of biomass – introduction. In: Pandey A, Bhaskar T, Stöcker M, Sukumaran RK (eds) Recent advances in thermochemical conversion of biomass. Elsevier, Amsterdam, pp 3–30. <https://doi.org/10.1016/B978-0-444-63289-0.00001-6>

2. Chen W, Chen Y, Yang H, Xia M, Li K, Chen X, Chen H (2017) Co-pyrolysis of lignocellulosic biomass and microalgae: products characteristics and interaction effect. *Bioresour Technol* 245:860–868
3. Arvindnarayan S, Prabhu KKS, Shobana S, Kumar G, Dharmaraja J (2017) Upgrading of micro algal derived bio-fuels in thermochemical liquefaction path and its perspectives: a review. *Int Biodeterior Biodegradation* 119:260–272
4. Chen CY, Yeh KL, Aisyah R, Lee DJ, Chang JS (2011) Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: a critical review. *Bioresour Technol* 102 (1):71–81
5. Koppejan J, Van Loo S (2012) *The handbook of biomass combustion and co-firing*. Routledge, London
6. Sticklen MB (2008) Plant genetic engineering for biofuel production: towards affordable cellulosic ethanol. *Nat Rev Genet* 9(6):433
7. Sørensen I, Pettolino FA, Bacic A, Ralph J, Lu F, O'Neill MA, Fei Z, Rose JK, Domozych DS, Willats WG (2011) The charophycean green algae provide insights into the early origins of plant cell walls. *Plant J* 68(2):201–211
8. Zhou X, Li W, Mabon R, Broadbelt LJ (2017) A critical review on hemicellulose pyrolysis. *Energy Technol* 5(1):52–79
9. Bajpai P (2016) Structure of lignocellulosic biomass. In: *Pretreatment of lignocellulosic biomass for biofuel production*. Springer, Singapore, pp 7–12
10. Pettersen RC (1984) The chemical composition of wood. In: *The chemistry of solid wood*, vol 207. US Department of Agriculture, Forest service, Forest Products Laboratory, Madison, pp 57–126
11. Fowden L (1954) A comparison of the compositions of some algal proteins. *Ann Bot* 18 (3):257–266
12. Markou G, Angelidaki I, Georgakakis D (2012) Microalgal carbohydrates: an overview of the factors influencing carbohydrates production, and of main bioconversion technologies for production of biofuels. *Appl Microbiol Biotechnol* 96(3):631–645
13. Yao L, Gerde JA, Lee SL, Wang T, Harrata KA (2015) Microalgae lipid characterization. *J Agric Food Chem* 63(6):1773–1787
14. Kruse A, Funke A, Titirici MM (2013) Hydrothermal conversion of biomass to fuels and energetic materials. *Curr Opin Chem Biol* 17(3):515–521
15. He C, Giannis A, Wang JY (2013) Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior. *Appl Energy* 111:257–266
16. Zhang S, Zhu X, Zhou S, Shang H, Luo J, Tsang DC (2019) Hydrothermal carbonization for hydrochar production and its application. In: *Biochar from biomass and waste*. Elsevier, Amsterdam, pp 275–294
17. Libra JA, Ro KS, Kammann C, Funke A, Berge ND, Neubauer Y, Titirici MM, Fühner C, Bens O, Kern J, Emmerich KH (2011) Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* 2(1):71–106
18. Funke A, Ziegler F (2010) Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod Biorefin* 4(2):160–177
19. Huang HJ, Yuan XZ (2015) Recent progress in the direct liquefaction of typical biomass. *Prog Energy Combust Sci* 49:59–80
20. Eboibi BEO, Lewis DM, Ashman PJ, Chinnasamy S (2014) Hydrothermal liquefaction of microalgae for biocrude production: improving the biocrude properties with vacuum distillation. *Bioresour Technol* 174:212–221
21. Jin F, Enomoto H (2011) Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: chemistry of acid/base-catalysed and oxidation reactions. *Energy Environ Sci* 4(2):382–397

22. Chopra J, Mahesh D, Yerrayya A, Vinu R, Kumar R, Sen R (2019) Performance enhancement of hydrothermal liquefaction for strategic and sustainable valorization of de-oiled yeast biomass into green bio-crude. *J Clean Prod* 227:292–301
23. Haiduc AG, Brandenberger M, Suquet S, Vogel F, Bernier-Latmani R, Ludwig C (2009) Sun Chem: an integrated process for the hydrothermal production of methane from microalgae and CO<sub>2</sub> mitigation. *J Appl Phycol* 21(5):529–541
24. Paidá VR, Brillman DWF, Kersten SRA (2019) Hydrothermal gasification of sorbitol: H<sub>2</sub> optimisation at high carbon gasification efficiencies. *Chem Eng J* 358:351–361
25. Matsumura Y (2015) Hydrothermal gasification of biomass. In: Recent advances in thermo-chemical conversion of biomass. Elsevier, Amsterdam, pp 251–267
26. Yin S, Tan Z (2012) Hydrothermal liquefaction of cellulose to biocrude under acidic, neutral and alkaline conditions. *Appl Energy* 92:234–239
27. Mok WSL, Antal Jr MJ (1992) Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water. *Ind Eng Chem Res* 31(4):1157–1161
28. Sasaki M, Hayakawa T, Arai K, Adschiri T (2003) Measurement of the rate of retro-aldol condensation of D-xylose in subcritical and supercritical water. In: Hydrothermal reactions and techniques. World Scientific Publishing, Singapore, pp 169–176
29. Kanetake T, Sasaki M, Goto M (2007) Decomposition of a lignin model compound under hydrothermal conditions. *Chem Eng Technol* 30(8):1113–1122
30. Zhang B, Huang HJ, Ramaswamy S (2007) Reaction kinetics of the hydrothermal treatment of lignin. In: Biotechnology for fuels and chemicals. Humana Press, Clifton, pp 487–499
31. Takeuchi Y, Jin F, Tohji K, Enomoto H (2008) Acid catalytic hydrothermal conversion of carbohydrate biomass into useful substances. *J Mater Sci* 43(7):2472–2475
32. Shi F, Wang P, Duan Y, Link D, Morreale B (2012) Recent developments in the production of liquid fuels via catalytic conversion of microalgae: experiments and simulations. *RSC Adv* 2(26):9727–9747
33. Tang S, Shi Z, Tang X, Yang X (2019) Hydrotreatment of biocrudes derived from hydrothermal liquefaction and lipid extraction of the high-lipid *Scenedesmus*. *Green Chem* 21(12):3413–3423
34. Tungal R, Shende RV (2014) Hydrothermal liquefaction of pinewood (*Pinus ponderosa*) for H<sub>2</sub>, biocrude and biocrude generation. *Appl Energy* 134:401–412
35. Cengiz NÜ, Eren S, Sağlam M, Yüksel M, Ballice L (2016) Influence of temperature and pressure on hydrogen and methane production in the hydrothermal gasification of wood residues. *J Supercrit Fluids* 107:243–249
36. Cheng S, D’cruz I, Wang M, Leitch M, Xu C (2010) Highly efficient liquefaction of woody biomass in hot-compressed alcohol – water co-solvents. *Energy Fuel* 24(9):4659–4667
37. de Caprariis B, Bavasso I, Bracciale MP, Damizia M, De Filippis P, Scarsella M (2019) Enhanced bio-crude yield and quality by reductive hydrothermal liquefaction of oak wood biomass: effect of iron addition. *J Anal Appl Pyrolysis* 139:123–130
38. Alper K, Tekin K, Karagöz S (2019) Hydrothermal liquefaction of lignocellulosic biomass using potassium fluoride-doped alumina. *Energy Fuel* 33(4):3248–3256
39. Liu Y, Yao S, Wang Y, Lu H, Brar SK, Yang S (2017) Bio-and hydrochars from rice straw and pig manure: inter-comparison. *Bioresour Technol* 235:332–337
40. Yuan XZ, Li H, Zeng GM, Tong JY, Xie W (2007) Sub-and supercritical liquefaction of rice straw in the presence of ethanol–water and 2-propanol–water mixture. *Energy* 32(11):2081–2088
41. Küçük MM, Ağırtaş S (1999) Liquefaction of *Prangmites australis* by supercritical gas extraction. *Bioresour Technol* 69(2):141–143
42. Khampuang K, Boreriboon N, Prasassarakich P (2015) Alkali catalyzed liquefaction of corncob in supercritical ethanol–water. *Biomass Bioenergy* 83:460–466
43. Çağlar A, Demirbaş A (2001) Conversion of cotton cocoon shell to liquid products by supercritical fluid extraction and low pressure pyrolysis in the presence of alkalis. *Energy Convers Manag* 42(9):1095–1104

44. Saber M, Golzary A, Hosseinpour M, Takahashi F, Yoshikawa K (2016) Catalytic hydrothermal liquefaction of microalgae using nanocatalyst. *Appl Energy* 183:566–576
45. Yang W, Li X, Liu S, Feng L (2014) Direct hydrothermal liquefaction of undried macroalgae *Enteromorpha prolifera* using acid catalysts. *Energy Convers Manag* 87:938–945
46. Yu G, Zhang Y, Guo B, Funk T, Schideman L (2014) Nutrient flows and quality of bio-crude oil produced via catalytic hydrothermal liquefaction of low-lipid microalgae. *Bioenergy Res* 7 (4):1317–1328
47. Reddy HK, Muppaneni T, Ponnusamy S, Sudasinghe N, Pegallapati A, Selvaratnam T, Seger M, Dungan B, Nirmalakhandan N, Schaub T, Holguin FO (2016) Temperature effect on hydrothermal liquefaction of *Nannochloropsis gaditana* and *Chlorella* sp. *Appl Energy* 165:943–951
48. Tian W, Liu R, Wang W, Yin Z, Yi X (2018) Effect of operating conditions on hydrothermal liquefaction of *Spirulina* over Ni/TiO<sub>2</sub> catalyst. *Bioresour Technol* 263:569–575
49. Vo TK, Kim SS, Ly HV, Lee EY, Lee CG, Kim J (2017) A general reaction network and kinetic model of the hydrothermal liquefaction of microalgae *Tetraselmis* sp. *Bioresour Technol* 241:610–619
50. Deniz I, Vardar-Sukan F, Yüksel M, Saglam M, Ballice L, Yesil-Celiktas O (2015) Hydrogen production from marine biomass by hydrothermal gasification. *Energy Convers Manag* 96:124–130
51. Promdej C, Chuntanapum A, Matsumura Y (2010) Effect of temperature on tarry material production of glucose in supercritical water gasification. *J Jpn Inst Energy* 89(12):1179–1184
52. Watanabe M, Sato T, Inomata H, Smith Jr RL, Arai Jr K, Kruse A, Dinjus E (2004) Chemical reactions of C1 compounds in near-critical and supercritical water. *Chem Rev* 104 (12):5803–5822
53. Ying GAO, CHEN HP, Jun WANG, Tao SHI, Hai-Ping YANG, Xian-Hua WANG (2011) Characterization of products from hydrothermal liquefaction and carbonation of biomass model compounds and real biomass. *J Fuel Chem Technol* 39(12):893–900
54. Tremel A, Stemann J, Herrmann M, Erlach B, Spliethoff H (2012) Entrained flow gasification of biocoal from hydrothermal carbonization. *Fuel* 102:396–403
55. Haarlemmer G, Guizani C, Anouti S, Déniel M, Roubaud A, Valin S (2016) Analysis and comparison of biocrudes obtained by hydrothermal liquefaction and fast pyrolysis of beech wood. *Fuel* 174:180–188
56. Zhang L, Wang Q, Wang B, Yang G, Lucia LA, Chen J (2015) Hydrothermal carbonization of corncob residues for hydrochar production. *Energy Fuel* 29(2):872–876
57. Gan J, Yuan W (2013) Operating condition optimization of corncob hydrothermal conversion for biocrude production. *Appl Energy* 103:350–357
58. Jena U, Das KC (2011) Comparative evaluation of thermochemical liquefaction and pyrolysis for biocrude production from microalgae. *Energy Fuel* 25(11):5472–5482
59. Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81(8):1051–1063
60. Jain A, Balasubramanian R, Srinivasan MP (2016) Hydrothermal conversion of biomass waste to activated carbon with high porosity: a review. *Chem Eng J* 283:789–805