Chapter

Valorization of Lignocellulosic and Microalgae Biomass

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Abstract

Lignocellulosic biomass has gained increasing recognition in the past decades for the production of value-added products (VAPs). Biomass feedstocks obtained from various sources, their composition, and pretreatment techniques employed for delignification into bioenergy production are discussed. The conversion processes of biomass into VAPs involve various methods. Notable among them are biochemical conversions; namely, anaerobic digestion and ethanol fermentation, and thermo-chemical conversions; namely, pyrolysis and gasification which are considered in this chapter. Microalgae can adapt to changes in the environment, producing biomass that serves as a precursor for a variety of biomolecules, such as proteins, which find their application in pharmaceutical, cosmetic, and biofuel industries. Suitable strains of freshwater microalgae biomass contain high levels of lipid which can be harnessed for bioenergy production. Hence, the advancement in the conversion of biomass into VAPs could help scientists and environmentalists for sustainable use of biomass in future developments.

Keywords: biomass, freshwater microalgae, lignocellulose, microalgae, value-added products

1. Introduction

Biomass resources are readily available globally as residual wastes derived from agricultural and industrial sources. Crop residues such as corn straw, wheat straw, and rice straw are classified as important and relatively abundant renewable biomass resources [1, 2]. With regards to the abundance of biomass resources, China still leads as one of the largest agricultural-based economies in the world, producing approximately about 216 million metric tons of corn straw per annum. For the aforementioned, more than half of that reported from China remain unutilized [3]. Lignocellulose arises from corn straw containing non-edible plant material, composed largely of cellulose, hemicellulose, and lignin. These three components comprise covalent cross-linkages between the polysaccharides (cellulose and hemicellulose) and lignin, making biomass a composite material [4]. The sources and compositions of lignocellulose play a very important role in predicting its potential as value added-products. The hemicellulose is present as the matrix that surrounds the cellulose skeleton, while lignin is present as an encrusting material and serves as a protective layer. However, biomass pretreatment is an essential tool for cellulose conversion processes as it changes the structure of cellulosic biomass to make

cellulose more available to the enzymes that convert the carbohydrate polymers into fermentable sugars [5]. Other studies have reported that pretreatment of lignocellulosic biomass (LB) aids to overcome recalcitrance through the combination of chemical and structural changes to the lignin and carbohydrates. Some of the different methods of pretreatment include physical; namely, mechanical pretreatment, physicochemical; namely, steam explosion, chemical; namely, alkali and acidic pretreatment, and biological; namely, manure addition or mixed microorganisms [6, 7]. Nonetheless, these traditional methods of pretreatment are cost-intensive, as additional chemicals or energy are required [8]. Also, useful information for policymakers and researchers on lignin biorefinery is presented in this chapter.

2. Lignocellulose biomass (LB)

LB is a composite, based on intertwined biopolymers on a dry basis, consisting of 35–45% cellulose, 25–30% hemicellulose, and 25–30% lignin [9]. These are classified into four major proportions based on their source, namely, woody biomass, agricultural residues (for example, rice/wheat/barley straws, corn stover, sugarcane bagasse), energy crops (switchgrass, *Miscanthus* and short-rotation hardwood is specifically grown for biofuel production) and a group of cellulosic wastes (for example, municipal solid waste, pulp mill and lumber mill wastes) [10]. Cellulose and hemicellulose are broken down by enzymatic saccharification into simple sugars which are further digested by microorganisms through the anaerobic digestion process to produce bioenergy such as biogas [11]. Nonetheless, the application of LB for the net reduction of CO_2 emissions from the transport sector is considered environmentally benign [12]. As a result, pretreatment becomes very important to improve the digestibility of the LB [5, 13]. **Table 1** shows the various chemical compositions of sugarcane bagasse, a lignin-rich residue obtained from the sugar industry.

2.1 Cellulose

Cellulose is a linear polymer of β-D-glucopyranose units linked to each other by 1,4-glycosidic bonds. The linear cellulose chain has a very strong tendency to form intra and inter-molecular hydrogen bonds, which promotes the collection of parallel chains into basic microfibrils. Most wood species contain 40–45% cellulose based on oven-dry (OD) wood. Compression wood of softwoods contains less crystalline cellulose than non-compression wood [13]. The chemical structure of cellulose is shown in **Figure 1**.

Components (%)			References
Cellulose	Hemicellulose	Lignin	
47.0	27.0	23.0	[14]
38.8	26.0	32.4	[15]
45.5	27.0	21.1	[16]
38.4	23.2	25.0	[17]
45.0	25.8	19.1	[18]
39.5	25.6	30.4	[19]
43.6	17.2	22.0	[20]

Table 1.
Chemical composition of raw sugarcane bagasse (%w/w, dry basis).

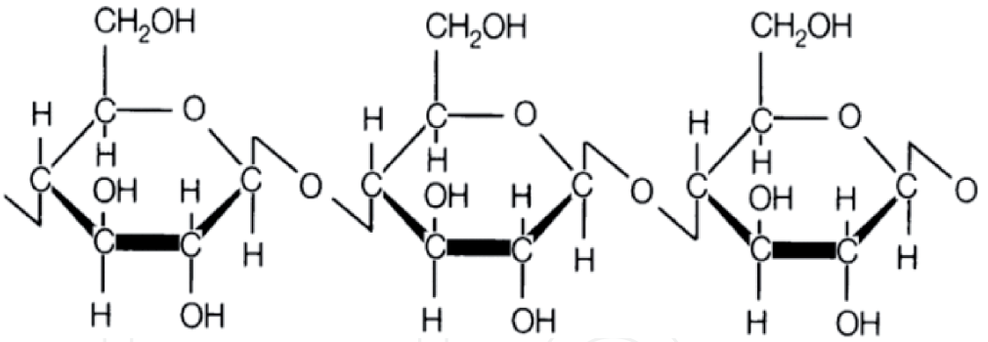

Figure 1.
Chemical structure of cellulose [21].

2.2 Hemicellulose

This is the second most abundant structural component of a typical plant cell wall after cellulose [21]. Cellulose microfibrils are thus linked together in a hydrogen bond with hemicellulose forming cellulose microfibrils (fibers). Hemicellulose has a random, amorphous structure and can be easily hydrolyzed by dilute acid or alkaline of various 5 and 6 carbon sugars, including arabion-xylans glucomannans, and galactans. Xylan is a family of polysaccharides most common to hemicellulose [22]. The schematic diagram is shown in **Figure 2**.

2.3 Lignin

Lignin is the third most abundant structural component in nature of a typical plant cell wall after cellulose and hemicellulose [14]. This amorphous heteropolymer consists of three different phenylpropane units, namely, p-coumaryl, coniferyl and sinapyl alcohol joined by different linkages (presented in **Figure 3**). Lignin was first discovered in 1813 by a Swiss botanist, A. P de Candolle who described it as fibrous, tasteless and insoluble in water and alcohol, but soluble in a weakly basic solution, thus, making it difficult for biodegradation [15]. It is a class of complex organic polymer forming structural materials for supporting tissues of vascular plants and offers impermeability and resistance to microbial attacks [16]. It strengthens stems and vascular tissue, allowing upward growth and permits

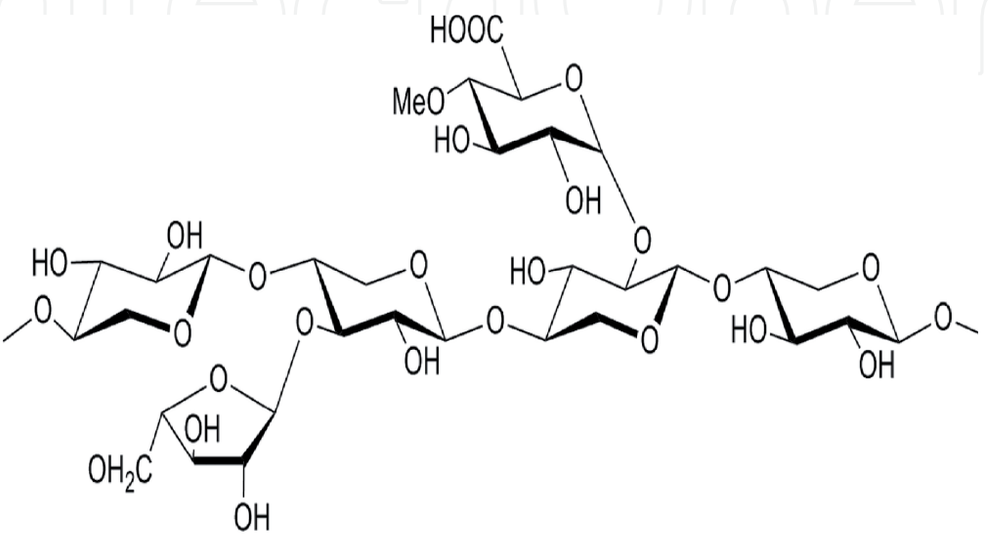

Figure 2.
Chemical structure of hemicellulose [14].

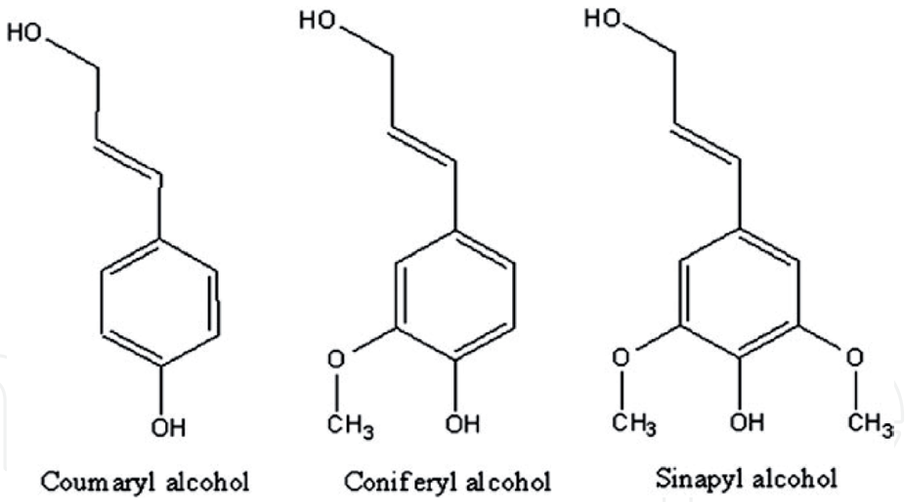

Figure 3.
Chemical structure of the main monolignols of lignin.

water and minerals to be conducted through the xylem under negative pressure without collapse of the tissue. In addition to mechanical support, lignin contributes to protective functions in plants by, for example, increasing resistance to biodegradation and environmental stresses, such as changes in humidity and water balance.

3. Lignocellulose pretreatment technologies

Application of biorefining to bagasse requires lignocellulose fractionation into cellulose, hemicelluloses and lignin [17]. This step involves pretreatment where a considerable part of hemicelluloses is solubilized. In this regard, the cellulose portion is activated initially towards enzymatic hydrolysis and subsequently, for ethanol/biogas production. The use of pretreatment in the conversion of LB for bioenergy production is to enhance the release of cellulose and disrupt lignin and hemicellulose [13]. The sole aim is to remove lignin and hemicellulose, thereby enhancing the cellulose crystallinity and porosity for easier accessibility of microbes to breakdown lignocellulosic feedstock [18]. Various feedstocks that have been employed in literature as pretreatments methods are presented in **Table 2**. Lignin is an amorphous and water-insoluble heteropolymer, and as stated earlier, it is composed of phenylpropane units (coniferyl, p-coumaryl and sinapyl alcohol) held together by different linkages as discussed earlier [19]. A simplified diagram of biomass pretreatment techniques showing the major components of lignocellulose is presented in this chapter (**Figure 4**). The fermentation of LB is difficult due to

Pre-treatment methods	Feedstocks	References
Hydrothermal	Sugarcane bagasse	[23]
Ultrasonic	Sugarcane bagasse	[24]
Ionic liquids	Water hyacinth	[25, 26]
Hydrothermal	Sugarcane bagasse	[14]
Alkali	Cattle dung	[27]
Thermochemical	Water hyacinth	[28]

Table 2.
Feedstocks and pretreatment methods.

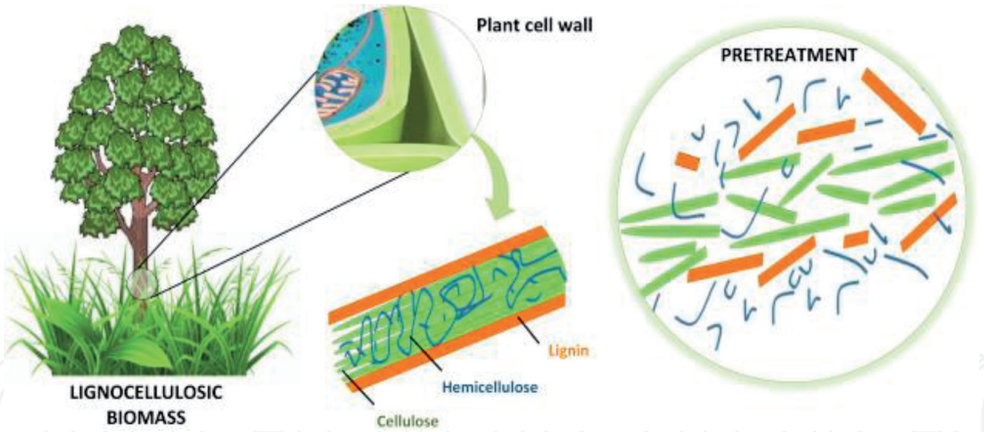

Figure 4.
Simplified diagram of biomass pretreatment technique showing the major components of lignocellulose (Accessed at: https://doi.org/10.1016/B978-0-12-802323-5.00001-3).

the high recalcitrant lignin and inadequate accessibility to sites for enzyme activity. Studies have shown that irrespective of its solubilization, the lignin content change is related to the solidification and re-deposition which is due to cooling after severe pre-treatment. Therefore, only re-allocation of lignin takes place, instead of lignin removal during pre-treatment at high temperatures and pressures [21]. Lignin inhibits hydrolysis by forming physical barriers and non-productive adsorption of cellulase enzymes. Thus, lignin restricts the enzymes from reaching the cellulose, thereby reducing the active enzyme sites for cellulose hydrolysis. Brandt et al. [20] observed that 80–90% of lignin was recovered from a solid fraction of hardwood through hydrothermal pre-treatment at 180–220°C. Therefore, as the severity of hydrothermal pre-treatment increases, the lignin content in the pre-treated solids also increases due to the simultaneous de- and re-polymerization reactions of lignin. Some pretreatment methods are summarized in the following sections.

3.1 Hydrothermolysis

During hydrothermolysis, the lignocellulosic changes that occur for bioenergy production were found to be an efficient method to disrupt lignin and hemicellulose and expose cellulose [20]. The authors [20] concluded that it is impossible for this pretreatment method to completely remove all the lignin present in a lignocellulosic feedstock. In the hydrothermolysis of sunflower oil cake for 1, 2, 4 and 6 h intervals at 25–200°C, it was observed that the cellulose solubilization rate was low (5%) while the hemicellulose content decreased from 13 to 6% at 200°C [29]. In the case of wheat straw at 200°C, cellulose crystallinity reduced as the cellulose hydrolysis rate was increased [30]. Lignin repolymerization occurred at 140°C -180°C for wood in 12–192 minutes with a removal of 75% of lignin [31]. Biogas production from sugarcane bagasse by hydrothermolysis was studied [25]. The authors [25] finding was that pretreatment by hydrothermolysis increased the biogas yield by approximately 15%.

3.2 Ionic liquid pretreatment

The search for a green solvent such as ionic liquids (IL) in the pretreatment of LB for biofuel production has gained increasing recognition for decades. ILs do solubilize complex biomass, thus providing industrial scale-up potential [23]. The unique abilities of ILs to selectively dissolve components of biomass or whole native biomass have been demonstrated [24]. Most ILs have been reported to be

viscous in nature, requiring the use of co-solvents to enhance its fluidity and the recovery by a commonly employed aqueous biphasic system, or the use of acetone, sodium hydroxide or water [25]. Commonly used co-solvents are dimethyl sulfoxide (DMSO) and dimethylacetamide (DMAC). The application of ILs to LB in areas such as fractionation, cellulose composites preparation and its derivative and removal of pollutants is a new avenue for the efficient utilization of these solvents [26]. ILs have been found to be the most expensive research-grade solvents under investigation for the dissolution of biomass and provides further challenges with solvent recovery [20].

3.3 Acidic and alkaline pretreatment

Lignocellulosic pretreatment with acids at ambient temperatures are carried out to enhance hemicellulose solubilization, thereby, making cellulose accessible for enzyme degradation with a dilute or a strong acid [14]. In this process, solubilized hemicelluloses are exposed by hydrolytic reactions to produce monomers, furfural, and other volatile products under acidic conditions [27]. In this regard, solubilized lignin quickly condenses and precipitates into acidic conditions. Hemicellulose solubilization and lignin precipitation are therefore noticeable during strong acid pretreatment. A disadvantage of this method is the risk of the formation of inhibiting compounds [14]. However, the use of dilute acid pretreatment has gained numerous research interests over the use of concentrated acids [28]. This is due to the fact that concentrated acids are toxic, corrosive, hazardous, and require reactors that need expensive construction materials which are resistant to corrosion.

3.4 Biological pretreatment

The delignification of LB could also involve application of biological methods using enzymes or microorganisms. Wood degrading microbes including white, brown, soft rot fungi, and bacteria are used in biological applications [28]. Biodegradation releases the chemical components and opens up the structure of the LB which promotes enzyme action leading to further breakdown. The brown and soft rots have been reported to attack cellulose leading to lignin modifications, whilst the lignin components are degraded by the white rot fungi [28]. The biological pretreatment of wood chips with four different white-rot fungi for a period of 30 days was studied [3]. The glucose yield of the pretreated wood by *Trametes versicolor MrP 1* reached 45% by enzymatic hydrolysis while 35% solid was converted to glucose during fungi incubation. Some microbes that have been employed in the past decades include *Ceriporia lacerate, Sterum hirsutum, Polyporus brumalis* and *Phanerochaete chrysosporium.*

4. Microalgae-based systems for CO_2 sequestering and industrial biorefineries

Microalgae have the capacity to adapt to changes in the environment, producing biomass that serves as a precursor for a variety of biomolecules; such as proteins, pigments, vitamins, lipids, and carbohydrates, in addition to finding applications in pharmaceutical, cosmetic, food and biofuel industries [32]. In **Figure 5**, a process flow diagram for micro-algal system in a combined biofuel production system is presented. Microalgae have a promising physiological plasticity in that they have a wide range of pH which allows for a range of species that can convert biomass to high value applications [33]. Pollutants in wastewaters present themselves as nutrients to microalgae, thus providing application of microalgae technology in the

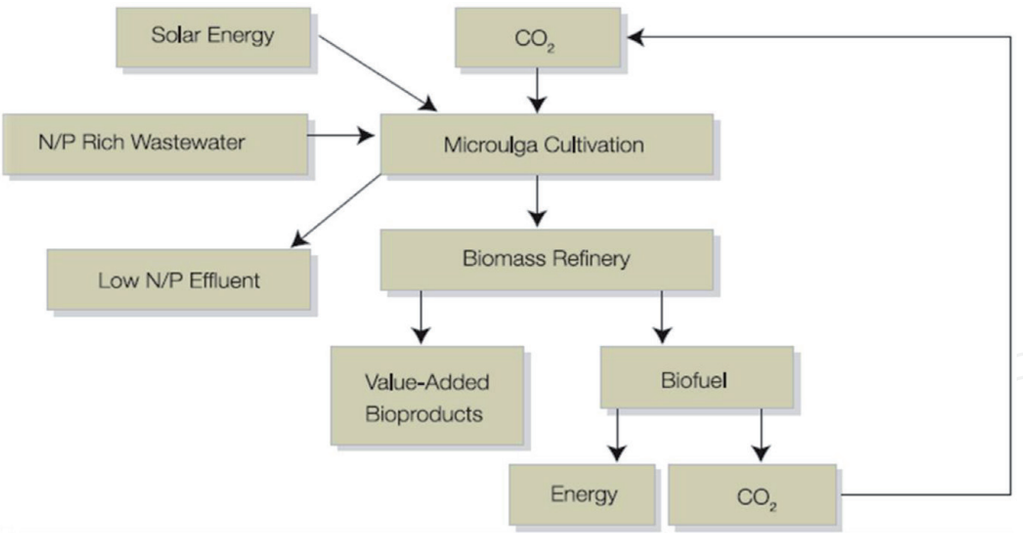

Figure 5.
Process flow for a micro-algal system for combined biofuels production, CO2 biomitigation, and N/P removal from wastewater [54].

wastewater treatment sector. These photosynthetic organisms grow under diverse luminous intensities and electromagnetic radiations to produce biomass of desired compositions. In addition, they sequester CO_2 from the environment and contribute to the global CO_2 balance, thus addressing the global warming phenomenon induced by emissions from fossil fuel combustion processes. Microalgae cultivation combined with metabolic techniques range from autotrophy and heterotrophy to mixotrophy, allowing the biomass a wide latitude for varied specific growth rate, productivity, and composition, which in turn can be enhanced by the hydrodynamics that are governed by the reactor configurations. Lipid recovery continues to be a significant bottleneck in biodiesel production due to high costs of harvesting the biomass in the first instance and the available lipid extraction techniques [34]. Microalgae growth is induced and sustained by factors such as (i) thermal energy, (ii) inorganic carbon supply, (iii) nutrient availability, (iv) luminous exposure, (v) organic carbon and (vi) water. Under photosynthesis protocol, these factors usually work in combination through different metabolic scenarios, which include autotrophy, heterotrophy and mixotrophy. The response to these factors and the nutritional programs depends on the microalgae species and strains. However, the quality of biomass produced from these photosynthetic metabolic scenarios depends on the hydrodynamic stress of the cultivation system [35].

4.1 Thermal energy

Most microalgae species are mesophilic in nature as they produce biomass in the temperature range of 15–35°C. However, some species are extremophiles, i.e. some strains are psychrophilic (*Chlamydomonas nivalis*, *Raphidonema* sp., *Mesotaenium berggrenii,* and *Chloromonas* sp. [CCCryo 020–99]) as they produce biomass under snowy conditions, while few other strains are thermophilic (*Phormidium sp.* and *Thermosynechococcus elongatus* BP-1 which are cyanobacteria; and *Desmodesmus sp.* F51, *Chlorella sorokiniana* UTEX 2805, *Desmodesmus sp*. F2 and F18 are green algae and; *Galdieria sulphuraria* 074G and *Galdieria sulphuraria* CCMEE 5587.1 are the red algae); they produce biomass at temperatures as high as 55–74°C. Depending on the species, microalgae at an optimum temperature with suitable nutrients media (nitrogen, phosphorus, and sulfur) and luminous exposure, produce biomass of varying properties and composition [36]. Temperature is a key variable that

influences the composition of microalgae biomass. For instance, Varshney and co-workers [37] reported that an increase in temperature from 20 to 25°C doubled the lipid content of *Nannochloropsis oculata* (from 7.90 to 14.92%), whilst an increase from 25 to 30°C brought about a decrease of the lipid content of *Chlorella vulgaris* from 14.71 to 5.90%.

4.1.1 Inorganic carbon

Inorganic carbon that is accessible to microalgae is mostly CO_2 gas. This gas is available in dilute concentrations in the atmosphere at 0.035 mole percent (dry basis) [38]. Microalgae absorb CO_2 from the atmosphere to produce sugars by the physiochemical process of photosynthesis. The biological conversion of CO_2 results in products of the photosynthetic metabolism such as cells, oxygen biopolymers which are soluble in the culture medium and volatile organic compounds (VOC's). Zhao and Su [39] described photosynthesis as a two-stage process. The first stage is the light-dependent reaction which captures the energy of light for oxidative phosphorylation in the metabolic cycle that produces the energy-storage molecules, adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) as shown in Eq. (1).

$$2H_2O + 2NADP^+ + 3ADP + 3P_i \xrightarrow{hv} 2NADPH + 2H^+ + 3ATP + O_2 \quad (1)$$

Eq. (2) shows the second-stage reaction, which is carbon dioxide fixation; and it is not directly light-dependent. This photosynthetic dark-reaction captures and reduces carbon dioxide to carbohydrates and releases molecular oxygen [40].

$$CO_2 + 2H_2O \xrightarrow{photons} [CH_2O] + O_2 \quad (2)$$

With a solubility of 0.1449 g CO_2/100 mL H_2O at 25°C and 101.325 kPa vapor pressure, carbon dioxide gas dissolves in surface water and slowly reacts with water to alter its chemistry as shown in Eqs. (3) and (4).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (3)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (4)$$

The release of H^+ ion in Eq. (4) causes the reduction in pH of the culture medium. However, the ability to thrive in a wide pH range has given microalgae the privilege to access nutrients from municipal and industrial wastewaters. In the presence of hydroxide ions, carbonate ions are also released as in Eq. (5).

$$OH^- + HCO_3^- \rightleftharpoons H_2O + CO_3^{2-} \quad (5)$$

When the dynamic ionization equilibrium is attained, dissolved inorganic carbon (DIC) is available in the form of CO_2, HCO_3^-, CO_3^{2-}, and H_2CO_3. However, only CO_2 and HCO_3^- are accessible to microalgae and both species are utilized simultaneously

to produce biomass [41]. The CO_2 conversion into biomass is increased only under conditions where the CO_2 mass loading rate is low. At a high CO_2 mass loading rate, the formation of VOCs is the main CO_2 biotransformation strategy [33].

4.1.2 Nutrients availability

Standard microalgae culture media have been developed and produced out of the need to produce desired products and are available in the market for freshwater microalgae growth management. Some of the media are the (i) Blue-Green medium, BG-11 (ii) Bold's Basal medium, BBM (iii) Bold's Basal medium modified, BBM-3 N (iv) CHU 13 and (v) Jaworski's Medium, JM. Both municipal and industrial wastewater have the basic nutrients common to all the artificial media designed for microalgae cultivation; and microalgae access these nutrients as nitrates and reactive phosphates from wastewaters to produce biomass and bioproducts [42, 43].

4.2 Metabolic flexibility of microalgae

Microalgae have three different metabolic pathways, namely, autotrophy, heterotrophy and mixotrophy. While all algae species are autotrophic, some stains have the ability to exhibit heterotrophy and mixotrophy; and any of the chosen photosynthetic metabolic depends on the microalgae species, and the quality of the biomass desired. Autotrophic metabolism utilizes inorganic carbon in the form of CO_2, gas and light energy. This mode of fixing CO_2 produces low density microalgal biomass. Heterotrophic metabolism takes advantage of the presence of organic carbon and utilizes it both as a source of carbon and energy. This is the dominant pathway during the night or dark phases. Some microalgae do metabolize mixotrophically. Under mixotophic mode, light energy is not the absolute growth limiting factor as organic carbon sources are also accessed and utilized for microalgal biomass production. Photoinhibition, a phenomenon that describes excessive light intensity thereby arresting photosynthetic metabolism, is overcome under the mixotrophic metabolic mode. Consequently, the growth rate is not interrupted and high density biomass is produced with recorded higher productivities when compared to autotrophic and heterotrophic metabolic scenarios [6].

4.2.1 Organic carbon

Organic carbon present in municipal and industrial wastewater are carbohydrates, fats, volatile fatty acids (VFAs), soaps, synthetic detergents, lignin, proteins and their decomposition products; as well as various natural and synthetic organic chemicals. Wastewater treatment and concomitant algal biofuel production has received increasing attention in recent years owing to its diverse environmental and economic benefits [44]. Organic carbon is accessible through monosodium glutamate wastewater, cheese whey permeates, sodium acetate, fruit peel, glucose, fructose, glycerol, etc. via mixotrophic microalgal growth mode. Tan and coworkers [45] reported that productivities of *C. vulgaris* cultured in wastewaters containing glucose and sodium acetate were 63.5 and 55.2 mg L^{-1} day^{-1}, respectively. This accounted for the leap of 2.61 and 2.27 times the productivities, respectively, achieved under autotrophic metabolic modes. Also, *Chlorella vulgaris* cultivated in sodium acetate and glucose wastewaters recorded productivities of lipid at 17.35 mg L^{-1} day^{-1} and carbohydrate at 18.75 mg L^{-1} day^{-1}, respectively, indicating that sodium acetate and glucose wastewaters have the potential to boost microalgal lipid production, which in turn may serve as feedstock for the biorefinery [46].

4.2.2 Hydrodynamic stress

Biotransformation kinetics in microalgae are driven by two cultivation systems: (i) open cultivation systems, (OCS) and (ii) closed cultivation systems, (CCS). Open cultivation systems employ open ponds, tanks and raceway ponds while the closed cultivations system utilizes closed photobioreactors (PBR), such as bubble column reactors (BCR), airlift reactors (ALR), tubular reactors (TR), plastic bag (single-use) reactors (SUR), stirred tank reactors (STR), and plate reactors (PR). The OCS attracts minimal capital, operating cost, and lesser energy for culture mixing. However, OCS require large land-mass for scale-up operations as they are prone to contamination and adverse weather conditions wherein they suffer evaporation and temperature fluctuations [47]. The CCS on the other hand, are operated at highly controlled conditions and are more efficient in terms of quality. PBRs can be designed and optimized to cultivate a chosen microalgal strain; since they occupy minimal landmass with enhanced luminous exposure to the microalgae cells and encounter little or no contamination. However, PBRs do have bio-fouling issues, cleaning difficulties, benthic microalgal growth, and high build-up of dissolved oxygen (DO) leading to growth obstructions, and high capital cost [48, 49].

The microalgae culture mixing regimes may vary from one PBR to another, and since the purpose of mixing is to ensure adequate exposure of all the microalgae cells to the growth index, variables such as thermal energy, nutrients adequate illumination, gas exchange, and the quality of microalgal biomass churned from each PBR varies in terms of cell density and biomass composition [50].

PBRs using microalgae to treat wastewater and to produce biomolecules are based on five basic criteria: (i) full control of the reaction conditions, (ii) increased efficient use of light energy, (iii) an adequate mixing system, (iv) reduced hydrodynamic stress on the cells and (v) flexible scale-up operations [51].

4.2.3 Luminous exposure

Biomass productivity depends largely on the quantity and quality of light available to microalgae cells during exponential growth, especially in the autotrophic metabolic mode. Lighting has a great influence on the synthesis of co-products in microalgal biomass as the cells increase pigmentation. Large quantities of solar radiation storage are enhanced as biomass, which can be transformed into solid, liquid, or gaseous fuels [52]. On the other hand, the exposition of microalgae cells to excessive illumination can cause photoinhibition, a phenomenon which describes termination of photocatalytic activity in the presence of illumination. Both photoperiod and light intensity influence microalgal growth, pigment production, biomass, and lipid productivities. High biomass and lipid productivities have been reported for stepwise strategic light-intensity increases during mixotrophic cultivation of microalgae. Cheirsilp and Torpee [53] reported the influence of light intensity on the growth and lipid accumulation of marine *Chlorella sp. and Nannochloropsis sp.*; and observed that the growth of marine *Chlorella sp.* increased when the light intensity was increased from 2000 to 8000 lux. Increasing the light intensity to 10,000 lux registered a slight decrease in the lux indices, which could be due to photoinhibition.

5. Conversion of biomass to bioenergy production

Generation of bioenergy from biomass is achieved in various ways and may be classified into three main categories, namely, physio-chemical, bio-chemical, and

thermo-chemical processes [54]. The following are common techniques utilized in the conversion of biomass into biofuels, i.e. mechanical extraction, transesterification, pyrolysis, anaerobic digestion, fermentation, gasification, liquefaction, and fuel cell systems as shown in **Figure 6**. This subsection gives an overview of the conversion process, the factors affecting each process and the main products derived.

5.1 Pre-treatment methods

Prior to the application of a specific technique of biofuel generation from biomass, various pre-treatment or pre-processing steps may be carried out to aid effective conversion. Two main pre-treatment methods broadly classified under physio-thermal and chemical methods are usually applied based on the lignocellulosic substrates as discussed in the latter sections on lignocellulosic and the related conversion techniques. Processes such as drying, sizing, crushing, powdering, pelletizing, torrefaction and heating are common physio-thermal methods for pre-treatment of lignocellulosic and algae biomass.

5.2 Physico-chemical means

This involves the mechanical extraction of oil from lignocellulosic and algae biomass, where the oil produced is further esterified to produce biodiesel. Biodiesel is

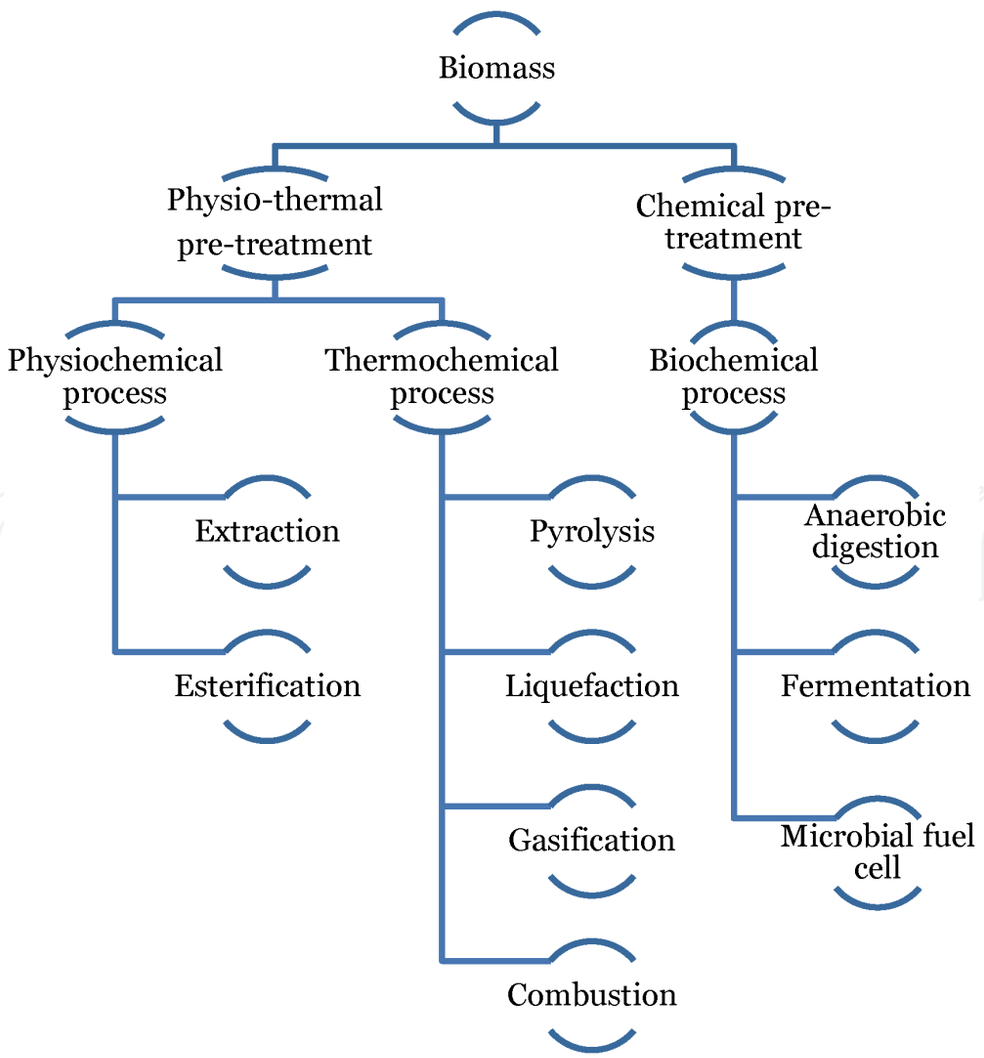

Figure 6.
Biomass conversion techniques.

usually blended with conventional diesel to be used as fuel for motor vehicles. The oil extracted from the biomass is highly viscous with polyunsaturated characteristics; therefore, transesterification processes which utilize either acids, bases, or enzymes as catalysts, convert the oil into fatty acid methyl esters (FAME) or fatty acid alkyl esters with glycerol as by-product. The esters produced from the transesterification process have lower viscosities and are comparable to conventional fuels [51].

5.3 Bio-chemical means

The biochemical conversion process utilizes the metabolic activity of microorganism for conversion of biomass into biofuel and by-products. Biomass conversion is environmentally friendly when compared to thermochemical methods where the residence time for the conversion process to be achieved is longer when compared to thermochemical conversion means. The main biochemical conversion methods are discussed below.

5.3.1 Anaerobic digestion

Anaerobic digestion (AD) is the microbial degradation of organic matter in the absence of oxygen to produce mainly biogas (biomethane and carbon dioxide). The conversion of organic matter into biogas is presented in **Figure 7**. It is a series of biochemical reactions where microorganisms anaerobically convert organic materials into products to be finally converted into biogas [2].

Microorganisms break down high molecular mass compounds such as polysaccharides, proteins, fats, cellulose, and hemicellulose into smaller molecular mass

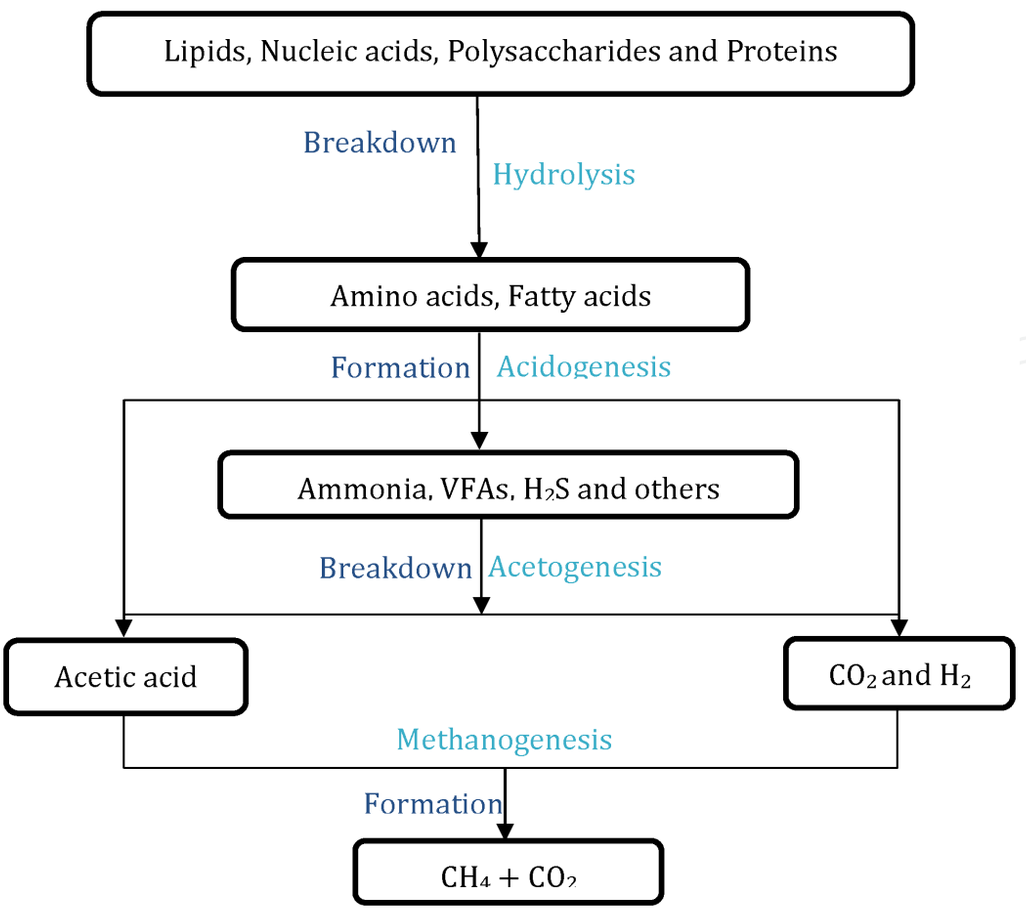

Figure 7.
Anaerobic digestion degradation process.

compounds which are later converted into biogas. The efficiency of AD processes is dependent on the components of the substrate and the activity of microorganisms. AD is a biochemical conversion process that is robust with proven reliable applications. AD has been widely applied in the treatment of organic waste streams, and its development for production of biogas goes far back as the 16th century [55]. The general equation to produce methane from organic matter is given as in Eq. (6).

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 \qquad (6)$$

5.3.1.1 Stages of AD process

The four main stages involved in the AD of lignocellulosic biomass are hydrolysis, acetogenesis, acidogenesis and methanogenesis. Theses stages occur successively as the product from a preceding stage is utilized in the next stage. Hydrolysis is the first stage in the AD process, and it involves the breakdown of high molecular mass compounds into smaller ones. This stage is followed by acidogenesis, which is the conversion of the smaller molecular compounds into identifiable lower molecular compounds. The acetogenesis stage converts the volatile fatty acids (VFAs) from acidogenesis into acetate, CO_2 and H_2, where after these intermediate compounds are converted into methane and CO_2 with other by-products in trace amounts in methanogenesis stage, with the aid of methanogens. The stages of the AD process are affected by various parameters and the biomass chosen.

5.3.2 Fermentation

The conversion of biomass to simple sugars with subsequent transformation into alcohol and CO_2 with the aid of microorganisms, mainly, yeasts is known as fermentation. This process has been applied for centuries to produce ethanol from sugar crops. It has been used for conversion of lignocellulosic material and algae to ethanol. The by-product from this process after the distillation process are the non-fermentable products which are further directed for use as animal-feed, or as raw feed for the thermochemical conversion. Ethanol produced from the process can be used as fuel for motor vehicles, or as compliment for existing conventional fuels. It has been used as an additive for petrol to improve the octane rating and vehicle emissions reduction in countries such as Australia, Brazil, Sweden, and United States [20]. Anaerobic or dark fermentation of pre-treated lignocellulosic biomass is used in the production of biohydrogen, where the process is like the acidogenic stage in AD. The microorganisms used in this process are mainly hydrogen producing microbes such as *Thermoanaero bacterales, Clostridiaceae* and *Enterobacteriaceae.* This process is gaining interest as the combustion of hydrogen is free of any harmful emissions [56]. The challenge encountered is the low yield of H_2 generated, though there has been research carried out into the upgrading of CH_4 into H_2.

5.3.3 Microbial fuel cell (MFC)

MFCs employ the activity of micro-organisms to convert pre-treated biomass into bioelectricity that can be fed into an existing electricity grid. The process involves the oxidation of the substrates (cellulosic biomass) at the anode chamber of the cell by microorganisms, (electrode-reducing organisms) to electrons which are transferred to the cathode chamber through a conductive material. In the cathode region, the electrode-oxidizing organisms utilize the electrons for

reduction of various compounds to other forms (such as CO_2 to acetate, nitrate to N_2 and O_2 to H_2O). It is an electrochemical reaction that utilizes microorganisms for catalysis; therefore, it is referred to as a bioelectrochemical process. The anode in an MFC is usually carbon based such as carbon cloth, felt, fiber, rod, and paper, while the cathode is either of the latter coated with platinum [57, 58]. **Figure 8** shows a schematic of the working principles of a microbial fuel cell. The catalyst used may differ based on the application of the fuel cell.

5.4 Thermo-chemical processes

Thermochemical conversion techniques involve the use of heat or chemicals for the conversion of biomass into fuel and heat (as in the case of combustion and gasification). The thermochemical means is sometimes preferred since it requires limited time, little or no pre-treatment, and generation of variable end-products as compared to biochemical means. The overview of the main thermochemical conversion techniques is summarized in the following section.

5.4.1 Pyrolysis

An irreversible chemical reaction impacted by heat in the absence of oxygen is known as pyrolysis. This method generally converts lignocellulosic biomass into solid, liquid, and gaseous fractions which are further processed into another product spectrum [59]. Pyrolysis is commonly adopted, since its end-product ranges from gaseous to solid fuels in varying percentages, when compared to other thermochemical biomass conversion methods. Pyrolysis can be a precursor to some other conversion processes such as gasification and combustion, as well as a succeeding step to some pre-treatment methods, such as torrefaction and degradative solvent extraction (DSE) [60]. Pyrolysis is a temperature, heating rate and time dependent process, and varying these conditions with addition of selected catalysts give a specified, desired end-product. Based on the specific conditions, pyrolysis is classified into slow, intermediate, and fast mode; and from which different percentages of solid, liquid, and gaseous product are derived. The classification of pyrolysis base on temperature and residence time is shown in **Table 3**, and it ranges from the low temperatures (~ 300°C) to high temperatures (approximately 900°C).

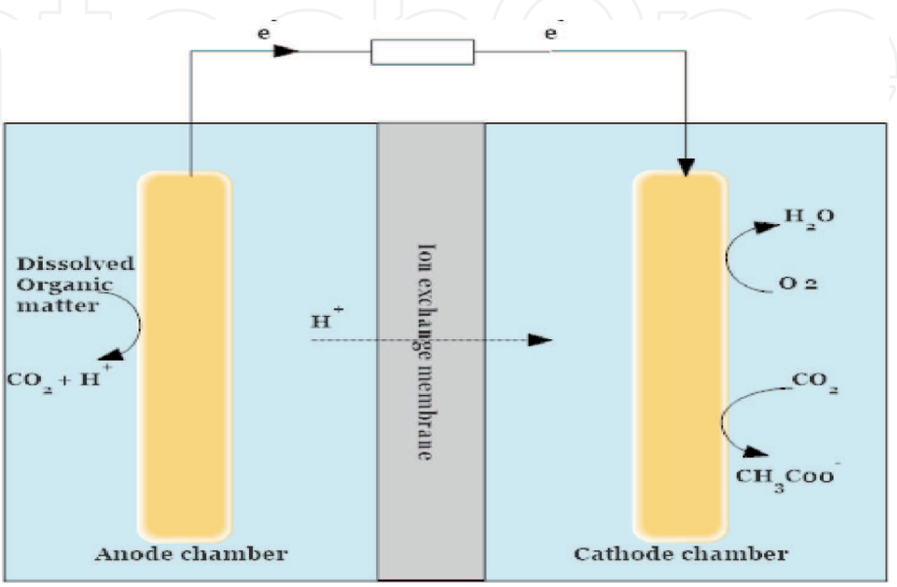

Figure 8.
Schematic of a microbial fuel cell.

Mode of pyrolysis	Heating rate	Temperature	Residence time	Product percent by weight (% wt)		
				Solid	Liquid	Gas
Slow		250–400°C	Long hours to days			
Carbonization	Low	~400°C*		35	30	35
Torrefaction Intermediate		~280°C	10–60 mins	80	3	20
	Medium	300–500°C	5–30 s	25	50	25
Fast	High	~500°C	< 2 s	12	75	13

**Approximate values.*

Table 3.
Mode of pyrolysis and product distribution [61, 62].

Slow pyrolysis involves lower heating rates between 0.1 and 2°C, and the products are mainly solids. Carbonization is a form of slow pyrolysis which is the old technique used in the production of charcoal (biochar) and the vapor produced during the process is usually not condensed, but rather used for heating. Torrefaction mainly aims at improving the energy density and biomass fuel properties, such as reduced weight and volume, which renders the fuel easy to transport and be crushed when needed. The intermediate pyrolysis process produces less solid and liquid with low viscosities. Fast pyrolysis is one of the biomass conversion technologies currently gaining prominence because of its ability to generate more liquid fuel (bio-oil) which could be easily upgraded to diverse valuable products, and transported [19, 61].

5.4.2 Gasification

Gasification is the conversion of biomass or carbonaceous feedstock into gaseous components at temperatures higher than 650°C. The gaseous component of the gasification process may vary depending on the operating temperature. At a lower temperatures below 1200°C, gas constituents may vary from CO, CO_2, CH_4 and H_2, which are collectively known as producer gas while at a higher temperatures, the constituents are CO and H_2, which are collectively known as synthesis gas or syngas [62]. Coal gasification is a well-known process in the generation of electricity which can also be used for biomass conversion into gas. The four steps involved in the gasification process are drying or heating, pyrolysis, gas–solid reaction, and gas phase reaction. These steps occur successively and may take a fraction of a minute depending on the reactor (gasifier) design [52]. Drying/heating is mainly adopted to remove the moisture content of biomass, thereby converting the biomass into dry mass. This is done to attain the required temperature for gasification and the desired products. This process is followed by pyrolysis. The gas–solid reaction step involves the reaction of the gas and solid (char) produced from the pyrolysis phase. The char which is carbon reacts with carbon dioxide, hydrogen, oxygen, and water (vapor) to form gaseous compounds as shown in the conversion Eqs. (7)–(10).

$$\text{Boudouard reaction}: C + CO_2 = 2CO \tag{7}$$

$$\text{Carbon} - \text{hydrogen reaction}: C + H_2 = CH_4 \tag{8}$$

$$\text{Carbon} - \text{oxygen reaction} : C + O_2 = CO_2 \quad (9)$$

$$\text{Carbon} - \text{water reaction} : C + H_2O = CO + H_2 \quad (10)$$

Thus, the gas phase reaction is shown in Eqs. (11)–(12).

$$CO + H_2O = CO_2 + H_2 \quad (11)$$

$$CH_4 + H_2O = CO + 3H_2 \quad (12)$$

5.4.3 Solvent liquefaction

This is the conversion of biomass into liquid or solubilized products at moderate temperatures (105–400°C) and pressure (2–20 MPa) with the aid of solvents. Solvents such as water, ethanol, phenol, tetralin, sulfuric acid, phosphoric acid, nitric acid, and other ionic solvents have been utilized. When water is used as the solvent in the liquefaction process, it is known as hydrothermal liquefaction [63]. For optimal efficiency of the process, the main parameter is the choice of solvent as the process requires the solvent to be in the liquid phase during the reaction. Solvents such as creosote have been utilized to achieve a bio-oil yield of 74 wt% as compared to water of 35 wt% yield or acetone of 10 to 60 wt% yield, for lignocellulosic biomass. This process has been mainly used for the processing of lignocellulosic biomass, algae, and other biomass feedstocks. Unlike other thermochemical conversion processes, this process does not need much residence time for intermediate drying/heating of the biomass as it could be used to process biomass with 15 to 80% moisture content.

5.4.4 Combustion

Combustion is the complete oxidation of carbon containing materials to CO_2 and H_2O in the presence of air (oxygen). For a complete combustion process, the four stages involved are heating or drying, pyrolysis, volatiles combustion (known as flaming) and char combustion (smoldering). These stages are similar to the stages in gasification and the only difference is that combustion requires excess air [64]. Combustion depends on the operating temperature, feedstock type, the particle size of the feedstock, the design of the reactor and atmospheric conditions. Other by-products of this process are nitrogen oxides, sulfur, ash, and particulate matter which are environmentally unfriendly [63].

6. Conclusion

The conversion of LB into value-added products is vital to meet the global demand for lignocellulosic products. The concept of biorefining arose since the potential of lignocellulosic and microalgae-based products were substituted for fossil fuel derived products, which accounted for increased usage of non-renewable fuels. The reduction in the demand on fossils, creation of opportunities in the job market and the provision of sustainable forms of energy has highlighted the role of

biorefineries in tackling climate change. This chapter presented the insights into the various components of lignocellulose and microalgae, the pretreatment techniques adopted in the past decades for delignification and conversion into useful products, and the applications coupled with future prospects for valorization of biomass.

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