

Sustainable Energy via Thermochemical and Biochemical Conversion of Biomass Wastes for Biofuel Production



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Abstract Environmental pollution is one of the major disadvantages of fossil fuel and their derivatives, but alternative energy resources have performed better in this area. A well-known example within these alternative energy sources that can increase total available energy for human's consumption is biomass, and it has been proven to be the most important renewable energy source. Its benefits include reduced emission, ease of growth (agricultural materials), more available when compared

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to non-renewable sources of energy and can be directly used by local methods. Biomass wastes heating is a major energy generation process. Processes that use heat on biomass wastes to generate energy are termed thermochemical conversion processes. The use of wood that store chemical energy in cooking is as far back as the creation of the world. Thermochemical conversion of biomass releases products which are extremely best when compared with other renewable energy source finding usefulness in automobile, power, chemical, production, and biomaterials industries. Pyrolysis is a heating process whereby carbon-based matter (organic material) such as lignocellulosic agricultural waste is heated to 450 °C and above in a non-O₂ atmosphere, e.g., N₂ atmosphere. Oxygen or air supports biomass combustion to generate heat, steam, and electricity. Gasification occurs at > 650 °C; it is a method of converting biomass waste into energy with the sole purpose of generating syngas useful for combustion, heating, and electricity generation. Liquefaction is a method of converting coal/biomass to petroleum through series of chemical reactions. Bio-oil, syngas, and char are useful products with stored chemical energy obtained from via thermochemical conversion. Biochemical conversion of biomass refers to the gradual and continuous release of biofuel from biomass waste through the activity of microorganisms and enzymes. Thermal and biochemical conversions are suitable processes to tap unused energy in largely available lignocellulosic biomass wastes to reduce reliance on the use of non-renewable fossil fuels as source of energy.

Keywords Biomass · Pyrolysis · Combustion · Liquefaction · Alternative energy

Abbreviation

GHG	Greenhouse gases
FC	Fixed carbon
AC	Ash content
VM	Volatile matter
BTL	Biomass to liquid
HHV	Higher heating value
NMOCs	Non-methane organic molecules in anaerobic circumstances (NMOCs)
MC	Moisture content
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction

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1 Introduction

1.1 *Need for Alternative Energy*

The modern world's ability to function without energy, primarily in the form of fossil fuels derived from the mining of coal, natural gas, and crude oil sources, appears to be a highly and practically impossible phenomenon. Fossil fuel has stood out as a significant source of world energy directly or via its wide range of derivatives [1]. Crude oil today is the primary energy source for the automobile/transportation industry, and this natural oil has served as more than 90% good source of other organic compounds [2]. Some of the crude oil that we are exploring now took millions of years and 107 years cycle to form, which brought about setting limitations to the exploration of crude oil to the world market because it is a limited, scarce, and non-renewable resource [3]. The output of fossil fuel follows Hubbert Curve, i.e., as the output increases, stabilizes, and then with time, decreases continuously [4]. All global oil output rises at the onset, then peaks, and later part falls constantly. According to various forecasts, crude oil which is a fossil fuel will begin to decline in the next 20 years to more than a century [5]. As the modern world relies on energy, demand for fossil fuel, majorly crude oil, is increasing, but its reserves are depleting as each day passes. As of 2014, [6] reported the daily consumption of crude oil stood at approximately 92 million barrels. By 2030, it was statistically projected to surge to the approximated value of 116 million barrels/day. This is an essential need, but we are not expected to keep exploring and consuming an entire planet's worth of oil [1].

Nonetheless, technical advances offer some hope for replacing less abundant crude oil with unconventional energy, e.g., shale oil, oil sands, and ultra-heavy oils. However, as everyone is aware, they are limited resources that will eventually be depleted. Furthermore, these oil extraction and utilization technologies can negatively impact the environment. Using fossil fuel for energy involves combustion, which releases toxic gases (CO_2 , N_2O , light hydrocarbons) into the atmosphere. In developing countries, activities that cut across domestic, industrial, and transportation burn fuel, but in particular, the transportation industry accounted for the most significant amount of greenhouse gases (GHG) [7].

The world population is increasing due to increased medical accessibility and the discovery of curable drugs for life-threatening diseases. In order to support this population boom, there is need for industrialization as done in Japan, China, and India. Gains of industrialization are tremendous but with reported increase in energy demand according to [3]. As a result, fossil supplies would rapidly deplete, and GHG emissions would rise. In addition, the ecosystem is endangered by the exploration of and burning of fossil fuels and products formed from it (derivatives). Domestic or industrial waste materials produced from petrochemicals includes: (rubber and plastics) are now commonly thrown into the sea in areas non-strict environmental protection laws making aquatic region unsafe for aquatic animals since they can

feed on them. These environmental pollutants (rubber and plastics wastes) have slow biodegradation rate hence could last hundreds of years in the deep oceans.

An energy shift from fossil fuel could be historically traced to “first-generation” biorefineries which used edible crops rich in carbohydrates and sugar, such as corn, wheat, sugar cane, and beets, as feedstocks for the production of biofuel [8, 9]. The most common fuel generated from the food crops listed as natural sugar source is ethanol, which not only provides energy but also serves as chemical additives. However, because these food crops are predominantly used for food and feed, their utilization in this context would compete for feedstock, fresh water, and fertile agricultural area for the food and feed sectors [10–12]. With these demerits, using food crops in first-generation biorefineries is a debate discussed under politics, environmental consequences, and ethical concerns [11]. Furthermore, these food crops are seasonal; therefore, the possibility of availability throughout the year is an issue to ponder. Additionally, the season’s availability is influenced by the agricultural technique and the soil’s organic/inorganic richness, and its conversion requires a significant quantity of energy [1]. Although these food crops serve as a good source of alternative energy (biofuel), their use as a feedstock in biorefinery concept raises critical questions as listed below (i–ii) that beg for answers:

- Can it produce sufficient crops without affecting our fundamental needs?
- Are conversion technologies effective and easily implemented?

Non-edible parts of biomass constitute waste, i.e., lignocellulose biomass such as wood waste, agro-residues (e.g., rice husk, sugar bagasse, cocoa pod, maize stover, grasses, and municipal solid wastes) have recently attracted several research studies [13]. Lignocellulose materials, like first-generation biorefinery feedstocks, have a high concentration of sugars (polysaccharides) with potential application in the biorefinery industry [8] and [14]. As a result, the constraints of first-generation biorefineries can be eliminated or reduced by using non-edible feedstocks (lignocellulose biomass wastes), and the process of converting these biomass wastes into biofuel is termed “second-generation” biorefinery [1] and [14]. There are currently few second-generation commercial biorefineries (dedicated to producing bio-oil), e.g., Borregaard in Norway that uses Nordic wood.

1.2 Biomass

Biomass is an organic material which has carbon, hydrogen, and oxygen as its principal elemental composition and some other trace amounts of nitrogen, sulfur, and minerals [15, 16]. In its wet form, the renewable resource (plant) manufactures its food through photosynthesis, where solar energy is trapped by chlorophyll and stored as chemical energy in the biomass. Biomass is an extensive term for a diverse range of plants, their derivative resources, and biodegradable waste. It also expands to all biological material, its residues, and dead biomass.

Crops and residues can be obtained from food processing companies, poultry, wood waste from the sawmill, municipal solid wastes, sewage sludge, trees, energy crops (water weeds, rushes, water, hyacinth, algae, seaweeds). Aquatic plants are also valuable biomass feedstock. Biomass wastes can be obtained from sorghum, maize, sugarcane, and rice. All crop residues have stored chemical energy that might fit as an alternative energy source, depending on its dry mass per unit of land (hectares). Increased output reduces the demand for land thereby reducing the cost of producing biomass energy.

Among all current renewable sources (solar, wind, hydro, tidal, and geothermal), biomass stands out as the only sustainable carbon carrier. It has been identified as an important source in the global transition to carbon-neutral energy [17]. Biomass accounts for around 10% of global energy use [18]. It includes photosynthesis-produced organic compounds such as hemicellulose, cellulose, lignin, moisture, extractives, and traces of various inorganic elements. Animal waste and sewage sludge are degradable biomasses from animals and microorganisms [19]. The composition of biomass is not fixed but determined by many factors such as biological origin [16]. Biomass is abundant as waste in various forms, including urban solid waste, wood residue, forest residue, agricultural waste, and industrial waste, making its acquisition more convenient, cost-effective, and environmentally friendly [15] and [20]. When biomass waste is left unmanaged in its huge mass, it constitutes an environmental nuisance. More than 75% of biomass utilized for energy generation comes from agro-wastes [21]. Agro-remnants are crop residues that would typically be discarded. If the residues are not combustible, they are usually burned or dumped in landfills.

The global energy potential of biomass is immense. The terrestrial standing biomass carbon on the globe was estimated to be 100 times the yearly world energy consumption. The forest biomass and its residues account for between 80 and 90% of total biomass carbon [22]. In terms of annual net energy output, marine biomass carbon (which has the lowest natural abundance) is predicted to outnumber forest biomass carbon [23]. The only renewable carbon source that can be converted into useable char, bio-oil, and volatile gaseous fuels, as well as high-value compounds, is biomass. The use of woody biomass and its residues as the oldest energy source cannot be disputed and still stand as the most used in developing and underdeveloped countries as a source of heat for cooking or charcoal production. It still serves the same purpose of heating. However, the direct combustion of these woody biomass contributes to a more hazardous environment via the release of CO₂ (a significant gas in GHG), SO₂, and NO_x (mix with moisture to form acid rain), and ash which makes such an environment becomes dusty. Compared to fossil combustion, biomass burning emits much less hazardous pollutants [24].

Forest residues, i.e., wood and its dust (sawdust), contribute about 64% of biomass energy, about 24% of biomass energy is possible with municipal solid waste, and 5% each is contributed by agricultural and landfill gases [24].

The general classification of biomass energy is:

Traditional biomass.

Modern biomass.

In developing and emerging countries, traditional biomass is the commonest used, comprising fuelwood, animal wastes, sugarcane bagasse, charcoal, and plant residues.

The concept of modern biomass is extended to wood and its wastes, agricultural residues, domestic and industrial wastes, and biofuels (biogas from animal wastes, energy crops, and so on), and it is widely employed to replace traditional energy sources [24].

1.3 Lignocellulosic Biomass as a Source of Renewable Energy

Lignocellulose biomass stood as the largest source of renewable carbon as it is expected that its production will be between at a minimum of 10 billion dry tons/yr and maximum of 50 billion dry tons/yr [25, 26] and then will assume that production of lignocellulosic biomass from energy crops and agricultural waste is a viable renewable source for transportation fuels and bio-based goods.

In simple terms, lignocellulosic biomass is composed of three major components of biomass: hemicellulose, cellulose, and lignin. They are preferred as feedstock biomass due to their abundance, renewable nature, low cost, and higher energy content in dried form [27]. According to [28], the per energy growth rate of lignocellulosic biomass is 30–240 barrels of oil equivalent hectare⁻¹ yr⁻¹.

Lignocellulose biomass feedstock includes: agricultural resources and their wastes, crop and its residues, forestry resources and wastes, carbon-rich domestic and industrial wastes, and animal waste.

Agricultural produce stood as the primary source of Nigerians' revenue before the discovery of oil and gas, accounting for almost half of her GDP and 75% of export [29]. Had the trend of farming continued, there would not be an issue of food shortage, and agro-waste from this source would have been easily diverted as a source of energy. Currently, the world is being driven by progressive usage of limited reserves of non-renewable fossil fuel resources which has adverse climatic repercussions [20]. Geologists and geophysicists are always charged with a continuous search for new oil fields, but lots of oil fields discovered are non-economical to be explored. Scientists must look for alternative energy sources to create energy balance, security, and sustainability.

A bio-based economy is built on the sustainable production of food, feed, chemicals, fuel, materials, and plant energy. It is impossible to store these energy sources (wind, water, solar energy, and nuclear) as a liquid fuel. Some selected thermochemical conversion techniques can be used to obtain liquid products useful as biofuels to serve the same function as oil in automobile engines. This means the successful use of bio-oil as an industrial raw material will significantly depend on biomass processing processes [20]. The adoption of biomass remains the only alternative to replace fossil fuels for transportation or automobile industry [20].

Photosynthesis is a process that uses solar energy to produce sugar, starch, and structural polysaccharides which are viable carbohydrates used to produce biofuel. Bio- C_2H_5OH , a suitable biofuel, is obtainable from these carbohydrates via biochemical extraction process and fermentation [30]. Since structural polysaccharides are the most predominant carbohydrates and integral components of plants' cell walls, they account for most plant biomass. However, since they can be converted into biofuel more easily than cell wall polysaccharides, soluble sugars and starch currently make up the majority of the production of bioethanol [9]. For example, the secondary cell wall of a plant is a strong, shielding biological structure that offers stability and resistance to deterioration. This is a result of its primary components which include the structural polysaccharides carbohydrate cellulose and hemicellulose as well as the phenolic polymer lignin, interlinking to create a strong matrix [31]. Plant biomass that contains cell walls, or lignocellulose, can be converted into bioethanol, but first, the cell wall structure needs to be treated to make it more pliable. This procedure combines thermal energy, mechanical pressure, and chemicals to break down the crosslinks between the major components of the cell wall and increase the exposure of the polysaccharides to enzymatic hydrolysis [32]. Hydrolysis is necessary to separate cellulose and hemicellulose into their monomeric sugar components. After that, by fermenting these components, bioethanol can be produced [30]. Although structural polysaccharides are rarely or never utilized in food and feed applications, they are the most widely used carbon source in the large-scale generation of biofuels [32].

Nigeria is a tropical area with a vast land mass covered in trees. A vast amount of residue, including bark, sawdust, and mill chips, is produced when these trees are felled and made into boards. They are made up of wood processing waste and scrap that cannot be used to make new wood, such as wood particles/dust, veneer rejects, veneer log cores, edgings, slabs, trimmings, and other wood wastes from carpentry and joinery. Biomass wastes from rice, cassava, sorghum, maize, millet, and bailey all contribute to the supply of lignocellulose in the form of residues from farming processes. Maize is typically grown for its grain, where the plant's leaf and stem parts are used (referred to as stover). There is huge energy harvest possibility when considering the overall collection of residues based on worldwide harvest and average residue production per hectare. The lack of technical know-how in most of Africa countries has made lots of useful forest residues untapped as biomass energy.

2 Biomass Chemistry

Organic and inorganic components, as well as water, make up biomass [33]. The chemical structure and essential organic constituents of biomass determine the appropriate technologies for converting it into fuels and chemicals [30]. Biomass comprises three primary categories of naturally occurring polymeric components in dry mass. These carbon-based polymers are [30]:

- i. Cellulose (approximately 50%),
- ii. Hemicellulose: its value is between 10–30% in forests, and for herbaceous biomass, it stood at 10–40%.
- iii. Lignin: this made up 20–40% of woods resources and stood at 10–40% in herbaceous biomass.

The amount of cellulose, lignin, and hemicellulose in biomass largely depends on the species, as stated above, and these variations are primarily noticed with hardwoods and softwoods. Of the three major components, cellulose and hemicellulose are in higher proportion in hardwood than softwood. Table 1 showed a comparison of compositions [30] and [34].

Proximate and ultimate analyses are used to determine the principal organic constituents of biomass (cellulose, hemicelluloses, and lignin) and the percentage elemental composition of biomass [19]. Ultimate analysis of biomass showed biomass contains largely carbon (30–60%), followed by oxygen (30–40%), hydrogen has about (5–6%), and other elements including S, N, and Cl make up < 1% of the biomass. Biomass elemental composition is listed in decreasing order of abundance as; $C > O > H > N > Ca > K > Si > Mg > Al$ [19].

The common inorganic components in biomass are: alkali metal compounds (K, Ca, Na, Si, P, Mg, and Cl in herbaceous biomass). However, the amounts of these inorganic compounds differ, and it depends on the biomass species; wood (< 1%), herbaceous biomass (15%), and agroforestry residues (25%) [35].

Extractives from biomass are majorly smaller organic molecules and some other giant molecules such as acids, protein, and salt. Plant stems, foliage, and barks contain equivalent amounts of the significant classes of food, ash, hydrocarbons, and other substances [35].

Carbohydrates are organic polyhydroxy molecules having the elemental formula $(CH_2O)_n$. They contain a homogeneous carbon content of about 40%, which is significantly lower than that of hydrocarbons. They have exceptional physicochemical qualities due to their oxygenation, which enhances conversion and utilization. Monosaccharides, disaccharides, oligosaccharides, and polysaccharides are the four

Table 1 Composition distribution in biomass

Wood type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)
Softwood	40–44	25–29	25–31	1–5
Hardwood	43–47	25–35	16–24	2–8

forms of carbohydrates. Starch and sugar are the primarily used feedstocks in first-generation refineries, while cellulose and hemicellulose stood as the feedstock in the second-generation refinery [36]. Of the three major biomass components, cellulose and hemicellulose are carbohydrates, while lignin is non-carbohydrate [37, 38].

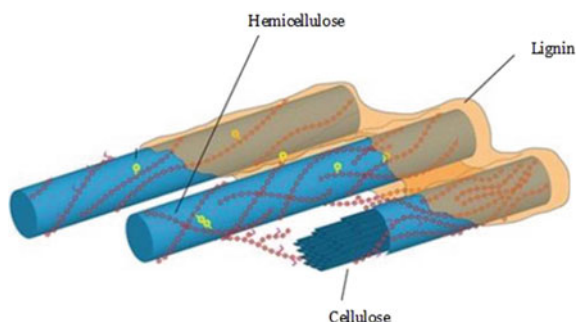
2.1 Chemistry of Biomass Components

The production of biofuel from any biomass depends on its three major components: cellulose, hemicelluloses, and lignin. These components stood as a fixed base for the production of fuels and other chemical additives. However, lignocellulosic biomass can generally be woody substrates and agricultural residues. In lignocellulosic biomass, cellulose and hemicelluloses are the two carbohydrate polymers that make a more significant percentage of the material. At the same time, the third principal component (lignin) is a non-carbohydrate but complex aromatic compound that is highly branched [39]. Apart from the fact that the variation of these components depends on plant specie type, other factors such as soil, age, and growth stage contribute to their variation [40].

In the order of abundance (%), the three significant components of biomass followed the order cellulose > hemicellulose > lignin [41]. The high content of cellulose and lignin is recorded in woody biomass, while soft tissue plants such as grasses are low in lignin but significantly high in hemicellulose [25].

Lignocellulosic biomass has cell wall extractives (proteins, pectin), macro- and micronutrients inform inorganic compounds, ashes, and the three major components. However, these have little effect on the buildup of the lignocellulose structure. The existence of lignin, hemicelluloses, pectin, and other plant cell wall components, as well as their spatial interlinks with cellulose, is hypothesized to have resulted in a plant cell wall with a robust and compact structure (Fig. 1) (physical barriers) that is resistant to microbial degradation [25].

Fig. 1 Arrangement of major components of biomass



2.2 The Structural Properties of Lignocellulose

2.2.1 Cellulose

Cellulose is a polysaccharide with a molecular weight of 162.1406 g/mol represented in Fig. 2. Cellobiose, an oligomer of two $C_6H_{12}O_6$ units linked together by fourteen glycosidic bond units. The cellulose polymer(s) $(C_6H_{10}O_5)_n$ has about 100 to 20,000 (14) linked D- $C_6H_{12}O_6$ molecules. Lignocellulose has the parallel linking of about 36 cellulose molecules via bonds and forces (hydrogen and van der Waal's) to form a non-amorphous structure with straight, stable supramolecular fibers of great tensile strength and limited openness. The basic fibrils are subsequently linked to other biomass components such as pectin, hemicelluloses, and lignin (Fig. 1). Cellulose microfibrils are little cellulose bundles that give plants mechanical strength and chemical stability. Some cellulose microfibrils are regularly joined to produce macro-fibrils [35].

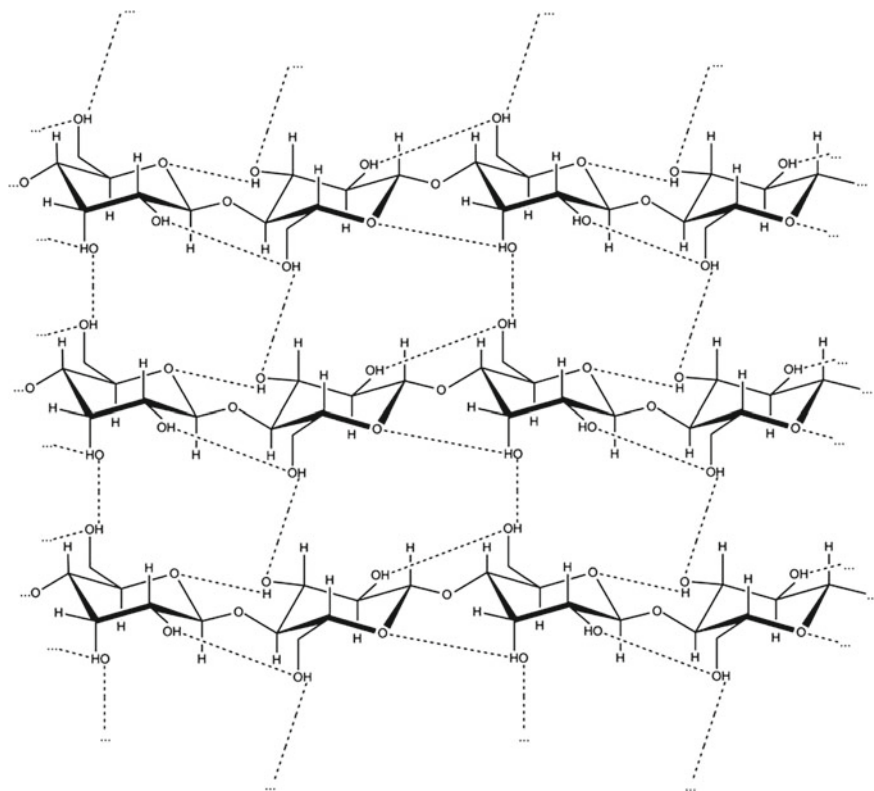


Fig. 2 Structure of cellulose

Cellulose has some degree of crystallinity, degrades less, and is typically insoluble in H₂O and common organic solvents. It is important to note that cellulose contains soluble, easily degradable, amorphous/non-ordered components. Many cellulose characteristics, however, are typically governed by its degree of polymerization.

2.2.2 Hemicellulose

After cellulose, hemicellulose (a polysaccharide grouping) is the second most significant carbohydrate component of lignocelluloses [41]. Hemicelluloses are heterogeneous short-chain linear and branching sugar polymers comprised of five different sugars, which are listed in (i–v) [25]; Fig. 3.

L-Arabinose (C₅H₁₀O₅)

D-Galactose (C₆H₁₂O₆)

D-Glucose (C₆H₁₂O₆)

D-Mannose (C₆H₁₂O₆)

D-Xylose (C₅H₁₀O₅).

The pentose (C₅) sugars are: L-arabinose and D-xylose, while the others are hexose (C₆) sugars. Xylan is the commonest hemicellulose family sugar, with examples listed in (i–vi). There are possibilities for minute amount of these sugars [42].

L-Rhamnose

L-Fucose

4-O-methyl glucuronic

Organic acids like acetic

Ferulic acid

Galacturonic.

Its sugar acetyl groups were replaced temporarily by –OH groups. However, the 1, 4-linked -D-hexosyl residues that make up most of the hemicellulose's backbone also occasionally include hexose(C₆) sugars, pentose (C₅) sugars, and uronic acids [25]. Unlike cellulose, hemicellulose's composition and structure vary depending on the source (such as the type of side chains and glycosidic linkages) [43]. Homopolymers, which are repeating units of a single sugar, include xylans, mannans, and glucans. Heteropolymers, on the other hand, are mixtures of various sugars, including arabinogalactan, arabinoxylans, arabinoglucuronoxylans, galactoglucomannans, glucomannans, glucomannans, glucomannans, and glucom. For instance, agricultural waste, O-acetyl-4-O-methylglucuronoxylans, and O-acetylgalactoglucomannan are utilized to create hardwood hemicellulose [44]. Due to their short-chain branching structure and acetyl groups attached to the polymer chains, hemicelluloses, unlike cellulose, lack crystallinity [42]. Its degree of polymerization ranges of minimum (70) to maximum (200) suggests that it is an amorphous polymer that degrades quickly [45].

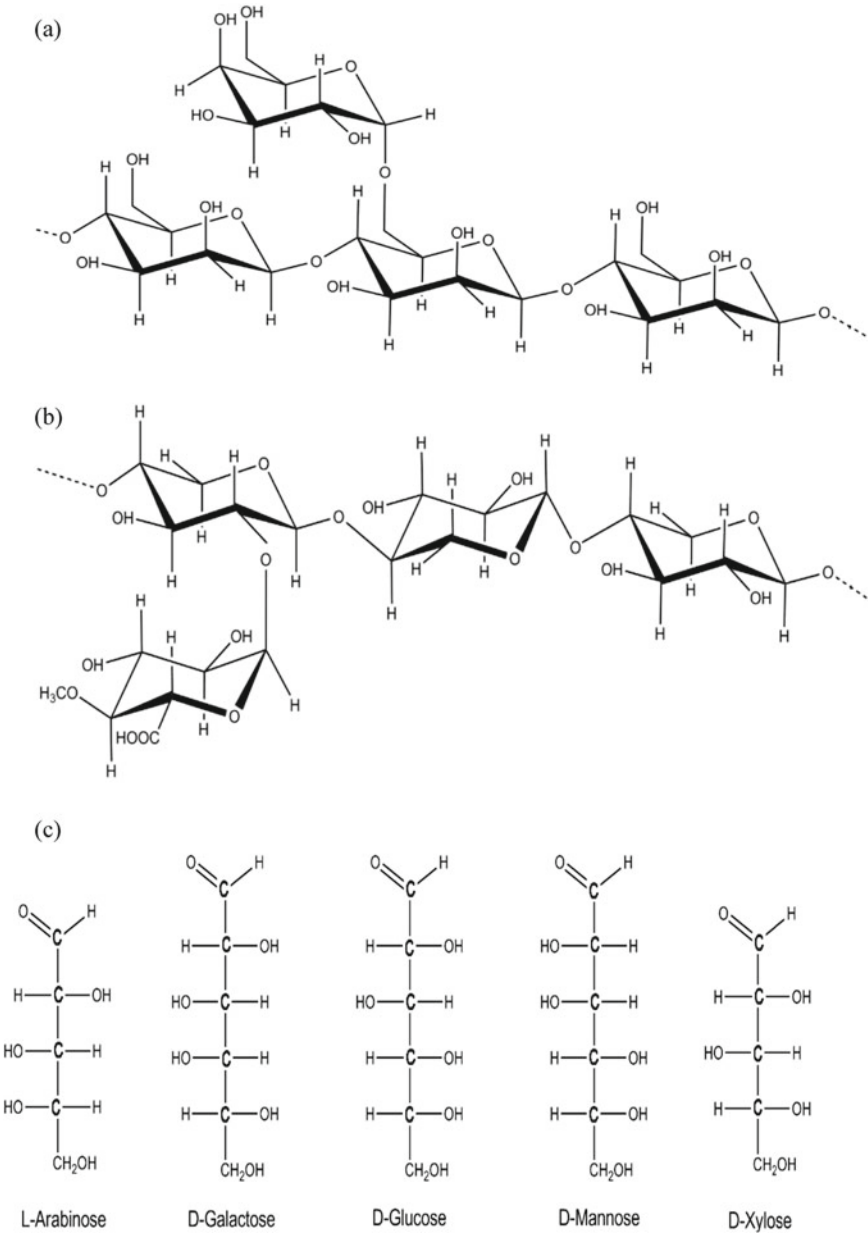


Fig. 3 Hemicellulose (a) represents galactomannan, (b) represents glucuronoxylan, (c) represents sugar monosaccharides

2.2.3 Lignin

After carbohydrates, lignin stood as the second-most available component of lignocellulose biomass on earth and the primary source of natural aromatic polymers [46]. The primary building units of lignin, an amorphous and highly branched rigid polymer, are three phenylpropane units. These three components, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, combine to form a random sequence of p-hydroxyphenyl (H-lignin), guaiacol (G-lignin), and syringyl (S-lignin) subunits [47]. Depending on the lignocellulose source, different H, G, and S-lignin compositions exist [48]. Herbaceous plants have high concentrations of all three lignins—G, S, and H—in various ratios, whereas hardwood lignins are largely composed of G and S monolignols with very little H. The G units make up the majority of the lignins in softwood, with H units making up the remaining fraction [43]. Lignin strengthens the cell wall by filling in the gaps between the two other major components of biomass (cellulose and hemicelluloses) and other cell wall components and acting as a cell, fiber, and vessel binding material [49]. Additionally, it has impact on how water, minerals, and metabolites are transported [39]. The development of lignocellulose's complex structure, the formation of plant cells, and the defense of plants against disease and insect attack all depend on it [42]. Although some bacteria and fungi may break down lignin, it can survive for a very long time [50].

2.2.4 Other Constituents

Proteins, ashes, extractives (including terpenoids, steroids, lipids, waxes, and phenolic compounds), and pectin, which is composed of neutral sugar side chains and acidic sugar backbones, are also present in the lignocellulose cell walls (often galacturonic acid) [51]. The homogalacturonan, rhamnogalacturonan, and xylogalacturonan subclasses make up the highly branching, complex heterogeneous polysaccharides known as pectins [52]. Their cross-linking influences plant morphogenesis and wall porosity and supports cell adhesion and wall hydration [51]. There are several uses for extractives; some safeguard plants, others act as precursors for certain compounds, and many others have unclear benefits [53].

2.3 *Lignin, Cellulose, and Hemicellulose Interactions* *Chemical*

The cellulose macro- and microfibrils embedded in lignin serve as the structural core (skeleton) of lignocellulose, whereas hemicelluloses are scattered between them

Table 2 Overview of significant connections between and among the three lignocellulose components

Linkage	Interpolymer	Interpolymer
ROR bond (Ether)	Lignin, (hemi)cellulose	Cellulose-lignin, hemicellulose-lignin
C–C	Lignin	NI
H- bond	Cellulose	Cellulose-hemicellulose, hemicellulose-lignin, cellulose-lignin
RCOOR bond (Ester)	Hemicellulose	Hemicellulose-lignin

NI: Not identified.

(Fig. 1). The crucial four interpolymers (between various components) and interpolymer (inside specific components) linkages that exist between these three components are ROR (ether), ester (RCOOR), carbon–carbon (C–C), and hydrogen bonds, as shown in Table 2 [45] and [54].

Ether (ROR) and H-bonds are the primary chemical bonds that hold cellulose polymers together. The glycosidic bonds in cellulose are comparable to ether bonds that bind 2-C atoms to an oxygen molecule [55]. The two –OH groups on various cellulose polymer chains interact to produce H- bonds. A number of the characteristics of natural cellulose, including its crystallinity, are thought to be caused by the hydrogen bonds between cellulose threads [56]. Similar to cellulose, hemicelluloses are connected mainly by either type of linkages. Several ester (carboxyl) groups are present instead of hydrogen bonds [45]. The C–C bonds make up 30% of the intrapolymer linkages between lignin monomer units, and ether bonds make up 70% of those linkages [45]. They can be found within and/or between the carbon atoms in allylic and aryl compounds [57]. Cellulose, hemicellulose, and lignin are joined by hydrogen via interpolymer bonds [54]. Hemicellulose and lignin are linked by ester (RCOOR) bonds, ether and ester bridges make up the majority of lignin and polysaccharide complexes. Although ether groups between lignin and the polysaccharides are known to exist, it is yet unknown if they also occur between lignin and cellulose or hemicellulose [45].

3 Role of Biomass in Energy Generation

3.1 Biomass Energy

The technologies applied to derive energy from biomass are: thermochemical and biochemical pathways. These two listed approaches are helpful in the transformation of lignocellulose biomass resources into three essential energy products: Biomass gasification has unique application since it is very promising for producing renewable chemicals and generating electricity in turbines or internal combustion engines [58].

Gasification of biomass is simply the use of a gasifier, which is a machine that uses a programmed mechanism involving heat (700 °C), steam, and O₂ to convert biomass into useful products such as syngas, biochar, biofuel, heat, power, and fertilizer without the use of combustion. The sustainable use of biomass for producing energy and chemicals depends on understanding its physicochemical properties. The variety and variations among biomass species are determined by chemical composition, MC, AC, and the presence of inorganic materials. Metals (Mn, Na, Al, Mg, K, Ca, Fe), metalloid (Si), and non-metals (Cl, S, N, H, O, and C) make up the majority of the components in biomass [59]. These elements are found in biomass in varying percentages.

Unlike fossil fuels, which have a high energy density, biomass has a low thermal efficiency. Low bulk density (typically 8.0×10^1 – 1.0×10^2 kgm⁻³ for agricultural straws and grasses and 1.5×10^2 – 2.0×10^2 kgm⁻³ for woody biomass) contributes to the low energy content of biomass in its original form [60]. Raw biomass is more expensive to handle, store, and transport than fossil fuels. Therefore, improving the biomass's handling, storage, and transport qualities are crucial for biomass's most efficient and productive valorization. Biomass is primarily converted via thermal and biochemical technologies to obtain improved biomass properties/products suitable for energy and lessen drawbacks associated with the use of biomass for energy purposes [61]. Fossil fuel serves as a better fuel when compared to bio-oil because bio-oil has low calorific values, a high percentage of moisture and oxygen, low energy density, high volatile matter, high density because of the presence of oxygenates, pH less than 5 (acidic), highly viscous and corrosive due to its water content attack on metallic engine and degradation with an increase in storage days [33].

3.2 *Biofuels*

Biofuel is an organic fuel derived from either live or dead carbon-based material. High-quality ethanol is produced from these sources using biomass conversion processes. This biomass conversion produces biofuels, which can be solid, liquid, or gaseous fuels. Biofuels include, among other things (a–c): **A. Solid biofuel:** Pelletized wood, briquettes, chips of wood, firewood; **B. Fluid biofuel:** Biodiesel, a bioethanol bioalcohols, **C. Gaseous biofuel:** Biogas \Syngas.

3.3 *Biofuel from a Few Familiar Biomass Sources*

3.3.1 *Cassava*

Cassava-Based Fuel: “Biomass” refers to all chemical energy sources that can be generated by converting plant and animal components into solid, liquid, and gaseous forms. To provide thermal energy for uses like cooking, propulsion, or the creation

of electricity, these fuels can be burned alone or in conjunction with traditional fossil fuels.

Ethanol is a biomass fuel type. By fermenting starchy substances like cassava and sugarcane, ethanol, a liquid fuel, can be produced. Other biomass fuel sources include biogas obtained from waste and rotting plant and animal matter in landfills or biogas digesters [62]. This part exclusively takes into account liquid biomass fuels, primarily ethanol.

Because cassava is commonly cultivated in Nigeria hence its preference for the production of C_2H_5OH . Government initiatives like the one that required cassava to be included in flour during the Obasanjo administration should have encouraged farmers to increase their cassava production in recent years. Most C_2H_5OH produced in Nigeria is made from petrochemicals, which has the unfavorable effect of taxing the country's petroleum reserves even more. So it is more than appropriate to adopt an alternative like cassava. This would have the desired result of creating employment in the rural areas where cassava is cultivated and lowering the dependence on petroleum components for ethanol synthesis. The lesson is that initiatives to support a biofuel sector of this kind must be pursued along with actions to ensure it does not affect the nation's food supply. Undoubtedly, these measures will involve educating farmers about the importance of giving food crop cultivation equal attention in the face of a cassava boom and subsidizing food crop production by providing farmers access to seedlings, farming equipment, fertilizer, financing, and other resources to make growing food crops simple.

3.3.2 Sugarcane

A perennial grass, sugarcane (*saccharin* spp.) grows well in tropical and subtropical climates. It needs an environment free from frost and with enough moisture during the growing season. Sugarcane uses chemical energy that it stores inside the plant to transform sunlight into energy as it grows. Approximately, one-third of the plant's stored energy is found in each of the following primary parts (a–c) below:

- a. Juice, which contains sucrose and is found inside sugarcane stalks, is used to produce ethanol and sugar.
- b. Bagasse: A ton of sugarcane yields 270 kilos of this dry, fibrous by-product after being crushed.
- c. Straw: The stalks of sugarcane leaves and tips.

Removing sugarcane bagasse in Nigeria is majorly via burning, and its straws are also usually burned to ward off snakes and other potentially deadly creatures. A third of the energy in sugarcane is destroyed via this procedure. Additionally, it has been found that burning the sugarcane field before harvesting is where the great bulk of emissions originate. According to experts, experts, straw, and bagasse can be burned together in high-efficiency boilers to provide up to 11,500 MW of bioelectricity [63]. Bagasse, a significant waste product, particularly during the dry season, offers a range of potential power output from 1000 to 9000 MW, depending

on the technology employed [63]. A significant source of both sugar and ethanol is juice. A biofuel known as bioethanol is increasingly frequently made from ethanol. The most crucial benefit of bioethanol for the environment is that it has the potential to be carbon neutral throughout its lifecycle, which means that the carbon dioxide (CO₂) released during production will be balanced by the amount absorbed from the atmosphere during usage. This guarantees a decrease in dangerous emissions and air pollution. Ethanol from sugarcane reduces greenhouse gas emissions by at least 60% compared to gasoline.

3.3.3 Husk of Rice

Rice husk is a typical agricultural by-product. Rice is one of the agricultural products designated for expansion by the Federal Government of Nigeria to diversify the country's current crude oil economy. In Nigeria, rice is a staple food, and if local production is expanded, this will lead to a rise in rice-processing wastes, including rice husk and straw. Igbinmo, Ebonyi, Isu, Kano, Ifon, Abeokuta, Jigawa, Cross-Rivers, and Sokoto are among towns that produce rice husk. In places, the number of dumps made of rice husks is rising alarmingly. Due to the impending environmental risks, deterioration, and pollution, it poses to people and the environment, disposing of and evacuating the rice dumps is urgently necessary. Most communities seek to dispose of rice husks by setting fire to the rice husk dumps, but a modest pile of rice husks takes months to burn to ashes. Even after being reduced to ashes, it still blights the neighborhoods, particularly during the rainy season. Air pollution and ash buildup are the results of burning rice husk dumps. Consequently, there is a pressing need to remove the rice dumps from these areas.

Rice husk, the main waste of the rice-processing industry, is one potential biomass-based energy source for generating electricity. With a calorific value of 3259 kcal/kg, rice husk is a renewable fuel source [64]. It is possible to produce electricity from rice husks using a gasifier and a modified internal combustion engine that drives a generator. Rice husk can be converted into fuel gas in a gasifier at high temperatures and in an atmosphere with just 1% oxygen. The generated clean gas (syngas) can be used right away in a gas-powered plant to generate electricity for local use as well as the powering of the rice mill. Rice husk power plants' by-product, rice husk ash, can be used in the cement and steel industries. It also increases the diversity and security of the electricity supply, is more environmentally friendly, creates more opportunities for local people to find work, and is a better way to dispose of agricultural waste.

3.3.4 Maize

Because it is the largest crop in the world in terms of overall acreage, maize is expected to be important in the development and widespread commercialization of cellulosic fuels [65]. Maize must be bred to function as a dual-purpose crop, demonstrating excellent grain production and quality features, high stem-biomass yield, and

Table 3 Biomass in bio-refinery

Biofuel	Description	Examples
First-generation biofuel	Made from raw materials that compete with those used in the food and feed industries	(i) Bioethanol from crops such as sugar beet, sugar cane, and starch (corn and wheat) (ii) Rapeseed, sunflower, soyabean, palm, and leftover food oil-based biodiesel biogas generated from starch
Second-generation biofuels	Produced from waste residues or non-food crops (energy crops)	(i) Biogas from leftovers and garbage (ii) Lignocellulosic material-based biofuel from energy crops, biofuel
Third-generation biofuel	From aquatic microorganisms, such as algae	(i) Biodiesel from algae (ii) Green hydrogen
Fourth-generation biofuels	Biofuels based on cultivation with high solar efficiency	(i) Technology that produces no carbon (ii) Future-day technology

higher processing amenability, in order to achieve this. The study [66] demonstrated that grain yield, agronomic fitness, and stover quality were not mutually exclusive breeding objectives and came to the conclusion that current maize breeding efforts might incorporate stover traits beneficial to the cellulosic ethanol sector without using foreign germplasm. With a wealth of genetic and agronomic resources, maize can be developed into a dual crop with the appropriate biomass quality characteristics and a significant amount of stover output. Given that it is widely produced, utilized as a feed crop, and generates enormous amounts of lignocellulosic wastes, maize is perhaps the most suitable model crop in the research of biomass quality. As shown in Table 3, maize and its waste can be used in biorefineries to generate electricity. Therefore, the main goals of research into maize bioenergy are to analyze and understand biomass recalcitrance as well as to specifically alter the composition of cell walls.

4 Chemistry of Biomass Conversion to Energy

4.1 The Use of Biomass

Lignocellulosic biomass is a significant organic embodiment of many components in which the major components are (hemicellulose, cellulose, and lignin); the carbohydrates components are (sugars, cellulose, and hemicellulose) and non-carbohydrate (lignin), with the presence H₂O, polysaccharides (starch, protein), fatty acids, oils, extractives, HC, AC, and other substances [34] and [67], in contrast to carbohydrates,

which make up < 30%, and lipids (oil), which make up < 10% of a biomass species, cellulose, lignin, and hemicellulose make up the majority of a biomass species. Lignin and the other two primary components of biomass term (carbohydrates) are typically recognized as lignocellulosic biomass [67].

Lignocellulosic biomass is a class of energy crops with distinct physicochemical properties (ultimate and proximate) or constituents (cellulose and hemicellulose) that are used as feedstock in second-generation refineries [36]. These compositions make biomass suitable for energy generation via thermochemical or biochemical conversion, and these factors are taken into account when selecting the appropriate conversion technologies for any biomass waste [68]. Biomass wastes have a high concentration of organic elements such as cellulose, hemicellulose, and lignin, as well as traces of other organic compounds or polymers, which are known to be a reservoir of solar converted to chemical energy [69]. Biomass contents vary; they can be converted to energy materials (bio-oil fuels, chemicals), and the selection of biomass depends on the required end products [70]. Bio-oil rich in lipids are frequently turned into biodiesel via the process of esterification (transesterification) with CH_3OH or $\text{C}_2\text{H}_5\text{OH}$, in contrast to carbohydrates (starchy and sugary components) which are typically converted through biological fermentation into $\text{C}_2\text{H}_5\text{OH}$. Naturally, lipids, proteins, and lignin are produced from sugars during photosynthesis. Long-chain hydrocarbon fatty acids with high calorific value contents are frequently produced when consumed by cyclic carbohydrates (glucose) [67]. As an alternative, solid biomass is commonly turned into syngas ($\text{CO} + \text{H}_2$), which, when subjected to Fischer–Tropsch (FT) process, produces liquid fuels and other chemicals. This process, however, requires several labor-intensive processes, energy, and financial investment. Direct liquefaction, often known as “biomass to liquid (BTL),” provides a more dependable and simple conversion of biomass leftovers to liquid. Numerous thermal and thermocatalytic BTL approaches are constantly being developed [67]. The choice of any biomass material for the generation of energy source is influenced by factors such as moisture content (MC), higher heating value (HHV), fixed carbon (FC), volatile matter (VM), ash slugging, and fouling indices via its group I metal content, and its cellulose/lignin ratio [37].

4.2 Criteria for Selecting Biomass

4.2.1 Ultimate and Proximate

There are two types of physicochemical parameters for determining the viability of any biomass waste as a source of biofuel. Proximate parameters commonly used are moisture content (%), volatile matter content (%), fixed carbon (%), and ash (%), while ultimate parameters are C, H, N, and S percentages.

MC Approximate Parameters

The moisture content of the same species of biomass varies greatly, making it an undesirable property of biomass for use in thermal conversion processes. Moisture content affects gross calorific value, combustion efficiency, and combustion temperature directly [16]. Sawdust moisture content (7.62%) is one of the factors that determined its HHV of 16.01 MJ/Kg, which is within the desirable range of 10% MC [15].

Ash Content (AC)

Ash is a residue that results from the thermal breakdown of organic and inorganic constituents of biomass waste. Higher ash content indicates higher carbon content, which favors gas yields. It is not a desirable property of a biofuel because depending on the elemental composition of ash, its constituents' catalytic influences thermal decomposition, slagging, fouling, and sintering.

Fixed Carbon (FC)

The fixed carbon fraction of a biomass is the carbon that exists in an uncombined state, that is, it is not chemically bonded to another element. FC produces biochar in a thermochemical conversion process of biomass, such as combustion, which is then burned in the reactor. A higher FC value is a property of herbaceous biomass wastes that favors combustion properties [71]. The expected FC range in such a waste is 7–20% [16].

$$FC = 100 - (\% MC + \% VM + \% Ash) \quad (1)$$

Volatile Matter (VM)

Volatile matter refers to the fraction of biomass that can escape and disappear from the reactor chamber during thermochemical conversion. Oxides of carbon (CO and CO₂), hydrogen gas, moisture, light hydrocarbons (CH₄), and tars are a few examples [24] and [71]. %VM is high in all biomasses, but values vary depending on the chemical composition of the biomass and range from 75 to 90% [16].

4.2.2 Gross Calorific Value (GCV)

The gross calorific value is a measurement of the chemical energy stored in biomass using an oxygen bomb calorimeter or a mathematical computation, as shown in Eq. (2). Equation (2) can be used to calculate the HHV or gross calorific value of

biomass [16].

$$\text{HHV} \left(\frac{\text{MJ}}{\text{kg}} \right) = 3491/10000 \times (C) + 1.1783(H) + 0.105(S) - 0.1034(O) - 0.015(N) - 0.0211(Ash) \quad (2)$$

4.2.3 Ultimate Parameters

The basic elements in biomass are C, H, N, and O. During the combustion process, the C component of biomass reacts with atmospheric oxygen to produce CO₂ and H₂O, a process known as an exothermic reaction. Equation (2) is a mathematical expression used to calculate HHV which demonstrated that these elements have a positive impact on biomass HHV and the combustion process itself.

Carbon is the most important element in thermochemical conversion processes; the higher its value, the higher the heating value of such biomass [15]. A very low percentage of hydrogen in biomass indicates a problem because it exists together with carbon to determine the heating value of biomass [15].

For a biomass waste not dried at 105 °C prior to CHNS analysis, Eq. (3) applies

$$O_2 = 100 \% - (\% C + \% H + \% N + \% S + \% M + \% AC) \quad (3)$$

Oven dried biomass waste before its ultimate analysis, Eq. (4) applies

$$O_2 = 100 \% - (\% C + \% H + \% N + \% S + \% AC) \quad (4)$$

The best biomass conversion methods (technically easy, cheap, and high yielding) must be selected for any biomass due to the nature of the polymers in lignocellulosic biomass to get fuels and chemicals.

Biomass is found worldwide, is highly abundant, and is renewable, which has sparked a growing interest in and driven current attempts to produce organic compounds with this diversity of biomass, with the sole aim of sugar conversions to value-added chemicals, e.g., ethanol. Hexoses, mainly glucose and D-fructose, are the best biomass sugar feedstock to use as chemical precursors or intermediaries [29].

5 Catalysis in the Conversion of Biomass

Biomass processing has historically used organic catalysis (also known as enzymatic catalysis). However, inorganic catalysis, utilized to transform unprocessed biomass feedstock into valuable products, is more economically efficient [67]. Due to their

higher capacity for molecular deoxygenation through various chemical processes, acid catalysis is commonly used in biomass valorization [72]

In converting biomass into alternative fuel and other chemical additives, catalysts are essential for either accelerating or improving the conversion products (liquids or gases). However, their properties and mechanism routes differ depending on the technology conversion employed.

5.1 Heterogeneous and Homogeneous Catalysis

Heterogeneous catalyst is largely employed as a crucial agent in the conversion of fossil fuels into fuels, power, and chemicals. Given the entirely different chemical make-up of these heterogeneous catalysts, their function in the digestion of biomass is still unknown. In recent years, zeolites have demonstrated tremendous progress for use in biomass valorization, particularly in converting lignocellulosic biomass into fuels and chemicals [73]. Catalyzing processes including dehydration, esterification, decarboxylation, and acylation play a crucial part in transforming oxygenates into hydrocarbons. Thus, it has been discovered that using zeolite catalysts in biomass processing is a feasible alternative technique for transporting fuels and chemicals [73]. However, a significant problem in the field of biochemicals is the discovery of innovative catalytic pathways for the selective, efficient, and direct conversion of biomass feedstock to manufacture specific compounds [74]. Both homogeneous and heterogeneous catalysts are typically used to catalyze the transesterification process for biodiesel production.

The chemical catalysts used in transesterification are classified as homogeneous or heterogeneous. Examples of homogeneous catalysts include potassium hydroxide (KOH), sodium hydroxide (NaOH), and sodium methoxide (CH_3ONa). NaOH is preferable to KOH because it dissolves quickly in solvents such as methanol (CH_3OH). It also has some intrinsic properties such as high purity and low cost when compared to KOH [75, 76]. The examples given above, in their concentrated/strong form, can help improve the quality of biodiesel production during transesterification.

When compared to homogeneous catalysis, heterogeneous catalysts are typically solid acid or solid alkali catalysts that improve transesterification by lowering costs and pollutant release [77]. Heterogeneous catalysts have several advantages, including low cost, ease of recovery after use, and reusability. Li/CaO, CaCO_3 rock, MgO/KOH, modified zeolites, anionic clays (hydrotalcite), Eni Slurry Technology (EST-4), and Na/NaOH/ Al_2O_3 are some examples of excellent heterogeneous catalysts used in transesterification reactions [78]. Solid acid catalysts promote both esterification and transesterification in the production of biodiesel from oils high in free fatty acid (FFA). $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$, SrO, CaO, MgO, $\text{KNO}_3/\text{Al}_2\text{O}_3$, [79], Li/CaO, KF/ZnO, basic hydrotalcite of Mg/Al, Li/Al, anion exchange resins, and base zeolites are some of the solid-base catalysts used in transesterification [80].

In a recent study [81], heterogeneous catalysts (acid or base) examples were reported and their applications in lab-scale biodiesel production. These include:

- i. Derivatives and oxides of Group I metals, e.g., (KOH), sodium hydroxide (NaOH), and sodium methoxide (CH₃ONa)
- ii. Derivatives and oxides of transition metals
- iii. Group II metal oxides and their derivatives; BeO, MgO, CaO, SrO, BaO and RaO.MgO and SrO
- iv. Products, metal oxides, and composites; Li/CaO, KF/ZnO, basic hydrotalcite of Mg/Al, Li/Al
- v. Sulfur dioxides
- vi. Ion exchange resins
- vii. Catalyst for carbon-based composites
- viii. Catalysts made of biological enzymes
- ix. Composite catalysts made of boron.
- x. Catalyst made from waste products.

Depending on the number and strength of active acid or main sites, they are extremely active, selective, and water-tolerant [81]. However, the production paths for biodiesel and bioethanol limit the use of heterogeneous catalysts in those processes (i.e., it favors the application of homogeneous bases in the fermentation of sugars and transesterification).

Heterogeneous catalyzed biodiesel production has emerged as a preferred route because it is environmentally friendly, requires no water washing, and product separation is much easier, and thus has a significant positive impact on the production of better biofuels (high energy density and fuel property compatibility). There are various important heterogeneous catalysts that have found use in pyrolysis, gasification, and catalytic upgrading of aqueous phase sugar processing, hydrotreatment of vegetable oils, and related feedstocks [74]. In this case, heterogeneous catalysts are pertinent, i.e., they are used appropriately and serve the required purposes.

Additionally, catalyst aids formation of gasification products. They increase conversion effectiveness, enhance gas quality, and lower tar content. Common gasification catalysts include dolomite, alkaline metal oxides, and oxides based on nickel. The importance of Fe, Co, ruthenium, and K catalysts in the FT synthesis of biofuel in liquid from biosyngas is well documented [30]. The effectiveness of various catalysts varies, though, and the choice of one depends on the desired end product and the catalyst's characteristics and reaction routes [30]. Catalysis has emerged as a key step to producing renewable chemical energy in recent years. Catalyst function has been demonstrated by the production of furan derivatives from biomass sugar in recent years, which have been used as alternatives to chemicals derived from crude oil or as building blocks for the synthesis of new products such as composite materials, metal casting, degrease metal, macrocyclic ligands, resins, agrochemicals, pharmaceuticals, liquid fuels, or solvents [29] and [82]. The commercialization of processes in which catalysts are used for biomass conversion to functional chemical additives has not been actualized. However, research is still going on in this area to improve these catalysts' selectivity and conversion efficiencies.

Furthermore, with recent improved research in the area of green chemistry, the choice of catalyst to be selected in biomass conversion should be the one that is cheap,

recoverable, and eco-friendly. Also, multipurpose catalysts derived from natural sources should be prioritized in catalytic chemistry. As a result, many reaction steps can be carried out in a single reactor without the need for pricey intermediary separation procedures. And also, the efficient recovery and separation of the desired products and the recycling of catalysts are crucial to catalytic research in general and biomass catalytic conversion. These, however, are complicated by the insufficient knowledge of the structure–property relationships of catalysts and the precise mechanisms underlying biomass conversion reactions, as well as the process compositions, catalyst optimization, and development, particularly for industrial scale production [29].

5.2 *Technologies for Converting Biomass*

Energy generation and environmental remediation were the two primary goals of biomass conversion technology. The toxic effect of released gases from the combustion of fossil fuels prompted the search for a low-cost and environmentally friendly alternative to energy generation. The use of readily available large biomass waste that constitute a nuisance to the environment is one approach that meets two objectives (energy generation and achieving of an environment cleaner and safer to live).

The two basic mechanisms for digesting biomass are biochemical and thermochemical reactions. Thermochemical pathways are frequently more efficient than biological routes due to their faster reaction times and greater capacity to break down the organic components of biomass [33]. The bulk density, MC, particle size, and intermittent availability of biomass conversion feedstock can all vary substantially. As a result, modern industrial technologies and fossil fuels are usually coupled so that in the case of a disruption in biomass supply, the fossil fuel serves these purposes (preheating, drying, and fuel supply maintenance) [83].

Different techniques are used to convert biomass into various energy sources. The quantity, kind, biofuel product, feedstock qualities, economic situations, legislation, and environmental requirements all play a role in selecting an appropriate conversion procedure [71]. The feedstock's desired energy form and accessibility are two important factors.

Biomass conversion into fuels, additive chemicals, and thermal energy materials is governed by three important processes. There are three types of chemical reactions: biochemical, thermochemical, and physicochemical. There are four main processing possibilities in the thermochemical pathway, which are outlined in (i–iv):

- Combustion
- Gasification
- Pyrolysis
- Liquefaction.

While the biochemical pathway consists of two primary processes (i–ii):

Anaerobic digestion
Fermentation.

The physicochemical route consists primarily of extraction followed by esterification, whereby oils are obtained from the hydrocarbons [70].

The listed biomass conversion methods are suitable for producing energy in the form of chemical/fuel, heat, and electrical sources. These processes can generate liquefied fuel (transport fuels), biochar, and gaseous fuels (H_2 , biogas, producer gas). The bioconversion of biomass predominantly yields biofuels, which are roughly categorized into four types and include bioalcohols, biodimethyl ether, syngas (bio- CH_4), FT fuels, and hydrogen (Table 2) [84]. Burning biomass to generate heat and power, converting it to gas-like fuels (CH_4 , H_2 , and CO), or turning it into liquid fuels are the three main ways to use biomass (biofuels). Currently, biomass energy accounts for about 4% of all energy utilized globally, compared to 12% from coal, 15% from gas, and 14% from electricity [34].

Simple sugars, lipids, starches, and vegetable oils are the primary raw materials used to make first-generation biofuels with commercialized methods. The second-generation biofuels, made mostly from lignocellulose biomass such as non-feed crops, forest leftovers, and household, agricultural, and industrial wastes, were developed in response to the debate between food and energy. The second-generation biofuels still need a lot of arable lands to grow the feedstock crops while having resolved the contentious food versus fuel dilemma faced by the first-generation biofuels. Consequently, food development is hindered, and a dispute similar to that around first-generation biofuels is implicitly imposed.

As described in Table 3, the third-generation biofuels that use algae and seaweed are grown on barren ground, marshy terrain, and sea waters overcome these concerns. These innovations are still being developed. The conceptual stage of the fourth-generation biofuel technology is still ongoing. They are designed to be made using technologies that successfully convert biomass into fuel, consuming more CO_2 during production than is created during usage or burning. As a result, these biofuels would be crucial in reducing gases responsible for global warming, which would help to mitigate climate change. They are produced by genetically modified algae, a carbon-negative energy source, with improved hydrocarbon yields, which results in the creation of an artificial carbon sink [84].

The majority of second-generation biofuels are produced utilizing bi thermochemical methods from lignocellulosic sources. The procedure's first thermochemical processes include gasification and/or pyrolysis, which are then followed by gas conditioning, cleaning, and FT synthesis to produce synthetic liquid fuels. According to the biochemical process, the cellulose and hemicellulose components of biomass are first broken down enzymatically into their unique sugars, which are then fermented to make bio- C_2H_5OH . Despite having a lower likelihood of being commercialized than the previous technology, this has a significant future cost reduction potential [81]. While biological processing works with lower efficiencies and

extremely slow reaction times (days, weeks, etc.) and is unable to completely break-down the majority of organic compounds in biomass, such as lignin, thermochemical processes work with higher efficiencies and faster reaction times and can completely decompose a lot of the organic compounds in biomass [70]. The pyrolysis, gasification, and hydrothermal processing of biomass are the three current thermochemical conversion pathways for producing fuels and chemicals discussed in the next section.

6 Thermochemical Conversion

Techniques commonly used to convert biomass or their wastes into higher calorific value fuel by increasing the energy density of the biomass, lowering its oxygen content, adding weight to the resulting hydrocarbon fuel, and creating carbon–carbon bonds are termed thermochemical conversion [84]. In addition to immediately generating sustainable energy from biomass, these processes yield more practical, portable, and energy-dense forms of energy carriers (-OH fuel, synthetic gases, light hydrocarbon, and so on) while preserving controlled temperatures and oxygen conditions [83]. They are influenced by the selected biomass feedstock, its ultimate properties, proximate properties, and the process operating parameters, and these factors are determining factors in thermo-converted product distribution and quality [35]. The end products of biomass thermochemical processing are typically categorized as the volatile and non-volatile fractions. The gases, vapor, and tar make up the volatile fraction while char or residual ash makes up the non-volatile component [30], and they usually take the form of the three states of matter with par or equivalent ecological and industrial significance [69].

Biomass can be thermochemically converted via processes listed below (i–v) and Fig. 5:

- Combustion
- Gasification
- Pyrolysis
- Torrefaction
- Liquefaction

Pyrolysis begins with any type of thermochemical conversion. These techniques liberate the energy store organic chemical energy in biomass by turning it into solid (charcoal), liquid (bio-oils), or gaseous fuels (synthetic gas) via pyrolysis, gasification, or liquefaction, as well as direct heat via combustion or co-firing. The most profitable of the listed thermochemical conversion processes is the one with the greatest potential for future advancement, producing higher yield intermediate energy carriers such as liquid or gaseous intermediate energy carriers [70]. Gasification is the most successful and economical method for producing bioenergy from lignocellulose biomass [84].

Variations in these processes' operational parameters, such as heating rate in °C/min, vapor residence time, reactor configuration, cause these processes to occur.

Biomass waste pyrolysis products exist in three states of matter: solid (biochar), liquid (pyro-oil), and gas (syn gas). The distribution of these products is determined by the feedstock used, pretreatment techniques, and pyrolyzer operating conditions. In most cases, fast pyrolysis techniques are used to achieve a maximum yield of bio-oil, which operates at a high heating rate (i.e., 1000 °C/s) suitable for achieving 60–70 wt% bio-oil, 15–25 wt% biochar, and 10–15 wt% syngas [85]. At lower heating rates and slower pyrolysis rates, all products (biochar/oil/gas) are capable of providing energy to sustain and drive the pyrolysis process.

A heated sand medium in an oxygen-deprived system quickly heats the biomass waste to the target pyrolysis temperature (450 °C -500 °C) to produce biochar, bio-oil, gas, vapors, and aerosol that exit the reactor via the conveying fluiding gas stream in a fluidized bed pyrolyzer.

A vacuum pyrolyzer is made up of stacked heated circular plates. A vacuum pump maintains a vacuum, which lowers the boiling point of gas products and prevents adverse chemical reactions. The top plate is around 200 °C, while the bottom is around 400 °C. Scrappers transport biomass from the top plate to successive lower plates. While moving across the plates, the biomass is dried and pyrolyzed. In this pyrolyzer, no carrier gas is required. When the biomass reaches the lowest plate, only char remains. The heating rate is relatively slow here, and vapor residence time in the pyrolysis zone is short. As a result, the liquid yield in this process is relatively low, ranging from 35 to 50% on dry feed, with a high char yield.

The longer the vapor residence time in a pyrolyzer, the more bio-oil is formed from the biomass.

Biochar, a solid by-product of pyrolysis, is widely used in soil management techniques to sequester carbon. Flue gas and syngas, which can be burned to provide heat and electricity or used as a feedstock for FT synthesis, are the primary products of the gasification process [35]. Only the production of liquid fuels under high pyrolysis pressure in various solvents like H₂O, CH₃COCH₃, CH₃OH, or their mixes is the focus of the liquefaction process (hydrothermal) [19]. The structural components of biomass (cellulose, hemicellulose, and lignin) thermally depolymerize and decompose, producing chemicals in the form of liquids, gases, and residual solid char-coal. Numerous compounds, including benzene, ethanol, isobutanol, methanol, 3-Pentanol, Butan-1-ol, 2-methylbutan-1-ol, and ethanol are present in bio-oil [15]. The process heating rate and temperature significantly impact these compounds' chemical make-up. Syngas (H₂ & CO), CH₃OH, dimethyl ether, C₂H₅OH, mixed alcohols, C1-C4 gases, hydrocarbons, FT liquids, styrenes, oxygenates, C₆H₅OH, cyclohexane, biphenyls, substituted C₆H₅OH, cresols, catechols, eugenols, resorcinols, syrinols, guaiacols, etc. are obtainable from biomass thermochemically converted.

6.1 Pyrolysis

In a system deprived of oxygen, thermal degradation of biomass is termed pyrolysis, which occurs at a temperature range of 350–450 °C to produce char, pyrolytic oil,

and non-condensable gas [33]. The variation in the distribution of pyrolysis products depends mainly on the process temperatures, residence times, and particle size distribution. Because of the composition of biomass, pyrolysis is a complex reaction. To achieve fast pyrolysis, it is critical to use a small but not extremely small particle size of biomass in order to achieve a kinetically controlled system at particle size of < 1 mm and low heating rates. Maximum yield of bio-oil can be achieved in fast pyrolysis with biomass particle size of < 1 mm. The higher the temperature, the faster the biomass composition is broken down to yield bio-oil and gas. At low temperatures (slow pyrolysis), a large amount of char is produced; as temperature rises, the char degrades further to produce bio-oil; and at higher temperatures ($550\text{ }^{\circ}\text{C}$ – $650\text{ }^{\circ}\text{C}$), gas yield is significantly enhanced. Higher vapor residence time in the pyrolytic chamber favors higher gas yields. It means gas production is principally favored at higher temperatures and extended vapor (hot) residence times. The need for high-quality and large quantity bio-oil is favored by a short residence time, and lower temperature $< 550\text{ }^{\circ}\text{C}$ while temperature below $350\text{ }^{\circ}\text{C}$ favors the large generation of charcoal [15]. The process condition or the modified process conditions determines how much of these three essential products are generated via pyrolysis [70]. This method produces fuels with high fuel-to-feed ratios, making it the most effective method for converting biomass. Additionally, the CV of biofuel products is optimized using thermal and catalytic processes. In comparison to other thermochemical conversion processes, pyrolysis offers a broader perspective and prospects for biomass valorization, which involves adding value to biomass wastes such as starch wastes, rice husk, corn husk, algae, grass, municipal waste, animal wastes, and so on by converting them to an energy source or biofuel and is roughly divided into two groups (i–ii): fast, slow, which are based on the operating circumstances [35]. In all practical thermochemical biomass conversion processes, pyrolysis is a key factor in reactor design, reaction kinetics, and the determination of product distribution, characteristics, and composition [30]

The four main pyrolysis-based processes (i–iv):

Slow pyrolysis and syngas upgrading

Fast pyrolysis and hydroprocessing

Catalytic pyrolysis and hydroprocessing

Hydropyrolysis and hydroprocessing, which are generally to provide transport fuels [86]. The combined hydrocracking and hydrotreating procedures are referred to as hydroprocessing. The quantity, kinds, and quality of the produced products are strictly controlled by the chemical make-up of selected biomass feedstock and the pyrolysis temperature [69]. The initial breakdown of the solid biomass species during pyrolysis results in char, light gases, and secondary tar, as well as the secondary reactions of the condensable volatile organic compounds. Pyrolysis of biomass in a thermogravimetric analyzer runs to the highest temperature of $700\text{ }^{\circ}\text{C}$, but most metallic components of this biomass degrades at higher temperatures, and also combustion and gasification occur at higher temperatures as compared to pyrolysis. Additionally, it happens at lower pressures (0.1×10^6 – 0.5×10^6 Pa) as opposed to hydrothermal liquefaction, which occurs at pressures between 10 and 25 MPa [35]. A key factor

in determining the distribution of pyrolysis products is temperature. Most of the products are made between 352 °C and 452 °C. As pyrolysis temperature increases, the breakdown of heavy molecules in the liquid and remaining solid enriches the gaseous portion with lighter molecules. High T (°C), a high heating rate (°C/min), and a short residence T(s) result in high liquid production. A long residence time, a moderate heating rate, and low temperatures encourage char formation. The production of charcoal is reduced as the temperature rises. High temperatures, a prolonged gas residence time, and a rapid heating rate are used to produce fuel gases [30].

The biomass components are typically thermally cracked into gases and vapor using heat from the outside, which leads to a vast spectrum of products [70]. Many variables influence performance, product kinds, distribution, and quality of biomass pyrolysis. Particle shrinkage and moisture content are a couple of them, as well as reactor design, catalysts, additives, and physicochemical characteristics like thermal conductivity and emissivity, permeability and density, specific heat capacity, and heat of reaction. Therefore, the variation in the parameters listed above will determine the outcome of any pyrolysis type [35]. The high interest in pyrolysis is due to its technological versatility, operational adaptability, and suitability for a wide range of biomass streams and products [70].

The pyrolysis technique is characterized by short hot vapor residence in 2 s, a high heating rate, and an overall rapid reaction time. It occurs at moderate temperatures of roughly 500 °C. The biomass is rapidly broken down into vapor, aerosols, biochar-coal, and gas. The process is best suited to obtain dark brown liquid bio-oil after condensing the syngas [70]. The process produces a lower amount of biochar when compared with slow pyrolysis [33]. Small particle size is also needed to achieve fast pyrolysis because the pyrolyzer is designed to remove any remaining vapor to avoid coming in contact with the hot feedstock particles again.

The following reactor types (i–iv) can be used for fast pyrolysis [35]:

Fluidized bed reactors

Ablative reactors

Vacuum reactors..

Stirred or moving bed reactors.

The acceptability of fast pyrolysis is due to its tremendous economic benefits. It produces liquids that can be utilized as energy carriers, fuels for transportation, and fuels for storage and energy. In this type of pyrolysis, about 60–70 w% pyrolytic oil, 15–25 w% biochar, and 10–20 w% non-condensable gases are produced. To optimize pyrolytic oil obtained from bio-oil, it is necessary to have conditions such as: low T (°C) high heating rate (°C/min), and short gas residence T(s), while high temperature, long residence time, and low heating rate are necessary to increase gas output [30]. However, rapid heating and quenching cause intermediate pyrolysis liquid to condense before its heavier elements break down into gaseous products [30] and [69].

The following are the salient characteristics of fast pyrolysis for pyrolytic oil products (high yields):

Biomass sieve to a diameter < 5 mm for quick volatilization and rapid heating.

A brief (2 s) vapor residence duration to reduce subsequent reactions.

For maximum liquid yields, a regulated reaction temperature of about 500 °C.

For biomass to ignite quickly, its moisture level must be < 10 w%, as all of the water from the feed's pyrolysis processes settles in the liquid phase with the feed.

Heating and heat transfer rates should be highly rapid at the interface of biomass particle reactions. Due to its poor thermal conductivity, this requires biomass that has been processed to a fineness of less than 3 mm. The rate-limiting phase in this process is the particle heating rate.

Quick removal of char to reduce vapor cracking.

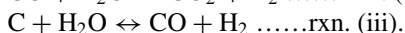
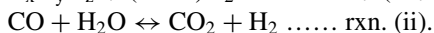
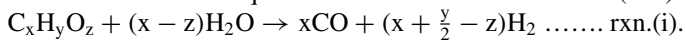
The production of bio-oil through the quick cooling of pyrolysis vapor and aerosols.

Mass and heat transfer processes, pyrolysis kinetics, and phase transition phenomena are critical since fast pyrolysis for liquids happens in a matter of seconds.

The ability to predict the maximum pyrolytic capacity of a pyrolyzer and feed-stock used is known as mass transfer, and the ability to predict the temperature/exit temperature to achieve this is known as heat transfer. It is critical to subject biomass to thermogravimetric analysis at various heating rates in order to confirm the thermal degradation pattern. The results of this analysis can be used in kinetic analysis to obtain useful parameters such as activation energy value (E_a), free energy G of the pyrolysis process, and so on. Understanding the thermal degradation pattern of biomass will reveal the state changes (solid–liquid–gas). Because fast pyrolysis is intended to produce a large amount of high-quality bio-oil, temperature data is critical. Thus, it is crucial in this process to quickly raise the reacting biomass particles to the ideal process temperature and reduce their exposure to lower temperatures (for the generation of charcoal) and higher temperatures (for thermal cracking) [70]. Fluidized bed reactors are primarily used to do this. For fast pyrolysis, reactors with bubbling fluidized beds, circulating fluidized beds, ablative flows, entrained flows, spinning cones, and vacuum reactors are frequently utilized [33].

Fast pyrolysis has the tendency to produce H_2 gas through steam reforming and water–gas shift processes. Study [87] used steam reforming of biomass pyrolysis oil to produce hydrogen (H_2). They carried out a steam reforming experiment on a bench-scale fluidized bed unit. The tubular reactor was heated electrically from the outside. 250 g of catalyst were loaded into the reactor. The researchers used Sud-C11-NK Chemie's catalyst commonly used for naphtha reforming and other four laboratory formulations catalyst which contains Ni, K, Ca, and Mg supported on alumina. These catalysts were first activated in an H_2/N_2 environment at 850 °C for about 2 h prior to the reforming reaction. Superheated steam, which is also a reactant in the reforming process, was used to fluidize the catalyst. Pyro-oil was loaded at the rate of 84 g/h through a temperature-controlled injection nozzle and sprayed as very fine droplets on the catalyst. A cyclone and a hot-gas filter were used to collect fine catalyst particles and possibly char generated in the reactor. The fluidized bed unit was incorporated with two heat exchangers for condensing the excess steam and obtained condensate weight was constantly monitored. A mass flow meter and a dry test meter were used to measure the outlet gas flow rate. Infrared spectrometer and a microgas chromatograph were used to measure the concentrations of hydrogen gas

(H₂), carbon oxides (CO₂ & CO), light hydrocarbons (CH₄), ethane (CH₂ = CH₂), and N₂ in the reformed gas. For all the catalysts, H₂ gas volume percentage in the product gas was around 70 vol.%, and the yield was 70–80% of the stoichiometric potential. The reaction sequence is as described in reactions (i–iii) below [87]:



The processes entail the conversion of CH₄, straightforward aromatics, various hydrocarbon vapors (C₂–C₅), and others that are primarily converted into H₂ gas. Generally speaking, steam reforming turns hydrocarbons into CO and H₂, and the CO then reacts with water to create H₂ and CO₂ [33]. Although it has been commercialized for the manufacturing of chemicals, the technology is still being worked on for the generation of liquid fuels. Lab-scale fast pyrolysis techniques have higher energy efficiency and comparatively lower capital cost than other thermochemical conversion methods [30]. Lab scale has small-scale size pyrolyzer reactor, hence heat transfer is effective throughout the reactor, and the smaller size dictates lower cost when compared to industrial pyrolyzer. The drawbacks of lab-scale fast pyrolysis are that the samples must be heated at high rates (around 200 °C/min), necessitating the use of high energy heating elements, and the small reactor size can only accommodate a limited amount of feedstock, resulting in a low bio-oil yield. An external energy is required to achieve fast pyrolysis which means the process itself is an endothermic reaction. The external heat supply degrades polymers (hemicellulose, cellulose, and lignin) at different temperature.

Liquids and gases are by-products of slow and intermediate pyrolysis, which focuses on the production of biochar. The process is characterized by longer vapor residence time and greater particle sizes compared to fast pyrolysis, and it takes place at low temperatures with mild heating. It is a well-known process that frequently occurs in the conventional charcoal kiln between 277 and 677 °C [69]. The most often used slow pyrolysis technologies include agitated (i–iv) [35]:

Drum kilns

Huge retorts (continuous or batch)

Rotary kilns

Screw pyrolyzers.

Slow pyrolysis is frequently used to decrease the amount of waste that needs to be disposed of and to lessen the adverse environmental effects of waste. Additionally, pyrolysis has been utilized for centuries to produce charcoal; nevertheless, it wasn't until recently (within the past 35 years) that rapid pyrolysis for the creation of liquids was created [70]. The petroleum equivalent of bio-oil is produced by the flash pyrolysis process, which runs at temperatures between 777 and 1027 °C and has a yield efficiency of up to 70%. Along with producing pyrolytic water, this procedure also has significant drawbacks. This bio-crude oil can be utilized as refined fuels for the production of heat and electricity or directly as fuel in boilers, motors, and turbines [69].

6.1.1 Energy Application of Pyrolysis Products

. The production of solid (char), liquid (tar), and gaseous products by the pyrolysis of biomass is a well-known process that can replace or provide an alternate energy source to fossil fuels. The liquids can either be catalytically transformed into liquid transport fuels or used directly as liquid fuels for boilers, diesel engines, and gas turbines to generate heat and power. Through catalytic cracking and hydrogenation, its oxygen content may need to be reduced and its alkalis content eliminated for other applications [30] and [69]. It mainly produces volatile materials or flue gas that is high in carbon. The flue gas is typically utilized to produce hydrocarbons, solvents (acetone, methanol), and power. Chemicals like CH_3COOH and levoglucosan, which can be converted into motor fuel or burned to produce energy, are abundant in the bio-oil component. The char could be used as activated carbon in industrial applications, slurry fuel, or soil enrichment agents [35].

In all thermochemical conversion processes, pyrolysis is crucial to determine reaction kinetics, reactor design, and the assessment of product distribution, composition, and characteristics [69].

6.1.2 Biomass Pyrolysis Oil

Pyrolysis oil is dark brown in color, a mixture of complex compounds with unknown quantification of the exact chemical composition. Its components are organic classes: hydrocarbon, aldehyde, aromatic, organic acids, ethanol, methanol, $\text{C}_6\text{H}_5\text{OH}$, anhydrosugars such as levoglucosan, pyrolytic lignin (a guaiacyl- and a syringyl-based fragment of the original polymeric lignin), and a limited amount of H_2O make up the majority of their chemical make-up (about 25%). Two distinct phases make up the pyrolysis liquid (i-ii) [30]:

An aqueous phase which is majorly organo-oxygen compounds of low molecular weight,

e.g., (higher CH_3OH , CH_3COOH , and acetone ratios).

ii. A non-aqueous phase that is primarily made up of high-molecular-weight insoluble organics called tar or bio-oil (aromatics).

A liquid mixture of oxygenated molecules with carboxyl, carbonyl, and phenolic groups makes up the bio-oil component of the pyrolysis products. Its chemical and physical composition differs significantly from that of fuels obtained from petroleum. Still, bio-oil is highly similar to the original biomass, making it difficult for pyrolytic oils to use as a substitute for fossil fuels. The chemical constituents of bio-oil are the same as those of the biomass from which it was derived [15]. The high water content of bio-oil content must be reduced before it could be suitable as engine fuel.

Components distribution in pyrolytic oil (i-vi):

About 20–25% H_2O

25–30% H_2O -insoluble pyrolytic lignin

5–12% organic acids

- 5–10% anhydrosugars
- 5–10% of non-polar hydrocarbons
- 10–25% oxygenated compounds.

Their low energy density is due to the water content of bio-oils, which decreases the flame temperatures of the oil, results in ignition problems, probable injection problems, and early oil evaporation during preheating. They are very polar and readily absorb over 35% water, in contrast to non-polar, insoluble petroleum oils. They also have a low heating value of 16 MJ/kg as opposed to 43 MJ/kg for ordinary diesel fuel because of their oxygenated nature and water content. The oils' pH range of 2.5–3.0 contributes to their mildly acidic nature. Additionally, compared to their petroleum equivalents, oxygenated bio-oils have significantly higher kinetic viscosities and densities [30].

Pyrolytic oils are typically used as fuel for boilers and turbines to produce heat energy and electricity. Through thermal or catalytic cracking, they can also be upgraded into transport fuels, or they can be used to produce useful chemicals and organic solvents. Bio-oils' low volatility, high viscosity, corrosiveness, and coking have, however, limited their applicability thus far.

Bio-oil does not dry off easily (low volatility); if directly used as engine fuel, large residue of carbon will be left in the ignition part of the engine.

One of the properties of fluid is viscosity, and for pyrolytic oil, its kinematic viscosity is the parameter usually measured at 40 °C. There is tendency for bio-oil viscosity to change during storage because of phase separation of its components (water and oil). Based on standard, bio-oil that could be use as fuel should have maximum viscosity is 125 cSt (or mm²/s) (ASTM D7544) while the standard viscosity of pure biodiesel is between 1.9–6.0 cSt (B100 and ASTM D6751). The composition of is bio-oil complex which depends on its source [15], i.e., the biomass and its water content which is responsible for variation in bio-oil viscosity. Addition of alcohol, e.g., small amount of CH₃OH, will decrease the rate of viscosity increase during storage.

Bio-oil derived from biomass pyrolysis was extremely corrosive to carbon steel and 214 Cr - 1 Mo steel, and some of the bio-oils corroded 409 stainless steels significantly. X-ray diffraction (XRD) analysis was used to identify compounds formed on the surface of the corroded carbon steel and 214 Cr - 1 Mo steel, which confirmed a hydrated form of iron formate. The study confirmed that formic acid is a significant corrodent in bio-oils, but it is almost certainly not the only corroding species, as evidenced by the lack of a direct correlation between formic acid concentration and measured corrosion rates [88].

SS410 alloy specimens were immersed in pyro-oil containing varying concentrations of four –COOH compound. Corrosion exposures revealed a linear relationship between the amount of formic acid added to the bio-oil and the amount of SS410 mass loss, indicating that formic acid is the most aggressive of the four acids tested [89].

Coking of bio-oil occurs during thermal cracking; coke has higher oxygen content than raw bio-oil and appears spongy [90].

Levoglucosan, furfural, HCOOH, guaiacol, cyclopentanone, CH₃COOH, methoxyphenyl, CH₃OH, CH₃COCH₃, C₆H₅OH, and their alkylated phenol are a few examples of these. The following chemical groups, as well as the minimum and maximum weights of the compounds that might probably be produced from fast pyrolysis oils, are listed in the study [30]: acids, ketones, aldehydes, aromatics, etc. that are organic.

6.1.3 Types of Pyrolysis

- i Slow pyrolysis is a thermochemical reaction typically occurring at 400 °C or lower. The three pyrolytic products are all used, although biochar is the most frequent. If some charcoal or oil is burned together with the pyrolytic gas, the heating process can be continuous and self-sufficient. This will give the reaction all the energy it needs to move forward. The heating process is often sluggish and low-rate, releasing gases with very little bio-oil. There is excellent potential for slow pyrolysis to produce biochar [16]. Due to a few process limitations, slow pyrolysis is not the best method for creating high-quality bio-oil. Data from Nigerian forestry and wood processing show that as of 2010, biomass wastes from solid and dust from logging, sawmilling, plywood, and particle board manufacturing totaled 65,753,628 m³ [65]. This might have been converted into charcoal through slow pyrolysis, providing clean energy for factories and peasants' boilers.
- ii. Fast pyrolysis: This method is typically used at 500 °C and a heating rate of 1,000 °C/s [16]. In a compartment with low oxygen levels, the pyrolyzer elevates the temperature of the biological materials to a high level. It occurs at a quick heating rate, which causes a substantial heat transfer to produce vapor with a short residence period, swiftly cooling and yielding a sizable volume of bio-oil [23]. The pyrolyzer uses this method to produce syngas, continuously burned to keep the system temperature constant. Fast pyrolysis can produce 15 to 25% char, 60 to 70% of pyrolytic liquid, and only 10–15% of pyrolytic gases; however, this mostly depends on the feedstock. Production of pyrolytic liquid for use as fuels, specialty compounds, and industrial chemicals has been a prominent application of fast pyrolysis technology. Agricultural waste, widely available in Nigeria, can also be used to extract bio-oil, the main by-product of this process, and transform it into biofuel. According to a study by [91], Nigerian maize cobs have an excellent potential for producing bio-oil, which may be used to generate electricity.
- iii Flash pyrolysis, a procedure that can create up to 75% of the bio-oil produced, can be used to produce the gas, bio-oil and char [24]. The biomass is rapidly devolatilized in an oxygen-free chamber with a gas residence time of < 1 s, a suitable high heating rate, and reactor temperatures in the range 450 °C–1000 °C [92]. Although this method generates a lot of bio-oil, it has significant technological restrictions. Flash pyrolysis has some technological limitations which include: poor thermal stability, char formed has catalytic properties that activate

the bio-oil to produce a more viscous bio-oil that sometimes contains some solid residues.

The produced pyrolysis oil has low heat stability, tendency for iron rustiness, incorporation of particles in the oil, produced char acts as catalyst reducing oil lubricating value over time, production of alkali in bio-oil, etc. [93].

- iv. Vacuum pyrolysis: In a vacuum, this form of pyrolysis occurs at lower pressure. Vacuum pyrolysis was first carried out in 1914 [94]. By removing the primary volatile products from the heated part of the pyrolyzer chamber, this type of pyrolysis slows down the breakdown processes that come after [95]. According to [96], inhibiting the cracking process and recondensation lowers gas production.
- v. Catalytic pyrolysis: This process, which produces primarily liquid that can be utilized as fuel or valuable compounds, occurs in an oxygen-deficient environment at moderate temperatures (about 500 °C), a high heating rate, and a brief residence period. This strategy has the best possibility of resolving the problems with polymerization, corrosion, low heat stability, and high viscosity that liquid pyrolysis products have. Additionally, it facilitates the handling and transportation of these liquid items [30]. A catalyst's effects during a pyrolysis process can include cracking reactions and upgrading biomass products, depending closely on the catalyst type and reactor design. Pyrolysis vapor is catalytically broken over a range of catalysts to create a variety of liquid and gaseous fuels. By reducing the oxygenates in a particular pyrolysis oil with the help of zeolites catalysts, the energy content of the oil is decreased [35]. In addition to promoting the synthesis of high-value products (hydrocarbons) that can raise the value of bioheating oil, catalysts are frequently employed to reduce oil viscosity, minimize the corrosiveness of bio-oil (by reducing carboxylic acid formation), and ultimately. Catalysts alter the pyrolysis procedure as illustrated below [35]:
 - i. Might cause a significant decrease in the temperatures at which biomass constituents decompose.
 - ii. Affect reaction networks as well as multifunctional phenols, which are precursors to polymerization and are used to stabilize bio-oil (deoxygenation).
 - iii. There is a chance that CO, CO₂, and H₂O will be emitted during the decarboxylation, decarbonization, and dehydration reactions.
 - iv. Promote coke production through dehydration procedures (mostly due to the very acidic catalysts).

6.2 Gasification

In the presence of gasifying agents like O₂, air, steam, CO₂, or their mixtures as well as impurities like nitrogen, sulfur, tars, and alkali compounds, the gasification process transforms carbonaceous materials (coal, petroleum coke, biomass, etc.) into combustible gases (CO, H₂, CO₂, CH₄, etc.) and trace amounts of light hydrocarbons

[33]; [86] and [97]. Syngas is the ultimate by-product after the production of bio-oil, an intermediate. In conjunction with a catalytic or chemical upgrading facility, the conversion unit frequently transforms syngas and bio-oil into usable biofuels and chemicals [84]). The process of partially oxidizing biomass at high temperatures to produce mostly gaseous products with very little tar and ash is known as “biomass gasification. “According to the gasifying agent, the gasification process is typically split into groups: steam, air, airstream, steam-oxygen, oxygen-enriched air, etc. [30]. Temperature increases favor gas production. Recently, advanced gasification techniques have been used for plasma gasification [61] and [70] and supercritical water gasification to break down biomass into primarily H_2 , CO , and CO_2 .

Hydrodynamics, or how the gasifying agent interacts with the solid fuel, operating circumstances (temperature, pressure, etc.), and the gasifying chemicals used by different biomass gasifiers all differ (air, oxygen, or steam).

Common types of gasifiers.

Entrained flow.

Fluidized bed.

Fixed-bed (updraft, downdraft, or cross draft).

The fixed-bed gasifiers are the most appropriate of these gasifiers [33] and [61]. The type of fuel, its properties (such as moisture content, particle size, density, ash content, and toxicity), how oxygen is delivered, and the type of combustion bed all affect how these gasifiers are constructed [69]. Supercritical water gasification (SCWG) is a highly effective method for converting high moisture biomass materials like algae, manure, olive mill water, sludge, etc. into H_2 (with little tar) [84].

6.3 Biomass Gasification Mechanism

Depending on the process temperature, this technology converts organic feedstock (solid fuel or liquid) into gases. Syngas is a gaseous mixture primarily made up of CO , H_2 , CH_4 , and CO_2 with traces of tar and ash at temperatures above $1200\text{ }^\circ\text{C}$ and below that. The effectiveness of the process and subsequent end-use are adversely affected by potential gasification by-products including tar and ash [70].

When the carbon in the feedstock material is partially oxidized in the presence of gasifying carriers (air, oxygen, steam, or CO_2), char is created. Char is a mixture of ash and unconverted carbon [59]. The inert component of the processed biomass is called char, which is the unconverted organic fraction. Producer gas, also referred to as syngas, is a gaseous mixture of nitrogen, light hydrocarbons (ethane, propane), heavy hydrocarbons (tar), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2). It condenses at temperatures between 250 and 300 degrees Celsius. Some of the contaminants include tar, particulate matter, alkalis, halides, sulfur, hydrogen sulfide (H_2S), chloridric acid (HCl), and inert gases like nitrogen (N_2). The amounts of each component, as well as ash and unconverted carbon, are influenced by the kind of biomass used as feedstock, the gasifying agent, and the gasification process operating parameters [14, 69, 84].

Table 4 Typical gasification reactions

Reaction	Calorific value (Kj/mol)
$2\text{C} + \text{O}_2(\text{g}) \leftrightarrow 2\text{CO}(\text{g})$	+ 246.4
$2\text{C} + \text{O}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{g})$	+ 408.8
$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$	-206
$\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$	-165
$\text{C} + \text{CO}_2(\text{g}) \leftrightarrow 2\text{CO}(\text{g})$	-172
$\text{C} + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CO} + \text{H}_2\text{O}(\text{l})$	-131

The basic example of biomass gasification is lignocellulosic biomass, which when burned in an oxygen environment produces CO, CO₂, H₂, CH₄, light hydrocarbons, tar, charcoal, ash, H₂S, NH₃, and trace species [84, 30]. The many chemical reactions that take place during biomass gasification are listed in Table 4 [97].

Based on temperature ranges and reaction chemistry, the entire gasification process is separated into primary, secondary, and tertiary reaction stages. At temperatures lower than 500 °C, biomass is first converted into oxygenated vapor and liquid species with water and CO₂. At temperatures between 700 and 850 °C, the initial moisture and liquid species react to create CO, H₂, CO₂, water vapor, phenols, gaseous olefins, and aromatics. The tar is made up of mixed oxygenates, phenolic esters, alkylphenols, heterocyclic esters, and PAHs. Processes like methanation, steam reforming, cracking, and water–gas shift also take place in addition to the tars and residual gases. At temperatures between 850 °C and 1000 °C, the tertiary reactions result in liquid tar, water vapor, PAHs, CO, H₂, and CO₂ [84].

To achieve optimum gasification, it is necessary to effectively control the process requirements for the biomass feedstock's homogeneity, bulk density, moisture and ash content, particle size, and energy content [70]. The woody biomass is first dried at temperatures above 200 °C before being gasified. Char and vapor are created early in the pyrolysis process. The char and vapor are oxidized by the oxygen in this atmosphere, releasing pollutants such as sulfur, tar, NH₃, and others as a gaseous mixture of CO, H₂, CO, and H₂O [70]. The energy required for the biomass oxidation step is frequently supplied by an allo-thermal technique (energy from an external source) as well as an auto-thermal procedure (internal heating of the gasifier by partial combustion) [61]. The process of gasification is entirely endothermic. The process of converting biomass into gas involves the following crucial techniques [97]:

Exchange of air (exothermic): This is necessary to generate the thermal energy that the endothermic processes (as a whole) require and to maintain the system's required operating temperature. In the absence of oxygen, the fuel only partially oxidizes while maintaining the stoichiometric ratio.

Dried (endothermic): In this instance, the feedstock's moisture content evaporates and directly impacts heat production.

Around 150 °C is the temperature at which this process is completed.

- i. Pyrolysis (endothermic): The breakdown of cellulose, hemicelluloses, and lignin occurs in biomass species between 250 and 700 °C, resulting in the generation of light molecules such as solids (char), liquids (tars), and gases (CO, H₂, CO₂, and light hydrocarbons) [30, 97]. Heat transfer, series reactions, and product diffusions are examples of process phenomena. At low temperatures, the reaction's kinetics is rate-limiting, but at high temperatures, the process is controlled by heat transfer or product diffusion.
- ii. Decrease (endothermic): Here, char and other remnants from the earlier steps are reduced through a series of reactions to create the final syngas [97]. Full-scale biomass gasification typically takes place between 800 °C and 1100 °C, while systems requiring oxygen for the gasification stage usually operate between 500 °C and 1600 °C [59]. The reduction temperatures influence the final qualities of the syngas constituents and the solid residue. The gasification pathway offers the best potential for incorporating flexible primary fuel input concepts and product mix ideas that could achieve zero or even negative carbon emissions [83]. The method improves the use of biomass and uses gas turbine technology to generate biomass electricity more effectively and at lower investment costs. Because the gas turbine's waste gases are collected and used to generate steam for the steam turbine, combined-cycle gas turbine systems can reach higher efficiencies of up to 50% [24].

Almost all hydrocarbon molecules, including C₂H₅OH, CH₃OH, transport fuels, dimethyl ether (DME), methane, and high-value compounds, can be created from syngas after it has been treated. Using the Fischer–Tropsch process, catalyzed by transition metal-based catalysts (cobalt or iron) at a higher temperature, syngas can also be upgraded into biomethane for injection into the gas grid or transformed into synthetic diesel. Separated hydrogen can be used to power both fuel cells and batteries in electric vehicles. However, the final end-use of the syngas is significantly influenced by end demand and plant scale [70]. Hydrocarbon waxes and long-chain alkanes are also produced when the clean syngas is processed by the Fischer–Tropsch method over a cobalt, platinum, or iron catalyst [86]. These products need upgrading and purification, but doing so consumes a lot of energy, is expensive, and necessitates further research and development to make them more effective for use on a large scale [70].

Catalysts are needed for the production of gasification products. They increase conversion effectiveness, enhance gas quality, and lower tar content. Common gasification catalysts include dolomite, alkaline metal oxides, olivine, and Ni-based oxides. It is well known that the Fischer–Tropsch process converts syngas into liquid fuels like diesel and hydrocarbons using iron, cobalt, ruthenium, and potassium catalysts. However, while selecting a catalyst, the intended end product should be considered in addition to the catalyst's characteristics and the reaction pathways [30]. For partial tar oxidations, catalytic steam reforming, and the catalytic upgrading of the gasification products into liquid biofuels, dolomite- or Ni-based catalysts are widely utilized in gasifiers. This is frequently carried out after a successful gas cleaning and composition modification [70].

6.4 Pretreatments and Feedstock for Gasification

Cellulose, hemicellulose, lignin, and protein breakdowns for the softwood, hardwood, and straw gasifiable biomass feedstocks are provided in Table 5 [59]. Saccharides that polymerize into long strands are the biomass fibers (cellulose and hemicellulose). Lignin, phenolic polymers that link fibers and are essential for maintaining the structural rigidity of proteins, serves as the binding agent between the fibers. The majority of proteins are produced by herbaceous plants [59]. These energy sources can be divided into the following groups: Biomass blends, wood, leftovers, animal and human waste, contaminated and industrial waste, waste biomass, and agricultural and horticultural waste are only a few examples [84].

The goal of biomass pretreatment is that biomass feedstock must be consistent in size, composition, and moisture content (25–30wt%) for the gasification process to function correctly. Torrefaction and hydrothermal upgrading (HTU) are the two non-drying pretreatment techniques for gasification [59]. Torrefaction increases the potential for gasification of biomass by reducing moisture, hydrogen, and oxygenated molecules at temperatures between 200 °C and 300 °C in an inert environment without oxygen. It might increase the biomass's ability to withstand moisture and improve its heating value as a form of mild pyrolysis. The biomass feedstock's high moisture content and solid fibrous structure are lost during this process, increasing the material's energy density. Pelletization and torsion can both occur at the same time [59] and [84]. Bio-crude is produced by hydrothermal upgrading (HTU), which breaks down biomass using water as a solvent. The procedure is typically carried out in two steps: first, the biomass feed is treated in water at pressures of approximately 30 bars and temperatures of 200 °C to 300 °C, and then the biomass (bio-crude) is converted at pressures of 120–180 bar and temperatures of 300 °C to 350 °C for a variable time of 5 to 10 min. The resulting bio-crude contains a range of hydrocarbons that can be used to make chemicals, a fuel that is synthetically made to resemble diesel, or as a co-fuel in coal-fired power plants [33].

Table 5 Biomass feedstocks for gasification

Supply sector	Example
Forestry	Wood chips, wood blocks, and willow
Agriculture	Herbaceous plants such as miscanthus, reed canary grass, giant reed, oilseeds for methyl esters such as rapeseed and sunflower, and sugar plants such as maize and wheat for ethanol production
Industry	Straw, wet and dry manure, industrial waste wood, sawdust from sawmills, fibrous vegetable waste from paper manufacturers, and pruning of fruit trees and vineyards
Waste	Grass and pruning remnants from parks and gardens, organic elements of municipal solid trash, biodegradable garbage buried in landfills, landfill gas, and sewage sludge

6.5 By-products of Biomass Gasification

The type and composition of the fuel, the gasifying medium or gasifier design, the temperature, the operating pressure, the moisture content of the fuel, and the method of contact between the reactants (biomass fuel and gasifying agent) within the gasifier all affect the precise components of the products produced by biomass gasification. Therefore, it is impossible to ascertain the precise composition of the gas produced by biomass [30]. The highest quantities of tar and dust in hardwood, lowest levels of char in softwood biomass, and highest levels of hydrogen are produced by straw [59]. The characteristics of the feedstock, such as its moisture content, ash content, volatile matter, char, organic contents, thermal conductivity, and inorganic elements, have a considerable impact on gasification [61]. By-products of gasification may be solid or gaseous, frequently divided into a gas and a condensable phase. Less than one weight percent of char is present in the solid phase (ash), composed of inert feedstock components and unreacted char. Char is acceptable for direct industrial application because it contains more carbon than 76%. The gas phase in the gas/vapor phase (syngas) is constituted of an incondensable gaseous mixture of CO, H₂, CO₂, CH₄, light hydrocarbons, and some C₂-C₄ hydrocarbons as well as a negligible amount of NH₃, H₂S, and HCl, depending on the make-up of the feedstock. They can be burned to produce heat or power or used to produce chemicals, hydrogen, or liquid transportation fuels. Syngas' dry mass basis generation can range from 1–3 Nm³/kg, and its low heating value (LHV) can range from 4 to 15 MJ/Nm³.

In gasification, products formed are bio-oil, gas, and tar, but gas has the highest percentage. Table 6 presents a physicochemical comparison of pyro-oil and diesel fuel, and Table 7 presents tar classes [59].

Table 6 Physicochemical comparison of pyro-oil and diesel fuel

Physical Properties	Bio-oil	Diesel Fuel
MC	20–30 wt.%	0.1 wt.%
pH	2.0–2.5	
Density	1.2 kgm ⁻³	0.94 kgm ⁻³
Ultimate Analysis (wt%)		
C	55–58	85
H	5–7	11
O	35–40	1
N	0–0.2	0.3
Ash	0–0.2	0.1
Gross CV	16–19 MJkg ⁻¹	40 MJkg ⁻¹
Viscosity	40–100 cp	180 cp
Biochar (wt.%)	0.1–0.5	1.0
Vacuum distillation residue	Up to 50 wt.%	One wt.%

Table 7 Classes of tar

Tar Type	Type Name	Peculiarity	Characteristics Compounds
1	GC-undetected	Very heavy tars that are not GC detectable	calculated by deducting the total gravimetric tar from the GC- detectable tar fraction
2	Heterocyclic aromatics	Tars with heteroatoms and other highly insoluble in water substances	Phenol, dibenzo phenol, pyridine, phenol, cresol, quinolone, and isoquinoline
3	Light aromatics (1 ring)	typically thin, single-ring hydrocarbons that don't have any issues with condensability or solubility	Xylene, styrene, toluene, and ethylbenzene
4	Light PAH compounds (2–3 rings)	compounds with 2 and 3 rings condense at low temperatures even when their concentration is relatively low	Fluorine, anthracene, indene, naphthalene, biphenyl, acenaphthene, and phenanthrene
5	Heavy PAH compound (4–7 rings)	These compounds, which have more than three rings, condense at high temperatures and low concentrations	Coronene, pyrene, chrysene, perylene, fluoranthene, and pyrene

The rate of the process of synthesizing gaseous fuels from biomass is governed by the rate-limiting phase known as char gasification [59]. Bituminous oil is believed to exist as the condensable phase (tar), composed of various chemical components.

The European Board of Standardization refers to all organic chemicals present in syngas with established analysis methodologies as “tar” (a complex mixture of condensable hydrocarbons), with the exception of the gaseous hydrocarbons C1–C6. The tar composition is greatly influenced by the gasification procedure, the operating circumstances, and the biomass feedstock. They are normally grouped into five major classes based on their molecular weights (Table 7) [59]. Tar is a by-product of the pyrolysis process and is degraded and recombined during the gasification stage. Depending on how they form, they are separated into three groups: primary, secondary, and tertiary tars. The primary tars are formed immediately during the pyrolysis cycle and are dependent on the biomass intake. Due to the high oxygen concentration of cellulose and hemicellulose as feedstock, primary tars made of oxygenated chemicals (carbon acids, aldehydes, alcohols, ketones, etc.) are produced from these materials. Aromatic compounds, especially bi- and tri-functional substituted phenols (xylenol, cresol, etc.), are the main by-products of lignin pyrolysis [59].

The oxidation cycle results in the production of secondary tars. At temperatures above 500 °C and in the presence of an oxidant such air, oxygen, or steam, their

manufacture involves the rearrangement reactions (dehydration, decarbonylation, and decarboxylation) of primary tars [59]. They include dioxin, furan, pyridine, thiophene, and other hetero- and mono-alkylated aromatics. Tertiary tars, often referred to as recombination or high-temperature tars, are produced at temperatures higher than 800 °C. They mostly consist of polynuclear aromatic hydrocarbons (PAH), such as phenanthrene, benzene, pyrene, and benzopyrene, as well as aromatics. Instead of during biomass gasification, tertiary tars are frequently created following the recombination and degradation of primary tars in the syngas reduction environment. They also do not live with primary tars; rather, they only emerge as secondary tars once all primary tars have been changed [59].

6.6 *Upgrading Methods for Bio-oil*

Bio-oil made from biomass is not suitable for use directly in engines due to its abnormally high moisture content, low energy density, and lack of a free-flowing physical form. Because of this, bio-oil needs to be cleaned and improved in order to increase its fuel efficiency, remove impurities, and increase its energy density [98]. Table 6 compares the differences between pyrolysis oil and diesel fuel [73].

Its major characteristics include bioviscosity, acidity, thermal instability, and a substantial proportion of oxygenated molecules. It can be difficult to produce high-quality bio-oil that perfectly replaces fossil fuels. To solve this issue, the bioquality oil must be raised in the manufacturing facility before total production or through product enhancement [30]. The three main procedures for converting bio-oil into high-quality transportation fuels are zeolite upgrading, hydrodeoxygenation using a hydrotreating catalyst (alumina supported sulfided CoMo or NiMo), and emulsion formation with diesel fuel. Char and bio-oil can also be combined with steam reforming to produce syngas or H₂ [30]. Bio-oil needs to be enhanced to improve its quality and purity because it is commonly generated with impurities. Physical, chemical, or catalytic methods can be used [70].

Integrated catalytic pyrolysis or decoupled liquid phase hydrodeoxygenation are two methods for catalytic bio-oil upgrading, which is the complete deoxygenation of the bio-oil and conventional refining. A partial upgrade into intermediate products compatible with refinery streams is additionally suggested to take advantage of the traditional refinery's substantial scale economies of scale and breadth of experience. The three fundamental ways of upgrading through refinery integration are gasification to syngas followed by synthesizing alcohols or hydrocarbons, in situ or ex situ catalytic vapor cracking, and hydrodeoxygenation [70].

To form saturated C–C bonds by removing oxygen, bio-oil is treated with high-pressure hydrogen at moderate temperatures (302 °C–602 °C) in the presence of heterogeneous catalysts, increasing the fuel's energy content and stability. When hydrotreating industrial feedstocks, sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ are frequently used [30]. A hydrogen supply, a temperature of around 400 °C, and a pressure of about 20 MPa are needed. Because of the phenols in bio-oil, complete

deoxygenation is frequently difficult. A naphtha-like by-product of full hydrodeoxygenation needs traditional refining to produce conventional transport fuels like gasoline. The estimated comparable output from biomass is 25 w%, or around 55% in terms of energy, without the addition of hydrogen. The yields are reduced to roughly 33% in energy and 15% in weight when hydrogen from biomass gasification is added [70].

Hydrogen must come from sustainable and renewable sources. It is possible to create H₂ locally by electrolyzing water, gasifying biomass, converting CO to H₂, and removing the H₂, steam-forming bio-oil, or the aqueous phase of a phase-separated product to H₂, converting CO to H₂ and removing the H₂, and more.

Given the high expenses of delivering and storing H₂, external supplies are improbable [70]. Zeolite cracking/upgrading, which removes oxygen primarily as CO₂ with a trace quantity of CO from catalyst coking, takes place in a closed system at pyrolysis temperatures between 352 °C and 502 °C and standard atmospheric pressure. The oil's thermal stability is enhanced as a result. It is estimated that the procedure will produce aromatics at a rate of about 18%. The chemical industry highly emphasizes the manufacture of aromatics, a crucial primary chemical [70].

Because the pyrolysis oil's negative side effects prevent direct use, it is frequently enhanced by being transformed into gasoline using zeolites (crystalline microporous aluminosilicate materials). This method generates hydrocarbons and by-products such as coke, water, and CO_x by forcing oil vapors over the catalyst at temperatures between 300 and 500 degrees Celsius. The impacts of unprocessed biocoking oil are eliminated by coke production (on the zeolites). Depending on the kind of organic component being treated, the catalyst extracts CO₂, CO, or H₂O [19]. Zeolite cracking of bio-oil is particularly advantageous because it does not require H₂, operates under atmospheric pressure, significantly lowers operating costs, and occurs at temperatures equivalent to those needed to produce bio-oil. The ZSM-5 zeolite catalysts transform oxygenated oil into mixtures of hydrocarbons ranging from C1 to C10 using their potent acidity, high activity, and shape selectivity. This method's primary limitations are its simple coking, poor yield (14–22.5%), and brief catalyst life [30].

The temperature range required for catalytic steam reforming over a nickel catalyst is 752 °C to 852 °C. The following technique has two steps reactions. (1 and 2), the shift response being one of them [30].

Pyro – oil + H₂O → CO + H₂ (Reaction 1) CO + H₂O → CO₂ + H₂ (Reaction 2)

6.7 Syngas Processing

Tar, particulate debris, nitrogen (NH₃, HCN), alkali, halides, sulfur (H₂S, COS), and trace elements are common contaminants in synthetic gas. These pollutants are leading causes of gasifier blockage, corrosion, and catalyst deactivation. Biofuels, chemicals, and electricity generation use synthetic gas as raw material. As a result,

Fischer–Tropsch synthesis, the production of biomethanol, the use of fuel cells, and other processes require syngas.

Syngas is typically used to generate biohydrogen (at a rate of 25%), NH_3 (at a rate of 50%), and other processes such as the production of biomethanol and FT.

The methods used to clean syngas are frequently divided into two groups based on the temperatures at which its constituent elements condense. Some of these pollutants are covered along with the techniques employed to purify them [84].

Flue gases and unwanted by-products like ashes and tar (the gasification bottleneck) are the principal by-products of biomass gasification used to produce electricity. The latter is typically discarded despite having significant chemical and fuel potential.

Recently, efforts have been made to valorize this biomass gasification waste into liquid fuels and chemicals due to the complicated nature of gasification tar, which contains hundreds of chemical components and has a significant potential for soil contamination when released into the environment untreated [58].

However, tar treatment, removal, or conversion severely impedes the development and use of biomass-derived gas (poor efficiency, fouling tendency, plugging pipes and tubes, operational problems, etc.). End pipe tar syngas cleanup, in-bed catalytic tar reforming, and in-bed thermal tar cracking technologies are a few techniques that are frequently employed [59]. By encouraging the transformation of tar into useable combustible gases through processes like steam reforming, thermal cracking, dry reforming, hydrocracking, water–gas shift reactions, and hydroforming, catalysts play a critical role in increasing reaction rates at low temperatures. They could serve as feedstock or bed materials [33].

Right now, the primary goal of biomass gasification is to produce fuel gases with low- or medium heating values for use in internal combustion engines that produce power.

Less emphasis has been given to gasification in the literature than to manufacturing liquid chemicals or transportation fuels. Gasification provides a great deal of flexibility and efficiency to value biomass. To promote future technologies, gasification systems and procedures must be complex, affordable, and highly effective. To increase process efficiency, boost gas quality and purity, lower investment costs, and improve the technology's performance in the future, additional research and development into biomass gasification are necessary. Fundamental conditions for attaining these include high-temperature gas cleaning, catalytic conditioning, and the development of novel catalysts, sorbents, and high-temperature filter media.

6.8 Hydrothermal Conversion of Biomass

Since hydrothermal energy was adopted as a high potential energy source, biomass hydrothermal conversion has attracted much interest. There was initially a lot of focus on selecting the proper solvent and especially on high temperature and pressure processing materials due to the lack of knowledge on chemical solubility and how

it affects the process as a whole [99]. It is a fantastic way of converting biomass with high energy and moisture content into a range of products, such as a solid (biochar), a liquid (bio-oil), or a gas (hydrogen, methane, etc.) [38]. This procedure involves heating organic wastes or aqueous biomass slurries at higher pressures and low to moderate temperatures to produce a high-density energy carrier or liquid product in the presence of a catalyst [24]. Subcritical and supercritical water is used as the processing medium whole [99]. The primary processing conditions are high pressures (4–22 MPa) and temperatures between 250 and 374 °C. Compared to other thermochemical processes, this technology's low temperatures, low tar production, and excellent energy efficiency are the critical reasons for the recent spike in interest [37] and [98]. Due to their high ash and moisture contents, manures, food wastes, anaerobic digestate, sewage sludge, aquatic biomass (micro and macroalgae), and municipal wastes are some examples of acceptable feedstock. The solid content of the slurries may reach 30% by weight [70].

In the four primary hydrothermal processing steps of carbonization, aqueous phase reforming (APR), liquefaction, and gasification, water functions as a reactant, solvent, and catalyst [70]. At pressures between 20 and 40 bar and temperatures between 180 °C and 250 °C, the mildest type of carbonization, known as hydrothermal carbonization (HTC), produces hydro-char, a solid with properties like those of low-rank coal. This process, which is influenced by temperature and residence time, allows for the reduction of the oxygen and hydrogen contents of the biomass feedstock through dehydration and decarboxylation processes [100].

Hydrothermal liquefaction (HTL) produces liquid bio-crude at pressures of up to 180 bar and temperatures of between 250 °C and 375 °C, which can subsequently be enhanced by catalytic hydrotreatment into a variety of distillate petroleum-derived products.

Hydrothermal gasification (HTG) or supercritical water gasification (SCWG) occurs at pressures larger than 200 bar and temperatures greater than 375 °C to create syngas, CO₂, CH₄, and C1-C4 hydrocarbon gases such C₂H₄ and C₃H₆ [38]. By-products, including char, tar, and microscopic bio-oil, are produced at low temperatures. At temperatures between 220 °C and 250 °C and pressures between 1.5 and 5 MPa, the aqueous phase reforming, a subset of HTG, generates H₂ syngas, alkanes, and a variety of biobased chemical products, including fibers and plastic compounds [99].

These processes utilize wet biomass without any initial dewatering, have high conversion rates, can collect, store, and sequester carbon, create a wide range of chemicals and fuels in the gaseous, liquid, or solid phases, and most importantly, capture, store, and sequester carbon [99]. Hydrothermal biomass processing has several drawbacks and benefits [37, 38]. Hydrothermal liquefaction (HTL) is a hydrothermal treatment used to create bio-oil. It is more energy-efficient than thermal processes (pyrolysis, gasification and combustion). A suitable biomass for pyrolysis and gasification must have a water content of less than 10%; otherwise, drying must be performed prior to use [101, 102]. Because HTL has a low oxygen content, upgrading bio-oil obtained through this process requires less hydrogen [37]. If HTL is implemented industrially, it is expected to result in a direct and continuous supply

of biomass wastes for effective valorization [103]. HTL technology implementation on an industrial scale is prone to operational issues. Corrosion of metallic parts by water in bio-oil, high operating costs, easy deactivation and sintering of catalyst, plugging due to solid deposition, corrosion, pumpability of feedstock, and safety process due to high pressure and temperature. For instance, managing large-scale separation and extraction operations involves managerial issues, more expensive and advanced reactors, extensive water handling equipment, etc. The hydrothermal processing of biomass is based on the critical water point (374 °C and 22.1 MPa), which determines both the subcritical and supercritical water conditions. Biomass constituents like cellulose and lignin are insoluble in water at ambient temperature but soluble in supercritical water (high-temperature water). When biomass is broken down hydrothermally, the water-soluble component disperses into the water at around 100 °C, and hydrolysis occurs above 150 °C. The solid biomass is transformed into a slurry at about 200 °C and 1 MPa, and liquefaction takes place at about 300 °C and 10 MPa, producing oily products. By altering the process variables, such as temperature, reactor pressure, reaction duration, and catalyst presence, biomass is converted here into solid (biochar), liquid (bio-oil), and gaseous products [37]. Supercritical water oxidation removes harmful compounds (pollutants) from biological and organic waste and power generation cycles. Understanding biomass hydrothermal processing and the many degradation processes require a thorough knowledge of water properties under hydrothermal conditions (subcritical and supercritical). At higher temperatures, water has a low dielectric constant. Non-polar compounds are therefore insoluble in water at room temperature, but in supercritical conditions, they are excellent solvents for non-polar substances [37].

6.8.1 Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction of biomass wastes has been extensively researched as a source of useful chemicals that could serve as biofuel obtained at moderate temperatures and high pressures sufficient to keep water in the liquid phase [99]. A technology that has promise for producing high-quality bio-oil from biomass is hydrothermal liquefaction. This process does not need the energy to dry biomass because it entails only wet feedstocks/high moisture content directly from the field. This does away with the necessity for energy-intensive feedstock drying, which is required in thermochemical processes such as torrefaction, combustion, gasification, and pyrolysis [104]. HTL produces liquid bio-crude with a high calorific value and aqueous, gaseous, and solid phase by-products in H₂O at high pressures (10×10^6 – 25×10^6 Pa) at moderate temperatures of around 280–370 °C [38]. This comprises several intricate reactions that result in products with high energy densities and an improved heat recovery mechanism. Two main feedstock groups defined the process mechanism. These are the wet feedstocks (algal biomass), which are made up of essential ingredients such as lipids, proteins, carbohydrates, and algaenans, and the dry feedstocks (lignocellulose biomass), which are composed of cellulose, hemicellulose, and lignin constituents [98].

Along with bio-crude, a variety of compounds can be obtained by HTL. Monoaromatic compounds, fatty acids, alkenes, alkanes, polyaromatic compounds, nitrogenous, and other oxygenated chemicals make up most of these, as described in detail by [98]. HTL concepts are highlighted in this section, including the process principles, the elemental make-up of bio-crude, the different types of feedstocks, the energy efficiency of the process, as well as its future potential.

HTL produces four distinct product phases, which are (i–iv) [104]:

Bio-oil

Light molecular weight gases (CO_2 and trace amounts of CH_4 , CO , and H_2)

Biochar

Water vapor rich in carbon

Process parameters that affect HTL (i–x):

Temperature (T)

Pressure (P)

Biomass waste composition

Residence time

Heating rate

Water ratio

Catalyst

Particle size

Solvent density and type

Reaction media.

As mentioned in a study, these factors significantly impact bio-oil output [105]. The transformation of crude bio-oil to high-quality liquid biofuel can be achieved via chemical additives upgrade, catalytic upgrade, and physical process (ultrasonication, distillation, extraction, solvent addition, or separation). The need for energy to dry the wet biomass does not arise in this process. Its uniqueness is that it uses water, making it an eco-friendly method that runs at lower and is slightly energy-efficient [19]. The products of these processes are characterized by high reduced H_2O content, a lower amount of oxygenated compounds, and higher yields which give it a gross calorific value comparable to that of pyrolytic/gasification oil but higher compared to fossil fuels. The drawback is that it requires high pressure, making such equipment expensive to run large-scale or industrial processing [104].

The reduced content of oxygen and high calorific value of bio-oil obtained from HTL is mainly due to dehydration and decarboxylation reactions which converted oxygen to H_2O and CO_2 , respectively [105]. This process can reduce biomass oxygen from 40 wt.% to about 10 wt.% [99]. According to [104], bio-oil yield can also be enhanced via temperature increase before bio-oil cracking and repolymerization reactions leading to a reverse trend. And also, bio-oil products can be improved by adding residence time in the 5–30 min range. However, if the reaction time is prolonged, lighter gases and char are produced in the cracking and polymerization reactions, which reduce the bio-oil yield. There are documented techniques for bio-oil components separation and extraction, chemical composition using CHNS elemental

analyzer, nuclear magnetic resonance (NMR) spectroscopy, and high-performance liquid chromatography (HPLC) [37].

The HTL process primarily transforms biomass into bio-oil, a fuel that can replace fossil fuels. However, this procedure faces difficulties under intense pressure, leading to severe economic problems. Organic fertilizer for agriculture, CO₂, and nutrients used to grow and photosynthesize algae in culture. Wastewater that can be recycled to require less processed water is all by-products from the HTL of algal biomass. This process is hugely energy-efficient since it creates between 85 and 90% of the energy it needs and only consumes 10% to 15% of the energy from the feedstock. Additionally, with minor upgrading, the resulting bio-crude may be used economically because it is similar to its petroleum equivalents [98]. If employed appropriately, all the by-products mentioned above could aid HTL in resolving its financial problems. Additional study to improve the mechanisms and parameters of the process is still needed to overcome the disadvantages of HTL and successfully commercialize the procedure.

Water is kept in the liquid phase throughout the operation by operating at or above its saturation point, which significantly reduces the enthalpy change caused by the latent heat of vaporization of water [70]. There has been a lot of interest in compressed hot water as a green reaction medium in recent years. It is currently widely used in a variety of fields, including waste treatment, inorganic and organic material synthesis, polymer recycling, biomass energy recovery, waste resource recovery, and others [99]. Subcritical processes are those that occur below the critical point of water. During the supercritical process, which occurs above the critical water point (274 °C and 22.1 MPa), the properties of water are in the liquid and gas phases. Water can act as a catalyst, a solvent, or a reactant at times. When the dielectric constant of insoluble organic compounds decreases, they become more soluble. Furthermore, because of the high diffusion coefficient, reaction rates increased as water viscosity decreased [104].

In recent years, considerable effort has been made toward using biomass and its derivatives to produce liquid fuels. This study area covers pyrolysis, gasification of biomass, HTL of lignocellulose, and strategies for upgrading bio-crude. The petrochemical sector has excellent hopes and goals for synthesizing fuels, fine chemicals, and raw materials because of the choice of biomass.

The HTL has recently received a lot of attention as one of the promising approaches for dry and wet biomass [98], as well as for converting biomass into fuels and chemicals. Currently, various pyrolysis and gasification techniques are used to produce fuels (biofuels) and chemicals, primarily from dry biomass feedstocks (dry wood). Despite the enormous potential of wet biomass feedstocks, as demonstrated by documentation [98], little interest or effort has been put into developing the HTL method for wet biomass valorization. Because of their high photosynthetic efficiency, rapid development, high biomass production, and lack of reliance on arable land, microalgae are recognized as a superior fuel and chemical source through wet biomass processing. To improve the performance, prospects, and applicability of this technology, particularly

for wet biomass, as well as to ensure HTL's financial viability, the best process feedstocks and operational conditions must be selected, as well as the current parameters and process mechanisms optimized (Figs. 6a and 6b).

6.9 *Dry Biomass HTL*

The complex routes shown in Fig. 4 are used to produce bio-crude in a continuous or batch reactor. The feedstock is pretreated to reduce particle size, remove impurities, and create a stable slurry that can be easily pumped. After the HTL process, which takes about 15 min at 350 °C and 150 bar pressure, a gaseous mixture of CO₂, bio-crude, solid trash, and traces of the aqueous phase (water) is formed as a result of phase separation. The HTL unit can use this gaseous mixture again to produce more bio-oil or use less process water. The other water stream is subjected to anaerobic or catalytic hydrothermal gasification, which produces hydrogen- or methane-rich syngas. The presence of phenols and furfurals, on the other hand, limits the anaerobic treatment process.

Because it contains less moisture and oxygen, the resulting bio-crude can be used directly or upgraded for commercial use through additional hydrotreatment. This technique uses relatively little energy because the hydrothermal gasifier can be operated effectively and efficiently with the overall heat generated [98].

6.10 *HTL for Wet Biomass*

Because it does not require pretreatment and has an HTL that is quite close to that of dry biomass, wet/algae biomass has a significant potential for nutrient recycling. Figure 5 provides a schematic representation of wet biomass hydrothermal processing.

In this process, the algae biomass feed from an algal culture is first dewatered to create a feed slurry with about 20% solids, which is then pumped into the HTL unit to create bio-crude and is then further hydrotreated to produce refined hydrocarbon fuels. The process is made more economically and sustainably feasible by the aqueous phase's production of CO₂ and nutrients that are then used to cultivate algae [98].

6.11 *Mechanism of HTL*

A dehydrogenation process, a dehydration process, a decarboxylation process, and a deoxygenation process are all methods of breaking down the components of biomass feedstock into smaller molecules after hydrolysis has broken down the biomass feedstock into smaller pieces after the hydrolysis process has broken down the biomass

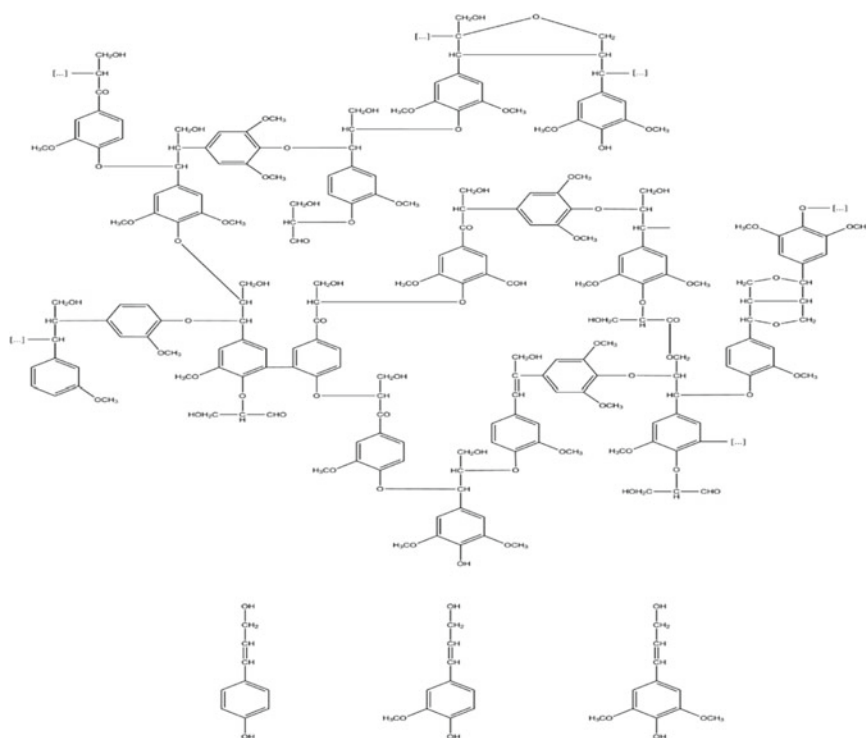


Fig. 4 Three main precursors of monolignol, (a) p-coumaryl alcohol, (b) coniferyl alcohol, (c) sinapyl alcohol, are shown in a schematic of lignin

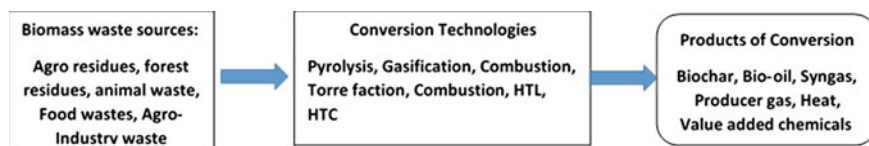


Fig. 5 Biomass waste thermochemical conversion processes

feedstock into smaller molecules. Aldehydes, phenols, acids, ketones, alcohols, and esters are a few complex chemicals that can be made by repolymerizing lighter molecules [98]. HTL begins with the solvolysis of the biomass in micellar forms, followed by the disintegration of the biomass's primary polymeric components (cellulose, hemicellulose, and lignin), and is finally completed by the thermal depolymerization of those components into smaller fractions [38]. The precise mechanism of HTL is currently unknown. Depolymerization is a step in the process; decomposition and recombination reactions come before it. To create simpler monomers, such as glucose and other products like acetic acid, furfural, and aldehyde compounds, the biomass must first be broken down and depolymerized into highly reactive

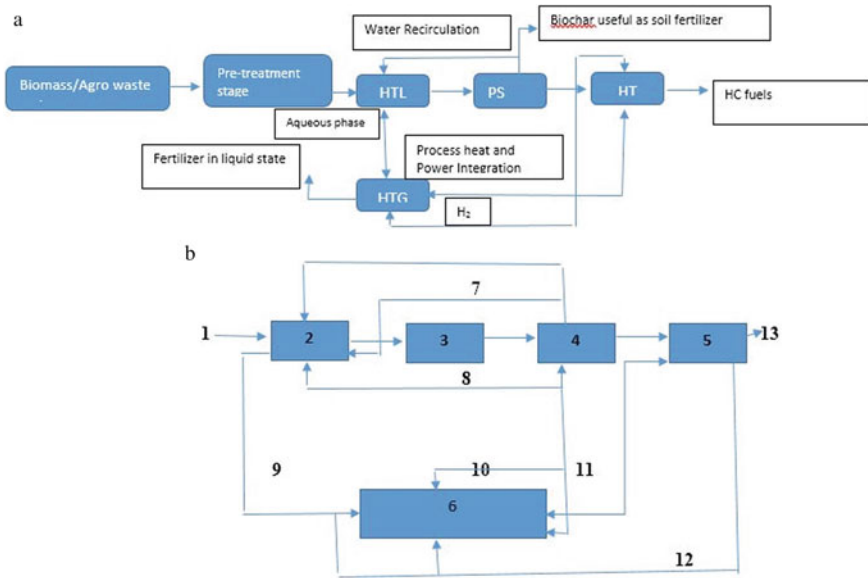


Fig. 6a a Consecutive pathway for lignocellulose biomass HTL [98], **b** Consecutive pathway for wet biomass HTL [98]:1. Water and nutrients 2. Algae cultivation 3. H₂O removal 4. Hydrothermal liquefaction 5. Hydrotreating 6. Catalytic hydrothermal gasification 7. Carbon (iv) oxide 8. Solid particle recycle 9. Nutrient and CO₂ 10. Aqueous phase 11. Process heat and power integration 12. H₂ gas 13. Hydrocarbon fuels

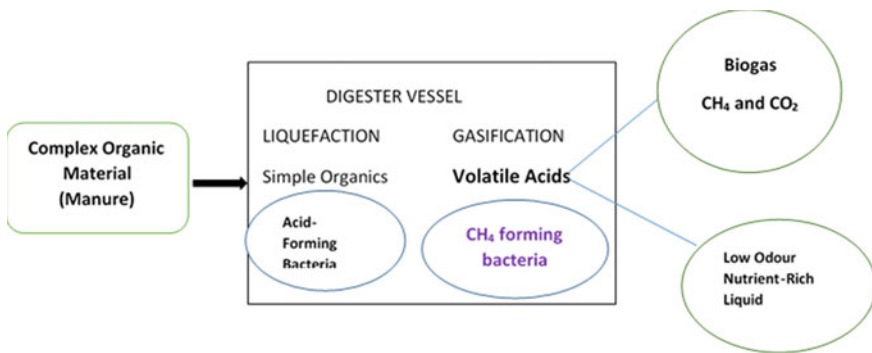


Fig. 7 Procedure for anaerobic digestion

lighter molecules (water-soluble oligomers) [38]. This repolymerization results in the production of bio-crude, gas, and solids.

The complexity of the biomass affects the mechanism and reaction chemistry as well as essential process factors such as residence time, temperature, process

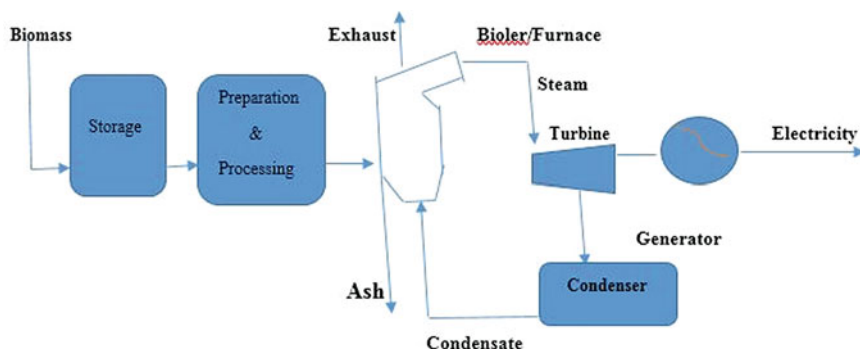


Fig. 8 Schematic representation of direct combustion/ steam turbine system

breakdown, Condensation, and polymerization of the constituents [98]. Temperature, pressure, particle size, and resection durations affect how much bio-oil may be produced using HTL [38].

The polymeric components of biomass are successively dissolved during biomass depolymerization, thanks to their physicochemical properties. The process temperature and pressure change the long-chain structure of the polymer, and the presence of water recycles the energy content of the organic components [98]. The biomass monomers are disassembled by cleavage, deamination, decarboxylation, and dehydration. Dehydration results in the loss of water molecules, decarboxylation results in the loss of carbon dioxide, and deamination results in the removal of the amino acid content. The polymers are hydrolyzed into polar monomers and oligomers by removing oxygen from biomass through the decarboxylation and dehydration processes as CO_2 and H_2O , respectively. When applied under high heat and pressure, water causes the hydrogen-bonded cellulose structure to split into glucose monomers. Compared to glucose, fructose is subject to greater isomerization, hydrolysis, reverse-aldol breakdown, dehydration, recombination, and rearrangement reactions. These reactions result in various products, such as furfural, polar organic molecules, phenols, organic acids, and glycolaldehyde, which are highly water-soluble [98]. The breakdown and deoxygenation reactions, among others, are the main processes that lead to the bio-crude, which is made of acids, aldehydes, and aromatics [105].

The repolymerization and recombination step result from the system's absence of hydrogen compounds. Free radicals, which are reactive by-products of earlier processes, have a propensity to repolymerize or recombine to generate heavier char molecules, which are notorious for producing coke when they are present in significant quantities [106, 107]. However, if there is sufficient hydrogen in the organic mixture during the liquefaction process, stable weight species will be produced by capping the free radicals with hydrogen molecules [98].

6.12 Catalytic Hydrothermal Liquefaction

Homogeneous and heterogeneous catalysts boost bio-oil production, lower biochar production, and raise conversion efficiency. Homogeneous catalysts (alkali salts, with the K salts being more active than the Na salts) such as KHCO_3 , KOH , K_2CO_3 , and NaOH , enable water–gas shift reactions by facilitating 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. Condensation, polymerization, and cyclization processes are then used in a cycle to create the final products. This group of catalysts favored inhibiting the formation of unstable and unsaturated molecules during dehydration processes (with high pH), enhancing the yield and properties of bio-crude, and minimizing solid yields [108–110].

The disadvantage of this method is that the catalyst recovery process costs a lot of money, uses a lot of energy, and requires a lot of capital [38].

Although heterogeneous catalysts are most typically used in HTG, incorporating a catalyst into the HTL process has been done in a select few instances to improve the quality of the bio-crude produced from lignocellulose biomass. Magnesium oxide, nickel oxide, manganese oxide, zinc oxide, cerium oxide, lauryl oxide, and other catalysts have been used [38]. The scarcity of Pt, Ni, and Pd stimulates the use of the above-mentioned heterogeneous catalyst.

Using CsOH and RbOH (very potent bases), the first catalytic hydrothermal liquefaction of wood biomass was conducted [37]. It was discovered that these potent bases, like other base catalysts, considerably boost oil yields by inhibiting char formation and creating mainly phenolic and benzenediol derivatives.

7 The Biochemical Transformation of Biomass

The biochemical conversion of biomass refers to the gradual and continuous release of biofuel from biomass waste through the activity of microorganisms and enzymes. Lignocellulosic biomass, which can produce chemicals, fuels, and other materials with energy value, is being adopted progressively as a renewable and alternative energy source to fossil fuels. Lignocellulose, which contains cellulose and hemicellulose, is primarily composed of sugars. Due to the difficulty in accessing this biomass polysaccharides content and the stiff and compacted assembly of plant cell walls, the synthesis of fermentable sugars has become constrained. Thus, using thermochemical pretreatment and an acid catalyst to overcome these challenging barriers, plant cell walls are frequently physically or chemically broken. After pretreatment, enzymatic hydrolysis is the preferred approach for creating sugars that microbial biocatalysts can later ferment to yield liquid fuels (such as $\text{C}_2\text{H}_5\text{OH}$). The release of inhibitory compounds, such as furfural, 5-hydroxymethyl furfural, $\text{C}_6\text{H}_5\text{OH}$, and aliphatic acids, is increased when biomass is pretreated with acid. These chemicals

have a considerable effect on both enzymatic hydrolysis and microbial fermentation. When Avicel cellulose and acid-treated spruce wood hydrolysate were mixed, the efficiency of enzymatic hydrolysis was discovered to be 63% lower than when Avicel was hydrolyzed in aqueous citrate buffer. The acid hydrolysates could seldom ever be fermented, either. As a result, the problems that come with lignocellulose conversion can be avoided by using less resistant feedstocks or by developing efficient pretreatment techniques that simultaneously yield high sugar yields and don't produce inhibitory by-products.

7.1 *Technologies for Biochemical Conversion*

The techniques for biochemical conversion include: anaerobic digestion (also known as biomethanation); ethanol fermentation. The recycling of waste such as poultry waste is usually done via anaerobic digestion. Anaerobic digestion can be done industrially. It is a fermentation process that converts organic waste into biogas, mainly composed of CH_4 (about 60%) and CO_2 (about 40%), comparable to landfill gas.

Anaerobic means a biological process taking in the absence of oxygen in which bacteria act as a catalyst in breaking down organic matter into biodegradable forms to produce biogas rich in CH_4 and CO_2 with some trace amounts of H_2S . This process takes place naturally.

In this method, biomass is fermented anaerobically without oxygen to produce biogas (also known as gobar gas) from cow dung, human waste, and other organic waste with high moisture content. Two distinct metabolic bacterial species carry out two degrees of fermentation.

The organic material undergoes the first hydrolysis to produce fatty acids, alcohols, sugars, H_2 , and CO_2 . Bacteria that produce methane transform the result of the first stage into CH_4 and CO_2 between 30 and 55 °C. The residual sludge is transformed into enriched fertilizer in a digester, a sealed tank used for fermentation (Fig. 7).

An anaerobic digestion facility can produce biogas and digestate, which can be processed further or utilized to make secondary goods. In addition to being a fuel for electricity and heat production, biogas can also be used for transportation. Biogas can also be enhanced and applied to gas distribution systems. The characteristics of anaerobic digestion were given in Table 8.

Digestate may be further processed to produce alcohol and a fibrous substance. Fiber, a bulky substance with little nutritional value that may be composted can be employed as a soil improver or a low-level fertilizer. The liquor preserves a significant portion of the nutrients and can be used as liquid fertilizer.

(ii) Ethanol fermentation.

Ethanol can be produced by dissolving sugar-containing biomass into sugar molecules like glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), such as sugarcane, and sweet cassava sorghum, beet, potato, corn, and grapes.

Table 8 Characteristics of anaerobic digestion

Characteristics	Anaerobic
Reaction in Anaerobic digestion	$C_6H_{12}O_6 \rightarrow CO_2 + 3CH_4$
Energy produced in KJ/mol. glucose	-393
C balance	95% $\rightarrow CO_2 + CH_4$ (= biogas)5% $\rightarrow biomass$
Energy balance	90% retained in CH_4 5% $\rightarrow biomass$ 5% $\rightarrow heat generated$
Biomass production	Slow growth of biomass

The biological fermentation of ethanol involves turning sugar into ethanol and CO_2 as part of the process.

Nowadays, gasoline is blended with ethanol, which serves as the primary alcohol fuel.

7.2 Biogas

“Biogas” refers to any gas produced when organic material decomposes anaerobically. It falls under the category of renewable energy. It may be produced using locally available raw materials such as recyclable rubbish and is environmentally friendly. Manure, sewage, municipal trash, green waste, and crops that have undergone anaerobic fermentation are among the sources of biogas.

A fuel gas called biogas has a CH_4 content of 65% and a CO_2 content of 35%. It is a renewable energy source made from biomass. Biogas is categorized based on its chemical composition and resulting physical characteristics. Nevertheless, “biogas” refers to various gases created from specific treatment processes, starting with various organic wastes from multiple enterprises, animal or domestic waste, etc.

7.3 Power Generation Based on Biogas

There are three methods for doing this (i–iii):

- Landfill
- Direct method
- Gasification.

i. Direct action.

For years, wood, by-products, and other solids were the only commercially feasible choices for producing electricity. The technique involves burning biomass

directly in a boiler connected to a steam turbine, which produces steam from the hot gases through a heat exchanger and generates electricity from the steam through a steam turbine (Fig. 8).

Burning fuel in the boiler produces steam, which powers a turbine or generator to produce electricity. The steam is then condensed into liquid in the condenser by cooling water circulating the tubes. The condensed water can be heated once more to create steam by being returned to the boiler.

Heat and power combined.

Combining heat and power (CHP), also known as cogeneration or distributed generation, generates heat and electricity simultaneously from a single fuel source, frequently natural gas.

Biogas cogeneration.

Renewable raw materials and the production of biogas anaerobic fermentation of organic material in a fermenter yields biogas. Between 45 and 70% of this gas is made of CH_4 . After burning, almost the same amount of CO_2 the substrates absorbed during growth is released. Cogeneration plants reduce the emissions that would otherwise be produced when burning fossil fuels by converting biogas into electricity.

An electric generator, a gas turbine, steam turbine, or combustion engine is a typical component of CHP systems. In addition to the electric generator, a waste heat exchanger is built. This device uses the heat or exhaust gas recovered from the generator to produce steam or hot water.

ii. Gasification as a Process.

The steps taken in gasification facilities are depicted in the image below. To ensure that the provided solid biomass fuel has the appropriate fuel parameters (particle size, water content), it must be modified (fuel conditioning and handling). The gasification process uses the cleaned fuel to create raw product gas. The gas quality of the raw material is required for further use. The washed product gas is employed in various procedures to produce fuel, heat, and power.

iii. Landfill.

Landfill gas is primarily CH_4 and CO_2 , with trace amounts of N_2 , O_2 , H_2S , and non-methane organic molecules in anaerobic circumstances (NMOCs). The amount of organic waste and moisture in a landfill is linearly related to the volume of landfill gas produced by bacterial decomposition. Gas can be extracted from landfills by drilling vertical wells into the trash connected by underground pipelines and “capping” a portion of the dump with clay. The gas is collected by vacuum compressors and then transported to a blower/flare station, where it is either fed to the electricity-generating plant or flared. Methane is converted into the less dangerous gas carbon dioxide during combustion. Even if stopping the process now reduces methane gas emissions, it does not utilize the heat energy generated during the conversion. After being gathered, the gas will be piped to a power plant, which will be burned to power engine generator sets.

Burning fuel in the boiler produces steam, which powers a turbine or generator to produce electricity. The steam is then condensed back into liquid form in

the condenser by cooling water being circulated around the condenser tubes. The condensed water can be heated once more to create steam by being returned to the boiler.

Acknowledgements We are grateful to the Petroleum Trust Development Fund (PTDF), Nigeria, for providing the financial assistance to carry out this work through Scholarship fund.

Contribution Abiodun Oluwatosin Adeoye (**Conceptualization, write-up, resource research, data presentation, and editing of manuscript**).

Olayide Samuel Lawal (**Supervision, Design, and Conceptualization**).

Rukayat Oluwatobiloba Quadri (**Resource research and editing of manuscript**).

Dosu Malomo (**Resource research and Editing**).

Muhammed Toyiyibb Aliyu, Gyang Emmanuel Dang, Emmanuel Oghenero Emojevju, Musa Joshua Maikato, Mohammed Giwa Yahaya, Oluyemisi Omotayo Omonije, Victor Great Edidem, Yakubu Khartum Abubakar, Onyeka Francis Offor, Ezeaku Henry Sochima, Boniface Eche Peter, Baba Nwunjuji Hikon (**Resource research**).

References

1. Cherubini, F.: The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manage.* **51**(7), 1412–1421 (2010)
2. Witcoff, H.A., Reuben, B.G.: *Industrial Organic Chemicals*, John Wiley & Sons, (1996)
3. Clark, H.J., Deswarte, E.I.F.: *The Biorefinery Concept—An Integrated Approach*. John Wiley & Sons (2008)
4. Hubbert: *Historical studies in the natural sciences* **44**(1), pp. 37–79. ISSN 1939–1811, electronic ISSN 1939–182X (1956)
5. Mousdale, D. M.: *Biofuels: biotechnology, chemistry, and Sustainable development*. CRC Press, pp. 328, USA, (2008)
6. Energy Information Administration (EIA), *Annual Energy Outlook* (2016)
7. Szulczyk, K.R.: Which is a better transportation fuel—butanol or ethanol? *Int. J. Energy Environ.* **1**(1), (2010)
8. Fernando, S., Adhikari, S., Chandrapal, C., Murali, N.: Biorefineries: Current status, challenges, and future direction. *Energy Fuels* **20**, 1727–1737 (2006)
9. Naik, S.N., Goud, V.V., Rout, P.K., Dalai, A.K.: Production of first and second generation biofuels: A comprehensive review. *Renew. Sustain. Energy Rev.* **14**, 578–597 (2010)
10. Zilberman, D., Hochman, G., Rajagopal, D., Sexton, S., Timilsina, G.: The impact of biofuels on commodity food prices: Assessment of findings. *Am. J. Agr. Econ.* **95**(2), 275–281 (2013)
11. Thompson, P.B.: The agricultural ethics of biofuels: the food vs. fuel debate. *Agriculture*. **2**, 339–358 (2012)
12. Rosillo-Calle, F.: Food versus fuel: toward a new paradigm—The need for a holistic approach. *ISRN Renew. Energy* (2012)
13. Cheng, S., Zhu, S.: Lignocellulosic feedstock biorefinery—the future of the chemical and energy industry. *BioResources* **4**(2), 456–457 (2009)
14. Menon, V., Rao, M.: Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Prog. Energy Combust. Sci.* **38**(4), 522–550 (2012)
15. Adeoye, A.O., Quadri, R.O., Lawal, O.S.: Physicochemical assessment, pyrolysis and thermal characterization of Albizia Zygia Tree Sawdust. *Int. J. Nanotechnol. Nanomed.* **7**(1), 91–99 (2022)
16. Adeoye, A.O., Quadri, R.O., Lawal, O.S.: Biomass pyrolysis in the context of Nigeria's oil and gas: An overview. *Int. J. Ambient Energy* (In press) (2023)

17. Sharma, S.K., Lee, J.: Design and Development of Smart Semi Active Suspension for Nonlinear Rail Vehicle Vibration Reduction. *Int. J. Struct. Stab. Dyn.* 20, 2050120 (2020). <https://doi.org/10.1142/S0219455420501205>
18. Bhardawaj, S., Sharma, R.C., Sharma, S.K.: Development of multibody dynamical using MR damper based semi-active bio-inspired chaotic fruit fly and fuzzy logic hybrid suspension control for rail vehicle system. *Proc. Inst. Mech. Eng. Part K J. Multi-body Dyn.* 234, 723–744 (2020). <https://doi.org/10.1177/1464419320953685>
19. Liu, H., Ma, M., Xie, X.: New materials from solid residues for investigation the mechanism of biomass hydrothermal liquefaction. *Ind. Crops Prod.* 108, 63–71 (2017). <https://doi.org/10.1016/j.indcrop.2017.06.026>
20. Adeoye, A.O., Quadri, R.O., Lawal, O.S.: Channeling biomass waste as an alternative industrial and domestic energy with pollution effects mitigation in Nigeria: An overview. *Int. J. Nanotechnol. Nanomed.* 7(1), 78–90 (2022)
21. Saleem, M.: Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source. *Heliyon* 48(2), e08905 (2022). <https://doi.org/10.1016/j.heliyon.2022.e08905>. PMID:35198772;PMCID:PMC8841379
22. Houghton R.A. Biomass. *Encyclopedia of Ecology*. pp. 448–453 (2008)
23. Chen, H., Wang L.: *Technologies for biochemical conversion of biomass*. Elsevier Inc., (2017)
24. Demirbas, A.: Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manage.* 42, 1357–1378 (2001). [https://doi.org/10.1016/S0196-8904\(00\)00137-0](https://doi.org/10.1016/S0196-8904(00)00137-0)
25. Zhao, X., Zhang, L., Liu, D.: Biomass recalcitrance. Part I: the chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose. *Biofuels, Bioproducts and Biorefining* 6(4), 465–482 (2012a)
26. Sánchez, Ó.J., Cardona, C.A.: Trends in biotechnological production of fuel ethanol from different feedstocks. *Biores. Technol.* 99(13), 5270–5295 (2008)
27. Vaibhav, D., Thallada, B.A.: Comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew. Energ.* 129, 695–716 (2018)
28. Huber, G.W., Iborra, S., Corma, A.: Synthesis of transportation fuels from biomass: chemistry, catalyst, and engineering. *Chem. Revol.* 106, 4044–4098 (2006)
29. Tong, X., Ma, Y., Li Y.: Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes”, *Appl. Catal. A Gen* 385 (1–2), 1–13, (2010). <https://doi.org/10.1016/j.apcata.2010.06.049>
30. Balat, M., Balat, M., Kurtay, E., Balat, H.: Main routes for the thermo-conversion of biomass into fuels and chemicals. Part I : Pyrolysis systems, *Energy Convers. Manage.* 50(12), 3147–3157, (2009). <https://doi.org/10.1016/j.enconman.2009.08.014>
31. Himmel, M.E., Ding, S.Y., Johnson, D.K., Adney, W.S., Nimlos M.R., Brady, J.W., Foust, T.D.: Biomass recalcitrance: engineering plants and enzymes for biofuels production. *Science.* 315 (2007)
32. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technol.* 96, 673–686 (2005)
33. Adeoye, A.O., Quadri, R.O., Lawal, O.S.: Assessment of biofuel potential of tenera palm kernel shell via fixed bed pyrolysis and thermal characterization, *Results in Surfaces and Interfaces.* 9(1), 100091(2022). <https://doi.org/10.1016/j.rsufri.2022.100091>
34. Demirbas, A.: *Biorefineries: For biomass upgrading facilities*. Springer (2010). <https://doi.org/10.1007/978-1-84882-721-9>
35. Sharma, A., Pareek, V., Zhang D.: Biomass pyrolysis—A review of modelling, process parameters and catalytic studies. *Renew. Sustain. Energy Rev.* 50, 1081–1096, (2015). <https://doi.org/10.1016/j.rser.2015.04.193>
36. Hayes, D.J.M.: Biomass composition and its relevance to biorefining. In *The Role of Catalysis for the Sustainable Production of Biofuels and Bio-chemicals*, pp. 27–65. Elsevier B.V. (2013)
37. Tekin, K., Karagoz, S., Bektaş, S.: A review of hydrothermal biomass processing. *Renew. Sustain. Energy Rev.* 40, 673–687, (2014). <https://doi.org/10.1016/j.rser.2014.07.216>

38. Kumar, M., Oyedun, A.O., Kumar A.: A Review on the Current Status of Various Hydrothermal Technologies on Biomass Feedstock (2017)
39. Sharma, S.K., Phan, H., Lee, J.: An Application Study on Road Surface Monitoring Using DTW Based Image Processing and Ultrasonic Sensors. *Appl. Sci.* **10**, 4490 (2020). <https://doi.org/10.3390/app10134490>
40. Pauly, M., Keegstra, K.: Plant cell wall polymers as precursors for biofuels. *Curr Opin Plant Biol.* **13**, 305–312 (2010)
41. Saha, B.C.: Hemicellulose bioconversion. *J. Ind. Microbiol. Biotechnol.* **30**(5), 279–291
42. Mussatto, S.I., Teixeira, J.A.: Lignocellulose as raw material in fermentation processes. In: A. Méndez-Vilas, A. (ed.) *Applied Microbiology and Microbial Biotechnology*. Formatex, pp. 897–907 (2010)
43. Chundawat, S.P.S., Beckham, G.T., Himmel, M.E. Dale, B.E.: Deconstruction of lignocellulosic biomass to fuels and chemicals. *Annu. Rev. Chem. Biomol. Eng.* **2**(6), 1–6.25 (2011)
44. Peng, F., Ren, J.L., Xu, F., Sun, R.C.: Chemicals from hemicelluloses: A review. In: Zhu, J.Y., Zhang, X., Pan, X. (eds.) *Sustainable Production of Fuels, Chemicals, and Fibers from Forest Biomass*. ACS Symposium Series, pp. 219–259. Washington DC, USA (2011)
45. Harmsen, P.F.H., Huijgen, W.J.J., Bermúdez López, L.M., Bakker, R.R.C.: Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass. Energy Research Centre of Netherlands (ECN) (2010)
46. Ragauskas, A.J., Beckham, G.T., Biddy, M.J., Chandra, R., Chen, F., Davis, M.F., Davison, B.H., Dixon, R.A., Gilna, P., Keller, M., Langan, P., Naskar, A.K., Saddler, J.N., Tschaplinski, T.J., Tuskan, G.A., Wyman, C.E.: Lignin valorization: improving lignin processing in the biorefinery. *Science* **344** (6185) (2014)
47. Ralph, J., Lundquist, K., Brunow, G., Lu, F., Kim, H., Schatz, P.F., Marita, J.M., Hatfield, R.D., Ralph, S.A., Christensen, J.H., Boerjan, W.: Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids. *Phytochem. Rev.* **3**, 29–60 (2004)
48. Guo, F., Shi, W., Sun, W., Li, X., Wang, F., Zhao, J., Qu, Y.: Differences in the adsorption of enzymes onto lignins from diverse types of lignocellulosic biomass and the underlying mechanism. *Biotechnol. Biofuel.* **7**(38) (2014)
49. Sticklen, M.B.: Plant genetic engineering for biofuel production: towards affordable cellulosic ethanol. *Nat. Rev. Genet.* **9**, 433–443 (2008)
50. Bugg, T.D.H., Ahmad, M., Hardiman, E.M., Singh, R.: The emerging role for bacteria in lignin degradation and bio-product formation. *Curr. Opin. Biotechnol.* **22**, 394–400 (2011)
51. Xiao, C., Anderson, C.T.: Roles of pectin in biomass yield and processing for biofuels. *Front Plant Science* **4**(67) (2013)
52. Caffall, K.H., Mohnen, D.: The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. *Carbohydr. Res.* **344**, 1879–1900 (2009)
53. Rowell, R.M., Pettersen, R., Tshabalala, M.A.: Cell wall chemistry. In: Rowell, R.M. (ed.) *Handbook of Wood Chemistry and Wood Composites*, Second Edition. CRC Press, pp. 33–72 (2012)
54. Faulon, J., Carlson, G.A., Hatcher, P.G.: A three-dimensional model for lignocellulose from gymnospermous wood. *Org. Geochem.* **21**(12), 1169–1179 (1994)
55. Sharma, R.C., Sharma, S., Sharma, S.K., Sharma, N.: Analysis of generalized force and its influence on ride and stability of railway vehicle. *Noise Vib. Worldw.* **51**, 95–109 (2020). <https://doi.org/10.1177/0957456520923125>
56. Poletto, M., Ornaghi Júnior, H.L., Zattera, A.J.: Native cellulose: Structure, characterization and thermal properties. *Materials* **7**, 6105–6119 (2014)
57. Adler, E.: Lignin chemistry—past, present and future. *Wood Sci. Technol.* **11**, 169–218 (1977)
58. Laksono, N., Paraschiv, M., Loubar, K., Tazerout M.: Biodiesel production from biomass gasification tar *via* thermal/ catalytic cracking. *Fuel Process. Technol.* **106**, 776–783 (2013). <https://doi.org/10.1016/j.fuproc.2012.10.016>
59. Molino A., Chianese S., Musmarra D.: Biomass gasification technology : The state of the art overview. *J. Energy Chem.* **25**(1), 10–25, (2016). <https://doi.org/10.1016/j.jchem.2015.11.005>

60. Mani, S., Tabil, L.G., Sokhansanj, S.: Specific energy requirement for compacting corn stover. *Bioresource Technol.* **97**(12), 1420–1426 (2006). <https://doi.org/10.1016/j.biortech.2005.06.01918:58>
61. Baruah, D., Baruah, D.C.: Modeling of biomass gasification: A review. *Renew. Sustain. Energy Rev.* **39**, 806–815 (2014). <https://doi.org/10.1016/j.rser.2014.07.129>
62. Sambo, A.S.: Renewable energy electricity in Nigeria: The way forward. In: *The Renewable Electricity Policy Conference 2016*, pp. 11–12, Abuja (2006)
63. Heinimö, J., Junginger, M.: Production and trading of biomass for energy—An overview of the global status. *Biomass Bioenerg.* **33**(9), 1310–1320 (2009). <https://doi.org/10.1016/j.biombioe.2009.05.017>
64. Awulu, J.O., Omale, P.A., Ameh, J.A.: Comparative analysis of calorific values of selected Agricultural wastes. *Nigerian J. Technol. (NIJOTECH)* **37**(4), 1141–1146 (2018)
65. FAOSTAT. FAO statistics division, <http://www.faostat.fao.org>. Accessed 31/08/2022
66. Lewis, M.L., Robenzon, J., Hans-Joachim N., Bernardo, R.: Potential for Simultaneous Improvement of Corn Grain Yield and Stover Quality for Cellulosic Ethanol. *Crop Science* (2010). 50. <https://doi.org/10.2135/cropsci2009.03.0148>.
67. O'Connor, P.: A general introduction to biomass utilization possibilities. In: *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, pp. 1–25. Elsevier (2013)
68. Adeoye, A.O., Quadri, R.O., Lawal, O.S.: Fixed-bed pyrolysis and thermal analyses of pressed oil palm fruit fibre as potential source of alternative energy. *FUOYE J. Innov. Sci. Technol.* (In press) (2022)
69. Panwar, N.L., Kothari, R., Tyagi, V.V.: Thermo chemical conversion of biomass—Eco-friendly energy routes. *Renew. Sustain. Energy Rev.* **16**(4), 1801–1816 (2012). <https://doi.org/10.1016/j.rser.2012.01.024>
70. Adams, P., Bridgwater, T., Lea-Langton, A., Ross A., Watson, I.: Biomass conversion technologies. In: *Greenhouse Gas Balance of Bioenergy Systems*. 1st Edition, pp. 107–139. Elsevier Inc. (2018). <https://doi.org/10.1016/B978-0-08-101036-5.00008-2>
71. Vassilev, S.V., Baxter, D., Vassileva, C.G.: An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel* **112**, 391–449 (2013)
72. Bhardawaj, S., Sharma, R., Sharma, S.: Ride Analysis of Track-Vehicle-Human Body Interaction Subjected to Random Excitation. *J. Chinese Soc. Mech. Eng.* **41**, 237–236 (2020). <https://doi.org/10.29979/JCSME>.
73. Taarning, E., Osmundsen, C.M., Yang, X., Voss, B., Andersen, I., Christensen C.H.: Zeolite-catalyzed biomass conversion to fuels and chemicals. *Energy Environ. Sci.* **4**, 793–804 (2011). <https://doi.org/10.1039/C004518G>
74. Serrano-Ruiz, J.C., Luque, R., and Clark, J.H.: The Role of heterogeneous catalysis in the biorefinery of the future. In: *The Role of Catalysis for the Sustainable Production of Bio-fuels and Biochemicals*, pp. 557–576. Elsevier B.V. (2013)
75. Fukuda, H., Kondo, A., Noda, H.: Biodiesel fuel production by transesterification of oils. *J. Biosci. Bioeng.* **92**, 405–416 (2001)
76. Renganathan, S.V., Narashimhan, S.L., Muthukumar, K.: An overview of enzymatic production of biodiesel. *Bioresour. Technol.* **99**, 3975–3981 (2008)
77. Xie, W., Huang, X., Li, H.: Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. *Bioresour. Technol.* **98**, 936–939 (2007)
78. İlgen, O., Akin, A.N.: Development of alumina supported alkaline catalysts used for biodiesel production. *Turk J Chem.* **33**, 281–287 (2009)
79. Gama, P.E., Lachter, E.R., Gil, R.: Characterization and catalytic activity of K₂CO₃/Al₂O₃ in the transesterification of sunflower oil in conventional and microwave heating. *Quim Nova* **38**, 185–190 (2015)
80. Vyas, A.P., Verma, J.L., Subrahmanyam, N.: A review on FAME production processes. *Fuel* **89**, 1–9 (2010)

81. Chouhan, A.P.S., Sarma, A.K.: Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renew. Sustain. Energy Rev.* **15**(9),4378–4399 (2011).<https://doi.org/10.1016/j.rser.2011.07.112>
82. Hu, L., Lin, L., Wu Z., Zhou S., Liu S.: Recent advances in catalytic transformation of biomass-derived 5-hydroxymethylfurfural into the innovative fuels and chemicals. *Renew. Sustain. Energy Rev.* **74**, 230–257 (2017). <https://doi.org/10.1016/j.rser.2017.02.042>
83. Sharma, S., Meena, R., Sharma, A., Goyal P. Biomass conversion technologies for renewable energy and fuels: A review Note, *IOSR J. Mech. Civ. Eng.* **11**(2), 28–35 (2014). <https://doi.org/10.9790/1684-11232835>
84. Sikarwar, V.S., Zhao, M., Fennell, P.S., Shab, N., Anthony E.J. Progress in biofuel production from gasification. *Pror. Energy Combust. Sci.* **61**, 89–248 (2017). <https://doi.org/10.1016/j.pecs.2017.04.001>
85. Rolando, Z., Krister, S., Emilia, B.: Rapid pyrolysis of agricultural residues at high temperature. *Biomass and Bioenergy.* **23**, 357–366. [https://doi.org/10.1016/S0961-9534\(02\)00061-2](https://doi.org/10.1016/S0961-9534(02)00061-2)
86. Brown T.R.: A techno-economic review of thermochemical cellulosic biofuel pathways. *Bioresour. Technol.* (2014). [PMID: 25266684]
87. Czernik, S., Evans, R., French, R.: Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catal. Today* **129**, 265–268 (2007)
88. Keiser, J. R., Warrington, G. L., Lewis, S. A., Connatser, R. M., Jun, J., Qu, J., Lee, K., Brady, M. P.: Corrosion and Chemical Characterization of Bio-Oils from Biomass with Varying Ash and Moisture Contents. USA (2021)
89. Sulejmanovic, D., Keiser, J.R., Su, Y., Kass, M.D., Jack, R., Ferrell, J.R., Marieffel, V., Olarte, M.V., Wade, J.E., Jun, J.: Effect of Carboxylic Acids on Corrosion of Type 410 Stainless Steel in Pyrolysis Bio-Oil. *Sustainability.* **14**(18), 11743 (2022). <https://doi.org/10.3390/su141811743>
90. Hu, X.Z., Zhanming, G., Mortaza, Z., Shu, L., Jason, C.-H., Zhe, W.Y.: Coke formation during thermal treatment of bio-oil. *Energy Fuels XXXX* (2020). <https://doi.org/10.1021/acs.energyfuels.0c01323>
91. Bamgboye, A.I., Oniya. O.: Pyrolytic conversion of corn cobs to medium grade fuels and chemical preservatives. *The Federal University of Technology Journal of Engineering and Environmental Technol.* **3**(2), 50–53 (2003)
92. Jahirul, M.I., Rasul M.: Recent developments in biomass pyrolysis for bio-Fuel production, its potential for commercial applications. In: *Recent Researches in Environmental and Geological Sciences*, pp. 256–265 (2012)
93. Cornelissen, T., Yperman, Y., Reggers, G., Schreurs, S., Carleer, R.: Flash co-pyrolysis of biomass with polylactic acid. Part 1: influence on bio-oil yield and heating value. *Fuel* **87**, 1031–1041 (2008)
94. de Jongh, W.A.: Possible applications for vacuum pyrolysis in the processing of waste materials. *Stellenbosch; SU (Thesis-M.Sc.)* (2001)
95. Kong, S.H., Lam, S.S., Yek, P.N.Y., Liew, R.K., Ma, N.L.: Self- purging microwave pyrolysis: an innovative approach to convert oil palm shell into carbon-rich biochar for methylene blue adsorption. *J. Chem. Technol. Biotechnol.* **94**(5), 1397–1405 (2019)
96. Goyal, H.B., Seal D., Saxena. R.C. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew. Sustain. Energy Rev.* **12** 504–517 (2008)
97. Damartzis, T., Zabaniotou, A.: Thermochemical conversion of biomass to second-generation biofuels through integrated process design—A review. *Renew. Sustain. Energy Rev.* **15**(1), 366–378 (2011). <https://doi.org/10.1016/j.rser.2010.08.003>
98. Gollakota, A.R.K., Kishore, N., Gu S.: A review on hydrothermal liquefaction of biomass. *Renew. Sustain. Energy Rev.* 1–15, (2017)
99. Hrcnc, M.K., Kravanja, G., Knez, Z.: Hydrothermal treatment of biomass for energy and chemicals. *Energy* 1–11 (2016)
100. Wang, T., Zhai, Y., Zhu, Y., Li, C., Zeng, G.: A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renew. Sustain. Energy Rev.* **90**, 223–247 (2018)

101. Yaashikaa, P.R., Kumar, P.S., Varjani, S., Saravanan, A.: A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports*. **28**: e00570 (2020). <https://doi.org/10.1016/j.btre.2020.e00570>
102. Lepage, T., Kammoun, M., Schmetz, Q., Richel, A.: Biomass-to-hydrogen: a review of main routes production, processes evaluation and techno-economical assessment. *Biomass Bioenergy* **144** 105920 (2021). <https://doi.org/10.1016/j.biombioe.2020.105920>
103. Ozdenkci, K., De Blasio, C., Muddassar, H.R.: A novel biorefinery integration concept for lignocellulosic biomass. *Energy Convers. Manage.* **149**, 974–987 (2017). <https://doi.org/10.1016/j.enconman.2017.04.034>
104. De Caprariis, B., De Filippis, P., Petruzzo, A., Scarsella M.: Hydrothermal liquefaction of biomass : Influence of temperature and biomass composition on the bio-oil production. *Fuel* **208**, 618–625 (2017). <https://doi.org/10.1016/j.fuel.2017.07.054>
105. Akhtar, J., Aishah, N., Amin S.: A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew. Sustain. Energy Rev.* **15**(3), 1615–1624 (2011). <https://doi.org/10.1016/j.rser.2010.11.054>
106. Sharma, S.K., Sharma, R.C., Sharma, N.: Combined Multi-Body-System and Finite Element Analysis of a Rail Locomotive Crashworthiness. *Int. J. Veh. Struct. Syst.* **12** (2020). <https://doi.org/10.4273/ijvss.12.4.15>
107. Bhardawaj, S., Sharma, R.C., Sharma, S.K.: Development in the modeling of rail vehicle system for the analysis of lateral stability. *Mater. Today Proc.* **25**, 610–619 (2020). <https://doi.org/10.1016/j.matpr.2019.07.376>
108. Sharma, R.C., Sharma, S., Sharma, S.K., Sharma, N., Singh, G.: Analysis of bio-dynamic model of seated human subject and optimization of the passenger ride comfort for three-wheel vehicle using random search technique. *Proc. Inst. Mech. Eng. Part K J. Multi-body Dyn.* **235**, 106–121 (2021). <https://doi.org/10.1177/1464419320983711>
109. Sharma, S.K., Sharma, R.C., Lee, J.: Effect of Rail Vehicle–Track Coupled Dynamics on Fatigue Failure of Coil Spring in a Suspension System. *Appl. Sci.* **11**, 2650 (2021). <https://doi.org/10.3390/app11062650>
110. Sharma, S.K., Sharma, R.C.: Pothole Detection and Warning System for Indian Roads. In: *Advances in Interdisciplinary Engineering*. pp. 511–519 (2019). https://doi.org/10.1007/978-981-13-6577-5_48