Sustainable energy and fuels from biomass: A review focusing on hydrothermal biomass processing

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ABSTRACT

Fossil fuels must be replaced with renewable energy resources (biomass and biomass waste, solar, geothermal, wind, etc.) to ensure sustainable development, reduce the dependence on fossil fuels, address environmental challenges including climate change. Today, biomass produces $5x10^{19}$ kJ of energy/year, which corresponds to 10% of the annual global energy consumption. Considering the variety of biomass resources, this value is predicted to reach $150x10^{19}$ kJ by 2050. Biomass may become even more important for use as an energy resource and chemical raw material in the 21st century. Hydrothermal biomass conversion stands out as a promising and alternative technology. Methods such as traditional gasification and pyrolysis require dry biomass. Hydrothermal techniques have been developed to eliminate the cost and time required for drying biomass. The purpose of this process is to decompose biomass with a high moisture content into small molecules and reduce its oxygen content to obtain liquid fuels or valuable chemicals.

This review presents the current and future state of energy, energy sources, biomass properties and biomass conversion technologies and the properties of water in hydrothermal media, focusing on hydrothermal technologies.

INTRODUCTION

The energy requirement of society constantly increases due to advancing technologies and the growing population and GDP. According to the Energy Information Administration (EIA), although the world's total energy consumption was 282.817 quadrillion Btu in 1980, the annual total energy consumption exceeded 500 quadrillion Btu in the 2010s [1]. The world's energy consumption is predicted to reach 815 quadrillion Btu in 2040, representing an increase of 48% [2]. Today, this energy demand is largely met by fossil fuels, which are finite and have serious negative effects. If we continue to accelerate the use of fossil fuels, greenhouse gases effects will increase, and contribute to global warming [3]. The greenhouse effect is caused by gases such as carbon dioxide (CO_2), methane (CH_4), nitrogen oxide (N_2O), and water vapor (H_2O) [4]. While the average atmospheric CO_2 concentration was approximately 285 ppm for the 400,000 years before the industrial revolution, the average atmospheric CO_2 concentration reached 376 ppm as of 2005 and is still increasing [5]. By the end of the century, the CO_2 concentration is predicted to double that of the preindustrial revolution, which may cause the average global temperature to increase from 1.5 to 4.5°C [5]. If the increasing use of fossil reserves does not end by 2050 the average global temperature increase will exceed the critical level of 2°C [6]. Nonrenewable fossil fuels must be replaced with renewable energy resources (biomass and biomass waste, solar, geothermal, wind, etc.) to facilitate sustainable development, rural development, and address environmental challenges [7-12]. This process of replacement must begin as soon as possible since it will require a considerable amount of time [13]. Among the alternative energy resources, lignocellulosic biomass, which is renewable and whose supply is abundant, is a promising resource for the sustainable production of valuable chemicals and fuels, which are largely obtained from oil as of today [14]. Presently, biomass produces $5x10^{19}$ kJ of energy, which corresponds to 10% of the annual global energy consumption. Considering the variety of biomass resources, this value is predicted to reach $150x10^{19}$ kJ by 2050 [15]. Biomass may become even more important for use as an energy resource and chemical raw material in the 21st century [16]. It is asserted that drugs, agricultural chemicals, plastics, and fuels, which are obtained from fossil fuel-based raw materials, will be produced using renewable biomass [17]. Additionally, while fossil fuels have taken millions of years to form, biomass forms in years or even months [18].

Since the CO_2 released due to biomass use has previously been used to grow plants through photosynthesis, unlike fossil fuels, biomass energy is regarded as carbon neutral [11, 18, 19]. For this reason, biomass is a promising alternative that can replace fossil fuels, which are finite and have detrimental on the environment [20]. Biomass is produced from CO_2 and water (H_2O) using sunlight as the energy resource, while oxygen (O_2) is released as a byproduct [21].

The use of biomass energy may provide several benefits:

- Decreased greenhouse gas emissions and, therefore, a cleaner environment;
- Decreased foreign-source dependence as a result of replacing imported fossil fuels with biomass;
- Development economical opportunities in rural areas; and
- Decreased waste disposal problems [15].

Despite its advantages, biomass has a low energy density (an upper heating value of 15-20 MJ/kg) and needs to be converted into valuable products, which can be achieved using various methods [22]. However, it is not an easy task to efficiently convert lignocellulosic biomass into valuable products because lignocellulosic biomass is heterogeneous and has a structure that is difficult to decompose [14]. Thus, various conversion technologies are used to produce biomass-based fuels, organic chemicals, polymers, and materials [12]. These conversion technologies can be divided into two main groups, thermochemical and biochemical technologies. Thermochemical conversion is performed by subjecting biomass to a thermal treatment. Thermochemical technologies include combustion, gasification, pyrolysis, and liquefaction [23]. Hydrothermal liquefaction (HTL) is an effective technique used to convert biomass into a liquid fuel resource [22]. Various catalysts are used in these technologies to reduce the production costs and increase the yields and selectivity [24-26]. This study provides a comprehensive overview of the hydrothermal processing of biomass.

1. ENERGY

Energy is the foundation of modern society. In classical physics, energy is defined as the ability to do work [27, 28]. Energy use is directly or indirectly related to the development of humanity [29]. In the past, fossil fuels had been consumed rapidly for energy, and their negative impacts on the environment had been ignored [30]. Although conventional energy resources based on oil, coal, and natural gas are significant contributors to economic development, they are growing concerns regarding their environment and human health impacts [31]. According to the 2016 report released by the World Energy Council (WEC), significant changes had been initiated in the use of energy resources over the previous 15 years [32]. As shown in Figure 1.1, in 2008, oil, natural gas, and coal accounted for 35.4%, 22.0%, and 29.9% of the world's energy consumption, respectively, while renewable resources accounted for 7.4% of the world's energy consumption. In 2018, oil, natural gas, and coal accounted for 33.6%, 23.9%, and 27.2% of the world's energy consumption, respectively, while renewable resources accounted for 10.9% [33].

As shown in Figure 1.2, the world extracted 36.037 quadrillion kilojoules from renewable resources in 2008, and this value reached 63.212 quadrillion kilojoules in 2018, representing an increase of approximately 75%. However, as shown in Figure 1.3, nonrenewable resources reached 517.155 quadrillion kilojoules, an increase of 15%, within the same period [33]. These data indicate that there substantial opportunities to further develop renewable energy resources.

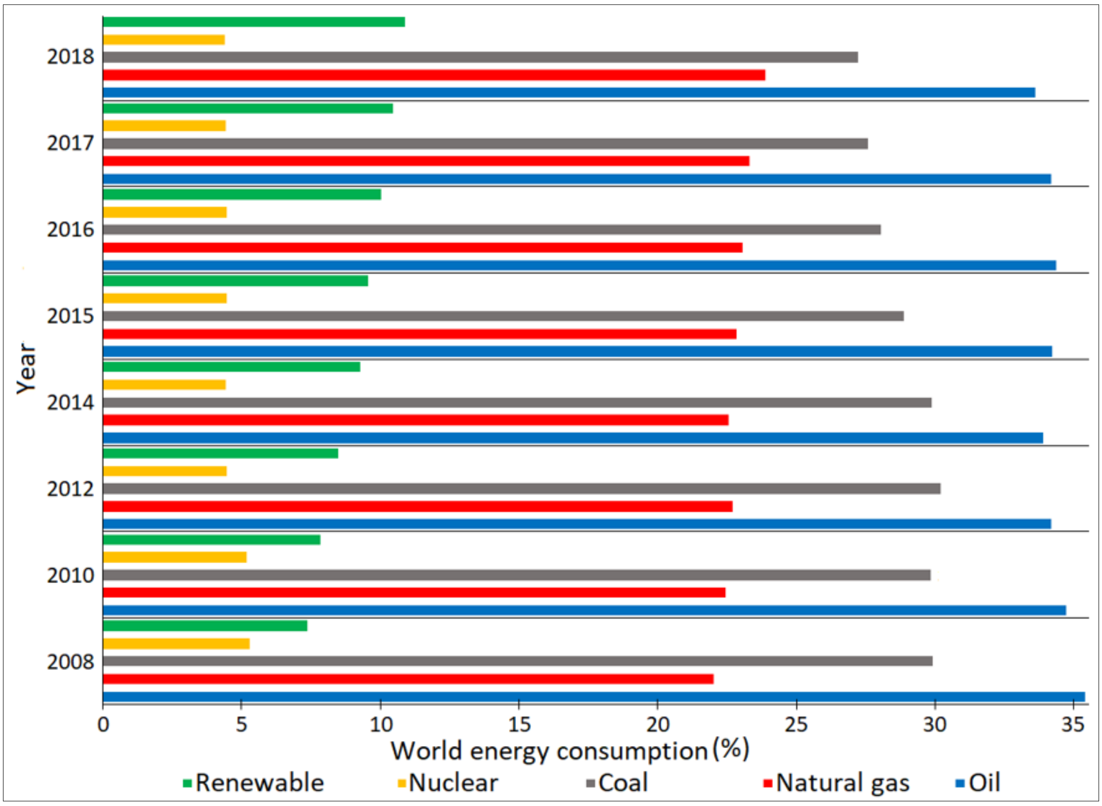

Figure 1.1. Distribution of the world's energy resources in percentages.

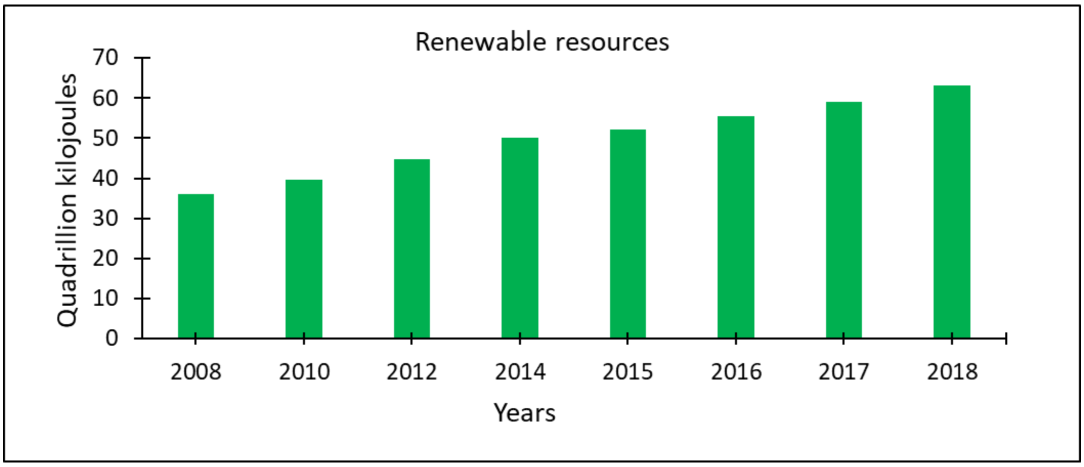

Figure 1.2. Distribution of renewable resources by year.

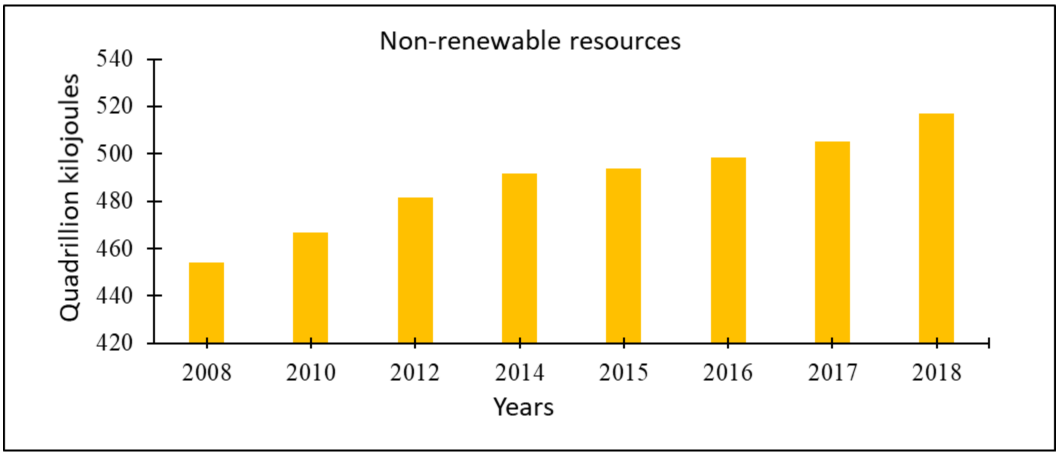

Figure 1.3. Distribution of nonrenewable resources by year.

1.1. Energy Resources

The main energy resource of the world is the sun [27]. All energy resources available on our planet, such as water, wind, fossil fuels, and biomass, are derived directly or indirectly from the sun [34]. As shown in Figure 1.4, the energy resources that meet the basic needs of humanity can be divided into two groups: primary and secondary resources. Primary energy resources include both renewable and nonrenewable energy resources. Secondary energy resources, on the other hand, are obtained from the conversion of primary energy resources.

1.1.1. Primary Energy Resources

Energy can be gathered directly from the environment. Primary energy resources include both nonrenewable (oil, natural gas, coal, and nuclear) and renewable energy resources (hydro energy, biomass, solar, wind, and geothermal) [28].

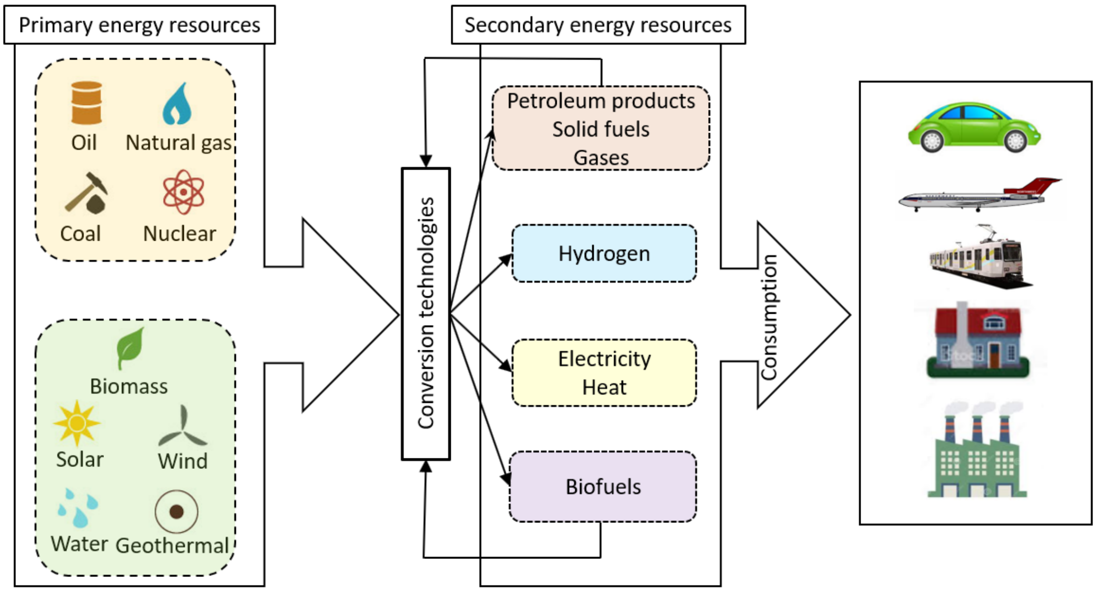

Figure 1.4. Primary and secondary energy resources.

Nonrenewable Energy Resources

Fossil fuels (coal, oil, and natural gas) and nuclear energy are considered to be nonrenewable energy resources. Although fossil fuels, which constitute the majority of nonrenewable energy resources, cause great harm to the environment, they guide modern technology and represent a billion dollar industry, which substantially impacts the global economy [35]. Fossil fuels have formed over millions of years by decomposing the remains of plants and animals under heat and pressure [28, 35].

Oil consists of hydrocarbons (paraffin, naphthalene, and aromatics), oxygen, nitrogen, sulfur, and trace amounts of metallic components [36]. The content of oil samples around the world is 82-87% carbon and 11-15% hydrogen, and the remaining components are oxygen, nitrogen, and sulfur. The oxygen and nitrogen contents rarely exceed 1.5%, while the sulfur content may be as high as 6% in exceptional cases [37]. Eighty-four percent of oil is converted to rich energy fuels such as gasoline, diesel, jet fuel, and liquefied petroleum gas (LPG), and the remaining oil is converted to lubricants, medicines, fertilizers, and plastics [28].

Natural gas is a type of fossil fuel consisting of various types of gases and has a combustion enthalpy per unit mass higher than that of gasoline or diesel and very similar properties to methane, its main component [38]. As shown in Table 1.1, the majority of natural gas consists of methane [39]. Natural gas is usually found in reserves, dissolved in oil under high pressures or accumulated on oil [35].

Table 1.1. Natural gas composition [39].

Gas	**Content (%)**
Methane	92.041
Ethane	3.241
Propane	0.654
Butane	0.016
Pentane	0.099
Nitrogen	3.008
Carbon dioxide	0.587

Coal is a brown or black, brittle, combustible organic sedimentary rock formed by the decomposition of vegetation under high temperatures and pressures and contains varying amounts of carbon, hydrogen, nitrogen, oxygen, and sulfur [40]. Coal is classified as anthracite, bituminous coal, sub-bituminous coal, and lignite depending on its heating value and carbon content [41]. Coal produces more CO_2 than other fossil fuels, such as crude oil, due to its high carbon content, and therefore, it has a significant effect on global warming [28]. Also, coal combustion gases, sulfur dioxide and nitrogen oxides, are released into the atmosphere and hydrolyzed to sulfuric and nitric acid causing acid rain [42, 43].

Table 1.2. Heating values and carbon contents of the different coal types [41].

	Heating value (Btu/kg)	**Carbon content (wt%)**
Anthracite	29762-34392	86-98
Bituminous coal	18298-34392	46-86
Subbituminous coal	18078-24692	42-52
Lignite	12125-18298	46-60

Although nuclear energy can be harnessed by two methods, fission and fusion, an effective fusion system remains a research challenge for power plants [44]. Available reactors are based on the fission system and process either uranium or thorium. The energy derived from fission reactions is used as thermal energy and transferred to a liquid (water, gas, liquid, metal, or molten salt) to generate steam. Steam is then sent to turbines to generate electrical energy [45]. As of February 12, 2019, there are 452 nuclear power plants in 30 countries around the world, generating 398667 MW_e of energy, and 55 nuclear power plants are under construction in 18 countries, with a capacity of 56643 MW_e. The Akkuyu Nuclear Power Plant in Turkey, which has a capacity of 1114 MW_e, is one of these power plants under construction [46].

Table 1.3. Pros and cons of nonrenewable energy resources [47].

Oil	**Pros**	Plentiful supply	Readily transported	Many uses	Source of revenue for exporters	
	Cons	Majority of supply in unstable nations	Risk of rapid depletion	Rising costs	Source of dependence for importers	Source of greenhouse gas emissions
Natural Gas	**Pros**	Plentiful supply	Readily transported	Many uses	Source of revenue for exporters	
	Cons	Significant supply in unstable nations	Rising costs	Source of greenhouse gas emissions	Source of dependence for importers	
Coal	**Pros**	Plentiful and high supply; diversity	Inexpensive	Many uses	Easily stored	Source of revenue for exporters
	Cons	Risk of rapid depletion	Mercury, CO_2, and other emissions	Key threat for climate change	Source of health problems	Source of dependence for importers
Nuclear	**Pros**	Low operating costs	Low-carbon pathway to cheap energy	Scientific benefits		
	Cons	Requires high level of expertise	Very high setup costs	Presents major health risks	Waste and safety challenges	Has troubling links with weapons proliferation

Renewable Energy Resources

The need to conserve energy and find alternative energy resources has increased due to the high demand for energy around the world, concerns related to global climate change, and the expectation that fossil fuels will become less available and more costly in the next century [48, 49]. Biomass, wind, geothermal, solar, and water energy resources stand out as renewable energy resources [50]. The potential of these resources is quite high, and these resources have the capacity to meet the world's energy requirement many times over [31, 51]. In addition to the significant decline in the costs of systems based on solar and wind energy during the last 30 years, uncertainties regarding oil and natural gas prices are accelerating the shift to renewable energy. Additionally, economic and societal support for these renewable energy systems are rapidly advancing [31].

Water, which moves due to the effect of gravity, contains energy by nature. When generating electrical energy, the work done by water is usually measured in units of kilowatt-hour (kWh). Water has two types of energy, potential energy caused by its location and kinetic energy due to its motion. Water energy is converted to electrical energy using a main carrier that is known as a water wheel or hydraulic turbine [52]. The electrical energy derived from water was 2100 terawatt-hours in 1997, 3000 terawatt-hours in the early 2000s and may reach 6000 terawatt-hours by 2050 [51]. According to the EIA, 3645 trillion kWh of electrical energy was generated from water energy worldwide in 2012, and this is estimated to reach 5571 trillion kWh by 2040 [2].

Solar energy is the most abundant of all renewable energy resources. The sun emits an energy of $3.8\text{x}10^{23}$ kW, and approximately 60% ($1.8\text{x}10^{14}$ kW) of earth's solar energy reaches the surface. The remaining energy is reflected into space or absorbed by the atmosphere. Converting 0.1% of the energy reaching the surface with a yield of 10% will make it possible to produce 4 times the total energy capacity of the world, approximately 3000 GW [53]. In 2012, 103 trillion kWh of electrical energy was generated from solar energy worldwide, while this is estimated to reach 962 trillion kWh by 2040 [2].

Wind energy is generated by turbines connected to grid networks, which convert wind power into electricity. The most common wind turbines generate an electrical energy of 10 kW or less, while there are also turbines that generate an electrical energy of 1.5 to 5 MW [54]. In 2012, 520 trillion kWh of electrical energy was generated from wind energy worldwide, while this is estimated to reach 2452 trillion kWh by 2040 [2].

Geothermal energy is the heat derived from volcanic activities, the radioactive decay of minerals, the formation of the planet, and the solar energy absorbed on the surface [28]. Although the geothermal energy potential is approximately $140000000\text{x}10^{18}$ J, even its reachable reserve (approximately 434x10^{18} J) exceeds the annual primary energy consumption [55]. Geothermal energy has great potential in terms of energy generation and domestic heating. However, geothermal energy contributes to a small portion of the world's primary energy consumption, and the electricity generated by geothermal energy accounts for less than 1% of the world's electricity generation [32]. There are four types of geothermal energy: hot water or steam at a depth of 100-4500 meters, hot water that contains methane dissolved at high pressures and exists at a depth of 3-6 kilometers, geological structures at abnormal temperatures with little to no water, and molten rock (magma) at temperatures of 700-1200°C [55]. In 2012, 68 trillion kWh of electrical energy was generated from geothermal energy worldwide, while this is estimated to reach 395 trillion kWh by 2040 [2].

Table 1.4. Pros and cons of renewable energy resources [47].

Hydroelectric	**Pros**	Domestic resource	Inexpensive	Clean source of energy	Easy to manage once established	
	Cons	Causes Environmental damage	Affected by drought, technical failures, and terrorist attacks	May entail the forced relocation of communities	Decommissioning can represent hidden costs	
Solar and Wind	**Pros**	Domestic resource	Easy to scale-up, decentralized	Clean source of energy	Can minimize impacts of fossil fuel price increases	
	Cons	Intermittency poses hidden costs	Can be undermined by environmental or climatic changes	Costs may rise		
Biofuels	**Pros**	Most nations have some supply	Variety of sources	Waste disposal	Enhances agricultural development	Can minimize oil imports
	Cons	Not enough to fully replace other fuels	Requires continued expansion of land-use to expand supply	Gives rise to deforestation and resulting environmental insecurity		

2. BIOMASS

Biomass contains organic substances that include all plant species that live or have recently existed on the planet and their waste, in which solar energy is stored as chemical bonds [18, 56, 57]. Biomass is a sustainable and renewable resource and is constantly formed, as shown in Figure 2.1, via photosynthesis using solar energy, CO_2 in the atmosphere and H_2O in the soil [21, 26, 56, 58, 59]. Annually, 170 billion tons of biomass, 75% of which is classified as carbon, is produced by nature via photosynthesis [21].

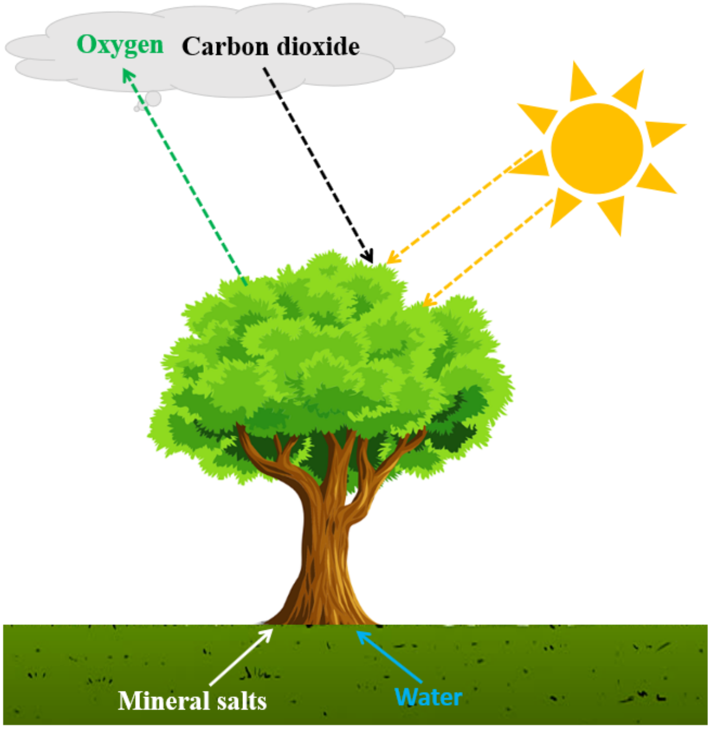

Figure 2.1. Regrowth of biomass via photosynthesis.

Biomass is also known as a heterogeneous mixture formed by organic substances and a small amount of inorganic substances. A typical dry biomass contains 30-40% oxygen, 30-60% carbon, and 5-6% hydrogen by weight, while nitrogen, sulfur, and chlorine account for approximately 1% of the biomass together with other inorganic elements [60]. Carbon (C) comes from atmospheric CO_2 during photosynthesis and is the element that makes the greatest contribution to the total heating value of biomass [23]. Hydrogen (H) integrated into the chemical structures of carbon and phenolic polymers, turns into water (H_2O) during combustion and is another important element of biomass [23, 61]. Nitrogen (N) returns to soil as fertilizer and enhances plant growth and yield. Sulfur (S) is found in amino acids, proteins, and enzymes and is an important nutrient for plant growth. Oxygen (O) is released during photosynthesis and is a vital element in the composition of biomass [23].

Biomass, which has always been an important energy resource for humankind, produces 50×10^{18} J of energy currently, corresponding to 10% of the world's energy consumption [15, 56]. In addition to being a renewable carbon resource for energy, fuel, and chemicals, biomass has allowed for less dependence on oil and reduced greenhouse gas emissions [62]. (such as that derived from herbal, herbaceous, ligneous, and organic wastes) possesses a great advantage over fossil fuels, which form over thousands or millions of years [63]. As shown in Figure 2.2, the use of fossil fuels causes the release of CO_2, which was stored millions of years ago, meaning additional CO_2 is released to the atmosphere; however, since the CO_2 released as a result of biomass use is taken from the atmosphere during plant growth, additional CO_2 release does not occur, and thus, there are no net greenhouse gas effects [19, 56, 58, 59, 63-65].

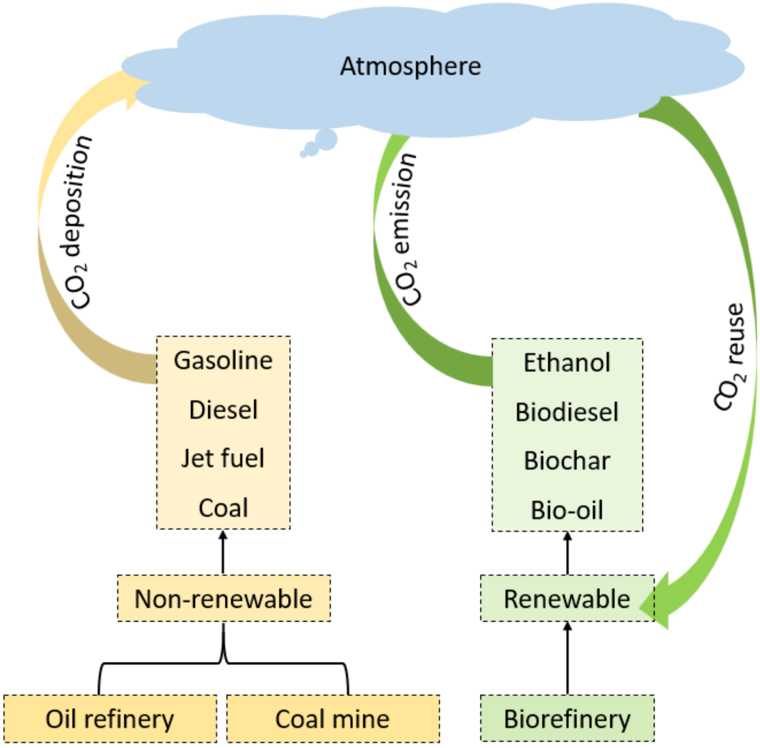

Figure 2.2. CO_2 cycle of fossil- and biomass-based fuels.

Biomass can be converted to electrical energy, thermal energy, vehicle fuels, and valuable chemicals [56, 66].

Biomass is quite attractive for biofuel production due to following reasons:

- Biomass is a renewable resource;
- Biomass is an important raw material for valuable chemicals;
- Biomass is environmentally friendly due to due to carbon neutrality; and
- Biomass has economic potential due to the unreliability of oil prices [50, 65].

Biomass resources contain less carbon and hydrogen and have a higher oxygen content than oil [67]. The H/C and O/C mol ratios indicate the heating value of a fuel. To convert biomass into liquid products, which can replace oil, the oxygen in the biomass structure must be removed in the form of H_2O, CO and CO_2, the O/C ratio must be reduced, and the H/C ratio must be increased [8, 59, 68]. However, the high O/C ratio in cellulosic biomass becomes an advantage in terms of extracting valuable chemicals, which cannot be obtained inexpensively from raw fossil fuel materials [69-71].

Biomass can be converted into gas fuels, such as hydrogen and methane; liquid fuels, such as biodiesel; Fischer-Tropsch diesel, vegetable oil, ethanol, and methanol; and solid fuels, such as biochar and hydrocarbons [65].

2.1. Chemical Structure of Biomass

Biomass consists of cellulose (40-50 wt%), hemicellulose (15-30 wt%), lignin (16-33 wt%) and extractive materials (1-10 wt%) [72]. Figure 2.3 shows the chemical structure of biomass.

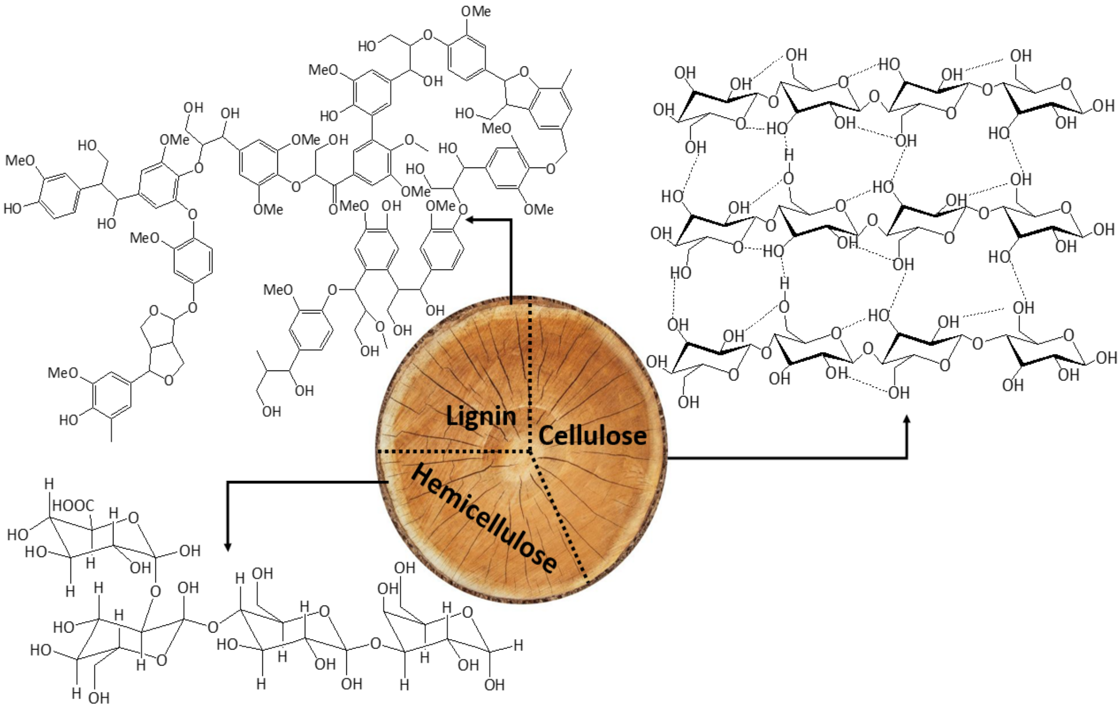

Figure 2.3. Representative chemical structure of biomass

2.1.1. Cellulose

Cellulose, the most abundant component of biomass, is considered as an infinite resource of chemicals and fuels [73]. Cellulose is found in plant cell walls and constitutes approximately one-third of all plant material [74, 75]. The French chemist Anselme Payen describes cellulose as a resistant fibrous solid that remains after the treatment of various plant tissues with acid and ammonia and extraction with water, alcohol, and ether [76]. Cellulose is composed of linear polymers, in which glucose units bond to each other by β-1,4 glycosidic ester bonds [56, 58, 77, 78]. The average molecular weight of native cellulose is ~100000 [50, 56]. Cellulose chains possess a structure that supports intramolecular and intermolecular hydrogen bonds [79]. Additionally, the hydrogen and van der Waals bonds in the cellulose structure impart cellulose with a high strength and high resistance against biological attacks. Cellulose is not water soluble due to its crystal structure and is resistant to hydrolysis [12]. Cellulose is a very important resource for paper and cardboard production. Additionally, cellulose derivatives are used in pavements, laminates, optical films, pharmaceuticals, foods, and textiles [80]. Figure 2.4 shows the structure of cellulose.

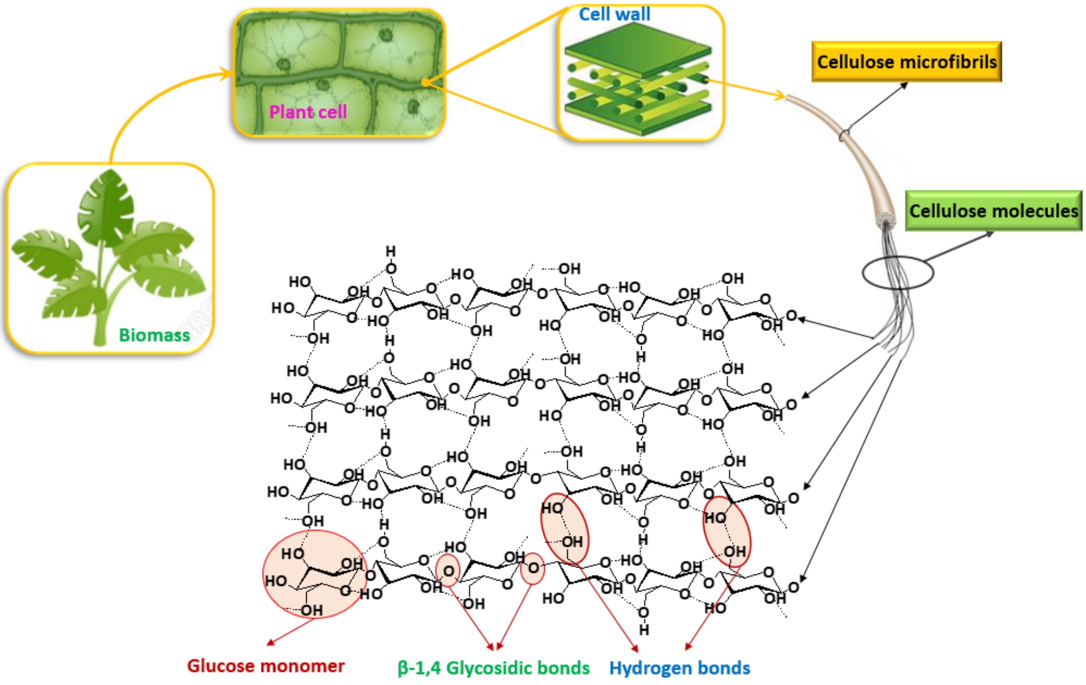

Figure 2.4. Structure of cellulose.

2.1.2. Hemicellulose

Hemicellulose, the second most important component of lignocellulosic biomass, is also known as polyose [81]. Hemicellulose is a heteropolysaccharide with β-1,4-linked sugar units [82]. Hemicellulose has a heterogeneous structure and consists of uronic acid, hexoses, and pentoses [83]. Hemicellulose contains various monosaccharides, such as *D*-xylose, *L*-arabinose, *D*-glucose, *D*-galactose, *D*-mannose, *D*-glucuronic acid, 4-*O*-methyl-*D*-glucuronic acid, and *D*-galacturonic acid [74, 81]. Hemicellulose exhibits a lower polymerization degree than cellulose, is largely soluble in alkali media and is easily hydrolyzed [83]. While hemicellulose is amorphous and hydrophilic, it serves as an interfibrous connective material that provides support to cellulose microfibrils [84]. In addition, hemicellulose is known to form covalent bonds with the functional groups found in lignin and interacts with cellulose via hydrogen bonds [75]. Figure 2.5 shows the building blocks of hemicellulose.

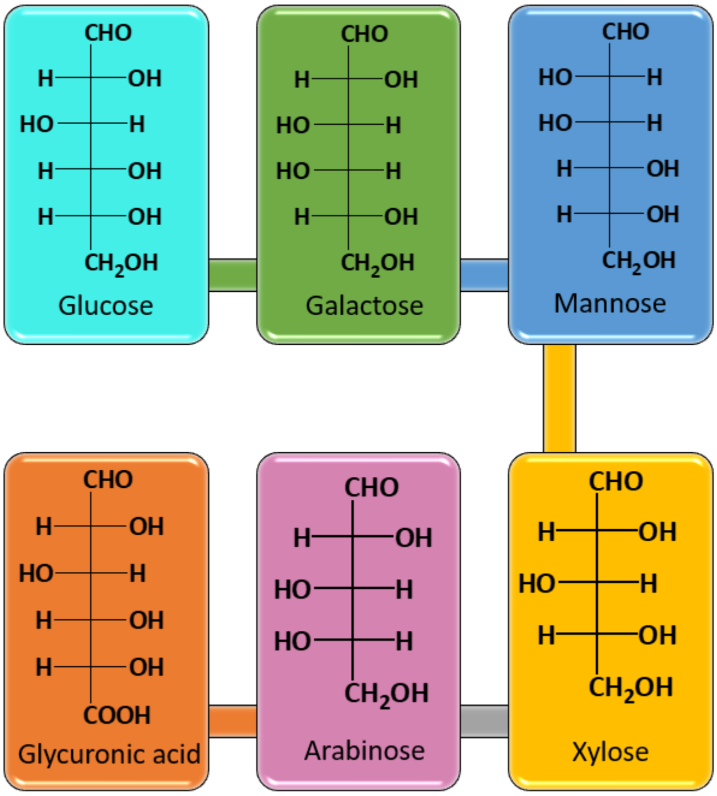

Figure 2.5. Building blocks of hemicellulose.

2.1.3. Lignin

Lignin is the most common organic polymer besides cellulose [75]. Lignin is a term that was introduced by Candolle in 1819 and is derived from the Latin word for wood (Lignum) [74]. Lignin is a complex polymer with a three-dimensional amorphous structure consisting of phenylpropane units [85]. Lignin constitutes 17-33% of wood [86]. Lignin has a very high molecular weight, which is difficult to measure [85]. Lignins are complex polymers that form by the dehydrogenation of *p*-coumaryl, sinapyl, and coniferyl [87]. Figure 2.6 shows the structures of lignin monomers. Softwood lignin consists of coniferyl alcohol and a small amount of coumaryl alcohol. Hardwood lignin consists of both coniferyl and sinapyl alcohols and a small amount of coumaryl alcohol. Herbaceous plant lignin consists of phenylpropane (*p*-coumaryl, sinapyl, and coniferyl alcohols) units and *p*-hydroxycinnamic acids (*p*-coumaric acid, ferulic acid, and sinapinic acid) [88].

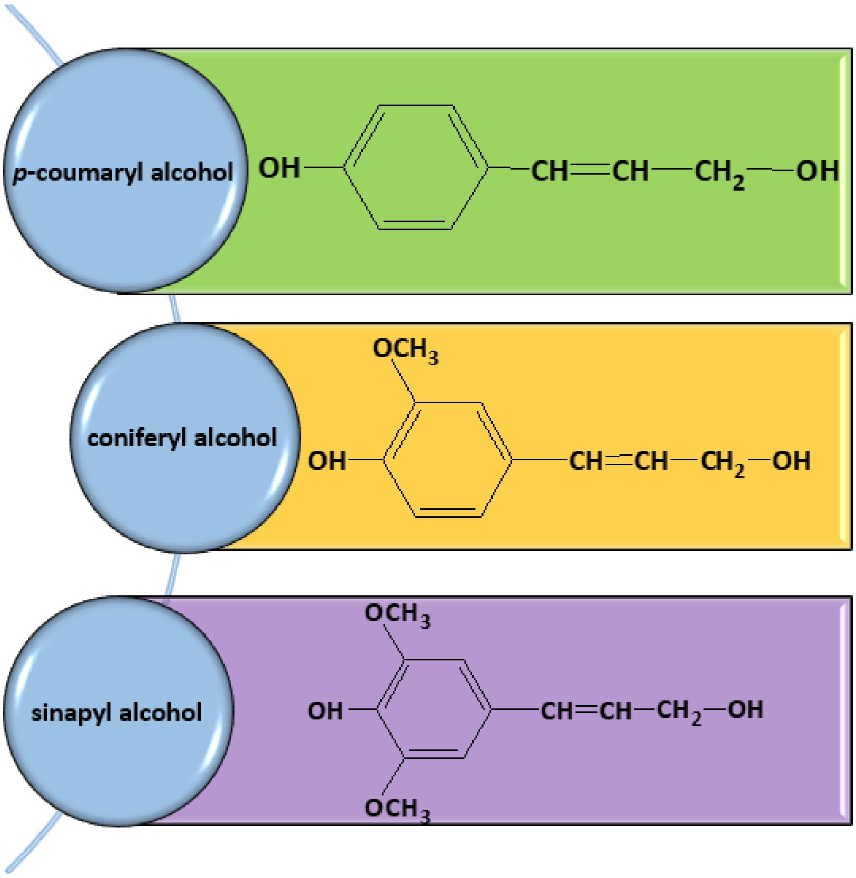

Figure 2.6. Lignin monomer compositions.

Compared to polysaccharides, lignin is more resistant to microbial decay due to its complex structure and diverse bonds [89, 90]. However, when efficiently depolymerized, lignin is an important resource of valuable chemicals, fuels, and fuel additives [20].

2.1.4. Extractive Substances

The term ‘extractive substances’ is used to refer to a wide variety of compounds that can be extracted by using polar and nonpolar solvents [75]. These extracts are usually compounds with low molecular weights [91]. Extractive substances, such as fats, free fatty acids, waxes, resins, tannins, gums, terpenoids, flavonoids, stilbenes, tropolenes, and volatile hydrocarbons, usually amount to only a small portion by weight of wood [37]. Each extractive substance has a different task, which allows a tree to maintain its biological functions. For example, fats are the energy providers of wood cells, while terpenoids, resins, and phenolic substances protect wood against microbial and insect attacks [74]. Figure 2.8 shows the composition of extractive substances, such as stilbenes, terpenes, and flavonoids.

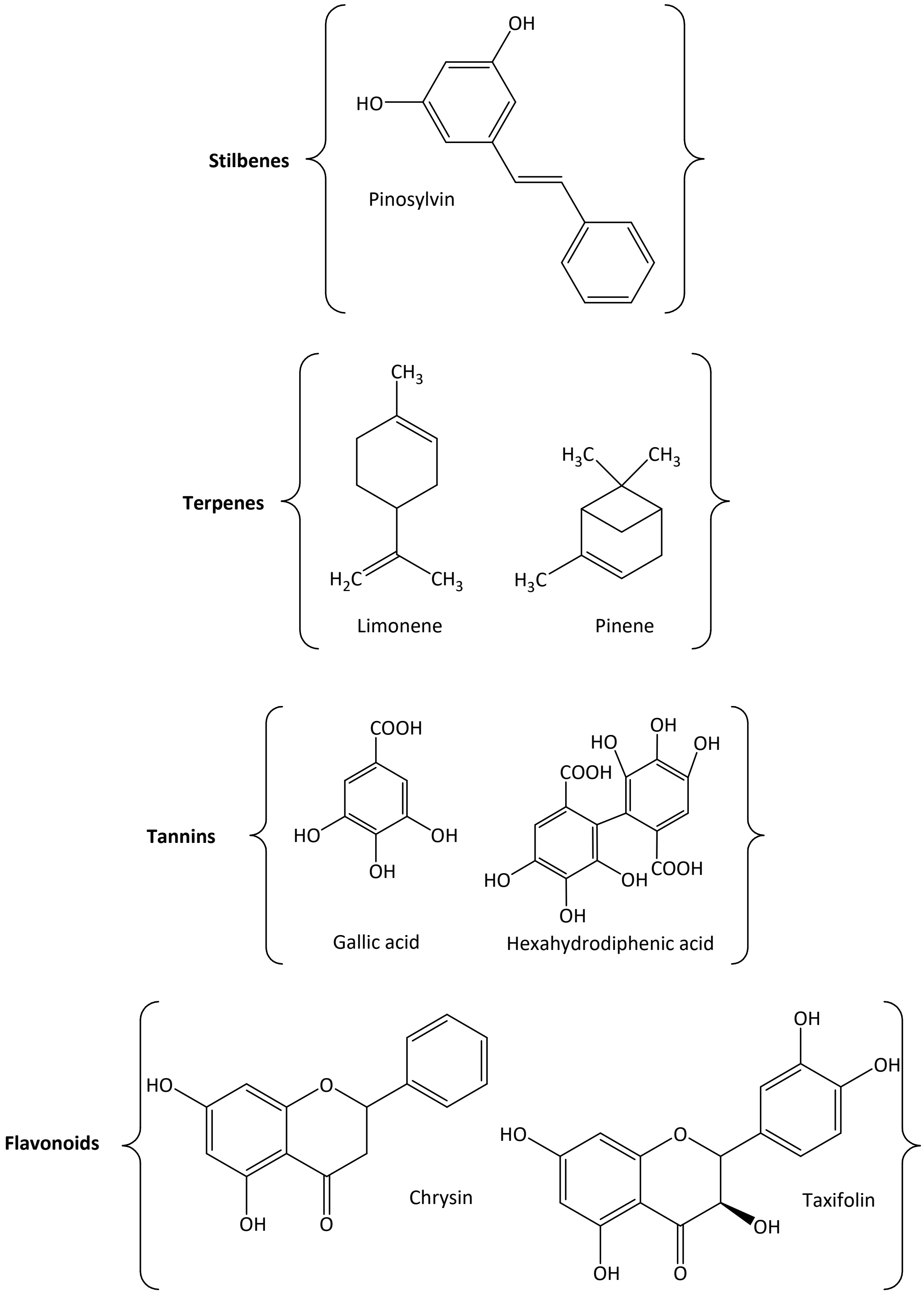

Figure 2.8. The compositions of stilbenes, terpenes, and flavonoids.

Tannins are defined as polyphenolic carboxylic acids frequently esterified to sugar, usually, glucose. They are further divided into two subgroups, hydrolysable tannins and condensed tannins [92]. The ester linkages of tannins can be readily hydrolyzed by acids, bases, or enzymes. Terpenes are hydrocarbons that bear the same isoprene unit and one or more carbon-carbon bonds; natural and synthetic derivatives of terpenes containing oxygen are referred to as terpenoids [21, 93]. Terpenoids are found in essential oils and are components of resins, steroids, and rubber. Readily available and inexpensive terpenoid types, such as pinene and limonene, are ideal starting compounds for the synthesis of some important chemicals [21]. Stilbenes are 1,2 diphenylethylene units and contain conjugated double bonds. The pinosylvin found in pine trees can is one example [74].

3. BIOMASS CONVERSION TECHNOLOGIES

Biomass conversion technologies are divided into two groups, biochemical and thermochemical technologies. As shown in Table 3.1, thermochemical processes have some advantages over biochemical processes [94, 95].

Table 3.1. Comparison of biochemical and thermochemical conversion processes [94].

	Biochemical conversion	**Thermochemical conversion**
Products	Alcohols	Various fuels
Reaction conditions	<70°C, 1 atm	100-1200°C, 1-250 atm
Duration	2-5 days	0.2 second to 1 hour
Selectiveness	Adjustable	Depends on reaction
Catalyst cost	0.5 USD/gallon ethanol	0.01 USD/gallon ethanol
Sterilization	Necessary	Not necessary
Reprocessing	Difficult	Possible for solid catalysts

3.1. Biochemical Conversion Technologies

The biochemical conversion of biomass involves the use of bacteria, microorganisms, and enzymes to convert biomass into a gas (i.e., biogas) or liquid (i.e., bioethanol) fuel [96]. This process is substantially slower than the thermochemical process and does not require significant energy [59]. Biochemical conversion involves two processes: fermentation (ethanol or other low MW alcohols production) or digestion (biogas production) [97]. During anaerobic digestion, bacteria receive oxygen from the biomass and generate methane and carbon dioxide as well as solid products. During aerobic digestion, microorganisms receive oxygen from the air and release carbon dioxide, heat, and solid products. During fermentation, part of the biomass, except for lignin, is converted into sugars using acids and enzymes, and the sugar is then converted into ethanol or other chemicals with the help of yeasts or other microbial agents [59]. There are now many examples of fermenting lignin to lipids There are two difficulties associated with biochemical conversion. The first is the high cost of breaking down the hard and complex cell walls of cellulosic biomass, and the second is the conversion of the sugar into biofuels [98].

3.2. Thermochemical Conversion Technologies

Thermochemical conversion technologies allow fuel, chemicals, or electricity to be obtained from biomass using heat and catalysts. The thermochemical process is performed at high temperatures (at least a few hundred centigrade and sometimes over 1000°C) with or without a catalyst [95]. Four techniques are used for the process: burning, pyrolysis, gasification, and hydrothermal techniques.

3.2.1. Burning

Burning is the oldest biomass conversion process used to obtain energy [59, 99]. Until the early 1900s, burning was used for various purposes, such as heating, chemical and coal production, and mechanical and electrical energy generation. The burning process takes place as a result of the chemical reaction occurring between biomass and oxygen, and the main products of the process are carbon dioxide and water [59, 95, 99, 100]. The flame temperature may exceed 1650°C depending on the heating value and moisture content of the fuel, the amount of air used to burn the fuel, and the structure of the furnace [95]. A low moisture content is desirable during the burning process [100].

3.2.2. Pyrolysis

Pyrolysis is the process of converting biomass into liquid, solid, or gas products by thermal decomposition in the absence of oxygen [59, 101]. Gases and bio-oils come from the volatile fraction of biomass, while the solid product, called char, comes mostly from the stable carbon component [100]. Bio-oils are dark brown organic liquids containing high amounts of oxygenated compounds [102]. This mixture, containing components such as acids, esters, alcohols, ketones, aldehydes, sugars, furans, and phenol, is obtained by depolymerizing and decomposing cellulose, hemicellulose, and lignin [7]. The resulting products present with differences depending on the pyrolysis method and reaction parameters [101]. Water is undesirable in raw materials and pyrolysis oils; the presence of water is complicated due to the stability, viscosity, pH, abrasiveness, and other properties [103]. The higher the water content is, the lower the net energy obtained from the pyrolysis oil [104]. Table 3.2 summarizes the pyrolysis techniques.

Table 3.2. Pyrolysis techniques [101].

		Reaction time	**Heating**	**Temperature (°C)**	**Main product**
Carbonization		Hours-days	Very slow	400	Biochar
Traditional		5-30 min.	Slow	600	Biochar, bio-oil, and gas
Fast		0.5-5 hours	Quite fast	650	Bio-oil
Flash	**Liquid**	<1 hour	Fast	<650	Bio-oil
	Gas	<1 hour	Fast	<650	Chemicals and gas
Ultra		<0-5 hours	Very fast	1000	Chemicals and gas
Vacuum		2-30 hours	Moderate	400	Bio-oil
Hydropyrolysis		<10 hours	Fast	<500	Bio-oil and chemicals
Methanopyrolysis		<10 hours	Fast	>700	Chemicals

3.2.3. Gasification

Gasification is the process of converting carbonaceous materials into a combustible or synthetic gas by reacting the material with air, oxygen, vapor, carbon dioxide, or a mixture of these gases at a temperature of 760°C or higher [105]. Gasification produces gases such as H_2, CO, H_2O, CO_2, and CH_4, which are used to generate electricity, heat, chemicals, and liquid fuels [105, 106]. For a successful gasification process, the raw material properties (moisture, ash, and volatiles) and pretreatment method (drying, particle size, fractionation, and leaching) are very important [107]. The biomass gasification process steps may involve drying, thermal decomposition or pyrolysis, partial combustion (of some gases, vapor, and coal), and the gasification of decomposed products [59].

3.2.4. Hydrothermal Techniques

Hydrothermal techniques are defined as chemical and physical conversion techniques performed at high temperatures (200-600°C) and high pressures (5-40 MPa) in liquid or supercritical water [108]. Water is indispensable for life and is a significant component of plant biomass; water accounts for 10-60% of lignocellulosic biomass and even higher ratios for microalgae [109].

Water acts as the reactant, solvent, and catalyst in hydrothermal techniques [110]. Many organic nonpolar compounds become water miscible under hydrothermal conditions [111]. In addition, water acts as an acidic and basic catalyst in reaction environments due to the H_3O^+ and OH^- ions that it contains [111-113]. Another catalytic function of water is its ability to participate in certain reactions at the transition states [112]. As the temperature increases, the hydrogen bonds between water molecules weaken, the dielectric constant decreases, and water behaves as a nonpolar solvent as a result [114].

Methods such as traditional gasification and pyrolysis require dry biomass [109]. Hydrothermal techniques have been developed to eliminate the cost and time required to dry biomass [109, 115]. Valuable plant chemicals, such as resins, oils, phenolic compounds, and phytosterols, are extracted during the hydrothermal process at approximately 100°C. At 200°C and under a 2 MPa pressure, the biomass is subjected to decomposition to obtain cellulose and hemicellulose decomposition products, such as furfural or 5-hydroxymethylfurfural. Biofuel, a nonaqueous soluble organic phase, is obtained at 300-350°C and under 12-18 MPa of pressure. Finally, a gas product containing a significant amount of methane is formed at 600-650°C and under 30 MPa pressure [111]. In addition to subcritical and supercritical water, hydrogen-donating solvents, such as alcohol, decalin, and tetralin, may be used for biomass conversion [116]. Hydrothermal techniques are classified as carbonization, gasification, and liquefaction. Table 3.3 shows the temperature ranges used by hydrothermal techniques.

Table 3.3. Hydrothermal techniques and temperature ranges.

Technique	Temperature (°C)	Reference
Hydrothermal carbonization	180-250	[117]
Hydrothermal liquefaction	280-380	[118]
Hydrothermal gasification	400-700	[108]

Subcritical and Supercritical Water

Water is an inexpensive and environmentally friendly solvent; it is not combustible, explosive, or toxic [119]. The interactions between water molecules are very strong due to its strong hydrogen bonds, and water has a high critical point [120]. Table 2.9 shows the physical and chemical properties of water under normal and subcritical/supercritical conditions [121]. Water reaches a critical point at 374.2°C and under a 22.1 MPa pressure [113, 122, 123]. Water close to its critical point displays significantly different thermophysical properties compared to water under normal conditions [124]. Water close to its critical point acts as a solvent, reactant, and catalyst in reaction environments [112]. Water below its critical point is referred to as subcritical water, while water above its critical point is referred to as supercritical water [120]. Below the critical point, the vapor pressure curve separates the liquid from the gas phase, and the properties of both phases become gradually more similar as the critical point is approached, and finally, become identical at the critical point [125]. While water is not a suitable solvent for many organic compounds under standard conditions (25°C and 0.1 MPa), it behaves as an apolar solvent and provides a quite effective reaction environment for organic compounds [123, 126]. The ionization constant of water ($K_w=[H^+][OH^-]$) under room conditions is approximately 10^{-14} but increases to approximately 10^{-11} near the critical temperature [127]. In this case, water provides an efficient environment for organic reactions with both acidic and basic catalysts [128]. The density and dielectric constant of water significantly impact the solubility of different compounds. For subcritical water, a low dielectric constant allows for a solution of organic compounds, whereas a high ionization constant provides an acidic environment for hydrolysis reactions [120]. Water exhibits properties similar to those of liquids under subcritical conditions; therefore, ionic reactions may be dominant, whereas the free radical reactions necessary for gasification are limited [129]. The density of supercritical water can be altered from high (as liquid) to low (as gas) without a phase transition occurring by changing the pressure and temperature values [122]. The density of water is lower under supercritical conditions, which means that the water ionization constant is substantial lower, and ionic reactions are somewhat inhibited due to the low dielectric constant, which supports the free radical reactions necessary for gasification [129]. The free radical reaction types are as follows: initiation, hydrogen transfer, radical isomerization, radical addition, radical dehydratization, radical substitution, and radical termination reactions [130]. This decrease in the density is associated with other properties, such as the resolving power, degree of hydrogen bonds, polarity, dielectric constant, molecular diffusivity, and viscosity [123]. Figure 3.1 shows the behaviors of water and the temperature and pressure ranges used by hydrothermal techniques.

Table 3.4. The dielectric constant of water depends on the temperature and pressure changes.

		Temperature (°C)											
		25	**50**	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Pressure (MPa)	**0.1**	78.46	69.91	1	1	1	1	1	1	1	1	1	1
	0.5	78.47	69.92	55.43	43.95	1.01	1.01	1.01	1.01	1.01	1	1	1
	1	78.49	69.94	55.44	43.96	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01
	2.5	78.55	69.99	55.50	44.02	34.79	1.06	1.04	1.04	1.03	1.03	1.02	1.02
	5	78.65	70.09	55.59	44.12	34.90	27.15	1.11	1.08	1.07	1.06	1.05	1.04
	10	78.85	70.27	55.76	44.30	35.11	27.43	20.39	1.23	1.17	1.14	1.11	1.10
	20	88.75	70.63	56.11	44.66	35.52	27.95	21.24	14.07	1.64	1.42	1.32	1.26
	30	89.20	70.98	56.44	45.01	35.91	28.43	21.95	15.66	5.91	2.07	1.68	1.51
	40	89.64	71.32	56.77	45.34	36.28	28.87	22.56	16.72	10.46	3.84	2.34	1.90

As shown in Table 3.4, while the dielectric constant of water is 78.46 at 25°C and 0.1 MPa, it decreases to 14.07 at 350°C and 20 MPa, and it is possible to decrease the dielectric constant of water to approximately 1 by modifying the temperature and pressure values [131]. When water reaches the supercritical point, the dielectric constant drops to approximately 6, and water behaves as a nonaqueous solvent at this level [122]. The dielectric behavior of water is similar to methane at ~200°C, acetone at ~300°C, methylene chloride at ~400°C, and hexane at ~500°C [132].

In an unconventional reaction environment, supercritical water displays a wide variety of conversions, including hydrogenation, carbon-carbon bond formation, dehydration, decarboxylation, partial oxidation and hydrolysis, and the rate and selectivity of these reactions can be adjusted by selecting the appropriate temperature, catalyst, and water density, which allows the functional group conversion reactions to be controlled [112].

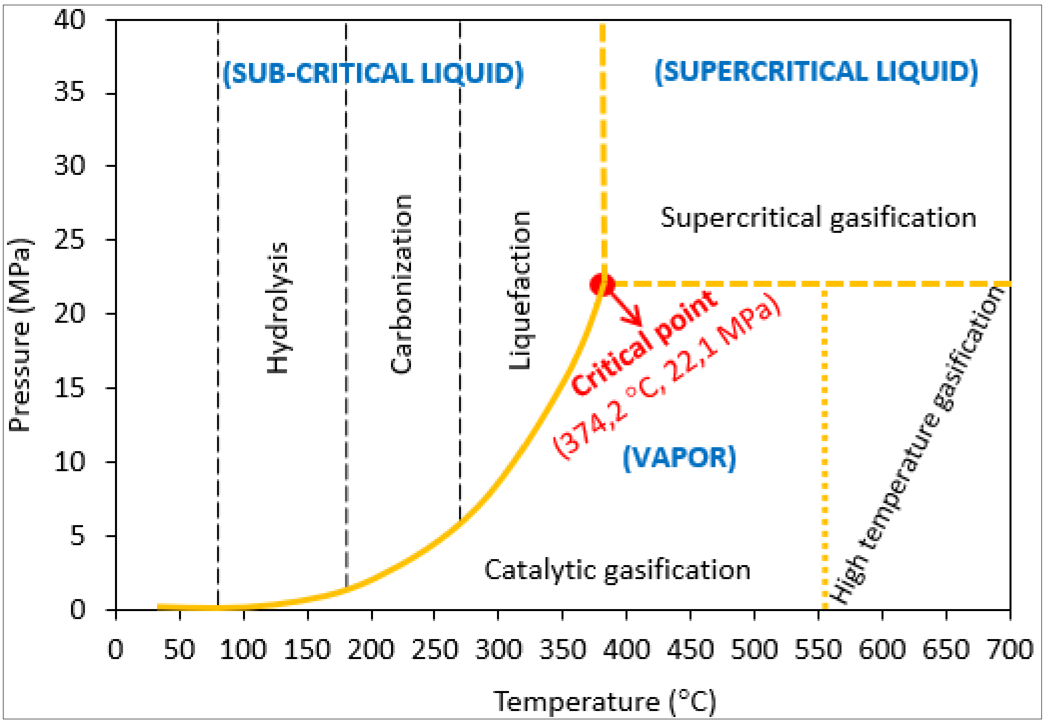

Figure 3.1. Properties of water and the uses of hydrothermal techniques [133, 134].

Table 3.5. The physical and chemical properties of water under normal and subcritical/supercritical conditions [121].

	Normal water	Subcritical water	Supercritical water
Temperature (°C)	0-100	100-374	>374
Vapor pressure (MPa)	0.003 (24°C)	22.1°C	> 22.1

Phase	liquid	liquid	no phase differentiation
Density (ρ) [g/cm^3]	0.997 (25°C)	0.692 (330°C, 30 MPa)	0.252 (410°C, 30 MPa)
Viscosity (μ) [Pa·s]	Liquid: 884 Gas: 9.9 (25°C)	Liquid: 50.4 Gas: 30.7 (371°C)	low
Thermal capacity (C_p) [J·g^{-1}·K^{-1}]	Liquid: 4.2 Gas: 2 (25°C)	Liquid: 69 Gas: 145 (371°C)	1300 (400°C, 25 MPa)
Dielectric constant (ε)	78.5 (25°C, 0.1 MPa)	18.2 (330°C, 30 MPa)	5.9 (400°C, 25 MPa)
Ionization constant (K_w) [mol^2·L^{-2}]	10^{-14} (25°C)	10^{-11} (300°C)	10^{-20} (400°C)

Hydrothermal Carbonization

The thermochemical conversion of the organic matter in biomass occurs in an anaerobic environment in the presence of subcritical water which is referred to as hydrothermal carbonization, and the resulting solid product is called hydrothermal carbon (HTC) or hydrochar [135]. Hydrothermal carbonization is a process that reduces both the oxygen and hydrogen contents (defined as the O/C and H/C molecular ratios) by dehydration and decarboxylation to increase the carbon content of biomass and obtain a higher calorific value [136]. Biomass with a high moisture content can be converted to fuel within a few hours in water at 180-250°C and under a 2-10 MPa pressure [117, 136]. The HTC process has been found to allow the formation of nano and microsized carbon particles with various properties, such as high energy value, high chemical and thermal stability, and an increased surface area and adsorption capacity [117, 137-139]. It is accepted that hydrolysis, dehydration, decarboxylation, aromatization, and condensation polymerization occur during hydrothermal carbonization [136].

Hydrothermal Gasification

The gasification process is an effective thermochemical method for converting biomass into gas products, such as carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4) [140]. Gasification is usually performed within a temperature range of 400 and 700°C to obtain methane or hydrogen in high yields [108][111]. The gasification process can be performed under subcritical conditions (a 225-265°C temperature and 2.9-5.6 MPa pressure) if a catalyst is used [141]. The wet biomass is almost completely gasified without predrying using hydrothermal gasification. The heating value of the resulting gas product depends on the reaction conditions [142].

Three temperature regions have been identified for hydrothermal gasification [143]:

- Region 1 (a 500-700°C temperature and 0-0.2 g/cm^3 water density): free radical materials are prevalent in low-density water, and the reaction is a second-order reaction

- Region 2 (a 374-500°C temperature and 0.2-0.6 g/cm^3 water density): radical mechanisms supporting ionic reaction mechanisms are prevalent together with an increased water density

- Region 3 (a <374°C temperature and >0.6 g/cm^3 water density): involves one vapor phase and one liquid phase. Slow hydrolysis reactions occur.

Hydrothermal Liquefaction

Hydrothermal liquefaction is a thermochemical process often used to obtain a liquid product, called a bio-oil, at moderate temperatures and under high pressures [144]. This process produces a bio-oil with an upper heating value of 35-40 MJ/kg, an aqueous phase containing dissolved organic compounds, a solid (called char), and a gas rich in CO_2 [145, 146]. The purpose of this process is to decompose biomass with a high moisture content into small molecules and reduce the biomass oxygen content to obtain liquid fuels or valuable chemicals [147, 148]. During the hydrothermal liquefaction process, biomass and oxygen are rapidly oxidized or mineralized to form CO_2 or H_2O, while harmful combustion products, such as NO_x, are converted into harmless products in a hydrothermal environment [149]. In a hydrothermal environment, water-soluble portions are dissolved at approximately 100°C, and extraction can be performed. Hydrolysis occurs above 150°C; polymers such as cellulose, hemicellulose, and protein are decomposed into monomers. At approximately 200°C and under 1 MPa pressure, the biomass turns into sludge [142]. Liquefaction is usually performed at a temperature range between 280°C and 380°C and under a pressure range between 7 and 30 MPa for 10 to 60 minutes [118]. The reactions that occur during hydrothermal liquefaction are as follows: larger molecules of the biomass are hydrolyzed and/or decomposed into smaller molecules. Since the majority of the resulting molecules are unstable and reactive, they may recombine with larger molecules. Furthermore, a considerable portion of the oxygen in the biomass is removed by dehydration or decarboxylation [144].

The parameters affecting the hydrothermal liquefaction performance (such as the bio-oil yield, char formation, bio-oil composition, H/C ratio, oxygen content, pH value, and upper heating value) include the biomass type, temperature, pressure, holding time, particle size, biomass/solvent ratio, reaction atmosphere, and catalyst [150]. These parameters are explained below.

The biomass type is one of the most important parameters affecting hydrothermal liquefaction. The products obtained from liquefaction vary depending on the biomass components and the amount of these components. High cellulose and hemicellulose contents of biomass usually provide higher bio-oil yields, while a high lignin content reduces the yield and increases the biochar amount [149, 151, 152]. Lignin decomposition in hydrothermal media mainly gives phenolic compounds (i.e., phenol, *m*/*p*/*o*- cresol, guaiacol, 2-/4-ethylphenol, veratrol, methylguaiacol, catechol, 4-methylcatechol, 4,5-dimethylresorcinol and syringol) (Table 3.6). The prominent oxygenated hydrocarbons from hydrothermal decomposition of lignin are phenol, guaiacol and catechol in most studies [153-157]. Hydrothermal liquefaction of cellulose mainly yields furfurals, ketones, and acids [158-163]. Recent studies demonstrated that phenolic compounds such as phenol, alkylphenols, catechol, acids and esters were also detected compounds in biocrudes from the hydrothermal liquefaction of cellulose [161, 162]. It is considered that condensation of reaction intermediates (such as furfurals) produced phenols or acids [161]. Notably, the type of formed compounds as well as their amounts are significantly affected by operating conditions. Moreover, the product selectivity can be accomplished by using catalysts [163].

Table 3.6. Hydrothermal liquefaction (HTL) of lignin and cellulose at different process conditions.

Component of Biomass	Temperature (°C)	Residence Time (min)	Pressure (MPa)	Main Findings	Reference
Kraft lignin from softwood (LignoBoost Kraft lignin)	350	11	25 (observed)	The experiments were carried out with phenol in the presence of K_2CO_3 (0.4-2.2 wt%). The biocrude contained mainly phenolic species including (phenol, anisole, 2-/4-methyl anisole, 2-ethylanisole, m/p/o- cresol, guaiacol, methylguaiacol, 4-ethylguaiacol, 4-Propylguaiacol, 2-Ethylphenol, dimethylphenol, 2-acetylphenol, 4-ethylphenol, propylphenol, catechol, 4-methylcatechol, 4-ethylcatechol and phenolic dimers.	153
Kraft pine lignin Indulin® AT	280-350	15	18.1-24 (observed)	The experiments were carried out without and with phenol in the presence of phenol with K_2CO_3 (1.7 wt%). Biocrude consisted of mainly phenols including phenol, m/p/o- cresol guaiacol, 2-/4-ethylphenol, veratrol, methylguaiacol, catechol, 4-methylcatechol, hydrocoumarine, vanillin, and phenolic dimers. The use of phenol in the HTL runs increased the total amount of phenols.	154
Soda wheat straw lignin (Protobind 1000)	300	30	17 (observed)	The experiments were conducted in the presence of 18.6 g 0.5 M NaOH. The selected phenolic compounds were quantified. The quantified phenolic species were anisole, phenol, guaiacol, catechol, 3-methoxycatechol, 1,2-dimethoxybenzene, 1,2,3-trimethoxybenzene, syringol, vanillin and acetosyringone. The amount of guaiacol, catechol, and 3-methoxycatechol was high.	155
Alkaline lignin	280	15	N/A	The experiments were carried out without using any catalysts. The identified prominent compounds in bio-oil were mainly phenols including guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol, phenol, 4-mehylphenol, catechol, 3-/4-methyl catechol, and 4,5-dimethylresorcinol. Among identified compounds guaiacol had the highest peak area.	156
Corncob lignin	210-290	0-40	N/A	The non-catalytic hydrothermal degradation of lignin mainly yielded phenolic compounds. The identified volatile organic compounds in the biocrude were phenols and its derivatives (i.e., phenol, 3-,4-methylphenol, 2-ethylphenol, 4-ethylguaiacol, syringol, 2-methoxy-4-propyl-phenol, and 2-methoxy-4-(1-propenyl)phenol. Among the identified compounds, 4-ethylguaiacol, phenol, and syringol were prominent with high peak areas.	157
Cellulose	275-320	0-30	N/A	Hydrothermal liquefaction of cellulose was carried out at different pHs. The identified compounds were hydroxymethylfurfural (HMF), acetic acid, propinoic acid, isobutyric acid, butyric acid, iso-valeric acid, isocaproic acid, n-caroic acid, heptanoic acid, lactic acid, levunulic acid, and dihyroxy acetone. The major compound was HMF at pH 3 and pH 7 whereas this compound did not observe at pH 14.	159
Microcrystalline cellulose	185-195	25-110	3.8-5.4 MPa (observed)	Microwave assisted non-catalytic degradation of cellulose produced two major products namely HMF and glucose. The product selectivity and yields changed depending on the operating conditions.	160
Cellulose (microcrystalline, Alfa Aesar)	350	30	N/A	Non-catalytic hydrothermal liquefaction of cellulose produced the following products: phenols, ketones and aldehydes, hydrocarbons, alcohols, and acids and esters.	161
Cellulose (medium fibers)	240-320	30	N/A	Non-catalytic hydrothermal liquefaction of cellulose yielded aldehydes, ketones, acids, and phenols.	162
Cellulose (Avicel®PH-101)	250	60	1.0 (initial)	Hydrothermal liquefaction of cellulose without and with catalyst (i.e., Fe powder, $FeO_{x,}$ Fe powder + Pd/Al_2O_3). The water -soluble (WS) fraction from the non-catalytic run contained 2-butanone, 2-pentanone, 3-hydroxy-2-butanone, hydroxyacetone, furfural, acetic acid, 2,5-hexanedione, 2,3-butanediol, 3-methyl-1,2-cyclopentanedione, and levulinic acid. Fe assisted HTL of cellulose mainly produced produced hydroxyketone while diols formed in WS fraction with the use of $Fe+Pd/Al_2O_3$.	163

Temperature is one of the decisive parameters of hydrothermal liquefaction [164]. The initial temperature increase in this process increases the bio-oil yield, while a further temperature increase triggers gasification and reduces the bio-oil yield [149]. Under subcritical conditions, the temperature increase usually leads to a bio-oil with a low oxygen content [165]. The widely used temperature range is from 250°C to 350°C, and the maximum bio-oil yield is usually achieved at approximately 280-310°C. Studies performed with several wood derivatives using the 280-360°C temperature range show that a temperature increase up to 300°C, the optimum temperature, leads to an increase in the bio-oil yield, while a further increase in the temperature leads to decreased yields [152, 166]. Very high temperatures are not appropriate for bio-oil production in terms of both operating costs and the liquid yield.

Catalysts play an important role in improving bio-oil properties. The functions of catalysts include increasing the H/C ratio of the bio-oil, reducing the bio-oil viscosity, and removing heteroatoms (such as O, N, and S) in bio-oils [167]. The hydrolytic cleavage of the ester bonds in lipids, peptide bonds in proteins, and glycosidic ether bonds in carbohydrates can be accelerated using catalysts in hydrothermal environments [148, 168]. Two types of catalysts, heterogeneous and homogeneous, are often used. Homogeneous catalysts may have a higher activity than heterogeneous catalysts [168]. However, it is often difficult to recover homogeneous catalysts at the end of the reaction [148]. When the concentration of the homogeneous catalyst is below a critical value, the bio-oil yield increases and the solid content decreases with increasing the catalyst concentration; exceeding this critical value decreases the bio-oil yield and increases the solid content [151]. Alkaline salts increase the bio-oil yield and reduce the solid content under subcritical conditions, while acids increase the production of water-soluble products (such as sugars, carboxylic acids, furfural, and 5-hydroxymethylfurfural) [144, 169]. Generally speaking, hydrothermal liquefaction of biomass with heterogenous catalyst produce lower yields of bio-oils than those with homogenous catalysts [22, 170-176]. The reason is that a heterogeneous catalyst is most likely affected by sintering, poisoning, internal diffusion limitation, and inactivation in the hydrothermal liquefaction of biomass [175]. Heating values of bio-oils obtained with heterogenous catalyst are comparable than those with homogenous [Table 3.7]. Notably, extraction procedure and solvent type for the extraction of biocrudes as well as the type of raw material have significant effect on the resulting biocrude yields obtained from hydrothermal liquefaction process. Homogenous catalyst such as potassium carbonate (K_2CO_3) is known to promote water gas shift (WGS) and steam reforming reactions as well as gasification under sub- and supercritical conditions [124]. The reason is that the presence of carbonate/bicarbonate increases hydrogen production due to changes in the gaseous equilibrium and accelerates WGS as well as steam-reforming reaction [124]. Heterogeneous catalysts usually have positive effects on gasification processes performed at low temperatures [144]. Moreover, the catalyst separation, recovery and reutilization are important for industrial applications, which are major challenges for the homogenous catalysts used in hydrothermal biomass processes.

Table 3.7. Yield (wt%), Elemental Composition (wt%), and HHV (MJ.kg−1) of the bio-oils produced from the hydrothermal liquefaction of various lignocellulosic biomasses in the presence of homogeneous and heterogenous catalysts.

Ref.	**Type of Lignocellulose**	**Catalyst**	**T (°C)**	**Reaction Time (min.)**	**Yield (wt%)**	**C (wt%)**	**H (wt%)**	**N (wt%)**	**O* (wt%)**	**HHV & (MJ/kg)**
170	Willow wood[a]	NaOH (NaOH/Biomass ratio=0.40)	400	10	31.0	84.00	9.40	1.60	5.00	40.92
170	Willow wood[b]	NaOH (NaOH/Biomass ratio=0.40)	400	10	42.0	82.00	9.00	1.60	7.40	39.25
22	Birch wood	K_2CO_3 (5 wt% of the biomass)	300	30	38.5	65.60	6.20	0.06	28.14	26.00
22	Birch wood	KOH (5 wt% of the biomass)	300	30	39.5	66.50	6.10	0.09	27.31	26.31
171	Paulownia wood	Iron powder (10 wt% of the biomass)	360	10	36.3	73.50	7.08	-	19.42	31.49
171	Paulownia wood	Na_2CO_3 (5 wt% of the biomass)	360	10	31.9	70.29	6.01	-	23.70	28.11
172	Scotch pine wood	t-BuOK (10 wt% of the biomass)	300	0	41.9	69.23[c]	7.22	-	23.55	29.51
172	Scotch pine wood	KOH (10 wt% of the biomass)	300	0	43.0	69.98[c]	6.97	-	23.05	29.49
173	Spruce wood	KF/Al_2O_3 (20 wt% of the biomass)	300	30	13.9	68.34	6.82	0.05	24.79	28.42
173	Beech wood	KF/Al_2O_3 (20 wt% of the biomass)	300	30	16.0	67.54	6.62	-	25.77	27.71

[176]	A mixture of pine and spruce biomass[d]	Co-precipitated Ni–Co/Al–Mg catalyst (25 wt%)	250	112.8	28.1	54.70	6.30	-	39.10	19.10
[177]	Beech wood	Colemanite (10 wt%)	300	0	29.8[c]	62.49	6.71	-	30.80	25.21
[22]	Birch wood	Synthetic hydrotalcite (5 wt%)	300	30	34.4	63.60	5.80	0.09	30.5	24.30

a-Non-pretreated b-Alkaline pretreated. c-Heavy bio-oil d-microwave assisted hydrothermal liquefaction

*by difference

& HHV was calculated according to the Dulong formula that is $HHV = 0.338C + 1.428(H–O/8) + 0.095S$.

There are some interactions between the solvent molecules and the biomass in hydrothermal medium, and the dissolution of the biomass components is suppressed as the biomass/solvent ratio increases during the hydrothermal process [151]. A low bio-oil yield is achieved, since the limited amount of water does not form a good suspension with the biomass, thereby delaying liquefaction in the reactor [178]. Very high biomass/solvent ratios support more gas production, as observed during pyrolysis [151]. On the other hand, low biomass/solvent ratios enhance biomass conversion and lead to high bio-oil yields; unfortunately, this is not economical [165]. However, the bio-oil yield has been observed to decrease at very low biomass/solvent ratios [179].

Although smaller particles with a large surface area can yield more bio-oil, as small particles can be highly hydrolyzed [180], reducing the particle size requires more energy. Thus, it is important to work with the most appropriate particle size. Water acts as both a heat transfer medium and an extractor in hydrothermal environments, which renders the hydrothermal liquefaction process relatively insensitive to particle size; therefore, it is not necessary to reduce the particle size excessively [149].

The reaction atmosphere may have various effects on the bio-oil yield and oxygen content [168, 181]. Since air causes the combustion of biomass, a low low bio-oil yield is obtained under air [149, 181][152]. Reducing gases (CO and H_2) and inert gases (N_2) are more favorable for obtaining large amounts of bio-oil [181]. These gases have important functions, including stabilizing the decomposed liquid products and preventing the cyclization, concentration, or repolymerization of free radicals [151], which inhibits char formation and achieves high bio-oil yields. Numerous studies have been performed to determine the effect of the reaction atmosphere and other liquefaction parameters on the hydrothermal liquefaction process, and although significant progress has been made, the mechanisms of action of these parameters have not been fully established [165]. This is because the structure of biomass is complex, and it is difficult to control the reactions in the hydrothermal environment.

The holding time is defined as the time required to maintain the maximum temperature of HTL and does not include the heating and cooling times [164]. The holding time is an important factor that affects bio-oil production and biomass conversion [165]. The holding time determines the composition of the liquefaction products and conversion rate of biomass [151]. While the bio-oil yield increases up to the optimum reaction time, the liquid products may re-decompose into gas products and repolymerize into solid products as the reaction time increases further [168]. High bio-oil yields are often achieved in 10-30 min [165]. The heat loss per unit mass of the bio-oil produced using prolonged heating times is significantly higher than that of a bio-oil produced with shorter heating times [182]. Shorter reaction times are often more favorable since they produce high bio-oil yields.

High heating rates lead to the formation of gaseous products due to redecomposition reactions, while low heating rates usually lead to the formation of char due to the repolymerization of intermediates [183]. Therefore, moderate heating rates should be preferred to overcome heat transfer limitations and achieve high bio-oil yields [184].

Pressure helps to maintain the single-phase environment of the liquefaction process [184]. A high pressure increases the solvent density and solubility of the biomass components, and the solvent spreads more efficiently into the molecular structure of biomass, thereby increasing the biomass decomposition and degradation degree [185]. In the subcritical region, the increased pressure leads to an increased water density. High-density water can penetrate the biomass structure more easily than low-density water, which increases the bio-oil yield and biomass degradation [150]. In the supercritical region, an increased pressure has a limited effect on the properties of the water environment; no significant change occurs in terms of the bio-oil yield, in particular [149]. Under supercritical conditions, an increased pressure causes an increase in the solvent density, which creates a cage effect for C-C bonds and prevents the C-C bonds from breaking [183].

CONCLUSION

This review describes state-of-art biomass processes and all of the steps of biomass processing, explaining the chemistry taking place in the background of the processes in a comprehensive manner. In hydrothermal media, the physicochemical properties of water change during the thermal treatment and differ from those of ambient water. Moreover, water acts as an acidic and basic catalyst in reaction environments due to H_3O^+ and OH^- ions, which makes it an excellent solvent and reaction medium. The handling of large volumes of water and the use of complex and expensive reactors are some of the drawbacks of hydrothermal technologies. However, the process is applicable for any type of biomass as well as waste treatment. Biomass with a high moisture content can be converted to liquid, solid and gaseous products within a few hours in water without any drying pretreatment, which requires a large amount of energy. The process has been found to form the following products: high-value chemicals that can be used as fuel or platform chemicals for synthesizing other commercial products, important nano and microsized carbon particles with various properties, such as a high energy value, a high chemical and thermal stability, and an increased surface area and adsorption capacity, and some gases that are used to generate electricity, heat, chemicals and liquid fuels. All the attractive and unique features make the "hydrothermal processing of biomass" a good candidate for converting biomass into value-added products, and this hydrothermal process has become an irrevocable alternative technology used to produce biofuels from various biomasses.

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