Biomass Conversion to Fuels and Value-Added Chemicals: A Comprehensive Review of the Thermochemical Processes

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Abstract: Fossil fuels have fueled the world economy for decades. However, given their limited nature, fluctuating prices and the escalating environmental concerns, there is an urgent need to develop and valorize cheaper, cleaner and sustainable alternative energy sources to curb these challenges. Biomass represents a valid alternative to fossil fuels, especially for fuel and chemical production as it represents the only natural organic renewable resource with vast abundance. A vast array of conversion technologies is used to process biomass from one form to another, to release energy, high-value products or chemical intermediates. This paper extensively reviews the thermochemical processing of biomass to fuels and high-value chemicals, with an emphasis on the process performance, conditions, and weaknesses. Technologies with great future prospects as well as those with possible linkage to CO₂ capture and sequestration are highlighted. The important chemical compositions of biomass feedstock, their conversion technologies and most importantly, the role of catalysis in their conversion to fuels, fuel additives, based chemicals, and added-value chemicals are also discussed. Special attention is given to biofuel production for transportation as this sector is responsible for the highest global greenhouse gas emissions, and has an emerging market with promising future prospects for sustainable large-scale biomass processing. The processes involved in the purification and upgrading of biomass-derived products into higher-value products are equally discussed and reviewed.

Keywords: Biofuel, biomass processing, biomass, biorefinery, green chemistry, thermochemical routes.

1. INTRODUCTION

Fossil fuels, the main source of global energy (81% of the energy supply) satisfactorily meet the current energy and chemical needs [1, 2], despite their environmental setbacks and other concerns. They are used mainly as fuels for transportation or combusted in gas/thermal engines or power plants for electricity production. The use of fossil fuels, however, leads to the emissions of Greenhouse Gases (GHGs). These emissions, together with their limited nature, rapid depletion, price fluctuations, environmental concerns (global warming or climate change), and the growing demand for energy has led to the current strong drive, widespread interest and investments in renewable energies [3-5]. Biomass energy is a sustainable substitute for fossil fuels (oil, natural gas, and coal) in the provision of energy, fuels, and chemicals [1, 6]. It is the only renewable organic resource, relatively cleanest and most abundant among the renewable energy resources [3], and is regarded as one of the most promising fossil fuel alternatives for energy, chemicals and biofuels production [7, 8]. The negligible amounts of nitrogen, sulphur, and ash in biomass make it a cleaner fuel compared to fossils due to its low SO₂, NOₓ and soot emissions. Zero net CO₂ emissions can be achieved with biomass due to the quantitative recycling or sequestration of its CO₂ released by plants during photosynthesis [9].

Also, the interest in the development and valorization of biomass as a source of fuel for the reduction of the environmental concerns from energy generation and in the expansion of domestic and renewable energy sources for both richer and poorer countries stems right from the 1970s energy crisis [10]. Apart from its direct energy production, there is currently a growing interest and attention to develop processes capable of converting biomass to fuels (bio-oil, bio-syngas, etc.) and vital industrial bio-based chemicals [7]. Currently, biomass fuels (agricultural residues, wood, and herbaceous materials) constitute the third largest primary...
energy resource worldwide. Their conventional conversion to energy is regarded as carbon neutral. However, the harvesting of biomass for energy purposes seemingly may be unsustainable as it depletes soil carbon and nutrients, leading to a reduction in soil productivity [5]. Recent studies [11] indicate that roughly 3 billion people globally rely on traditional biomass for heating, lighting, and cooking, resulting in the annual premature death of about 3.1 million due to indoor pollution mainly in developing countries. In addition, about 2.7 billion people lack clean cooking facilities in sub-Saharan Africa and Asia-Pacific, necessitating improved cooking facilities through biogas from anaerobic biomass processing [12].

The abundant and sustainable availability of biomass feedstocks is continuously being dominated and challenged by biomass-derived wastes and residual materials with the inclusion of municipal solid waste, which when unprocessed causes serious problems [5]. The use of biomass wastes (agricultural, domestic, etc.) as bioenergy feedstocks compared to energy crops, will among others reduce GHG emissions, stress on land usage, as well as other associated impacts, conflicts and ethical issues arising from food crops usages. This stands as a strong booster for bioenergy production and in the sustainability of biofuels and chemicals feedstocks [12]. The optimal use and applications of renewable energy resources and technologies can potentially minimize waste generations, enhance energy access and security, promote sustainable development, and above all redress the current environmental concerns associated with fossil use and dependency [14].

Biomass energy resource is utilized in two ways: directly through combustion and indirectly by transforming it into solid, liquid and gaseous fuels or intermediate energy carriers [10]. A variety of techniques, categorized into biochemical, thermochemical, biotechnological and physiochemical, are currently being employed to convert biomass into various energy forms (heat, power, fuels, chemicals and other value-added products) [3]. The thermochemical processes make use of heat energy and chemical catalysts to decompose biomass into valuable energy-rich products, while the physical methods use densification techniques that include crushing, heat and pressure applications, to convert biomass into biofuels. Also, the biochemical processes utilize naturally occurring micro-organisms and enzymes to process biomass into desirable energy products. Biomass direct combustion primarily produces thermal energy, used for electricity production, in Combined Heat and Power (CHP) systems or remotely for cooking and heating especially in developing countries. The indirect processing (gasification and pyrolysis) gives rise to mainly liquid fuels (biofuels), chemicals, charcoal, electricity and CHP generations with internal combustion engines, turbines, and boilers. The liquefaction process (hydrothermal) directly converts biomass into crude oil for use as premium fuels after upgrading or for heat and power generation [10].

Given that the required infrastructural developments for electric vehicles or hydrogen may last longer, biomass energy provides a huge potential for oil substitution in the transport sector [1]. The development of new processes is very crucial for the assurance of a smooth transition to renewable carbon sources in the future. As such, pathways for the generation of bio-derived chemicals and alkanes required for the production of various transport fuels, chemicals and materials are urgently needed. Alkanes (linear, branched and cyclic), mainly obtained from fossils are vital chemical intermediates and end products of the chemical industry, and biomass is an important alternative for the production of these chemicals and fuels [15]. Recent studies [16-18], has shown that several value-added chemicals (halocarbons, aromatics, alkanes, arenes, alkenes, ethers and epoxides, alcohols and phenols, carbonyls, and many other bifunctional organic species), energy and transport fuels can be derived directly from biomass or indirectly as biomass-derived intermediates via both thermochemical and biochemical pathways. However, more research is still required to optimize these processes to make them commercially viable for large-scale applications. These processes will in the nearest future become competitive with a continuous decrease in fossil supply and their rising costs. The transition to biomass-based economy is presently being demonstrated by the current multidisciplinary drives towards the development of biorefineries that can successfully transform biomass to chemicals, high-volume commodities, and platform molecules. This is challenged by the lack of novel separation, refinement and transformation techniques that will maximize feedstocks conversion, thereby minimizing waste and promoting large-scale applications [18].

This study presents a comprehensive review of the thermochemical processes for biomass conversion to fuels, chemicals, and vital material products, with special reference to the concept of the biorefinery as well as recent developments in this area. Considering the rapid progress so far in biomass conversions into energy, this review concentrates mainly on the available thermochemical routes of biomass transformations into fuels and value-added chemicals, with a special focus on the role of catalysis in these conversions. Recent developments and future prospects of these conversion processes are also discussed. Details about reactors technologies and designs are not covered in this review.

2. BIOMASS RESOURCE, CONSTITUENTS, AND CHEMISTRY

2.1. The Biomass Resources

Biomass is generally referred to any mixture of hydrocarbon material comprising carbon, hydrogen, and oxygen, with small amounts of nitrogen, sulphur and some minerals [9, 10, 19]. This very important and versatile renewable resource is an indirect source of solar energy and stores its solar energy in the form of chemical energy via photosynthesis [14, 20]. Biomass covers a broad range of plant and plant-derived materials, including biodegradable wastes. It comprises of all biological materials, including biological waste or dead biomass. They include: agricultural crops and residues, forestry crops and residues, wood and wood wastes, sewage, municipal solid waste, industrial residues, animal residues, food processing wastes, dedicated crops and resi-
dyes, seaweeds, algae and aquatic plants [3-5], and these biomass resources are divided into the following categories: wastes, standing forests, agricultural residues, and energy crops and aquatic plants (algae, water weeds, water hyacinth, reeds and rushes) [14, 21]. The energy crops include corn, sugar cane, grains, sorghum, sugar beets, elephant grass, seaweeds (kelp) and many others. The choice of an energy crop for energy production is dependent on the crop’s dry materials yield per unit of land (hectare). Higher yield reduces land requirements, thereby lowering the production cost of the biomass energy [10].

Virgin biomass has vast global energy potential. The world’s terrestrial standing biomass carbon is estimated to around a hundred times the total annual global energy consumption. Forest biomass comprises between 80% to 90% of the total biomass carbon. Marine biomass carbon (with least natural abundance) is highly concentrated in oceanic and marshy land environments and is projected to precedes forest biomass with respect to the net annual energy production [22]. Biomass is the only renewable carbon source capable of being converted into convenient solid, liquid and gaseous fuels, as well as added-value chemicals. Woody biomass is the oldest form of energy used by humans and is applied traditionally in many parts of the world (especially in the poorer countries) through direct combustion for heating and cooking or indirectly through conversion into liquids or gaseous fuels. However, biomass combustion produces pollutants such as CO₂ (the major component of greenhouse gases), SO₂ and NOₓ (both constituents of acid rain) and dust. The amount of these pollutants released from biomass combustion is far less compared to that emitted from fossil combustion [21]. The majority of biomass energy is produced from wood and wood wastes (64%), municipal solid wastes (24%), agricultural wastes (5%) and landfill gases (5%) [10]. Biomass energy can be classified as traditional or modern biomass. Traditional biomass includes fuelwood and charcoal, animal wastes, rice husk, and plant residues, used in small scales in developing countries. Modern biomass consists of wood and agricultural wastes, urban wastes, and biofuels (biogas, energy crops, etc.) and they are involved in large-scale uses aimed at substituting for the conventional energy sources [21].

The biomass resource can be processed into three major end products: transport fuels, chemical feedstock, and pow

er/heat generation through two principal conversion technologies: thermochemical and biochemical pathways. Among the four thermochemical technologies, biomass gasification has a great future prospect for renewable chemical production and for power generation via internal combustion engines or turbines [23]. Good knowledge of the physicochemical properties of biomass is instrumental for its sustainable use for energy and chemical production. Parameters such as chemical composition, moisture content, the content of ashes and inorganic substances account for the diversity and disparities among biomass species. The principal elements present in biomass in increasing order of abundance are: manganese, sodium, chlorine, iron, Sulphur, aluminum, magnesium, silicon, potassium, calcium, nitrogen, hydrogen, oxygen and carbon [24].

Biomass utilization is mainly challenged by its low energy density, inconvenient form, and bulkiness. As such, the handling, storage, and transportation of raw biomass are costlier compared to fossils. Therefore, to optimally and fruitfully valorize biomass, an improvement of the biomass properties that enhances its handling, storage and transport is very paramount. Biomass conversion technologies, therefore, seek to elevate these properties and ameliorate these prominent setbacks of biomass utilization [6]. When compared to fossil fuels, biomass-derived fuels have low heating values due to their high moisture and oxygen contents, low energy density, high content of volatiles (about 80%), high ignition stability, high density due to the presence of oxygenates, acidic, corrosive and are very viscous [25].

2.2. Biomass Chemistry and Conversion

Biomass (terrestrial) consists mainly of the following biological molecules: carbohydrates (sugars, cellulose, and hemicellulose), proteins, lignin and lipids (fatty acids, oils), extractives, starches, water, ash, hydrocarbons and other compounds [26, 27]. Lignin, cellulose, and hemicellulose made up the bulk of a biomass species whereas sugars occupy less than 30% and lipids (oil) less than 10% of a bulk biomass species. Lignin and carbohydrates are usually regarded together as lignocellulose biomass [26]. Biomass feedstocks vary greatly with respect to their chemical constituents and physicochemical properties, and these have a strong influence on their appropriate choice of conversion technologies [1]. Agricultural wastes are known to possess very high energy and chemical content as they have a higher composition of organic constituents like cellulose, hemicellulose, lignin and trace amount of other organic compounds or polymers [14].

The conversions of biomass vary and are dependent on the desired end products (energy, fuels or chemicals) and biomass streams available [13]. Whereas carbohydrates (starches and sugars) are usually converted through biological fermentation into ethanol, lipids (fatty acids) are often transformed into biodiesel through esterification (transesterification) with methanol or ethanol. The sugars from photosynthesis are usually metabolized into lipids, proteins, and lignin. Cyclic carbohydrate (glucose) are often converted into fatty acids with long-chain hydrocarbons having high energy contents and excellent liquid properties [26]. Alternatively, solid biomass is often converted into synthetic gas (CO + H₂), which is later transformed into liquid fuels and other chemicals through the Fischer-Tropsch (FT) process, requiring several complex steps, energy, and capital investment. Direct liquefaction provides a simpler and more robust solid biomass to liquid (BTL) conversion. Several BTL methods (thermal or thermocatalytic) are still under development [26].

The choice of biomass as a source of energy depends on its moisture content, calorific value, fixed carbon and volatile matter content, alkali metal content, ash, and residual matter content, and the cellulose/lignin ratio [28]. The conversion of lignocellulosic biomass to fuels and chemicals is often difficult, expensive and low-yielding due to the com-
plexities and the exact chemistry of the lignocellulose biomass polymers. Some of the processes available for the processing of lignocellulosic biomass, together with their products and possible pretreatments steps are illustrated in Fig. (1) [1]. The worldwide distribution, vast abundance and the renewable nature of biomass have led to growing interest and the devoted efforts currently employed for organic chemical production from various biomass streams, with particular focus on sugar conversions to value-added chemicals. The most suitable of the biomass sugar feedstocks used as chemical precursors or intermediates are the hexoses, especially glucose and D-fructose [29].

2.3. Biomass Composition

Biomass is generally composed of organic and inorganic constituents and a fraction of water [25]. The development of processes for the generation of fuels and chemicals from biomass is strictly dependent on its chemical structure and the basic organic constituents [9]. Biomass is composed of three main groups of naturally occurring polymeric materials on a dry mass basis. These are cellulose (about 50%), hemicellulose (10-30% in woods and 10-40% in herbaceous biomass), and lignin (20-40% in woods and 10-40% in herbaceous biomass). It also consists of other constituents such as inorganic minerals compounds like the alkali metals compounds (potassium, calcium, sodium, silicon, phosphorus, magnesium and chlorine in herbaceous biomass) and extractives (usually smaller organic molecules and polymers such as proteins, salts, and acids). However, the quantities of these inorganic compound vary from one biomass species to another (wood (less than 1%), herbaceous biomass (15%), and 25% in agricultural and forestry residues) [10]. Lipids, simple sugars, proteins, water, starches, hydrocarbons, ash, and other compounds are equally present and these components are mainly found in the trunks, foliage, and barks of plants [10].

The distributions of the three major biomass constituents are also species-dependent, with very prominent disparities between hardwoods and softwoods. The deciduous woods (hardwoods) have a relatively higher amount of cellulose, hemicellulose, and extractives compared to the softwoods which only have a higher lignin content. Overall, hardwood is made up of around 43-47% cellulose, 25-35% hemicelluloses, 16-24% lignin, and 2-8% extractives, whereas softwood is compose of about 40-44% cellulose, 25-29% hemicellulose, 25-31% lignin and 1-5% extractives [9, 27]. As discussed by [28] and [30], biomass is composed of the following major elemental composition on the dry mass basis: oxygen (30-40%), carbon (30-60%), and hydrogen (5-6%) depending on the ash content. Sulphur, chlorine, and nitrogen make up less than 1% of the biomass. These elemental composition in increasing order of abundance are: Al, Mg, Si, K, Ca, N, H, O, and C. The typical levels and description of the main biomass constituents are summarized in Table 1 [25]. The major biomass organic constituents (cellulose, hemicelluloses, and lignin) and biomass elemental composition are characterized using the proximate and ultimate analysis [31].

Carbohydrates are polyhydroxy organic compounds generally represented elementally as (CH$_2$O)$_n$. They have a uniform carbon of about 40%, far less than in hydrocarbons. However, their oxygenated nature gives them superior physicochemical properties that enhance their conversion and utilization. Carbohydrates are classified as monosaccharides, disaccharides and oligosaccharides, and polysaccharides.
First-generation biofuels feedstocks mainly comprise starch and sugar, whereas cellulose and hemicellulose carbohydrates constitute the second generation biofuels feedstocks [1]. Cellulose and hemicellulose make up the carbohydrate portion of biomass, whereas the non-carbohydrate portion is composed of lignin [28, 30].

### 2.4. Catalysis in Biomass Conversion

Organic catalysis (enzymatic catalysis) has traditionally been used in biomass processing. However, inorganic catalysis used in the conversion of raw biomass feedstocks to valuable products is to some extent more economically performant [26]. Acid catalysis is widely applicable in biomass valorization owing to their superior ability towards molecular deoxygenation through multiple chemical reactions [18]. Catalysts play a key role in biomass processing either in promoting the conversion processes or in the upgrading of the conversion products (liquids or gases) into high-value fuels or chemicals. However, their nature and action vary, depending on the conversion of technology being used.

Heterogeneous catalysts play a central role in fossils conversion to fuels, power, and chemicals. However, their role in biomass processing is still unclear, given the diametrically opposing chemical nature of both resources. Zeolites over the past years have shown great potential for use in biomass valorization, especially in the conversion of lignocellulosic biomass to fuels and chemicals. They play a key role in the conversion of oxygenates to hydrocarbons, catalyzing reactions like dehydration, esterifications, decarboxylation, and acylation. Thus, the use of zeolite catalysts in biomass processing is found to be a promising alternative method for the production of transport fuels and chemicals [32]. However, the design of novel catalytic routes for the selective, efficient, and direct conversion of biomass feedstocks for the production of targeted chemicals is a major challenge in the field of biochemicals [2]. The transesterification process for biodiesel production is usually catalyzed by both homogeneous and heterogeneous catalysts.

Heterogeneous catalysts (acid or base) like alkali metal oxides and derivatives, transition metal oxides and derivatives, alkali earth metal oxides and derivatives, mixed metal oxides and derivatives, sulfated oxides, ion exchange resins, carbon-based catalysts, enzyme base catalysts, boron-based catalysts, waste material-based catalysts, have all been reported in literature recently and their applications in lab-scale biodiesel production. They are highly active, selective, and water-tolerant depending on the amount and strength of the active acid or basic sites [33]. However, the role of heterogeneous catalysts in the production of biodiesel and bioethanol is limited due to their production pathways (bacterial fermentation and transesterification using homogeneous bases). Heterogeneous catalysis is vastly applicable in the production of advanced biofuels (high energy density and infrastructural compatibility). This involved some relevant catalytic routes like pyrolysis/gasification accompanied by catalytic upgrading, aqueous-phase processing of sugars and platform molecules, and hydrotreating of vegetable oils and related feedstocks [2].

Catalysts also play a fundamental role in the gasification products. They improve the gas quality, conversion efficiency and reduce the tar content. Dolomite, alkaline metal oxides and Ni-based oxides are widely used gasification catalysts. Iron, cobalt, ruthenium and potassium-based catalysts are well known for their role in the FT synthesis of diesel, hydrocarbons and other liquid fuels from bio-syngas. However, the performance of these catalysts varies and their choice is determined by their properties, reaction pathways and the desired end product [34]. Recently, catalysis has become one of the principal processes required for the achievement of sustainable chemicals and energy production. This is evident from the production of furan derivatives in the past decades from biomass sugar, used as substitutes for oil-derived chemicals or as starting materials for new product synthesis like vital polymeric materials, pharmaceutical agents (fungicides), liquid fuels or solvents, macrocyclic ligands [8, 29].

Despite the great and intriguing progress made in the catalytic transformation of biomass sugars into essential chemicals and chemical precursors, there is still an urgent need for further research to enhance the selectivities of the catalysts and to improve their conversion efficiencies in order to fully commercialize those processes. Also, further catalytic progress for biomass processing should be focused on the rapid, economical and environmentally benign production of organic chemicals with recent developments and the concepts of green chemistry. In addition, priorities in catalytic chemistry should be given to multi-purpose catalysts originating...
from the incorporation of transition metals with acid/base solid catalysts. This will permit several reaction steps to be conducted in a single reactor, avoiding the costly intermediate separation processes. Moreover, catalysts recycling and the efficient recovery and separation of the targeted products are also very instrumental in biomass catalytic conversion and in catalytic studies as a whole. However, these are challenged due to lack of perfect understanding of the catalysts structure-property relationships and exact biomass conversion reaction mechanisms, multi-purpose catalysts and their suitable solvent systems, process compositions, catalyst optimization, and development, especially for large-scale production systems [29].

3. BIOMASS CONVERSION TECHNOLOGIES

3.1. Overview of Biomass Conversion Processes

Biomass conversion processes mainly achieved two goals: energy production and environmental clean-up. Two major pathways are used for biomass processing: the biological (biochemical) and the thermochemical pathways. The thermochemical pathways usually have higher efficiencies than the biological processes due to their low reaction times and superior ability to destroy the organic constituents of biomass [25, 28]. The feedstocks for biomass conversion can be highly variable in terms of mass and energy density, moisture content, size, and intermittent supply. As such, modern industrial technologies are often hybridized with fossil fuel such that in case of biomass supply irregularities, the fossil fuel is used for preheating, drying and in the maintenance of fuel supply [22].

The pathways for biomass conversion into various energy forms vary. The choice of an appropriate conversion process depends on the biomass quantity, type, desired energy or chemical end product, the feedstock characteristics, economic conditions, policy and environmental standards [13]. Among these, the dominant factors are the desired energy form and feedstock availability. Three principal process technologies govern biomass conversion into energy, fuels, and chemicals. These are the biochemical, thermochemical and physiochemical processes. The biochemical pathway consists of two main processes (anaerobic digestion and fermentation), the thermochemical pathway consists of four major processing options (combustion, gasification, pyrolysis, and liquefaction) and the physiochemical route mainly consists of extraction, followed by esterification, whereby oils are obtained from the crushing of oilseeds [13].

Through these conversion processes, biomass can be used to produce different forms of energy (heat, electrical, chemical energy or fuels). Its energy density is often upgraded through the production of fuels such as liquid fuels (transport fuels), charcoal, gaseous fuels (H₂, biogas, producer gas). The bioconversion processes of biomass mainly give rise to biofuels (bio-alcohols, bio-dimethyl ether, synthetic natural gas (bio-methane), Fischer-Tropsch fuels, and hydrogen), broadly classified into four groups (Table 2) depending on the biomass feedstock used [3, 19]. Biomass is mainly utilized through combustion for heat and power generation, conversion into gas-like fuels (CH₄, H₂, and CO), or conversion into liquid fuels (biofuels). Presently, biomass energy contributes about 14% of the total global energy consumption, compared to 12% from coal, 15% from gas and 14% from electricity [27].

The first-generation biofuels, with commercialized technologies, are primarily produced with food or feed raw material feedstock like simple sugars, fats, starch, and vegetable oils. The controversy of food versus energy lead to the development of second-generation biofuels, produced mainly from lignocellulose biomass such as non-feed crops, forest residues, domestic, agricultural and industrial wastes. Although the second-generation biofuels overcame the controversial food versus fuel challenge of the first-generation biofuels, they still require vast arable land to cultivate the feedstock crops. Thus, depriving food cultivation and indirectly imposing the same controversy with the first-generation biofuels. These issues are addressed with the third-generation biofuels that use algae and seaweeds which are grown on unproductive land, marshy land, and sea waters. These tech-

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<tr>
<th>Biofuel Type</th>
<th>Description</th>
<th>Examples</th>
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<td>First generation biofuels</td>
<td>Produced from raw materials competing with the food and feed industry</td>
<td>• Bioethanol from sugar cane, sugar beet and starch crops (corn and wheat)</td>
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<td>• Biodiesel from oil-based crops (rapeseed sunflower, soyabean, palm oil, and waste edible oils)</td>
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<td>• Starch-derived biogas</td>
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<td>Second-generation biofuels</td>
<td>Produced from non-food crops (energy crops), or waste residues</td>
<td>• Biogas from waste and residues</td>
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<td></td>
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<td>• Biofuels from lignocellulosic materials</td>
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<td>• Biofuels from energy crops</td>
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<td>Third-generation biofuels</td>
<td>Produced from aquatic microorganisms like algae</td>
<td>• Algal biodiesel</td>
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<td>• Algal hydrogen</td>
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<td>Fourth-generation biofuels</td>
<td>Biofuels based on high solar efficiency cultivation</td>
<td>• Carbon-negative technology</td>
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<td>• Technology of the future</td>
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Table 2. Classification of biofuels [3, 19].
nologies are still under development. The fourth-generation biofuel technologies are still at the conceptual stage. They are intended to be produced by technologies that will successfully transform biomass into fuel in a way that the CO₂ consumed in their generation is larger than that produced during their use or combustion. As such, these biofuels would be very vital in mitigating climate change through the reduction of atmospheric GHGs. They result from genetically engineered algae, a carbon-negative energy resource, with enhancing hydrocarbon yields, giving rise to an artificial carbon sink [3, 19].

The second-generation biofuels are mainly produced via biochemical and thermochemical methods from lignocellulose materials. Thermochromically, the process consists of gasification and/or pyrolysis, followed by the processes for gas cleaning and conditioning and finally the FT synthesis to generate synthetic liquid fuels. Biochemically, the cellulose and hemicellulose components of biomass are first broken down enzymatically into their constituent sugars, which are then fermented to bioethanol. This pathway is less prone to commercialization than the former but shows great future cost reduction potentials [35]. Whereas the thermochemical processes occur at higher efficiencies with short reaction times and have the ability to completely decompose vast organic compounds in biomass, the biological processing shows low efficiencies with higher reaction times (days, weeks, etc.) and is unable to completely breakdown most organic compounds in biomass such as lignin [13]. The next sub-sections of this paper present an overview of the current biomass thermochemical conversion routes for fuels and chemical production - pyrolysis, gasification, and hydrothermal processing (precisely hydrothermal liquefaction).

3.2. The Thermochemical Conversion Pathways

They are commonly used to convert biomass into higher heating value fuels, reducing the biomass oxygen content to increase their energy density as well as increasing the weight of the final hydrocarbon fuel via the creation of carbon-carbon bonds [19]. These processes do not solely produce useful energy from biomass directly, but also convert biomass into more convenient, easily transportable and more energy-dense forms of energy carrier (producer gas, oils, alcohols, etc.) under controlled temperatures and oxygen condition [22]. They are dependent on the biomass feedstock type, physicochemical properties, and the process operating conditions and these affect process conversion time, product distribution and quality [10]. The products of biomass thermochemical processing are usually classified as a carbon-rich residual fraction and the volatile fraction (gases, vapor, and tar) [9], and are generally in the form of solid, liquid and gaseous fuels with equal ecological and industrial importance [14].

The thermochemical processing of biomass occurs via combustion, gasification, pyrolysis, carbonization, and liquefaction processes, with pyrolysis being a preliminary stage in all the processes. These processes release the energy content of biomass by transforming it into solid (charcoal), liquids (bio-oils) or gaseous fuels (synthetic gas) via pyrolysis, gasification or liquefaction and directly as heat through combustion and/or co-firing. The most valuable of these technologies are those with liquid or gaseous intermediate energy carriers with higher potentials of upgrading to more energetic molecules or fuels [13, 36]. Among these processes, gasification is the most efficient and cost-effective for bioenergy generation from lignocellulose biomass [19]. These processes occur by varying their operating conditions, namely heating rate, vapor residence time, reactor configuration, etc. The pyrolysis solid product (biochar) is highly applicable in the sequestration of carbon through soil management systems. The gasification process mainly generates flue gas, together with syngas which is the feedstock for the production of synthetic liquid fuels via the FT synthesis or burnt for heat and power generation [10]. The liquefaction process (hydrothermal) focuses only on liquid fuels production under high pressures in various solvents like water, acetone, methanol or their mixtures [31]. The stages, processes, and products involved in biomass thermochemical transformations are illustrated in Fig. (2) [13], and their characteristics are summarized in [13, 36].

The thermal depolymerization and decomposition of the structural constituents of biomass (cellulose, hemicellulose, and lignin) give rise to chemicals in the form of liquids, gases, together with residual solid charcoal. Pyrolysis oil comprises of an array of chemicals such as cyclopentanone, methanol (most valuable), methoxyphenol, acetone, acetic acid, phenol, levoglucosan, furfural, guaiacol and their alkylated phenol derivatives, and formic acid. The composition of these chemicals is mostly dependent on the process heating rate and temperature. Lignin conversions give rise to chemical like syngas, methanol, dimethyl ether, ethanol, mixed alcohols, C₁-C₄ gases, hydrocarbons, Fischer-Tropsch liquids, styrenes, oxygenates, phenol, cyclohexane, biphenyls, substituted phenols, cresols, catechols, aromatics, and so on [27].

3.2.1. Pyrolysis

Pyrolysis refers to the thermal breakdown of biomass (mainly lignocellulosic biomass) to liquid (tar or bio-oil), carbon-rich solid (char or biochar) and a mixture of non-condensable gases in the absence of oxygen at elevated temperatures [25]. Gases results when the process temperatures are high with longer residence times, and longer vapor (hot) residence times. Lower process temperatures favor charcoal production whereas short vapor residence times and lower temperatures are best for liquid production. The proportion of these three key products produced during a pyrolysis process is dependent on the process condition or how the process conditions are varied [13]. This process generates fuels with high fuel-to-feed ratios, and this makes it the most efficient biomass conversion route. In addition, the optimization of the high-value fuel products via thermal and catalytic
pathways is the main objective of this process [9]. In a nutshell, pyrolysis offers a broader perspective and opportunities for biomass valorization than the other thermochemical conversion processes and is broadly classified into two groups (fast and slow) depending on the operating conditions [10]. Pyrolysis plays a fundamental role in reactors design, reaction kinetics, and in the determination of product distribution, properties, and composition, in all the viable thermochemical biomass conversion processes [9].

Generally, four key pathways generate transport fuels via pyrolysis: slow pyrolysis and syngas upgrading, fast pyrolysis and hydroprocessing, catalytic pyrolysis and hydroprocessing, and hydropyrolysis and hydroprocessing [37]. Hydroprocessing refers to the integrated hydrocracking and hydrotreating processes. The feedstock chemical composition and the process temperature strictly determine the quantity, types, and quality of the resulting products [14]. Table 3 highlights the various types of pyrolysis, process conditions, and product distribution [13]. The end products of pyrolysis originate both from the primary breakdown of the solid biomass species and the secondary reactions of the condensable volatile organic products into char, lightweight gases, and secondary tar. Contrary to combustion and gasification that occur at higher temperatures, pyrolysis is conducted at lower temperatures, ranging from 400-700°C, and are found to be much lower in biomass species containing metallic compounds. Also, it occurs at lower pressures (0.1-0.5 MPa) compared to higher pressures ranging from 10 MPa to 25 MPa with hydrothermal liquefaction [10]. Temperature is a major determinant for the distribution of pyrolysis products. The products are mainly produced between 352°C-452°C. At higher temperatures, the gaseous fraction is enriched with lighter molecules through the breakdown of heavier molecules found in the liquid and residual solid. High liquid production arises at high temperatures, high heating rate and short residence time, while high residence time, low heating rate and low temperatures favor char production. Increasing temperatures reduces charcoal yield. The fuel gases are produced under high temperatures, long gas residence time and high heating rate [9].

Heat is usually provided externally to thermally crack the biomass constituents into gases and vapor, which through secondary reactions give rise to the broad product spectrum [13]. A number of factors affect biomass pyrolysis performance, product types, distribution, and quality. These include: feedstock type, temperature and heating rate, volatiles residence time and pressure, particle size, shape and orientation, reactor configuration, catalysts, additives, and physico-

**Table 3. Biomass pyrolysis modes, process conditions, and product distribution [13].**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Conditions</th>
<th>Liquid (wt.%)</th>
<th>Solid (wt.%)</th>
<th>Gas (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>~500°C. Shot hot vapor residence time &lt;2s</td>
<td>75</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Intermediate</td>
<td>~500°C. Moderate hot vapour residence time 5-30s</td>
<td>50 (2 phases)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Carbonization (slow)</td>
<td>~400°C. Long hot vapour residence time (hours to days)</td>
<td>30 (2 phases)</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Gasification (allothermal)</td>
<td>~750-900°C. Moderate hot vapour time &gt;5s</td>
<td>3</td>
<td>1</td>
<td>96</td>
</tr>
<tr>
<td>Torrefaction (slow)</td>
<td>~280°C. Solid residence time, -10-60mins</td>
<td>0, unless vapours are condensed, then up to 15%</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>
chemical properties such as thermal conductivity and emissivity, permeability and density, specific heat capacity and heat of reaction, particle shrinkage and moisture content, and the external heat transfer coefficient. The outcome of any pyrolysis process, therefore, depends on how these parameters are varied [10]. The much interest in pyrolysis arises from its operational flexibility, technology versatility, and its adaptability to a wide range of biomass streams and products [13].

Fast pyrolysis (thermolysis) operates under moderate temperatures of about 500°C and is characterized by high heating rate, short hot vapor residence time (<2s), and overall short reaction time. Here, the biomass is broken down swiftly to mainly vapor and aerosols, with some charcoal and gas. Thereafter, the vapor is cooled and condensed into a dark brown homogeneous liquid [13]. It favors the production of liquid products but inhibits solid char formation [25]. Its feedstocks generally have small particle size, with a provision in the system for the rapid removal of the vapor to prevent further contact with the hot solid particles. The reactor systems for fast pyrolysis include: fluidized bed, ablative systems, vacuum pyrolysis systems and the stirred or moving beds reactors [10]. Fast pyrolysis is currently of great commercial interest as it gives rise to liquids which can be stored, transported, used as energy, efficient energy carriers, chemicals, fuel precursors and transport fuels. It produces about 60-70wt.% of liquid bio-oil, 15-25wt.% of solid char, and about 10-20wt.% of non-condensable gases. To maximize liquid production, the process is kept under low temperature, high heating rate and short gas residence time and to maximize gas production, high temperature, long residence time and the low heating rate is required [9]. However, with rapid heating and quenching rates, intermediate pyrolysis liquid results which condense prior to the further decomposition of its higher weight constituents into gaseous products [9, 14]. The key features of fast pyrolysis for liquid productions (high yields) are [9, 13, 14, 25]:

- Particle size of less than 5mm for fast devolatilization and high heating rates.
- Short vapor residence time (<2s) to minimize secondary reactions.
- A controlled reaction temperature of around 500°C to maximize liquid yields.
- Feedstock moisture content of less than 10 wt.% as all the feed in water settle in the liquid phase together with water from the pyrolysis reactions.
- Very high heating and heat transfer rates at the biomass particle reaction interface. This requires a finely ground biomass fed of less than 3mm due to its low thermal conductivity. The particle heating rate is the rate-limiting step in this process.
- Rapid char removal to minimize vapor cracking.
- Rapid cooling of pyrolysis vapor and aerosols to produce bio-oil.

As fast pyrolysis for liquids occurs in few seconds, mass and heat transfer processes, reaction kinetics and phase transition phenomena play a major role. Thus, bringing the reacting biomass particles quickly to the optimum process temperature and minimizing their exposure to lower temperatures (charcoal production) and higher temperatures (thermal cracking) is very important in this process [13]. This is mainly achieved in fluidized bed reactors. The reactor commonly used for fast pyrolysis includes bubbling fluidized-bed, circulating fluidized-bed, ablative flow, entrained flow, rotating cone and vacuum reactors [25].

Fast pyrolysis is also reported to produce hydrogen gas at elevated temperatures (700-100°C), through steam reforming and water-gas shift reactions. These reactions mainly convert methane, simple aromatics, other hydrocarbon vapors (C₂, C₃), and others, into hydrogen. Overall, steam reforming converts the hydrocarbons into CO and H₂, and the CO then combines with H₂O to produce H₂ and CO₂ via the water-gas shift reactions [25]. It is a commercialize technology for chemical production but is still under development for the production of liquid fuels. Compared to the other thermochemical conversion processes, small scale fast pyrolysis processes have higher energy efficiencies and relatively low investment costs [9].

Slow and intermediate pyrolysis focus on the production of solid char with liquids and gases as by-products. Slow pyrolysis occurs under gentle heating at low temperatures with longer vapor residence times and larger particle sizes. It is a well-known process that occurs between 277-677°C and often appears in the traditional charcoal kiln [14]. The agitated drum kilns, large retorts (continuous or batch), rotary kilns and screw pyrolyzers are commonly used slow pyrolysis systems [10]. Slow pyrolysis has often been used to reduce the harmful effects of waste on the environment as well as reduces waste quantities for disposal. Also, pyrolysis has been used for centuries for the production of charcoal, until recently (last 35 years) that fast pyrolysis for liquid production was developed [13]. The flash pyrolysis process operates at temperatures within 777-1027°C to produce the petroleum equivalent of bio-oil of up to 70% yield efficiency. This process also gives rise to pyrolytic water, posing major setbacks to this process. This bio-crude oil can be used directly as fuels in boilers, engines, and turbines or as refined fuels for heat and power generation [14].

3.2.1.1. Pyrolysis Products and Uses

Biomass pyrolysis is a very prominent pathway for the generation of solid (char), liquid (tar) and gaseous products which are potential alternative energy sources or substitute for petroleum fuels. The liquids may be used directly as liquid fuels for boiler, diesel engine, and gas turbine for heat and power production added to the feedstock of the petroleum refinery or catalytically upgraded into liquid transport fuels. Other applications may require its alkalis content to be removed and oxygen content lowered via catalytic cracking and hydrogenation [9, 14]. It mainly gives rise to a carbon-rich solid and volatile matter or flue gas. The flue gas is generally used as solvents (acetone, methanol), hydrocarbons...
and electricity productions. The bio-oil component is a major source of chemicals like acetic acid and levoglucosan, which can be upgraded into motor fuel or combusted for electricity generation. The produced char could either be used as slurry fuel, soil enrichment agent or used as activated carbon in industrial applications [10]. Pyrolysis plays a fundamental role in reaction kinetics, reactor design and in the determination of product distribution, composition and properties in all the thermochemical conversion processes [14].

The pyrolysis liquids are dark brown viscous oils with well-known chemistry and no exact precision on their exact quantitative constituents. They are mainly composed of ketones, aldehydes, organic acids, phenols, anhydrosugars like levoglucosan, pyrolytic lignin (guaiacyl- and a syringyl-based fragment of the original polymeric lignin), and a significant amount of water (about 25%). The pyrolysis liquid consists of two distinct phases: the aqueous phase (higher methanol, acetic acid, and acetone ratios) comprising a broad range of low molecular weight organo-oxygen compounds, and a non-aqueous phase (tar or bio-oil) of high molecular weight insoluble organics (aromatics) [9]. Table 4 shows the chemical composition of fast pyrolysis liquids [9].

<table>
<thead>
<tr>
<th>Major Components</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20-30</td>
</tr>
<tr>
<td>Lignin fragments: insoluble pyrolytic lignin</td>
<td>15-30</td>
</tr>
<tr>
<td>Aldehydes: formaldehyde, acetaldehyde, hydroxyacetalddehyde, glyoxal, methylglyoxal</td>
<td>10-20</td>
</tr>
<tr>
<td>Carboxylic acids: formic, propionic acid, butyric, pentanoic, hexanoic, glycolic (hydroxy acetic)</td>
<td>10-15</td>
</tr>
<tr>
<td>Carbohydrates: celllobiosan, α-β-levoglucosan, oligosaccharides, 1,6-anhydroglucofuranose</td>
<td>5-10</td>
</tr>
<tr>
<td>Phenols: phenol, cresols, guaiacols, syringols</td>
<td>2-5</td>
</tr>
<tr>
<td>Furfurals</td>
<td>1-4</td>
</tr>
<tr>
<td>Alcohols: methanol, ethanol</td>
<td>2-5</td>
</tr>
<tr>
<td>Ketones: acetol (1-hydroxy-2-propanone), cyclopentanone</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Table 4. Chemical constituents of fast pyrolysis liquid [9].

for conventional diesel fuel due to their oxygenated nature and water content. Their moderately acidic nature (pH range 2.5-3.0) contributes to the corrosive nature of the oils. Also, the kinetic viscosities and densities of oxygenated bio-oils are much higher than their petroleum counterparts [9].

Bio-oils are generally used as fuels in engines, boilers, turbines, and CHP plants for heat and power generation, upgraded through thermal or catalytic cracking into transport fuels or can be used for the synthesis of valuable chemicals and organic solvents. However, bio-oils applications are so far limited by their poor volatility, high viscosity, corrosiveness, and coking. The range of chemicals that can be derived from the fast pyrolysis oils, their minimum, and maximum weights are found in study [9] and it covers the following chemical groups: organic acids, ketones, alcohols, aldehydes, esters, sugars, oxygenates, phenolics, hydrocarbons, and steroids. These consist of a range of compounds like cyclopentanone, acetic acid, methoxyphenol, methanol, acetone, phenol, levoglucosan, furfural, formic acid, guaiacol, and their alkylated phenol derivatives.

3.2.1.2. Catalytic Pyrolysis

This occurs in the absence of air under moderate temperatures (about 500°C), high heating rate, and short residence time, to produce mainly liquid, used as a source of fuel or valuable chemicals. This is the most attractive approach to minimize the polymerization, corrosivity, low thermal stability and high viscosity challenges associated with the liquid pyrolysis products, as well as facilitates the handling and treatments of these liquid products [9]. Cracking reactions and the upgrading of biomass products are the influence of catalyst during a pyrolysis process, with strict dependence on the catalyst type and reactor configuration. Various liquids and gaseous fuels arise from the catalytic cracking of pyrolysis vapor over different catalysts. Zeolites catalysts are particularly useful in the reduction of oxygenates (which decreases the energy content) of the specific pyrolysis oil [10]. Catalysts are mainly used to facilitate the cracking of heavier molecules in bio-oil to lighter ones, giving rise to a less vis-
cous oil, less corrosive bio-oil (by reducing the synthesis of carboxylic acids), and lastly to promote the synthesis of high-value products (hydrocarbons) capable of raising the heating value of bio-oil [9]. Catalysts modify the pyrolysis process as follows [10]:

- May cause a remarkable decrease in the breakdown temperatures of biomass constituents.
- Affects reaction networks (deoxygenation), as well as reduces polymerization precursors (multifunctional phenols) for stabilizing bio-oil.
- May lead to the release of CO, CO₂, and H₂O during decarboxylation, decarbonization and dehydration reactions.
- Promote coke formation via dehydration reactions (arises mainly from catalysts high acidity).

### 3.2.1.3. Bio-oil Upgrading to Fuels and Chemicals

Biomass-derived bio-oil in its unprocessed form has very high moisture content, low energy density, and no free-flowing physical form, making it unsuitable for direct use in engines. Therefore, these necessitated the need for bio-oil cleaning and upgrading, to enhance its energy density, fuel properties and remove any impurities present [38]. Table 5 highlights the distinct characteristics of pyrolysis oil compared to diesel fuel [32].

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Pyrolysis Oil</th>
<th>Diesel Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>20-30wt%</td>
<td>0.1wt%</td>
</tr>
<tr>
<td>pH</td>
<td>2.0-2.5</td>
<td>-</td>
</tr>
<tr>
<td>Density</td>
<td>1.2kgL⁻¹</td>
<td>0.94kgL⁻¹</td>
</tr>
<tr>
<td>Elemental analysis (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>55-58</td>
<td>85</td>
</tr>
<tr>
<td>H</td>
<td>5-7</td>
<td>11</td>
</tr>
<tr>
<td>O</td>
<td>35-40</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>0-0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0-0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>HHV as produced</td>
<td>16-19 MJkg⁻¹</td>
<td>40 MJkg⁻¹</td>
</tr>
<tr>
<td>Viscosity</td>
<td>40-100 cp</td>
<td>180 cp</td>
</tr>
<tr>
<td>Solids (char) (wt%)</td>
<td>0.1-0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Vacuum distillation residue</td>
<td>Up to 50 wt%</td>
<td>1 wt%</td>
</tr>
</tbody>
</table>

Biodegradation of high-quality bio-oil capable of substituting fossil fuels perfectly is often very challenging. To overcome this challenge, the bio-oil quality needs to be enhanced either at source before full production or via the product upgradation [9]. The upgrading of bio-oil to quality transport fuels is done through the following three principal routes: hydrodeoxygenation with a hydrotreating catalyst (alumina supported sulphided CoMo or NiMo), zeolite upgrading and emulsions formation with diesel fuel. Also, steam reforming can be used to convert char and bio-oil into syngas or H₂ [9]. Bio-oil is often produced with impurities and therefore needs to be upgraded to enhance its quality and purity. This can be done either physico-chemically or catalytically [13].

The catalytic bio-oil upgrading consists of the full deoxygenation of bio-oil and conventional refining, achieved either by integrated catalytic pyrolysis or decoupled liquid phase hydrodeoxygenation. The partial upgrading into intermediate products compatible with refinery streams is also envisaged to exploit the benefit of the economy of scale and the broad experience in the conventional refinery. The main upgrading methods through refineries integration are hydrodeoxygenation, catalytic vapor cracking (in-situ or ex-situ) and gasification to syngas followed by the synthesis of alcohols or hydrocarbons [13].

Hydrodeoxygenation involves the treatment of bio-oil with high-pressure hydrogen at moderate temperatures (302°C-602°C) in the presence of heterogeneous catalysts to form saturated C-C bonds via oxygen removal, raising the fuel energy content and stability. Sulphided CoMo/Al₂O₃ and NiMo/Al₂O₃ are often used to hydrotreat industrial feedstocks [9]. This requires a source of hydrogen, moderate temperature of about 400°C and high pressure of about 20 MPa. Complete deoxygenation is often challenging due to the presence of phenols in bio-oil. Full hydrodeoxygenation produces a naphtha-like product, requiring conventional refining to derived conventional transport fuels such as gaso-
line, diesel, methane, LPG, and kerosene. The naphtha equivalent yield from biomass without hydrogen provision is projected to about 55% in terms of energy or 25wt.%. With the inclusion of hydrogen from biomass gasification reduces the yields to about 33% in terms of energy and 15wt.% [13]. The hydrogen supply should be renewable and sustainable. This can be done through biomass gasification, CO shifting to H₂ followed by CO₂ scrubbing, or steam-reforming to H₂ of bio-oil or the aqueous phase from a phase-separated product or H₂ locally generated through the electrolysis of water. External H₂ supply is unlikely due to high transport and storage costs [13].

Zeolite cracking/upgrading takes place under atmospheric pressure at temperatures within 352°C-502°C in a closed process coupled to pyrolysis and removes oxygen mainly as CO₂ with race amount of CO due to catalyst coking. This improves the thermal stability of the oil. The process yield is projected to around 18wt.% aromatics. The production of aromatics, a very important base chemical through this process is of great significance to the chemical industry [13]. Due to the undesirable effects of pyrolysis oil that disfavors its direct use, the oil is often upgraded via conversion into gasoline using zeolites (crystalline microporous aluminosilicate materials). In this process, the oil vapors are passed through the catalyst between 300°C-500°C to produce hydrocarbons and by-products like H₂O, COₓ, and coke. Coke formation (on the zeolites) eliminates the coking effects of the unprocessed bio-oil. The catalyst removes the oxygen content of the oil in the form of water, CO₂ and CO, depending on the class of organic compound involved [32]. Zeolite cracking of bio-oil is highly beneficial in that there is no requirement for H₂, takes place under atmospheric pressure and this greatly reduces the operating cost, and the process occurs under similar temperature to those for the production of bio-oil. The ZSM-5 zeolite catalysts with strong acidity, high activities and shape selectivities convert oxygenated oil into hydrocarbon mixture ranging from C₁ to C₁₀. The major drawbacks to this process include easy coking, low yield (14-22.5%), and short catalyst lifespan [9].

Catalytic steam reforming occurs over a Ni-based catalyst at temperatures between 752°C-852°C. It is a two-step process that includes the shift reaction, and occurs as follows [9] (equations 1 and 2):

\[
\text{Bio-oil} + H_2O \rightarrow CO + H_2 \tag{1}
\]

and

\[
CO + H_2O \rightarrow CO_2 + H_2 \tag{2}
\]

3.2.2. Gasification

The gasification process converts carbonaceous materials (coal, petroleum coke, biomass, etc.) into combustible gases (CO, H₂, CO₂, CH₄, etc.) and small amounts of light hydrocarbons [37], in the presence of gasifying agents, such as oxygen, air, steam, CO₂ or their mixtures [25, 36], with impurities like nitrogen, sulphur, tars and alkali compounds [35]. Bio-oil is produced as an intermediate that gives rise to the final product, syngas. A catalytic or chemical upgrading unit is usually coupled to the conversion unit to transform syngas and/or bio-oil to potential biofuels and chemicals [19]. Biomass gasification is a well-known technology that produces mainly gaseous products at high temperatures through the partial oxidation of biomass, alongside a small amount of tar and ash. The gas production is optimized at higher temperatures and the process is often classified based on the gasifying agent: steam, air, air-stream, steam-oxygen, oxygen-enriched air, etc. [34]. Advanced gasification processes, such as plasma gasification and the supercritical water gasification have recently been employed for the decomposition of biomass into mainly H₂, as well as CO and CO₂ for the plasma gasification process [6, 13, 25].

Biomass gasification occurs in gasifiers which vary based on their hydrodynamics (precisely the manner of contact between the gasifying agent and solid fuel), operating conditions (temperature, pressure, etc.), and the gasifying agents (air, oxygen or steam). The most common types of gasifiers are fixed-bed (updraft, downdraft or cross draft) gasifiers, fluidized-bed gasifiers, and the entrained flow gasifier. Among these gasifiers, the most suitable are the fixed-bed gasifiers [6, 25, 34, 35]. The designs of these gasifiers, however, depend on the energy requirement, fuel type and characteristics (moisture, particle size, density, ash content, and toxicity), nature of oxygen injection and the combustion bed type [14, 19]. The Supercritical Water Gasification (SCWG) is a highly efficient gasification pathway for H₂ (with low tar) production from high moisture biomass species like algae, manure, olive mill waste, sludge, etc. [19]. In this subsection, design details, operation principles, performance characteristics and comparisons of biomass gasifiers are not included or discussed. However, the gasification process, product transformations, purification, and upgrading are highlighted and deeply discussed.

3.2.2.1. Principles of Biomass Gasification

This process converts organic feedstocks (solid fuel or liquid) into gases depending on the process temperature. Syngas is primarily produced at extremely higher temperatures (>1200°C) and at lower temperatures, a gaseous mixture comprising CO, H₂, CH₄ and CO₂, with small amounts of tar and ash. Tar and ash are potential by-products of gasification and have adverse effects on the process performance and downstream end-uses [13]. Char (the unconverted organic fraction and the inert material found in the treated biomass) production arises from the partial oxidation of carbon in the feedstock material in the presence of gasifying carriers (air, oxygen, steam, or CO₂), and is largely a mixture of ash and the unconverted carbon [24]. The main product of gasification (producer gas or syngas) is a gaseous mixture of Carbon Monoxide (CO), methane (CH₄), carbon dioxide (CO₂), Hydrogen (H₂), and nitrogen, together with light hydrocarbons (ethane, propane) and heavier hydrocarbons (tar), which condense at temperatures within 250°C to 300°C. Impurities such as tar, particulate matter, alkalis, halides, Sulphur, Hydrogen Sulfide (H₂S), Hydrochloric acid (HCl), and inert gases such as Nitrogen (N₂) are also present. However, the relative presence of each component, as well as ash and unconverted carbon depends on the biomass feedstock spe-
cies, the gasifying agent, and the operating conditions of the gasification process [14, 19, 34, 24]. Overall, biomass gasification is generally represented as: Biomass + O₂ (or H₂O) gives rise to CO, CO₂, H₂, CH₄ + other CH₄ + tar + char + ash + H₂S + NH₃ + C + trace species [19, 34]. The individual chemical reactions that take place during the biomass gasification process are shown in Table 6 [14, 35].

Table 6. Typical biomass gasification reactions [14, 35].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heating Value (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C + O₂ ↔ 2CO</td>
<td>+246.4</td>
</tr>
<tr>
<td>C + O₂ ↔ CO₂</td>
<td>+408.8</td>
</tr>
<tr>
<td>CH₄ + H₂O ↔ CO + 3H₂</td>
<td>-206</td>
</tr>
<tr>
<td>CH₄ + 2H₂O ↔ CO₂ + 4H₂</td>
<td>-165</td>
</tr>
<tr>
<td>C + CO₂ ↔ 2CO</td>
<td>-172</td>
</tr>
<tr>
<td>C + H₂O ↔ CO + H₂O</td>
<td>-131</td>
</tr>
</tbody>
</table>

The overall gasification process is grouped into primary, secondary and tertiary reaction stages based on the temperature ranges and reaction chemistry. Below 500°C, biomass is converted to oxygenated vapor and liquid species, together with water and CO₂ during the primary reactions. The secondary reactions take place between 700°C-850°C to produce CO, H₂, CO₂, water vapor, phenols, gaseous olefins, and aromatics, from primary vapor and liquid species. The produced tar consists of mixed oxygenates, phenolic esters, alkyphenols, heterocyclic esters, and PAHs. Methanation, steam reforming, cracking, and water gas shift reaction occurs with the remaining gases and tars. At temperatures between 850°C-1000°C, CO, H₂ and CO₂ together with water vapor, PAHs, and liquid tar results during the tertiary reactions [19].

This process is limited by the biomass feedstock requirements, homogeneity, bulk density, moisture and ash content, particle size and energy content, which all require effective control for efficient gasification [13]. During the gasification process, the woody biomass is first dehydrated before the process temperatures exceed 200°C. Then pyrolysis is initiated, producing vapor and char. The presence of oxygen here oxidizes the char and vapor into a gaseous mixture of CO, H₂, CO and water, as well as sulphur, tar, ammonia, and other impurities [13]. The overall gasification process is endothermic and the biomass oxidation stage normally provides the required energy through either an autothermal (internal heating of gasifier via partial combustion) or an allothermal process (energy supplied from an external source) [6]. The major stages of biomass gasification process include [6, 24, 25, 35]:

- **Oxidation** (exothermic). This is required to generate the thermal energy needed by the endothermic processes (whole process) and to maintain the required operating temperature of the system. It occurs in the absence of oxygen and respecting the stoichiometric ratio so as to only partially oxidize the fuel.

- **Drying** (endothermic). Here, the moisture contained in the feedstock is evaporated and the heat required is proportional to the moisture content of the feedstock. This process is complete at temperatures around 150°C.

- **Pyrolysis** (endothermic). This process occurs at temperatures between 250°C to 700°C to produces lightweight molecules such as solid (char), liquid (tars) and gases (CO, H₂, CO₂ and light hydrocarbons) via the thermo-chemical breakdown of the biomass species (the decomposition of cellulose, hemicelluloses, and lignin) [34, 35]. Process phenomena such as heat transfer, series reactions, and product diffusions are involved. The kinetics of the reactions acts as the rate-limiting step at low temperatures whereas heat transfer or product diffusion controls the process at high temperatures.

- **Reduction** (endothermic). Here the products of the previous stages together with char are reduced through a series of reactions to produce the final syngas [35]. The reduction temperatures determine the final properties or constituents of syngas and the solid residue.

The normal operating temperatures of full-scale biomass gasification vary between 800°C to 1100°C, whereas for processes requiring oxygen for the gasification stage, the process temperature ranges from 500°C to 1600°C [24]. The gasification pathway offers ideal possibilities of combination with cheap CO₂ capture and storage technologies, giving rise to both primary fuel input flexibility and product mix concepts with possibilities achieving zero or even negative carbon emissions [22]. The process enhances the utilization of biomass and is currently being used to increase the efficiency and reduce the investment costs of biomass electricity generation through integration with gas turbine technology. A combined-cycle gas turbine system is capable of achieving higher efficiencies up to 50%, as the gas turbine’s waste gases are recovered to produce steam for the steam turbine [21]. Apart from its use for heat and power generation, nearly all hydrocarbon compounds, as well as premium fuels (ethanol, methanol, transport fuels, Dimethyl Ether (DME) and methane) and high-value chemicals, can be synthesized from syngas after purification. Syngas can also be upgraded into biomethane for injection into the gas grid or converted to synthetic diesel via the Fischer-Tropsch process, a process catalyzed by transition metal-based catalysts (Cobalt or iron) at a higher temperature. Hydrogen can equally be isolated for use in fuel cells for electricity generation and to power electric vehicles. However, the final end-use of the syngas is largely dependent on the end demand and plant scale [4, 13]. Also, reacting the clean syngas over a cobalt, platinum or iron catalyst via Fischer-Tropsch pathway gives rise to hydrocarbon waxes and long-chain alkanes [37]. The purification and upgrading of these products are energy-intensive, costly and require more R & D to improve their efficiencies for large scale use [13].
Catalysts play a fundamental role in the gasification products. They improve the gas quality, conversion efficiency, and reduce the tar content. Dolomite, alkaline metal oxides, olivine, and Ni-based oxides are widely used gasification catalysts. Iron, cobalt, ruthenium and potassium-based catalysts are well known for their role in the Fischer-Tropsch synthesis of diesel, hydrocarbons and other liquid fuels from bio-syngas. However, the performance of these catalysts varies and their choice is determined by their properties, reaction pathways and the desired end product [34]. Dolomite or Ni-based catalysts are used in most gasifiers for the partial tar oxidations, catalytic steam reforming as well as to enable the catalytic upgrading of the gasification products into liquid biofuels. This is usually done after effective gas cleaning and composition adjustments are made [13].

### 3.2.2.2. Gasification Feedstocks and Pretreatments

The gasifiable biomass feedstocks (Table 7) are composed of cellulose, hemicellulose, lignin, and proteins, with their percentage composition in softwood, hardwood, and straw indicated in [24]. The fibers of biomass (cellulose and hemicellulose) consist of saccharides that polymerize into long chains. Lignins are phenolic polymers which play a pivotal role in ensuring the structural stiffness of proteins and also functions as the fibers glue. Mainly the herbaceous species produce proteins [24]. These feedstocks are broadly classified as wood and residues, agricultural and herbaceous, marine biomass, human and animal waste, contaminated and industrial biomass waste, and biomass mixtures [19].

Biomass pretreatment is aimed to provide homogeneous feedstocks with respect to composition, size and moisture content (25-30 wt.%) required for the smooth and efficient operation of the gasification process. Apart from drying, the other gasification pretreatment methods are torrefaction and Hydrothermal Upgrading (HTU) [24]. Torrefaction occurs in the absence of oxygen at temperatures between 200°C to 300°C, under an inert atmosphere to enhance biomass potentials for gasification through moisture, hydrogen and oxygenated species loss. As a form of mild pyrolysis, it potentially enhances biomass resistance to moisture and its heating value. During this process, the biomass feed loses both its moisture content and the rigid fibrous structure, resulting in an increase in the energy density of the material. A combination of torrefaction and palleltization is also possible [19, 24]. Hydrothermal Upgrading (HTU) breakdown biomass using water as a solvent to produce bio-crude. It is mainly conducted in two stages: treating the biomass feed in the water at pressures of around 30 bars and temperatures between 200°C to 300°C, and the biomass (bio-crude) conversion at temperatures of 300°C-350°C and pressures of 120-180 bar and in a variable time period from 5-10 minutes. The produced bio-crude is made up of a variety of hydrocarbons that can be used as a co-fuel in coal plant, for chemicals or synthetic diesel-like fuel production in the chemical industry [24].

### 3.2.2.3. Biomass Gasification Products

The exact constituents of biomass gasification products depend on the fuel type and composition, the gasifying medium or gasifier design, the temperature, operating pressure, fuel moisture content and the way the reactants (biomass fuel and gasifying agent) are brought into contact within the gasifier. As such, it is impossible to predict the exact composition of biomass producer gas [34]. Straw produces a high hydrogen content, highest char content in softwood biomass, lowest char content in straw, higher dust content in straw and higher tar content in hardwood [24]. The feedstock properties with a strong influence on the gasification process are moisture content, ash content, volatile matter, char, organic constituents, thermal conductivity, and inorganic constituents [6]. The gasification product can be in a solid phase, and a gas/vapor phase - often split into a gas and a condensable phase. The solid phase (ash) is made up of the unreacted char and the inert materials found in the feedstock, with char having <1 wt. % in the quantity of ash. Char has a carbon content greater than 76%, making it possible for its direct industrial use. In the gas/vapor phase (syngas), the gas phase comprises of an indesoluble gaseous mixture of CO, H2, CO2, CH4, light hydrocarbons, and some C2-C4 hydrocarbons, at room temperature as well as minor quantities of NH3, H2S, and HCl depending on the feedstock composition. They can be burnt for electricity or heat generation, or use to synthesize liquid transport fuels, hydrogen or chemicals. The quantity of syngas produced on dry mass basis may range from 1-3

### Table 7. Biomass gasification feedstocks [24].

<table>
<thead>
<tr>
<th>Supply Sector</th>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forestry</td>
<td>Dedicated forestry, forestry by-products</td>
<td>Short rotation plantations (e.g. willow, popular, eucalyptus), wood blocks, wood chips from thinning</td>
</tr>
<tr>
<td>Agriculture</td>
<td>Dry lignocellulosic energy crops, oil, sugar, and starch energy crops</td>
<td>Herbaceous crops (e.g. miscanthus, reed canary grass, giant reed), oilseeds for methyl esters (e.g. rapeseed, sunflower), sugar crops for ethanol (e.g. sugar cane, sweet sorghum), starch crops for ethanol (e.g. maize, wheat)</td>
</tr>
<tr>
<td>Industry</td>
<td>Agricultural residues, livestock waste, industrial residues</td>
<td>Straw, pruning of vineyards and fruit trees, wet and dry manure, industrial waste wood, sawdust from sawmills, fibrous vegetable waste from paper industries</td>
</tr>
<tr>
<td>Waste</td>
<td>Dry lignocellulosic contaminated waste</td>
<td>Residues from parks and gardens (e.g. pruning, grass), demolition wood, organic fraction of municipal solid waste, biodegradable landfilled waste, landfill gas, sewage sludge</td>
</tr>
</tbody>
</table>
Table 8. Classes of tar [24].

<table>
<thead>
<tr>
<th>Tar Type</th>
<th>Type Name</th>
<th>Peculiarity</th>
<th>Characteristic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GC-undetected</td>
<td>Very heavy tars, cannot be detected by GC</td>
<td>Determined by subtracting the GC-detectable tar fraction from total gravimetric tar</td>
</tr>
<tr>
<td>2</td>
<td>Heterocyclic aromatics</td>
<td>Tars containing heteroatoms, highly water-soluble compounds</td>
<td>Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzo phenol</td>
</tr>
<tr>
<td>3</td>
<td>Light aromatics (1 ring)</td>
<td>Usually light hydrocarbons with a single ring; do not pose a problem regarding condensability and solubility</td>
<td>Toluene, ethylbenzene, xylenes, styrene</td>
</tr>
<tr>
<td>4</td>
<td>Light PAH compounds (2-3 rings)</td>
<td>2 and 3 ring compounds; condense at low temperature even at very low concentration</td>
<td>Indene, napthalene, methylnaphthalene, biphenyl, acenaphthene, fluorene, phenanthrene, anthracene</td>
</tr>
<tr>
<td>5</td>
<td>Heavy PAH compounds (4-7 rings)</td>
<td>Larger than 3 rings, these compounds condense at high temperature at low concentration</td>
<td>Fluoranthen, pyrene, chrysene, perylene, coronene</td>
</tr>
</tbody>
</table>

Nm³/kg, with a Low Heating Value (LHV) range between 4-15 MJ/Nm³.

In the production of gaseous fuels from biomass, char gasification determines the rate of the process (rate-limiting step) [24, 34]. The condensable phase (tar), consist of various organic compound which is considered as bituminous oil in condensed form. Tar (a complex mixture of condensable hydrocarbons), according to the European board of standardization refers to all organic compounds present in syngas with defined analysis procedures, except the gaseous hydrocarbons C₁-C₆. The composition of tar is strictly dependent on the gasification technology used, the operating conditions and the biomass feedstock. They are generally divided into five major groups (Table 8) according to their molecular weights [24]. In the gasification process, tar originates from the pyrolysis stage and are subject to decomposition and recombination. They are classified as primary, secondary and tertiary tars according to their respective formation mechanisms. The primary tars are dependent on the biomass feed and are produced directly during the pyrolysis step. Primary tars containing oxygenated compounds (carbon acids, aldehydes, alcohols, ketones, etc.) arise from cellulose and hemicellulose feedstocks due to their high oxygen contents. Lignin pyrolysis principally gives rise to aromatic compounds, mainly bi- and tri-functional substituted phenols (xylene, cresol, etc.) [24].

The secondary tars are produced during the oxidation stage. They are alkylated mono- and di-aromatics, as well as hetero-aromatics such as furan, pyridine, thiophene, and di-oxin. Their formation arises from the transformations of primary tars through rearrangement reactions (dehydration, decarboxylation, and decarboxylation), at temperatures above 500°C and in the presence of an oxidant such as air, oxygen or steam [24]. At temperatures above 800°C, tertiary tars (also known as recombination or high-temperature tars) are formed. They comprise mainly of aromatics and Polynuclear Aromatic Hydrocarbons (PAH) such as napthalene, benzene, pyrene, benzopyrene, and phenanthrene. Biomass gasification generally does not produce tertiary tars but they arise from the recombination and decomposition of primary tars in the syngas reducing environment. They also do not co-exist with primary tars, but only appears when all the primary tars are converted into the secondary tars [24]. Fig. (3) depicts a schematic representation of the different classes of tars as a function of temperature.

### 3.2.2.4. Syngas Processing

Synthetic gas, a raw material for biofuels, chemicals and power generation, usually contains impurities such as tar, particulate matter, nitrogen (NH₃, HCN), alkali, halides, sulphur (H₂S, COS) and trace elements mainly responsible for gasifier clogging, corrosion and catalyst deactivation. Thus, rendering syngas unfit for Fischer-Tropsch synthesis, biomethanol production, fuel cell uses, and other applications. The majority of syngas is used for ammonia synthesis (50%), bio-hydrogen production (25%), and the remaining used for bio-methanol production, FT synthesis, and other processes. The processes for syngas cleaning are broadly classified as cold or hot gas clean-up based on the condensation temperatures of its various constituents. Some of these impurities and their cleaning processes are discussed in [19].

Biomass gasification for power generation produces mainly flue gases and unwanted by-products such as ashes and tar (gasification bottleneck) which are often left unutilized especially tar despite its rich fuel and chemical potentials. Due to the complex nature of gasification tar with hundreds of chemical constituents, there has been a recent interest in the valorization of this biomass gasification waste to liquid fuels and chemicals, given its high potential for soil contamination when discharged to the environment untreated [23]. However, the complete treatment, removal or conversion of tar is a huge technical challenge (low efficiency, fouling, plug pipes and tubes, operational difficulty, etc.) in the development and in the successful application of biomass-derived gas. Some commonly used methods are: end pipe tar syngas clean-up, in bed catalytic tar reforming and in bed thermal tar cracking processes [24]. Catalysts play a key role in enhancing reaction rates at low temperatures and also promote the conversion of tar into valuable combustible gases through steam reforming, thermal cracking, dry reforming, hydrocracking, water-gas shift reactions, and hydrore-
forming. They are used either as bed materials or as feedstock additives [25].

At present, biomass gasification is mainly focusing on the production of low- or medium heating value fuel gas for use in the internal combustion engines for power generation. Lesser research has so far been documented on gasification for liquid transport fuels or chemicals generation. Gasification is a very promising technology for biomass valorization with high flexibility and efficiency. The promotion of this technology in the future requires advanced, cost-effective, and highly efficient gasification systems and processes. This, therefore, ushers need for further research and development in biomass gasification in order to improve the future performance of this technology necessary to enhance the process efficiencies, improves gas quality and purity, and to lower the investment costs. To achieve these, the development of innovative catalysts, sorbent, and high-temperature filtration media are fundamental requirements, coupled with high-temperature gas cleaning and catalytic conditioning.

3.2.3. Hydrothermal Processing of Biomass

Biomass hydrothermal conversion has drawn much attention since the adoption of hydrothermal energy as a high potential energy resource. At first, much focus was on the selection of the right solvent and mainly on high temperature and pressure processing materials, given the omission on compound solubility knowledge and its effect on the overall process [5]. It is an excellent approach for converting high moisture energy-rich biomass into various products, such as solid (biochar), a liquid (bio-oil), or a gas (hydrogen, methane, etc.) [30]. This involves the heating of organic wastes or aqueous biomass slurries at higher pressures and low or moderate temperatures to generate a high-density energy carrier or liquid product in the presence of a catalyst [21], using the subcritical and supercritical water as the processing media [5]. The basic processing conditions are high pressures (4-22 MPa) and temperature between 250-374°C. This process low temperatures, low tar yield, and high energy efficiency compared to other thermochemical processes are the key factors responsible for the recent widespread interest in this technology [28, 38]. Suitable feedstocks are those with high ash and moisture contents such as manures, food wastes, anaerobic digestion digestate, sewage sludge, aquatic biomass (micro- and macroalgae) and municipal wastes. The slurries can be fed up to 30wt.% solids [13].

Four main processes (carbonization, Aqueous Phase Reforming (APR), liquefaction and gasification) make up hydrothermal processing (Table 9), with water acting as a reactant, solvent, and a catalyst [5, 13]. Hydrothermal Carbonization (HTC) is the mildest, occurs at pressures between 20 bar to 40 bar and temperatures between 180°C to 250°C to produce hydro-char (solid), which is similar in properties to low-rank coal. This process is governed by temperature and residence time and allows for the reduction of both the oxygen and hydrogen content of the biomass feedstock via dehydration and decarboxylation reactions [39]. Hydrothermal Liquefaction (HTL) occurs at pressures up to 180 bar and temperatures between 250°C and 375°C to produce liquid bio-crude, which can be upgraded via catalytic hydro-treatment to a wide range of distillate petroleum-derived products. Hydrothermal Gasification (HTG) or Supercritical Water Gasification (SCWG) occurs at pressures beyond 200 bar and temperatures above 375°C in the absence of oxidants to produce syngas, CO₂, CH₄ and C₁-C₄ hydrocarbon gases like C₂H₄ and C₃H₆ [13, 30]. At low temperatures, by-products like small bio-oil, tar and char are formed. The aqueous phase reforming (a subsection of HTG) takes place within a temperature range of 220°C-250°C and pressures 1.5-5 MPa to generate H₂ syngas, alkanes and a range of bio-based chemical products including fibers and plastic chemicals [5].

These processes produce a broad range of chemicals and fuels in the gaseous, liquid or solid state with opportunities for carbon capture, storage, and sequestration, have high conversion rates, and most importantly uses wet biomass without any prior dewatering [5]. Despite these benefits of hydrothermal biomass processing, it uses more complex and expensive reactors, requires large water handling equipment and capabilities, challenging to manage large-scale separation and extraction processes and also difficult to compute gas yield due to a complex mass balance resulting from the variabilities in the hydrothermal media [28, 30]. The hydrothermal biomass processing takes place under two main process conditions: the subcritical and supercritical water conditions, which are each determined by the critical point of water (374°C and 22.1 MPa). Table 10 shows the various properties of water at these process conditions. Biomass constituents like cellulose and lignin are insoluble in water at ambient temperature but are soluble in supercritical water (high-temperature water). The hydrothermal breakdown of biomass takes place as follows: the water-soluble biomass portion disperses into the water at about 100°C, and above 150°C
Table 9. Main hydrothermal processes and operating conditions [5].

<table>
<thead>
<tr>
<th>Hydrothermal Reaction</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Reaction Time</th>
<th>Catalyst</th>
<th>Main Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HT carbonization</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low temperature</td>
<td>523</td>
<td>2</td>
<td>Several hours</td>
<td>Not essential</td>
<td>Hydrochar</td>
</tr>
<tr>
<td>High temperature</td>
<td>573-1073</td>
<td>2</td>
<td>Several hours</td>
<td>Optional</td>
<td>hydrochar</td>
</tr>
<tr>
<td><strong>HT liquefaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High temperature</td>
<td>553-643</td>
<td>10-25</td>
<td>Few seconds</td>
<td>Optional</td>
<td>Bio-oil</td>
</tr>
<tr>
<td>Low temperature</td>
<td>573-873</td>
<td>10-25</td>
<td>Few seconds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkaline salts: Na2CO3, KCl, KOH, heterogeneous catalysts under high pressure H2</td>
<td>Increasing bio-oil yield, improved to transport fuel by increasing C/H ratio</td>
</tr>
<tr>
<td><strong>HT gasification</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Near-critical</td>
<td>573-773</td>
<td>Various</td>
<td>Few seconds</td>
<td>Metal catalysts and alkaline salts</td>
<td>CH4</td>
</tr>
<tr>
<td>Supercritical</td>
<td>773-1073</td>
<td>Various</td>
<td>Few seconds</td>
<td>Metal catalysts and alkaline salts</td>
<td>Syngas H2 with minor, CO2, C1-C4 gases</td>
</tr>
<tr>
<td>Aqueous phase reforming</td>
<td>493-523</td>
<td>1.5-5</td>
<td>Few seconds</td>
<td>Pt/Al2O3, Pt/ZrO2, Rh, Ni and on SiO2, etc.</td>
<td>H2 and CO2 with minor C1-C4 alkanes</td>
</tr>
</tbody>
</table>

Table 10. Properties of water under ambient, subcritical and supercritical conditions [28].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ambient Water</th>
<th>Subcritical Water</th>
<th>Supercritical Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, T (°C)</td>
<td>25</td>
<td>250</td>
<td>400</td>
</tr>
<tr>
<td>Pressure, p (MPa)</td>
<td>0.1</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>Density, ρ (g cm⁻³)</td>
<td>0.997</td>
<td>0.80</td>
<td>0.17</td>
</tr>
<tr>
<td>Dielectric constant, (ε)</td>
<td>78.5</td>
<td>27.1</td>
<td>5.9</td>
</tr>
<tr>
<td>pKₐ₂</td>
<td>14.0</td>
<td>11.2</td>
<td>19.4</td>
</tr>
<tr>
<td>Heat capacity, cᵥ (kJkg⁻¹K⁻¹)</td>
<td>4.22</td>
<td>4.86</td>
<td>13</td>
</tr>
<tr>
<td>Viscosity, μ (mPa s)</td>
<td>0.89</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Thermal conductivity λ (nWm⁻¹K⁻¹)</td>
<td>608</td>
<td>620</td>
<td>160</td>
</tr>
</tbody>
</table>

hydrolysis occurs. The solid biomass is transformed into the slurry at about 200°C and 1 MPa, and finally, at about 300°C and 10 MPa, liquefaction takes place giving rise to the oily products. Here, biomass is converted into a solid (biochar, a liquid (bio-oil) and gaseous products via the variation of the process conditions like temperature, reactor pressure, reaction time and catalyst presence [28]. Supercritical water oxidation is used for the removal of toxic compounds (pollutants) from biological and organic waste, and in power generation cycles for power generation. To better understand biomass hydrothermal processing and the various degradation pathways, a thorough knowledge of water properties under hydrothermal conditions (subcritical and supercritical) is required. At higher temperatures, water has a low dielectric constant. As such, under supercritical conditions, water is a very good solvent for non-polar substances but these substances are insoluble in water at room temperatures [28].

3.2.3.1. Hydrothermal Liquefaction (HTL)

This is one of the most investigated hydrothermal processes for the conversion of waste biomass into chemicals and bio-based fuels at moderate temperature and high pressure enough to keep the water in the liquid phase [5]. Hydrothermal liquefaction is a promising technology for the production of high-quality bio-oil from biomass. Here, mainly wet feedstocks or those with high moisture content are used. This eliminates the need for feedstock drying (energy-consuming) as performed with traditional thermochemical processes such as gasification and pyrolysis, that requires only dry feedstocks [7]. This process is performed in water under moderate temperature of about 280-370°C and at high pressures (10-25 MPa), to generate liquid bio-crude with high energy content, together with aqueous, gaseous and solid-phase by-products [30, 38]. This involves several com-
plex reactions, giving rise to high energy density products and an enhanced heat recovery process. Two major feedstock classes characterized the process mechanism. These are the dry feedstocks (lignocellulose biomass) comprising of cellulose, hemicellulose and lignin constituents, and the wet feedstocks (algal biomass) made up of vital components such as proteins, carbohydrates, lipids and algaenans [38]. A broad range of chemicals can be obtained through HTL alongside bio-crude. These mainly consist of monoaromatic compounds, fatty acids, alkenes, alkanes, polyaromatic compounds, nitrogenous and other oxygenated compounds, detail constituted by [38]. In this section, key concepts of HTL such as the process principles, bio-crude elemental composition, feedstock types, process energy efficiency, as well as, future scope and prospects, are highlighted.

HTL gives rise to four distinct product phases comprising of the bio-oil, light gases, CO2 and trace amounts of CH4, CO and H2, a solid residue, char, and a carbon-rich water phase [7]. As discussed in a study [40], process parameters, such as temperature, pressure, feedstock composition, residence times, heating rate, water ratio, catalyst, particle size, solvent density and type, and reaction medium, greatly affect bio-oil yield. The bio-oil generated can be improved into high-quality liquid fuels via chemical, catalytic and physical (extraction, solvent addition, or separation) methods. This process is advantageous in that it uses wet biomass which does not require drying, uses water which is a unique and environmentally friendly solvent, occurs at lower temperatures, highly energy-efficient and does not require drying [28, 31], produces high quality bio-oil, higher yields, lower water and oxygen content, which give it an HHV compared to pyrolysis or gasification oil but higher compared to fossil fuels. However, the high-pressure process leads to high equipment cost for large-scale or industrial processing [7]. The low oxygen content and HHV of the bio-oil main product originates from the high contribution of the dehydrogenation and decarboxylation reactions in the HTL process, removing oxygen in the form of water and CO2 respectively [40], which reduces biomass oxygen from 40wt.% to about 10wt.% [5]. According to [7], increasing the HTL process temperature correspondingly raises bio-oil yield prior to the occurrence of bio-oil cracking and repolymerization reactions that lead to an opposite trend. In addition, increasing the residence time (normal range of 5-30 minutes) equally increases bio-oil yield. However, a further increase in the reaction time rather leads to a decrease in bio-oil yield originating from cracking and repolymerization reactions to form lighter gases and char respectively. A detailed review of the techniques for the separation and extraction of HTL products, chemical composition and products analysis using the mass spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, elemental analyzer, Nuclear Magnetic Resonance (NMR) spectroscopy, High Performance Liquid Chromatography (HPLC), etc. are discussed in [28].

The HTL process mainly converts biomass to bio-oil which can substitute fossil fuels. This process is however challenged by its high-pressure conditions, making its economics very questionable. The HTL of algal biomass gives rise to by-products such as CO2 and nutrients which are reused for algal cultivation in the algal culture for growth and photosynthesis, and wastewater which can be reused to reduce the process water need, as well as organic fertilizer for agricultural use. The process generates about 85-90% of energy, consuming only 10-15% of the feedstock energy, thus a very energy efficient process. Moreso, the resultant bio-crude is very similar to their petroleum counterparts, and thus require very little upgrading for commercial use [38]. All the above-listed by-products and applications if properly valorized, can potentially overcome the economic challenges of HTL. However, further research to optimize the process mechanisms and parameters are still needed to overcome the setbacks of HTL and to effectively commercialize the process.

During the process, water is kept in the liquid phase by operating at or above its saturation point which greatly minimizes the enthalpy change linked with the latent heat of vaporization of water [13]. In the past decades, compressed hot water has attracted much attention as a green reaction medium. Presently, it is widely applicable in resource recovery from wastes, polymers recycling, and biomass energy recovery, waste treatments, homogeneous and heterogeneous catalysis, inorganic and organic materials synthesis, and others [5]. When the process occurs below the critical point of water, it is known as subcritical. The supercritical process takes place above water critical point (274°C and 22.1 MPa), with the water properties within the liquid-like and gas-like phase. Under these conditions, water functions both as a solvent and a catalyst or reactant. Its dielectric constant decreases, raising the solubility of insoluble organic compounds. Also, the reaction rates are higher due to the high diffusion coefficient as the water viscosity decreased [7].

In the past few decades, there has been a strong drive and interest in the use of biomass and biomass derivatives for the production of liquid fuels. Research studies within this scope range from biomass gasification, pyrolysis, HTL of lignocellulose material and the upgrading processes of the derived bio-crude. The choice of biomass generates high prospects and expectations for fuels, fine chemicals and raw material synthesis for the petrochemical industry. Among the biomass to fuels and chemicals processing methods, the HTL has drawn huge attention recently as one of the promising routes for both dry and wet biomass [38]. Presently, fuels (biofuels) and chemicals production rely mainly on dry biomass feedstocks (dry wood) through various pyrolysis and gasification processes. Only very little interest and attempts are reported [38] which have so far been made towards the development of the HTL process for wet biomass valorization, despite the huge prospects in wet biomass feedstocks. Microalgae due to their high photosynthetic efficiency, fast growth rate, maximum biomass production, and the lack of arable land requirements, is regarded as an excellent fuel and chemical source through wet biomass processing. Thus, the selection of the best process feedstocks and operational conditions, as well as the optimization of the existing parameters and process mechanisms to enhance HTL process efficiency and yields are very important for enhancing future performance,
prospects and applicability of this technology especially for wet biomass, as well as in assuring the economic viability of HTL.

### 3.2.3.1.1. Dry Biomass HTL

This produces bio-crude either in a continuous or batch reactor, with detailed pathways as shown in Fig. (4). The feedstock is pretreated to reduce the particle size, removes impurities and to make a stable slurry for easy pumping through alkaline treatment. The HTL process then takes place at around 350°C and 150 bar for around 15 minutes, followed by phase separation to produce a gaseous mixture of CO₂, bio-crude, solid residue and traces of the aqueous phase (water) which can be re-used in the HTL unit to enhance the yield of the bio-oil or reduce the process water requirement. Anaerobic or catalytic hydrothermal gasification treatment of the other water stream results in a hydrogen-rich or methane-rich syngas. However, the presence of phenols and furfurals limits the anaerobic treatment process. The resulting bio-crude has less moisture and oxygen content, thus can be used directly or upgraded by further hydro-treatment for commercial use. This process is highly energy-efficient as the overall heat generated can be used efficiently and effectively to operate the hydrothermal gasifier [38].

### 3.2.3.1.2. Wet Biomass HTL

The HTL of wet/algae biomass differs only slightly (no pretreatment) from that of dry biomass and offers great potential for nutrient recycling. Fig. (5) depicts a schematic representation of wet biomass hydrothermal processing. Here, the algae biomass feed from an algal culture is first dewatered to obtain a feed slurry with about 20% solid, which is then pumped into the HTL unit to produce bio-crude which is then further hydrotreated to generate fine hydrocarbon fuels. The CO₂ and nutrients that result from the aqueous phase are re-used for algal cultivation, making the process more economically viable and sustainable [38].

### 3.2.3.1.3. HTL Process Mechanism

Prior to the degradation of the biomass constituents into smaller molecules via dehydrogenation, dehydration, decarboxylation, and deoxygenation, the biomass feedstock is initially fragmented by hydrolysis. Repolymerization of the lighter molecules results in the synthesis of some complex chemicals, containing aldehydes, phenols, acids, ketones, alcohols, esters, and other aromatics [38]. HTL is initiated by solvolysis of biomass in micellar forms, followed by the disintegration of biomass major polymeric constituents (cellulose, hemicellulose, and lignin), and then concludes with its thermal depolymerization into smaller fractions [30]. The actual mechanism of HTL is still unclear. However, the process comprises depolymerization, preceded by decomposition and recombination reaction. The biomass is first decomposed and depolymerized into highly reactive lighter molecules (water-soluble oligomers), preceded by the cleavage of the inter- and intramolecular hydrogen bonds to produce simpler monomers (glucose and other products like acetic acid, furfural, and aldehyde compounds) [30], which subse-
quently repolymerizes to form bio-crude, gas, and solids. Due to the complex nature of biomass, the process mechanism and reaction chemistry is also complex and the major process parameters like residence time, temperature, process decomposition, condensation and repolymerization of the constituents also vary within the phases [38]. Temperature, pressure, particle size and resection times affect bio-oil production via HTL [30].

Biomass depolymerization sequentially dissolves the polymeric components of biomass, aided by their physico-chemical properties. The process temperature and pressure modify the polymer long-chain structure, while the organic materials’ energy contents are recycled in the presence of water [38].

The decomposition of the biomass monomers occurs via dehydroyation, cleavage, deamination, and decarboxylation. Here, water molecules are lost via dehydroyation, CO₂ lost by decarboxylation and deamination removes the amino acid content. The decarboxylation and dehydroyation processes remove oxygen from biomass as CO₂ and H₂O respectively, and this hydroylation converts the polymers to polar monomers and oligomers. The applications of water at high temperature and pressure dissociates the hydrogen-bonded cellulose structure into its glucose monomers. The isomerization, hydroylysis, reverse-aldol breakdown, dehydroxyation, recombination and rearrangement reactions of fructose compared to glucose results in a broad stream of products like furfural, polar organic molecules, phenols, organic acids, and glycoaldehydes, which are highly water-soluble [28, 38]. Among these reactions, the decomposition and deoxygenation reactions are the key reactions that give rise to the resulting biocrude, consisting of acids, aldehydes, and aromatics [40].

The repolymerization and recombination stage arises from the non-availability of hydrogen compounds in the system. As such, with high concentrations of free radicals (reactive fragments from previous reactions), the fragments tend to repolymerize or recombine into heavier char molecules, noted for their coke formation. However, with sufficient presence of hydrogen in the organic mixture during the liquefaction process, stable weight species will be formed from the capping of the free radicals with the hydrogen molecules [38].

3.2.3.1.4. Catalytic Hydrothermal Liquefaction

Homogeneous and heterogeneous catalysts are generally employed in HTL to enhance the process efficiency through the reduction in tar and char formation while improving oil (product) yields. The homogeneous catalysts (alkali salts, with the K salts more active than Na salts) like KHCO₃, KOH, K₂CO₃, Na₂CO₃, and NaOH, improve the product yield of the HTL process by facilitating water-gas shift reactions through ester formation via decarboxylation reaction between biomass hydroxyl groups and the formate ions in the alkali carbonates, followed by dehydration, deoxygenation, decarboxylation and dehydration of micellar-like fragments into lighter ones. Then, the cycle of rearrangement reactions via cyclization, polymerization, and condensation gives rise to the final products. This group of catalysts preferably decreased solid yields, increased bio-crude yield and properties and decreased dehydration reactions (with elevated pH) that produces unstable and unsaturated molecules. However, the recovery of these catalysts is costly, owing to the energy and cost-intensive separation process [30]. Heterogeneous catalysts are most commonly used in HTG, with only a few applications so far with HTL especially with the improvement of the bio-crude quality from ligno-cellulose biomass. Platinum, nickel, and palladium are common heterogeneous catalysts, but due to the rareness of these metals, attention has been shifted to metallic oxides like ZrO₂, MnO, MgO, NiO, ZnO, CeO₂, La₂O₃, and so on [30].

The very first catalytic hydrothermal liquefaction of wood biomass with CsOH and RbOH (very potent bases) has been performed [41] and noted that these strong bases (CsOH and RbOH) like other base catalysts greatly improve oil yields by hindering char formation, producing mainly benzenediol derivatives and phenolic compounds. Also, Karagöz et al. [42] investigated the effect K and Na carbonates and hydroxides on the product yields and boiling point distribution of oxygenated hydrocarbons from low-temperature HTL of wood biomass (pine). They found that the treatment of wood biomass with catalytic alkaline solutions (NaOH, Na₂CO₃, KOH, and K₂CO₃) produces mainly phenolic compounds whose distribution depends solely on the exact base solution used and thermal treatments produce mainly furan derivatives. They reported the catalytic activity of these bases as follows: K₂CO₃ > KOH > Na₂CO₃ > NaOH. The effects of various catalysts and process parameters on the product yields, distribution and chemical constitution from various biomass streams like bagasse [43], waste biomass [44], food waste using CeZrO₃ [45], aquatic biomass [46, 47], and barley straw [48] are also reported in literature. The use of bifunctional catalysts like Ni/HZSM-5 [49] has also been investigated and seen to exhibit better catalytic activity on bio-oil production as it integrates the cracking and hydrodeoxygenation reactions. The production of feedstocks for other biomass conversion technologies like gasification is also feasible with catalytic HTL. This has been demonstrated [50] by using K₂CO₃ catalyst to produce aqueous gasification liquids and gases from pine sawdust. This in a nutshell integrates a biomass to liquid gasifier to a catalytic HTL process and this improves the overall gasification efficiency. Biocrude quality in algae HTL is best improved using Ni/SiO₂-Al₂O₃, Ni-Mo/Al₂O₃, Pt/C, Pt/Al₂O₃ and Ce/HZSM-5 catalysts, with Ce/HZSM-5 catalyst presently seen as the first-choice option. The highest catalytic denitrogenation, deoxygenation and desulfurization activities are exhibited respectively by Ce/HZSM-5, Co/Mo/Al₂O₃ and Ni/SiO₂-Al₂O₃. Also, Ru supported catalysts like Ru/C, Ru/C+alumina, show higher deoxygenation, denitrogenation, and hydrogenation performances in biocrude upgrading whereas Pt supported catalysts, such as Pt/C and Pt/γ-Al₂O₃ showing optimal catalytic activities in heteroatom content reduction and in improving algal HTL biocrude quality and upgrading, especially with respect to catalytic hydrogenation, deoxygenation and denitrogenation [47].
4. CURRENT DEVELOPMENTS AND FUTURE OF BIOMASS CONVERSION PROCESS

4.1. Current Developments

Current research and development in renewable energy technologies have led to significant engineering advances and discoveries for all renewable energy resources. Some of these advances in biomass conversion technologies are [22]:

- Advanced biorefinery system designs for the sustainable production of multiple products.
- Advanced gasification processes for the efficient production of medium energy content fuel gas and power.
- Advanced plantation designs for multicultivation of virgin biomass species for integrated biomass production and conversion systems.
- Closed-coupled biomass gasification-combustion systems for the production of steam and hot water for schools and commercial buildings.
- Advanced catalysts for thermochemical gasification for high yield chemicals, gases, and fuels production.
- Zero-emission biomass waste combustion systems for energy recovery, waste disposal, and recycling.
- Fast pyrolysis processes for liquid fuels and chemicals production from biomass
- Genetically engineered microorganisms for the simultaneous conversion of pentose and hexose sugars to ethanol for cellulotic biomass

4.2. Future of Biomass Processing

Biomass has the full potential to provide a cost-effective and sustainable supply of energy in the future, while simultaneously helping countries to meet their targeted GHG emission reduction. Biomass integrated gasification-gas turbine technology with high energy conversion efficiencies holds the future of biomass electricity generation. The renewable, flexible and adaptable biomass resource is expected to favorably compete for niches with fossils in the chemical industry. However, the success of the biomass-derived chemicals depends on the demand and supply of feedstock, primary chemicals and key intermediates such as lactic acid, cellulose, levulinic acid, etc., that the petrochemical industries shall be unable to make [21]. Biomass resource, with its great natural abundance, is a perfect substitute for fossil fuels for energy generation if fully harnessed. Third and fourth generation biofuels processing technologies shall have great future prospects and impact on climate change mitigations, thereby creating a more carbon-neutral environment free from greenhouse gases.

The present biorefineries generate and attempt to generate costlier fuels and value-added products (chemicals) with an almost negligible cost of the initial raw materials, making biomass processing a great attraction to investors in the chemical and energy industries owing to its potentially huge benefits and sustainability. Efficient feedstock upgrading and refining processes would be employed in future biorefineries. This would greatly improve biorefinery efficiency given the added uniformity of the process with the fractionating of the biomass feedstock into its core constituents before usage. As such, a complete biomass usage will be assured as only the residual biomass shall be used for heat and power generation. Nanoparticles-based catalysts would more likely be used to improve the catalytic upgrading/cracking processes of the products of biomass thermochemical conversion. Also, greener processes with higher efficiencies shall be applicable for biomass conversions under mild conditions through bio-catalysts development.

Biodiesel and bioethanol in the near future completely replace gasoline, given the unlimited scope and rapid advances of biomass biochemical processing and algal biomass conversion processes. In addition, the production efficiencies of cellulases and hemicellulases shall be improved through genetic engineering (genetic manipulation) and this would greatly reduce the conversion times for the biochemical processing of lignocellulosic biomass. Furthermore, transgenic plants with less lignin content and an upregulated biosynthesis of cellulose shall be grown. These plants would have the capacity to capture and store more carbon so as to enhance the energy density of biomass. Conclusively, the bright future of biomass to energy conversion is evident with the vast number of integrated biorefineries already planted globally [3].

CONCLUSION

Biomass can be converted to solid, liquid, and gaseous fuels and high-value chemicals or high-density energy and chemical precursors. Biomass energy is released directly through combustion or co-firing with fossils (natural gas or coal) for heat and power generation, or indirectly through thermochemical processes (gasification, pyrolysis, liquefaction, etc.) to produce fuels (syngas, bio-oils, charcoal, etc.) and value-added chemicals or intermediates. The vast array of biomass feedstocks for chemicals and biofuels production vary substantially with respect to their physicochemical constituents, which greatly influence their choice of conversion technology.

A number of processes transform biomass into fuels and chemicals. However, all these processes show some major shortcomings. This ushers the need for a modern biorefinery to maximize environmental and economic benefits through the combination of the various processes. The use of small, local or mobile pyrolyzers could make the transformation of agricultural waste and forestry materials into liquid attractive and this can easily be shipped and further processed in a central biorefinery. Biomass conversion technologies comprise of both biochemical and thermochemical processes, suitable for both direct conversion or the formation of high energy or chemical intermediates. The sufficient variability of these processes enabled the gaseous or liquid fuels produced to be identical or non-identical to fossil fuels. Virtually, all fossil-derived fuels and chemicals can be produced from biomass. The modern biorefinery uses almost all of the processes in-
involved in the refining of petrochemicals and fuels in the petroleum refinery. Also, many chemical species, natural polymers, pharmaceuticals, and other value-added products are derived from specialized biomass feedstocks. Gasification and pyrolysis processes play a key role in the production of fuels and chemicals from biomass. They both show great future prospects for use in biomass valorization, especially in small scale applications. However, further research and development are still needed to enhance their conversion efficiencies, reactor configurations, process parameters, and product upgrading to transportation fuels or valuable chemicals as well as in-process integrations with diesel engines, turbines, boilers and CHP plants for heat and power generation.

The knowledge and productivity of energy crops have reasonably advanced recently. Thus, modern biotechnological research provides an opportunity for more advances in this trend, thereby encouraging and promoting the development of cost-competitive biofuels worldwide. In addition, high-pressure studies will play a central role in future bioenergy research and in the deployment of suitable economic viable technologies for biomass processing into biofuels (liquid or gaseous) and useful biochemicals (organic acids, ketones, furfurals, aldehydes) via the application of supercritical fluids. This will significantly contribute and enhances both upstream and downstream processing in the energy industry and most importantly in the future biorefinery.

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REFERENCES
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