



## Review Article

### Lignocellulosic Biomass as a Potential Source of Biofuels for Sustainable Development: A Review

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#### ABSTRACT

*Lignocellulosic biomass has gained interest as a potential feedstock for biofuel production and other biorefinery processes. However, its complex structure poses challenges for efficient conversion into biofuels or other valuable products. Biofuels are renewable fuel which can be produced from biomass mainly through thermochemical and biochemical methods. Thermochemical process consists of combustion, gasification and pyrolysis while biochemical process consists of pretreatment, hydrolysis, fermentation and purifications. All these processes are explained in this paper, The advantages and disadvantages of each of the process are also given. Biochemical methods offer significant advantages in terms of efficiency, versatility, mild reaction conditions and improved enzymatic process, while thermochemical method produce a high value of fuels and mitigation of environmental effect. The formation of Inhibitory compounds is the major disadvantage of the method which may increase the cost and efficiency of production. These set back can be reduced by detoxification strategies, use of appropriate catalyst or by using liquid-liquid extraction method of pretreatment. Production of biofuels from lignocellulosic materials can help to sustain development in Africa and the world in general.*

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## 1. INTRODUCTION

Rising uncertainties over the environmental impact of using fossil fuels, security of supply, and price instability have led to a mounting interest in the production of alternative fuels from renewable resources (Demirbas, 2017; Evans & Smith, 2012). Biofuels are liquid or gaseous fuels produced from organic materials (biomass) which can be used as transportation fuel, heating, and for electricity generation (Patinvoh

& Taherzadeh, 2019). Biomass means organic matter such as plants, trees, crops, forest crops and residues after processing. The residues include crop residues (such as straw, stalks, leaves, roots etc.) and agro-processing residues (such as oilseed shells, groundnut shells, husk, bagasse, molasses, coconut shells, saw dust, wood chips etc.). Human waste, and organic fractions of sewage sludge, industrial effluents and household wastes also consider as a biomass (Rawat, 2016). Biomass is a renewable energy resource which comprises carbon, hydrogen, oxygen, traces of nitrogen and some minerals (Sikarwar et al., 2017). Biomass offers an abundant and environmentally friendly source of clean energy that can help alleviate greenhouse gas emissions (Prasertpong et al., 2017), a greenhouse gas is any gaseous compound that traps heat in the atmosphere causing the greenhouse effect. The main greenhouse gases are water vapor ( $H_2O$ ), carbon dioxide ( $CO_2$ ), and methane ( $CH_4$ ). Greenhouse effect is a process by which the atmospheric greenhouse gases absorb a part of infrared radiation of the sun making the atmosphere and thus the surface of the earth warmer (Itskos et al., 2016). Biomass is the organic material that comes from plants and animals, and it is a renewable source of energy (Houghton, 2008; Itskos et al., 2016) contain stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis (Rawat, 2016). When biomass is burnt, the chemical energy in biomass is released as heat (Rawat, 2016).

Renewable energy is the energy that is endlessly and freely produced in the nature and are not exhaustible (Rawat, 2016). Renewable energy includes solar energy, solar photovoltaic {photovoltaics gets its name from the process of converting light(photons) to electricity(voltage), which is called the photovoltaic effect}, biomass and wood energy, geo thermal energy, hydrogen fuel cell, wind energy, tidal energy and ocean energy (Rawat, 2016). Lignocellulose biomass, the most abundant renewable resource materials from plants mainly composed of polysaccharides (cellulose and hemicellulose) and an aromatic polymer(lignin) in the world, is a capable resource for sustainable biofuel production (Avci et al., 2013). This paper review focuses on the various biomasses for biofuels production, pretreatment processes and the conversion techniques used in the production of biofuels from lignocellulosic materials. The objective is to highlight the advantages and weaknesses of different technologies and to find a pretreatment method suitable for industrial-scale production of biofuels, identify the areas that need improvement and provide some useful information for policy makers and researchers.

## 2. CHEMICAL COMPOSITION OF LIGNOCELLULOSIC BIOMASS

Lignocellulose is a complex structural material found in the cell walls of plants, particularly in woody tissues. It is composed mainly of cellulose, hemicellulose, and lignin. Cellulose consists of linear chains of glucose molecules linked by  $\beta$ -1,4-glycosidic bonds and provide structural support to the plant cell walls and also serve as source of energy for microorganisms capable of digesting it (Prasad et al., 2019). Unlike cellulose, hemicellulose is a heterogeneous polymer composed of different sugars, including xylose, mannose, galactose, and arabinose. It acts as a cementing material in the cell wall, binding cellulose fibers together, and also provides some rigidity to the cell wall structure. Lignin is a complex, amorphous polymer that provides rigidity and hydrophobicity to the cell wall. It is formed from phenylpropanoid units and is highly cross-linked with other cell wall components which is responsible for the strength and resistance of wood to microbial degradation. (Kucharska *et al.*, 2018). In terms of elemental analysis, biomass elements can be classified into major, minor, and trace, according to their elemental concentrations on a dry basis. Major elements include Carbon, Oxygen, Hydrogen, Nitrogen, Calcium, and potassium, while minor elements include Silicon, Magnesium, Aluminum, Sulphur, iron, Phosphorus, Chlorine, and sodium. Trace elements may include Manganese and Tin. Most biomass is composed of roughly 40% cellulose, 25% hemicellulose, and 25% lignin by mass, with ash and miscellaneous compounds making up the remaining 10% (Dahman et al., 2019).

### 2.1. Cellulose

Cellulose is a long-chain complex carbohydrate which composed of glucose molecules. It is the structural component of the cell walls of green plants, algae, and some bacteria. The molecules of cellulose are made up of linear chains of glucose units linked by  $\beta$  (1 $\rightarrow$ 4) glycosidic bonds arranged in a way to allows hydrogen bonding between adjacent chains to form microfibrils. The microfibrils, in turn, are bundled together to form larger structures like fibers, which contribute to the strength and rigidity of the plant cell wall. (Li, et al., 2021). The molecular formula of cellulose is  $(C_6H_{12}O_6)_n$ . Where n is the degree of polymerization which range from hundreds

to thousands of glucose monomers. Total hydrolysis of cellulose yields D-glucose (a monosaccharide), but partial hydrolysis yields a disaccharide (cellobiose) and polysaccharides in which  $n$  is in the order of 3 to 10. Cellulose has a crystalline structure and great resistance to acids and alkalis (Prasad, et al., 2019). Humans and many animals lack the enzyme necessary to break down cellulose, so it is indigestible to them. However, certain microorganisms such as bacteria and fungi possess the necessary enzymes, allowing them to break down cellulose and use it as a food source through a process called cellulolysis. Additionally, cellulose is of great industrial importance, being used in the production of paper, textiles, and various other products. (Li, et al., 2021)

## 2.2 Hemicellulose

Hemicellulose are diverse complex plant materials composed of different  $C_5$  and  $C_6$  sugars like xylose, arabinose, mannose and galactose. L-arabinose and D-xylose are pentoses or ( $C_5$ ) sugars while the rest are hexose ( $C_6$ ) sugars with the average molecular formula of  $(C_5H_8O_4)_n$ . Hemicelluloses may also contain small amounts of other sugars such as  $\alpha$ -L-rhamnose and  $\alpha$ -L-fucose, organic acids such as acetic, 4-Omethyl glucuronic, galacturonic, and ferulic acid (Jedvert, & Heinze, 2017). They are made up of about 25 % to 35 % of the dry weight of wood and are the second-most abundant type of carbohydrate on earth. Several biosynthetic processes are used to convert lignocellulosic biomass into hemicellulose. (Zhou et al.,2017). The chain of hemicellulose is smaller than that of cellulose. When contrasted with cellulose, hemicellulose molecules exhibit fewer branches and shorter lengths, with degree of polymerization (DP) values ranging from 2 to 20. They are made up of several heteroglycan sugar units. According to this composition, the hydrolysis process causes hemicellulose to break down more quickly. In addition, the amorphous nature of hemicellulose makes it simple to hydrolyze. The hydrolysis of the hemicellulose structure yields pentose sugars like xylose and arabinose, along with hexose sugars such as galactose, mannose, and glucose. Because of its sensitivity to heat, hemicellulose can disintegrate more quickly when exposed to heat (Zhou et al.,2017).

The characteristics of hemicellulose in different biomass sources can vary based on their branching pattern, degree of polymerization (DP), and carbohydrate composition. Furthermore, the composition of hemicellulose is influenced by factors such as the species, origin, and specific features of the biomass. (Fu et al., 2019). Hemicellulose is primarily composed of xylan and contains various sugar components, including  $C_5$  sugars like xylose and arabinose, as well as  $C_6$  sugars like mannose, glucose, and galactose, along with sugar acids. In softwood, the predominant hemicellulose components are galactoglucomanan and mannose, which constitute the major monomers of this complex carbohydrate. The two primary monomers... that make up the hemicellulose in hardwood are glucuronoxylan and xylose. As a result, the hemicellulose compositions of softwood and hardwood varied slightly. While the utilization of hemicellulose is currently at an early stage and subject to certain restrictions, it holds significant promise in the advancement of bio-based products such as Xylooligosaccharides (Fu et al., 2019)

## 2.3. Lignin

Lignin is an amorphous and highly branched irregular complex polymer, predominantly constituting of three phenylpropane units as the major building blocks: p-coumaryl alcohol( paracoumaryl  $C_9H_{10}O_2$ ), coniferyl alcohol, and sinapyl alcohol, which give rise to a random sequence of p-hydroxyphenyl (Hlignin), guaicyl (G-lignin), and syringyl (S-lignin) subunits in the polymer, respectively and it has also many biological functions such as water transport, mechanical support and resistance to stresses (Quingquan *et al.*, 2018). The composition of H, G, and S-lignin's vary depending on source of lignocellulose. It has been identified that softwood lignin is mostly composed of G units with the remaining being H units, hardwood contain G and S monolignols with trace amounts of H units, and herbaceous plants contain significant amounts of all three G, S, and H lignans but in different ratios(ref) The present of lignin in lignocellulose biomass played the two major roles this include physical and chemical role. Physically, lignin reduces the accessibility of cellulose to enzymes by covering cellulose fibrils and by restricting fiber swelling. Chemically, lignin is causes recalcitrance by irreversibility binding cellulose enzymes and also preventing further enzymatic activity on cellulose (Soudham, 2015).

## 2.4. Pectin

Pectin is part of a complex family of polysaccharides, which are primarily found in primary walls that surround growing and dividing cells and in the middle lamella and cell corners. Pectin is also present in very small proportion in the secondary cell wall. Structurally, pectin is a galacturonic acid-rich polysaccharide, and part of a

family of polymers including homogalacturonan (HG), rhamnogalacturonan I (RG-I), substituted galacturonans rhamnogalacturonan II (RG-II), and xylogalacturonan (XGA). There is evidence that indicates pectin is utilized by the plant for variety of functions including binding the cell wall composite together, plant growth, defense, cell-cell adhesion, cellular signaling, cell wall porosity, binding of ions, etc. (Foston, 2014).

### **2.5. Other Constituents**

Lignocellulose cell wall also contain some other substances such as extractives which include terpenoids, steroids, fats, waxes, and phenolic constituents, proteins, and ashes. The characters of extractives are diverse, some are involved in plant protection, some are forerunners of certain chemicals, and for many the character has not been completely understood (Soudham, 2015).

## **3. GENERATIONS OF BIOFUELS**

Biofuels are fuels produced from biomass, which can include organic materials such as plants, algae, and animal waste. They are considered renewable energy sources because the biomass used in the production can be replenished relatively quickly compared to fossil fuels. Biofuels are classified in First, Second, Third and Fourth Generations (Patinvoh & Taherzadeh, 2019).

### **3.1. First Generation Biofuels**

First-generation biofuels refer to biofuels produced from feedstocks that are edible or easily convertible into food, such as corn, sugarcane, soybeans, and vegetable oils which include ethanol and biodiesel and biogas (Itskos et al., 2016; Alalwan et al., 2019). Ethanol is typically produced by fermenting sugars or starches found in crops, while biodiesel is produced from vegetable oils or animal fats by transesterification process (Safari et al., 2024). Biogas is generated from anaerobic digestion of organic matter such as agricultural waste, manure, or sewage, biogas is primarily composed of methane and carbon dioxide and can be used for electricity generation or as a vehicle fuel. First-generation biofuels have faced criticism due to concerns over their impact on food prices, land use change, and their limited ability to significantly reduce greenhouse gas emissions. As a result, there has been increasing interest in second-generation biofuels (Mat Aron et al., 2020).

### **3.2. Second Generation Biofuels**

Second-generation biofuels also known as advanced biofuels are produced from non-food crops, agricultural residues and waste materials that are not directly compete with food production. They are derived from lignocellulosic Biomass like corn stover, wheat straw, and rice husks, as well as energy crops like switchgrass and miscanthus. Second generation biofuels can also be obtained from algae which can be cultivated in ponds, photobioreactors, or open water systems and can produce high yields of oil, which is converted into biodiesel or other biofuels (Aro, 2016; Itskos et al., 2016; Amin et al., 2017). Algae have the advantage of potentially higher productivity per unit of land compared to terrestrial crops. Organic waste such as municipal solid waste, sewage sludge, and food waste can be converted into biofuels through anaerobic digestion, gasification, or fermentation). The merits of this type of fuel are reduction of concerns about competition with food production and land use, lower greenhouse gas emissions, more sustainably with less environmental impact and offer the potential for increased energy security by diversifying energy sources away from fossil fuels. However, second-generation biofuels also face challenges such as technological and economic feasibility, scalability, and competition with low-cost fossil fuels (Binod et al., 2019).

### **3.3. Third Generation Biofuels**

Third-generation biofuels are advanced biofuels gotten from non-food feedstocks, typically from algae, seaweed, and other non-food crops. algae in particular have been making a strong case as the best candidate to completely revolutionize the energy market because they only need CO<sub>2</sub>, nutrients, water, and sunlight to grow (Aro, 2016; Itskos et al., 2016; Alalwan et al., 2019). Third generation biofuels are aimed to overcome some of the limitations associated with the first two generations. While there has been significant research and development in the field of third-generation biofuels, large-scale commercial production is still limited. The industry continues to work on improving efficiency and reducing costs to make these biofuels competitive with traditional fossil fuels. Third-generation biofuels promising for sustainable alternative to traditional fossil fuels, offering potential benefits in

terms of feedstock diversity, environmental impact, and resource efficiency. Further research, development, and investment are needed to realize their full potential and enable widespread adoption. (Neto, *et al.*, 2019).

### 3.4. Fourth Generation Biofuel

In fourth-generation biofuels, genetically modified microorganisms such as microalgae, yeast, fungi, cyanobacteria and certain types of grasses, waste materials like agricultural residues, municipal solid waste, and forestry residues are utilized. The ability of microorganisms to convert CO<sub>2</sub> to fuel through photosynthesis is utilized. The multiple advantages of microalgae such as their high growth rate and oil content and low structural complexity enhance their numerous commercial applications (Shokrav, *et al.*, 2022). In addition to genetic modification, some fourth-generation technologies involve pyrolysis, gasification, upgrading, and solar-to-fuel, pathways. The general purpose of these modifications is to improve the hydrocarbon yield and create an artificial carbon sink to eliminate or minimize carbon emission. Despite these advantages, fourth-generation biofuels still face challenges related to technological and economic viability, scalability, and sustainability. Research and development efforts are ongoing to improve production processes, reduce costs, and address environmental concerns associated with biofuel production (Aro, 2016; Itskos *et al.*, 2016; Alalwan *et al.*, 2019).

## 4. TYPES OF BIO-FUEL

There are different types of Bio-fuels which include the following; Vegetable oil, Biodiesel, Bio alcohols, Biogas, Solid biofuels, Syngas and Bio hydrogen (Rastegari *et al.*, 2019).

### 4.1. Vegetable Oil

Vegetable oil can be directly used as diesel fuel without any changes to engine. The very first engine (by Rudolf Diesel) was tested using vegetable oil as fuel. The primary concern with vegetable oil as fuel is its high viscosity (atomization of vegetable oil is difficult), which leads to problems in the long run. Advantages of vegetable oil as diesel fuel are: Liquid nature and portability, High heat content (80 percent of diesel fuel), Ready availability, and Renewability (Thangapandian & Lucas, 2015).

### 4.2. Biodiesel

Biodiesel is a fuel obtained from organic sources such as vegetable oils, animal fats, or recycled cooking grease. It is produced by transesterification, in which the fats or oils are chemically reacted with an alcohol (usually methanol or ethanol) in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide to breakdown the fats and oils into methyl or ethyl esters (biodiesel) and glycerin. Knothe and Razon. (2017). Biodiesel can be used in diesel engines either pure or blended with petroleum diesel in various proportions. Common blends include B5 (5% biodiesel, 95% petroleum diesel), B20 (20% biodiesel, 80% petroleum diesel), and B100 (100% biodiesel). It is considered a cleaner alternative to conventional diesel fuel because it produces lower emissions of certain pollutants such as carbon monoxide, particulate matter, and sulfur oxides. One of the major advantages of biodiesel is its renewable nature and potential to reduce greenhouse gas emissions, as the carbon dioxide released during combustion is offset by the carbon dioxide absorbed during the growth of the feedstock plants. Additionally, biodiesel can help reduce dependence on fossil fuels and promote energy security. The challenges associated with biodiesel production and use is the competition with food production, land use concerns, and problem of biodiversity. Additionally, the energy balance of biodiesel production, which considers the energy input required for cultivation, processing, and distribution compared to the energy output, can vary depending on the feedstock and production methods (Gebremariam & Marchetti, 2018).

### 4.3. Bioethanol

Bioethanol is a volatile, flammable, colorless liquid made by fermenting and distilling starch crops. It is a sustainable and renewable form of energy from Agricultural feedstock. These feedstocks include waste straw, milk, rice, beetroot, recently grape, banana and dates, sugar cane, potatoes, corn, cassava and yam etc. The production process involves fermenting the sugars in the substrate with yeast or bacteria and the ethanol is then distilled to increase the purity. Apart from fermentation process, bioethanol can be manufactured by the chemical reaction of ethylene with steam (Adiomre, 2015). One of the key advantages of bioethanol is its potential to reduce greenhouse gas emissions compared to fossil fuels. While burning bioethanol still releases carbon dioxide, the plants used to produce it absorb carbon dioxide from the atmosphere during their growth, effectively balancing

out the carbon emissions when bioethanol is burned for energy. Bioethanol production has faced criticism and concerns due to impact on food prices, land use, and biodiversity. The cultivation of feedstocks for bioethanol can result in land use changes, including deforestation and habitat destruction. (Azhar, et al.,2017).

#### 4.4. Biogas

There are four main steps in biomethane production: hydrolysis acidogenesis, acetogenesis/dehydrogenation, and methanogenesis. Hydrolysis procedure, the first step for biomethane or biogas depends on the molecular structure of the substrate used such as carbohydrate, proteins, lipids, and lignocelluloses structures. In hydrolysis process, the fermenting bacteria (FB) such as *Bacterioides*, *Clostridia*, and *Bifidobacteria* convert complex biopolymers (carbohydrate, proteins, and lipids) into soluble organic molecules (sugar, amino acids, and fatty acids). In the next steps, i.e., acidogenesis and acetogenesis, the biohydrogen, carbon dioxide, and acetate is produced from soluble organic molecules using different fermentative bacteria. In the final step, i.e., methanogenesis, the biomethane and carbon dioxide (Ferrer et al., 2008).

#### 4.5. Solid Biofuels

Solid biofuels are obtained from organic materials like wood, crop residues, or organic waste. These materials are burned to generate heat or electricity, providing an alternative to fossil fuels like coal or natural gas. Examples of solid biofuels are logs, chips, pellets, and sawdust from trees and forestry residues, agricultural byproducts such as straw, husks, stalks and organic Waste such as municipal solid waste, sewage sludge, or food processing byproducts. Solid biofuels offer many advantages such as renewability and carbon-neutral properties, potential for waste reduction through the utilization of agricultural and forestry residues, and the ability to provide energy by utilizing local biomass resources. On the other hand, competition with food production, land use conflicts, and deforestation are some of the challenges (Manandhar, et al.,2022).

#### 4.6. Syngas

Syngas (Synthesis Gas) is produced by the combined processes of pyrolysis combustion, and gasification. Syngas consists of a mixture of CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> (primary components) and H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, tar, and other trace species (secondary components), with a composition dependent on feedstock type and characteristics, operating conditions (i.e., gasifying agents, gasifier temperature and pressure, type of bed materials), and gasification technology (Molino et al., 2018).

#### 4.7. Biohydrogen

Biohydrogen is produced from biological sources by fermentation or anaerobic digestion of organic materials. The process involves breaking down of organic materials in the absence of oxygen by microorganisms, resulting in the release of hydrogen gas as a byproduct. Biohydrogen is considered a renewable and sustainable energy source because it can be produced from many biomass feedstocks such as agricultural residues, organic waste, algae, and energy crops. The common method for producing biohydrogen by dark fermentation which involves the anaerobic fermentation of organic materials by bacteria in the absence of light using organic substrates such as carbohydrates, sugars, and organic acids. Photo fermentation can also be used to generate biohydrogen by photosynthetic bacteria, such as purple non-sulfur bacteria (Rastegari et al., 2019). The organisms utilize light energy to produce hydrogen gas from organic compounds in the presence of specific co-factors. Photo fermentation typically requires light as an energy source and can be more efficient than dark fermentation under certain conditions. (Usma et al.,2019). The advantages of biohydrogen as an energy is its renewability, potential for carbon neutrality when produced from biomass, and compatibility. However, biohydrogen production faces low conversion efficiency, problem of substrate availability, downstream and technological limitations. (Ananthi, et al., 2022).

### 5. CONVERSION OF BIOMASS TO BIOFUEL

Converting biomass into biofuel involves several processes depending on the type of biofuel being produced. Biomass often undergoes pre-treatment to make it more amenable to the conversion process. This may involve physical, chemical, or biological methods to break down the complex structure and facilitate subsequent processing steps. Pre-treatment methods include drying, milling, grinding, chemical and biological treatment using enzymes or microorganisms. (Hossain al., 2019). Thermochemical conversion include pyrolysis in which

biomass is heated in the absence of oxygen to produce bio-oil, biochar, and syngas and gasification in which biomass is partially oxidized at high temperatures to produce syngas (a mixture of carbon monoxide and hydrogen), which can be further processed into liquid fuels like ethanol or diesel. Biomass can also be burned directly to produce heat or electricity. (Karimi-Maleh, et al.,2022). Biochemical conversion involves fermentation and anaerobic digestion using microorganisms. The biofuel can be separated from the reaction mixture and purified to remove impurities and water by common separation techniques such as distillation, filtration, and centrifugation. Further refining processes may be required depending on the type of biofuel produced. This can include processes such as hydrotreating, hydrocracking, or esterification to improve the quality of the biofuel and make it suitable for use in engines. (Karimi-Maleh, et al.,2022).

### **5.1. Thermochemical**

Thermochemical conversion of biomass involves the use of heat to transform biomass (organic materials derived from plants and animals) into useful products such as biofuels, chemicals, and heat or electricity. The processes are categorized into many methods, each with its own advantages and applications such as Pyrolysis, Gasification, Combustion, Torrefaction and Hydrothermal carbonization (HTC) (Wang & Wu, 2023).

#### **5.1.1. Combustion**

Combustion is the process of burning biomass in the presence of oxygen to produce heat, which can be used directly for heating or converted into electricity through steam turbines. While combustion is the simplest and most widely used thermochemical conversion method, it generates emissions such as carbon dioxide, nitrogen oxides, and particulate matter, which can be mitigated through advanced combustion technologies (Wang & Wu., 2023).

#### **5.1.2. Gasification**

Gasification converts biomass into a synthesis gas (syngas) composed primarily of hydrogen, carbon monoxide, and methane by reacting it with a controlled amount of oxygen and/or steam at high temperatures. Syngas can be used as a fuel for power generation or as a precursor for the production of chemicals and fuels like methanol and synthetic natural gas (SNG). (Bridgwater et al., 2008).

#### **5.1.3. Pyrolysis**

Pyrolysis involves heating biomass in the absence of oxygen to break it down into solid char, liquid biooil, and gases such as hydrogen, methane, carbon monoxide, and carbon dioxide. The produced bio-oil can be further upgraded to transportation fuels or used as a feedstock for various chemical processes. (Oyeleke et al., 2021).

#### **5.1.4. Liquefaction**

Liquefaction is a thermochemical biomass conversion technology that produces high-quality bio-oil in the presence of catalyst at high pressures and controlled reaction rates. The process is typically operated at pressures ranging from 1 to 20 MPa and temperature between 250 and 450°C. Compared to pyrolysis that produces a highly oxygenated bio-oil, liquefaction results in lower oxygen-containing biooil (Nanda et al., 2015). In liquefaction drying of the product is unnecessary unlike pyrolysis (Yufu Xu et al., 2011).

#### **5.1.5. Torrefaction**

Torrefaction is a mild pyrolysis process carried out at temperatures between 200°C and 300°C in the absence of oxygen. It removes moisture and volatile organic compounds from biomass, resulting in a dry, energy-dense material called torrefied biomass. Torrefied biomass has improved properties such as increased energy density, water resistance, and grindability, making it suitable for co-firing with coal or as a feedstock for gasification and combustion processes. (Ong et al.,2019).

#### **5.1.6. Hydrothermal Carbonization (HTC)**

Hydrothermal carbonization is a wet thermochemical process that converts biomass into a carbon-rich solid called hydrochar by treating it with hot, pressurized water at temperatures typically ranging from 180°C to 250°C. HTC can process a wide range of biomass feedstocks, including wet and waste materials, and the resulting hydrochar can be used as a solid fuel, soil amendment, or precursor for activated carbon production (Ong et al.,2019).

## 5.2. Biochemical

Biochemical conversion of biomass involves utilizing biological processes, such as fermentation or enzymatic hydrolysis to break down complex biomass and then converted them into useful products such as biofuels, biochemicals, or other value-added products (Hakeem et al., 2023). These biochemical conversion processes offer environmentally sustainable alternatives to conventional fossil fuel-based processes and can contribute to reducing greenhouse gas emissions and dependence on finite fossil resources. However, challenges such as cost-effectiveness, technological and scalability are the major constraint of this process. Other advantages of biochemical process over thermochemical process include, low cost of production, effective pretreatment process, improved fermentative enzymes, lignin utilization, recycling of enzymes and use of cost-effective bioreactor design (Patinvoh & Taherzadeh, 2019). Pretreatment, hydrolysis, fermentations and purification are the basic stages in biochemical conversion of biomass into biofuel as shown in Figure 1 (Avci et al., 2013; Hakeem et al., 2023).

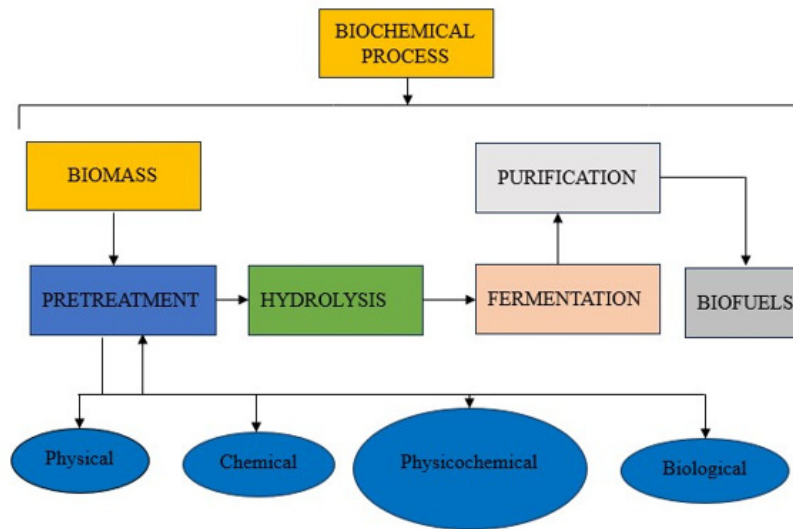


Figure 1: Biochemical process for biomass conversion to biofuels

### 5.2.1. Pretreatment

Pretreatment is crucial in biochemical conversion processes in order to expose the physical and chemical biomass of lignocellulose to make the cellulose polysaccharide more accessible for the enzymatic degradation (Kumar et al., 2009). Pretreatment is actually the process with an objective of removing the recalcitrant barriers of biomass by altering its indirect factors such as pore size and volume, particle size, and specific surface area and improving direct factors such as accessible surface area to enhance the cellulose accessibility to enzymes that would degrade carbohydrate polymers into simple sugars. Also, a partial or complete removal of hemicelluloses and/or lignin would help in improving the hydrolysis of cellulose (Qian, 2013). Pretreatment is categorized in to four main categories these include physical, chemical, physicochemical and biological pretreatment (Tomás-Pejó et al., 2011; Soudham, 2015). Severity factor is used to assess the effect of various pretreatment techniques as indicated in Equation (1) (Saha et al., 2015; Soudham, 2015).

$$SF = \text{Log} [t \exp ((T - T_{ref})/14.75)] \quad (1)$$

Where SF = Severity factor, t = Holding time of Treatment (minute), T = Treatment temperature,  $T_{ref}$  = Reference temperature that is 100°C and 14.75 = Empirically determine constant.

Other factors for the assessment of effect of various pretreatment techniques includes: Enzymatic digestibility of pretreated solids, Sugars degradation, Inhibitors, cost effective, Sugar concentrations, Fermentation compatibility of hydrolysates, Lignin recovery and Heat and power requirements (Soudham, 2015).



### **5.2.1.1. Physical Pretreatment**

Physical pretreatment such as mechanical comminution, extrusion, microwave irradiation, liquid hot water, pyrolysis, torrefaction, freezing, pulsed electric field and ultrasonic pretreatment (Peral, 2016) are among the various physical pretreatment used in biofuel production. The objective of physical pretreatment is to increase surface area and reduce particle size of lignocellulosic materials and also it leads to decrease degree of polymerization and de- crystallization of feedstock (Tomás-Pejó et al., 2011).

#### **5.2.1.1.1. Mechanical comminution**

Mechanical comminution pretreatment Coarse size reduction, cutting, shredding, chipping, grinding, or milling are among the different mechanical comminution methods that can be used to reduce the particle size and crystallinity of lignocellulose in order to increase the specific surface area and reduce the degree of polymerization (Tomás-Pejó et al., 2011). there is different equipment used for mechanical comminution this include feeders, conveyors, separators, hopper, washer, chipper (Arora et al., 2018). However, also there are different type of mills used to break down the lignocellulosic material and reduce the material's crystallinity which include attrition mills, ball mills, centrifugal mills, colloid mills, hammer mills, extruders, knife mills, pin mills and vibratory mills (Amin et al., 2017).

#### **5.2.1.1.2. Extrusion**

Size reduction is one of the most effective methods for increasing the enzymatic accessibility to lignocellulose. However, many of the physical methods for size reduction (milling, grinding, etc.) are not economically feasible because a very high-energy input is required. In this context, extrusion is a novel and promising physical pretreatment method for biomass conversion to ethanol production. In extrusion, materials are subjected to heating, mixing, and shearing, resulting in physical and chemical modifications during the passage through the extruder. The extruder has many advantages such as the ability to provide high shear, rapid heat transfer, and effective and rapid mixing (Tomás-Pejó et al., 2011). Main advantages of this method include short residence time, moderate temperature, no formation of inhibitors such as furfural or 5-hydroxymethylfurfural (HMF), no need of washing step, no solid loss, rapid mixing, feasibility of scale-up, and possibilities of continuous operation (Peral, 2016).

#### **5.2.1.1.3. Microwave irradiation**

Microwave irradiations increase the physical, chemical, and biological processes by generation of heat from electric and magnetic components, and the performance of this method is influenced by dielectric properties of lignocelluloses (Rastegari et al., 2019). lignocellulose materials required energy to break the hydrogen bonds in order to improved polysaccharides hydrolysis, the irradiation treatment will be employed (Qian, 2013; Soudham, 2015). This process is effective only under lab conditions but not effective in potential industrial projects (Rastegari et al., 2019).

#### **5.2.1.1.4. Liquid hot water pretreatment**

Liquid hot water pretreatment. Concept: solvolysis, hydro thermolysis, aqueous fractionation, and aqua Solv are all terms that have been used to describe the use of liquid hot water for biomass pretreatment. Liquid hot water pretreatment uses water in the liquid state at elevated temperatures instead of steam. Liquid hot water pretreatment results in hemicellulose hydrolysis and removal of lignin, rendering cellulose in the biomass more accessible while avoiding the formation of fermentation inhibitors that occur at higher temperatures (Agbor & Cicek, 2011).

#### **5.2.1.1.5. Pyrolysis**

Pyrolysis is another physical pretreatment method which leads to rapid decomposition of lignocellulosic materials to gaseous products and residual char at above 300 °C. The high rate of biomass decomposition can be achieved at a lower temperature when zinc chloride or sodium carbonate is used as a catalyst (Rastegari et al., 2019).

#### **5.2.1.1.6. Freezing**

Freezing or thaw pretreatment is a new method for physical pretreatment of biomass. In this process, biomass is frozen in a straight freezer at temperature below  $-20^{\circ}\text{C}$  from 2 to 24 hours and then immediately melted in hot water or at room temperature. This method favors enzyme digestibility of substrates for the pretreatment of

lignocellulosic biomass. Few studies have been carried out, its limitations are it is cost and its advantage is it is environmentally friendly because less released of dangerous chemicals (Peral, 2016).

#### **5.2.1.1.7. Pulsed electric field**

Pulsed electric field pretreatment is a physical pretreatment of lignocellulosic biomass that involves the application of a short burst of high voltage to a sample (biomass) situated between two electrodes. The sample can be either placed or transported between the electrodes, and the electric discharge is applied in the form of pulses. High intensity electric field produced structural changes in the cell membrane, resulting in an increase in mass permeability and mechanical rupture (Peral, 2016).

#### **5.2.1.1.8. Ultrasound**

Ultrasound pretreatment is used to remove lignin from biomass in solution, lignin is a chemical compound that binds cellulose and hemicellulose together in plant cell walls. Commonly, enzymes or chemicals are used to remove it from biomass and allowed the freed sugars to be dissolved for further processing in to biofuel. This method is highly important which could remove lignin and sugars dissolve in minutes rather than in hours with the traditional methods (Oliveira et al., 2018).

#### **5.2.1.2. Chemical pretreatment**

Chemical pretreatment methods include acid pretreatment, alkali, organosolv, ozonolysis, peroxyformic acid and peroxide pretreatment (Tomás-Pejó et al., 2011; Soudham, 2015; Peral, 2016). The main advantage of chemical pretreatment is that 95% of lignocellulose material can be converted to soluble sugars and also improvement of hydrolysis of cellulosic fractions to glucose in the impending enzymatic process (Soudham, 2015). The main drawback of this method is the production of various inhibitors compounds for microorganisms which increasing overheads by requiring a detoxification step (Panahi et al., 2020).

#### **5.2.1.3. Physicochemical pretreatment**

Physicochemical is dependent on the joint action of both physical and chemical processes. The physicochemical pretreatment methods including wet oxidation, ionic liquids (ILs), ammonia fiber explosion, sulfite pretreatment to overcome recalcitrance (SPORC), supercritical fluid and steam explosion are been used to treat lignocellulose biomass as describe by (Mood.H. & Tabatabaei M., 2013; TomásPejó et al., 2011). (Tomás-Pejó et al., 2011) describe physiochemical pretreatment in details also Peral, 2016 and Soudham *et al.*, 2015 explained this method of pretreatment in details. Combined methods of lignocellulose pretreatment were carryout by many researchers in order to get the best pretreatment method, the combined pretreatment method include alkaline pretreatment and gamma irradiation, alkaline and mechanical pretreatment, alkaline pretreatment and wet oxidative pretreatment, combinatorial biological pretreatment (Peral, 2016), also (Mood & Tabatabaei, 2013) explained the combined pretreatment like Combination of alkaline and dilute acid pretreatments, Combination of alkaline and IL pretreatments, Combination of dilute acid and steam explosion pretreatments, Combination of supercritical CO<sub>2</sub> and steam explosion pretreatments , Combination of organosolv and biological pretreatments (bio-organosolv), Combination of biological and dilute acid pretreatments, Combination of biological and steam explosion pretreatment, Microwave-assisted alkali pretreatment, Combination of dilute acid and microwave pretreatment and Combination of IL and ultrasonic pretreatment (Mood & Tabatabaei, 2013).

#### **5.2.1.4. Biological pretreatment**

In this method of pretreatment, the use of lignocellulose degrading microorganism, commonly brown, rot, white and soft rot fungi, can be applied for decomposition of lignocellulose through the action of enzymes such as laccase and peroxidase. Since these fungi can also decomposition lignocellulose, cellulase-less mutant with ability for selective degradation of lignin was developed. The hydrolysis is very slow with this method (Tomás-Pejó et al., 2011). The advantages of biological pretreatment include low energy demand, mild environmental conditions, and no chemical requirement (Peral, 2016; Sindhu et al., 2016).

### 5.2.2. Hydrolysis

Hydrolysis simply means the chemical break down of a biomass compound with the reaction of water. The conversion of cellulose and hemicellulose can be expressed by the reaction of glucan (for hexoses) and xylan (for pentose) with water as shown in the Equations (2) and (3).



The maximum theoretical yield of hexoses and pentoses is 1.136 kg and 1.111 kg per kg of glucan and xylan, respectively (Kang et al., 2014). Under this pretreatment two methods are employed viz: acid hydrolysis and enzymatic hydrolysis (Patinvoh & Taherzadeh, 2019).

#### 5.2.2.1. Acid hydrolysis

Biomass can be treated with mineral acid such as  $H_2SO_4$  or  $HCl$  at low temperature and high acid concentrations. Hydrolysis of hemicellulose will release the sugars in to hydrolysate and leaving worthy lignin in the solid phase (Peral, 2016). When dilute acid hydrolysis is used a subsequent enzymatic hydrolysis is needed but this is not required for concentrated acid hydrolysis (Patinvoh & Taherzadeh, 2019). The disadvantages of acid hydrolysis include: high pressure and temperature needed, cellulose hydrolysis is not effective, formation of inhibitors and equipment corrosion (Soudham, 2015).

#### 5.2.2.2. Enzymatic hydrolysis

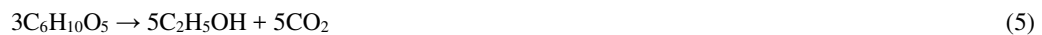
Enzymatic or biological hydrolysis is carried out using enzymes as a catalyst to hydrolyze the lignocellulose biomass compound (cellulases and hemicelluloses) with water to release monomeric pentose and hexose sugars from cellulose, and hemicellulose, respectively. Considering many advantages, enzymatic hydrolysis is regarded as the most attractive way over concentrated acid hydrolysis. Due to the complex chemical structure of lignocellulose, multiple enzymes are often needed for the degradation of its carbohydrate polymers. For instance, cellulose is hydrolyzed by a mixture of cellulose enzymes and hemicellulose is hydrolyzed by the action of different hemicelluloses e.g., xylenes, manganese, and others (Kumar et al., 2009).

##### 5.2.2.2.1. Constituents of lignocellulose biomass hydrolysate

The constituents of lignocellulose biomass after hydrolysis are glucose from cellulose and arabinose, galactose, glucose, mannose and xylose from hemicelluloses (Patinvoh & Taherzadeh, 2019).

### 5.2.3. Fermentation

Fermentation is the biological process to convert the sugar rich lignocellulose hydrolysates such as hexoses (C6) and pentoses (C5) obtained from pretreatment and enzymatic hydrolysis to biofuel using different types of microorganisms, such as bacteria, yeast, or fungi as depicted in Equations 4 and 5 (Kang et al., 2014).



#### 5.2.3.1. Fermentation technology

Fermentations can be performed either in batch, fed-batch or continuous modes operation as explained by Lugani et al., 2019.; Rastegari et al., 2019.

#### 5.2.3.2. Fermentation process

Fermentation process can be carried out by one of the processes either by Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), Consolidated Bioprocessing (CBP) or Simultaneous Saccharification and Co-fermentation (SSCF) as explained by (Rastegari et al., 2019).

#### 5.2.3.3. Methods of minimize inhibition problems in fermentation processes

Several approaches have been used by researchers to minimize inhibition problems in fermentation processes to increase strain robustness, improve existing metabolic pathways, and reduce capital investment and production

costs. The approaches include Detoxification approach, Genetic modification approach and High cell-density approach (Patinvoh & Taherzadeh, 2019).

#### **5.2.3.3.1. Detoxification approach**

Detoxification is a general method for removing inhibitors from lignocellulosic hydrolysate so that the fermenting microbes can easily access the available sugars leading to increased fermentation rate. Different detoxification methods have been investigated prior to the fermentation process, such as enzyme treatment (laccase and peroxidase), alkaline treatment [ $\text{Ca}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$  and  $\text{NaOH}$ ], liquid-liquid extraction (supercritical  $\text{CO}_2$ , ethyl acetate, trialkylamine), solid-liquid extraction (activated carbon treatment, ionexchange, lignin), and microbial treatment (Patinvoh & Taherzadeh, 2019).

#### **5.2.3.3.2. High cell-density approach**

The activity of yeast cells during fermentation of lignocellulose hydrolysate can be improved by increasing the concentration of the cells in the bioreactor. This approach will result in a very high fermentation rate, thereby improving productivity, minimizing the risk of contamination, possibility of operation beyond the washout rate, and easy recycling and recovery of cells, thereby aiding downstream processing in continuous, fed-batch, and batch reactors. Several techniques for increasing cell density during the fermentation process have been demonstrated, such as flocculation, encapsulation, sedimentation, surface adsorption (zeolite, bentonite, kaolinite, sands, silicates, carbonates, and phosphates), and the use of membrane bioreactors. Some of these techniques have been reported suitable for application on an industrial scale (Patinvoh & Taherzadeh, 2019).

#### **5.2.3.3.3. Genetic modification approach**

Realizing a high ethanol yield from lignocellulose hydrolysate required the use of strains that can metabolize hexoses and pentose, tolerate inhibitors, retard contaminants, and releases rare byproducts. There is no single strain that meets this entire requirement, hence, the need for genetic modifications to achieve desired properties in ethanol-producing strains. This strategy allows integration of recombinant gene while retaining gene expression for optimum ethanol production; this circumvents limitations of potential fermentative microorganisms (Patinvoh & Taherzadeh, 2019).

#### **5.2.4. Purification**

The fermentation by-products such as starch (esters, organic acids, and higher alcohols) and lignin (cyclic and heterocyclic compounds) are obtained after fermentation process. These by-products must be rid out in order to obtain pure biofuel, with the help of one of the following purification processes which include distillation, adsorption, ozonation and gas stripping (Onuki *et al.*, 2008). The solid residual unreacted products such as lignin, cellulose, hemicelluloses, enzymes, microorganisms, and ash can be further collected from the bottom of the distillation column and processed into other fuels (De Bhowmick *et al.*, 2023). The biofuel can be analysed by the following which include Gas chromatography, High performance liquid chromatography, infrared spectroscopy, and Olfactometry as explained by (Shinnosuke *et al.*, 2023).

### **6. DEGRADATION PRODUCTS OF LIGNOCELLULOSE PRETREATMENT**

Pretreatment of lignocellulose biomass may produce degradation products (inhibitors), mostly from sugars and lignin, such as Furan aldehyde (furfural and 5-hydroxymethyl furfural), Organic acids (acetic acids, formic acids, levulinic acids) and phenolic compounds (4-hydroxybenzaldehyde, vanillin, 4-hydroxybenzoic acid, dihydroconiferyl alcohol, syringic acid and coniferyl aldehyde). Presence of these compounds affects both saccharification and fermentation steps in the bio-conversion of lignocellulose (Panahi *et al.*, 2020). Using acid catalyst for pretreatment at high temperatures, pressure and longer residence time (reaction time) are responsible for degradation product such as furanlaldehydes from cellulose and hemicellulose sugars while aldehydic, aromatic, phenolic, and polyaromatic compounds are degradations from lignin as studies shown.

#### **6.1. Methods in Preventing Inhibitory Problems in Lignocellulose Pretreatment**

Different methods have been studied to overcome inhibitors formation in the pretreatment products, these include the use of chemical additives, microbial treatments, enzymatic treatments, heating and vaporization, liquid-liquid extraction, and liquid-solid extraction (Soudham, 2015). Physical treatments such as evaporation is used to

eliminate volatile compounds which include acetic acid, furfural and vanillin but this method has disadvantages that is high energy requirements and the nonvolatile product will not be eliminated and they remain in the hydrolysates. After evaporation then adsorption will follow where activated charcoal will be used removed acetic acid, formic and levulinic acids as well as HMF and furfural (Soudham, 2015). Chemical treatment include treatment with hydrogen peroxide ( $H_2O_2$ ) and ferrous sulphate ( $FeSO_4$ ), Alkaline treatments ( $NH_4(OH)$ ,  $Ca(OH)_2$ , and  $NaOH$ ), Use of reducing agents (sodium sulphite, sodium dithionite, dithiothreitol (DTT), and sodium borohydride) and other techniques such as Liquid-solid extraction, Use of surfactants (fatty acid esters of sorbitan polyethoxylates, polyethylene glycol) and Ion exchange resins. Biological detoxification Several biological methods including treatment with enzymes such as laccases or use of the natural or targeted genetic engineered micro-organism are proposed to overcome the inhibitory effects of pre-treated lignocellulose materials. Micro-organisms, such as some species of yeasts (Soudham, 2015).

## 7. ADVANTAGES AND LIMITATIONS OF BIOFUELS

### 7.1 Advantages

Biofuels have the following advantages High-quality fuel, less emission of greenhouse gases (GHGs), Less pollution to the planet, Process is biodegradable and environmentally friendly, can be easily distributed with mild modifications to existing infrastructure, Reduced use and import of fossil fuels, add jobs to the economy, Renewable source of energy and contributes to sustainable development and No need of changes on existing engines and keeps the engine running for longer (Patinvoh & Taherzadeh, 2019).

### 7.2. Limitations

The limitations of biofuels are as follows: High cost of production, Enhances the use of genetically modified plants, Requirement of large quantities of water to irrigate biofuel plants, Formation of monoculture, resulting in loss of biodiversity, Use of edible crops in first-generation biofuels can have negative impacts on agriculture and food industry, The cost of biofuel production is governed on the type of raw material which is sometimes greater than the price of fossil fuel production and Contamination of water and soil due to intensive cultivation of biofuel crops (Rastegari et al., 2019).

## 8. CONCLUSION

Lignocellulosic materials are vast sustainable substrate that can be processed into biofuels and other useful products. This review paper focused mainly on thermochemical and biochemical conversion of biomass to biofuels. Energy conversion using thermochemical, and biochemical conversion processes produce fuels such as bioethanol, biobutanol, biomethane, biohydrogen and biodiesels. Additionally, the paper highlighted the advantages and disadvantages of each of the processes for the conversion of biomass to biofuel. Thermochemical and biochemical method of lignocellulose pretreatment offers significant advantages in terms of efficiency, versatility, mild reaction conditions and improved enzymatic digestibility which can easily be integration with biorefinery concepts. The formation of inhibitory compounds such as furfural, hydroxymethylfurfural (HMF), and organic acids is the major disadvantage of thermochemical and biochemical method of lignocellulose pretreatment which may increase the cost of production and reduction of the efficiency of biofuel production. However, using detoxification strategies such as the use of activated charcoal adsorption, choosing appropriate catalyst or liquid-liquid extraction during the pretreatment process can help remove or neutralize the inhibitory compounds. Adoption of this suitable pretreatment techniques and the accessibility of these easily obtained local raw materials will enable significant production of biofuels and other important products,

## 9. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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