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VALORISATION OF LIGNOCELLULOSIC BIOMASS TO BIOFUELS, BIOPRODUCTS AND BIOCHEMICALS: PAVING THE PATHWAY TOWARDS CIRCULAR ECONOMY

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INTRODUCTION

Rapid growth in the world's population, along with vast global industrialisation, has prompted the rise in consumption of fossil fuels followed by increase in pollution and issues related to climate change. In light of the pressing needs to provide alternatives to fossil fuels, there has been a surge of interest in lignocellulosic biomass, which is a renewable feedstock that does not contribute to carbon emissions. Lignocellulosic biomass can be converted to various products such as biofuels, paper products, nanocellulose, biochemical etc. Global production of lignocellulosic biomasses is approximately 181.5 billion metric tonnes per year (Dahmen et al. 2019, Ashokkumar et al. 2022). The high production rate coupled with its low price, lignocellulosic biomass is a potentially viable yet sustainable material for use in development of value-added products and energy generation towards achieving a circular economy. Lignocellulosic biomass must be managed efficiently according to the concept of reuse and recycle, which focuses on product retrieval and restoration for each product's life cycle (Blades et al. 2017, Velvizhi et al. 2022a).

SOURCES AND PROPERTIES OF LIGNOCELLULOSIC BIOMASS

The most prevalent sources of lignocellulosic biomass, either as a crop or as a residue, are woody crops and herbaceous plants. In addition, forest and agricultural residues (e.g. oil palm residue, rice straw, sugar cane bagasse, saw dust), energy crops, municipal organic wastes, and industrial wastes (e.g. waste paper, pulp) are some of the examples of the major source of lignocellulosic biomass. It mainly consists of cellulose (35-50%), hemicellulose (20-35%), lignin (10-25%) (Ning et al. 2021) and relatively small amount of extractives, proteins, pectin and inorganic matters (Bhowmick et al. 2018; Goswami et al. 2022). These components vary according to the type and source of lignocellulosic biomass. Table 1 depicts the common lignocellulosic biomass and its major composition.

Table 1 Compositions of various common lignocellulosic biomass (adopted from Ning et al. 2021)

Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood			
Hardwood stem	40–55	24–40	18–25
Poplar	42–49	16–23	21–29
Eucalyptus	34–51	9–30	21–39
Acacia	35–47	31	23–31
Softwood			
Softwood stems	45–50	25–35	25–35
Pine	34–46	20–35	26–34
Spruce	25–47	10–21	32–35
Crop residues			
Rice straw	36–47	16–35	6–36
Sugarcane bagasse	38–45	17–33	4–36
Grasses			
Miscanthus	40–53	18–26	20–27
Bamboo	37–47	17–19	26–39

Polysaccharides (cellulose, hemicellulose) and aromatic polymer lignin which make up 75% of lignocellulose content are mainly found in the secondary cell wall of plant. Cellulose $(C_6H_{10}O_5)_n$, a high molecular weight linear homopolymer is composed of repeating units of β-D-glucopyranosyl linked by β-(1,4) glycosidic bonds. The glucose monomer is polymerised into long chain of cellulose through van der Waals, intra- and intermolecular hydrogen bonds. The strong hydrogen bond networks formed by hydroxyl groups in cellulose lead to the stiffening of the cellulose chain and cellulose insolubility in many common solvents. The strong axial stiffness of cellulose and insolubility is also due to the arrangement of highly ordered crystalline and disordered amorphous regions in cellulose microfibrils. Due to its inherent characteristics such as hydrophilicity, reactive hydroxyl groups and biocompatibility, cellulose is used as a flexible material for applications in films, composites, fibres, fuels and chemicals (Ashokkumar et al. 2022).

Hemicellulose is a short-chain heteropolymer which consists of varying sugars of C_5 and C_6 such as xylose, arabinose, glucose, galactose, rhamnose and fructose. The content of these sugars varies based on the type of lignocellulose biomass. Hemicellulose structure differs from cellulose where it has branched chain and acetyl group. Due to its amorphous and random nature, and the inability to form crystalline structure by hydrogen bond networks, hemicellulose is easier to be hydrolysed compared to cellulose. Pre-treatment process is essential to release hemicellulose before being used in any product development. Hemicellulose is used in various applications such as hydrogels, cosmetics and drug carriers in biomedical fields (Ashokkumar et al. 2022).

Lignin, an aromatic and water insoluble polymer, acts to maintain the structural integrity of plants. Lignin is the most challenging component to be extracted from lignocellulosic biomass as it is highly recalcitrant and bonded by hydrogen and covalent bonds. The properties of lignin are influenced by the composition of its three monolignols (phenyl polymer) namely p-coumary alcohol, coniferyl alcohol and sinapyl alcohol. The monolignols make up of three primary units namely syringyl, guaiacyl and hydroxyphenyl group. The difference in the composition affects the delignification (extraction of lignin) of lignocellulosic biomass. The higher composition of lignin requires more chemicals and energy to remove it.

The intricate structure of cellulose, hemicellulose, and lignin makes them chemical and biologically resistant. The reasons are believed to be due to the poor accessibility of cellulosic fibre (connected by glycosidic bond) and the presence of hemicellulose and lignin that hampers chemical or biological substrate's access to cellulose. Hemicellulose is the easiest of the three to hydrolyse, followed by cellulose. Different pre-treatment techniques must be employed in lignocellulosic biomass valorisation to remove trapped polysaccharides in the conversion to value-added products.

PROCESSING TECHNOLOGY

Lignocellulosic biomass is subjected to different processing steps or pre-treatments depending on the type of product. Generally, pre-treatment modifies the biomass' physical, chemical, and rheological properties, resulting in a suitable substrate for further product development. In particular, pre-treatment aims to disrupt the lignin bond, removal of hemicellulose, and obtaining full access to the cellulose in the plant cell wall (Velvizhi et al. 2022b). The following characteristics must be taken into consideration for an effective pre-treatment (Bhowmick et al. 2018):

i) Energy minimisation
ii) Reduction in biomass particle size
iii) Low cost of catalyst
iv) Costs related to biomass, downstream processing, operating and capital must be balanced
v) Minimising formation of degrading product that inhibits the growth of fermentative microorganism

Pre-treatments can be classified into physical, chemical, biological or a combination of them (Figure 1). Each pre-treatment has its own advantage and disadvantage. Individual pre-treatment will not be sufficient in accommodating for all the lignocellulosic biomass feedstock. Therefore, a combination of two or three pre-treatment techniques could be adopted to improve the overall process efficiency, or lowering the energy requirement and overall costs. Physical pre-treatment techniques include mechanical comminution (e.g. ball milling, compression milling), extrusion, microwave, ultrasounds etc. Physical techniques will reduce not only the size of the particles, but also the degree of polymerisation and crystallinity, which will make the next process easier (Velvizhi et al. 2022b). A combination of physical and chemical pre-treatments (physico-chemical) leads to techniques such as steam explosion, ammonia fibre expansion (AFEX), wet oxidation etc. Steam explosion is an effective and economical technique as it only uses water without any catalyst. In this process, both mechanical force and chemical are employed to cleave the biomass. A novel technique known as sulfite pre-treatment to overcome recalcitrance of lignocellulose (SPORL) has been established. SPORL is reported to be able to dissolve partial lignin and all hemicellulose, and reduces cellulose depolymerisation through lignin sulfonation (Ning et al. 2021). Another recent advancement in pre-treatment is the usage of deep eutectic solvent. Deep eutectic solvent is a promising new green solvent that has similar physical and chemical properties with ionic liquids but has lower melting point, increased stability and is much cheaper (in terms of their starting material) (Mbous et al. 2017). In biological pre-treatment approach, the use of enzyme and microbes is considered as an eco-friendly method that can reduce energy consumption.

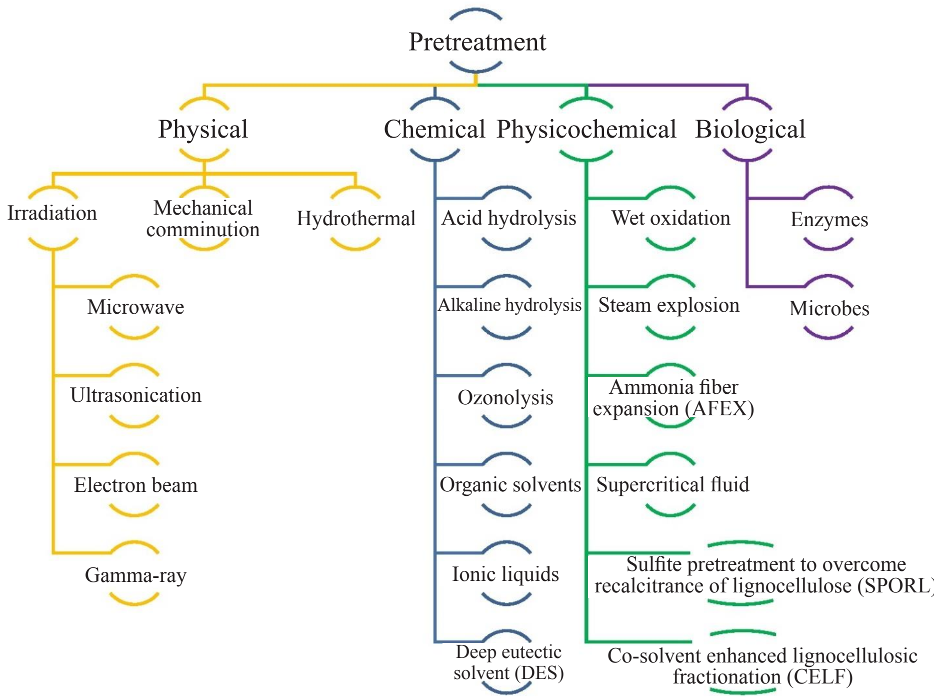

Figure 1 Pre-treatment of lignocellulosic biomass (adopted from Ning et al. 2021)

Thermochemical pre-treatment techniques such as pyrolysis, torrefaction, gasification, hydrothermal treatment and combustion are able to convert biomass into heat and electricity as well as various products such as chemicals, gaseous or liquid fuel precursor. Thermochemical processing is categorised according to their associated oxidation environment, particle size, and heating rate whether in an oxygen-free environment or full oxidation (Tanger et al. 2013).

USES AND POTENTIAL USES OF LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass can be converted into diverse products, namely cellulose-based, hemicellulose-based, lignin-based and glycerol-based products. Figure 2 shows the overview of lignocellulosic biomass valorisation and Figure 3 illustrates further details on the product derivation from lignocellulosic biomass.

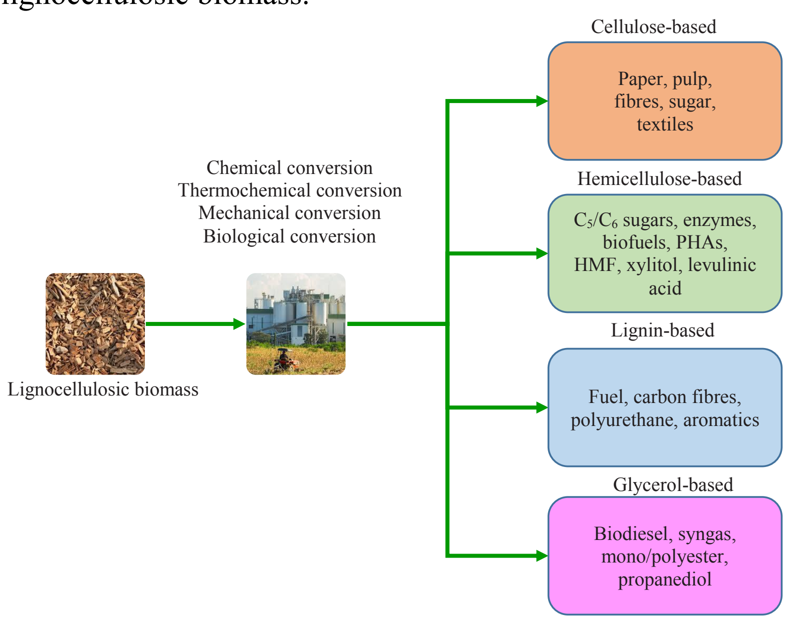

Figure 2 Overview of value-added products from lignocellulosic biomass (adopted from Culaba et al. 2022)

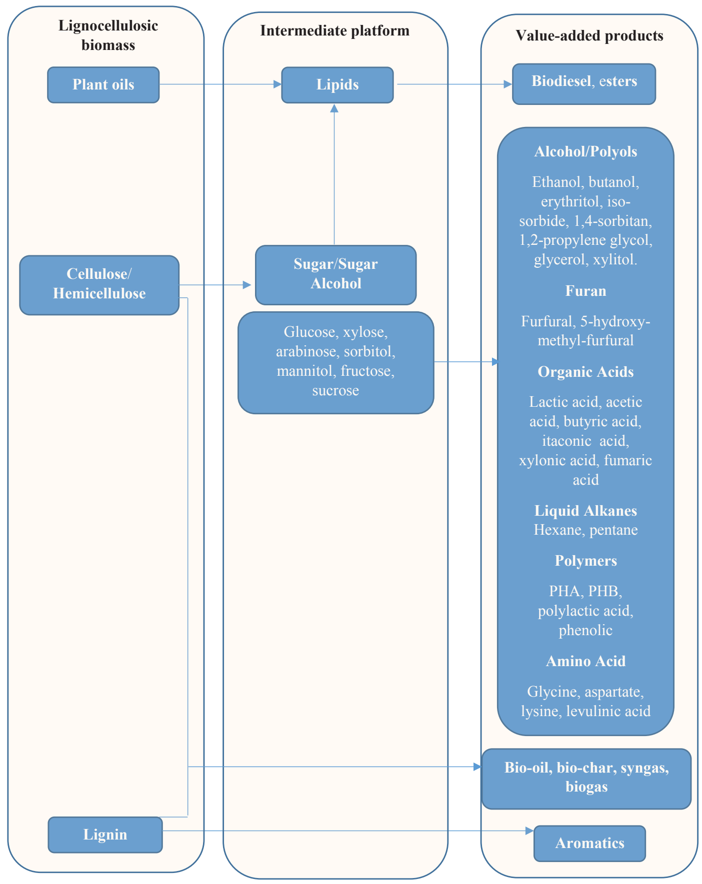

Figure 3 Details on derivation of value-added products from lignocellulosic biomass (adopted from Ning et al. 2021)

Cellulose-based products

Cellulose is traditionally used in papermaking where lignocellulosic biomass undergoes several processing steps such as alkaline pulping, bleaching and papermaking processes, to produce various pulp and paper products. Of late, nanocellulose (nanostructured cellulose) is receiving widespread interest as it can be produced from any type of lignocellulosic biomass and possesses unique properties (e.g. high surface area, exceptional mechanical strength, low toxicity). Given its remarkable properties, nanocellulose could be used as strength additive, rheology modifier, drug carrier, thin film in wide range of applications, including pharmaceutical, automotive, cosmetic, packaging, energy storage and many others.

Apart from paper products, cellulosic textile can also be produced from lignocellulosic biomass such as viscose, rayon, acetate etc. In the production process, wood pulp is converted to regenerated cellulose by the use of several chemicals to produce fibres. They are then knitted or woven to produce fabrics.

Sugars can also be isolated from cellulose for production of biofuels especially bioethanol and biobutanol. Nevertheless, it involves complicated and multiple steps such as pre-treatment and fractionation to extract cellulose followed by saccharification and microbial fermentation. The fermentable sugar is a substrate for the manufacture of biofuels as well as other bioproducts, including organic acids e.g. acetic, lactic, gluconic, itaconic, butyric acids, polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB) or polyesters (Karp et al. 2021). Other chemicals such as hydroxymethylfurfural (HMF) and levulinic acid can also be produced via chemical route in acidic medium.

Hemicellulose-based products

Pre-treatment via dilute acid hydrolysis releases hemicellulosic sugars i.e. pentose, fermentable substrate for microbial growth and metabolite production. Pentose-rich substrate requires certain microorganism that is capable of converting the sugar into biofuel. Fermentation of pentose-rich substrate can also lead to the production of organic acids.

Catalytic hydrogenation of xylose produces xylitol, a five carbon polyalcohol sugar used in various applications, specifically in pharmaceutical and food industries (Karp et al. 2021). Biological pathway can also be applied to transform xylose to xylitol using various strains. Fermentation of xylose produces bioethanol, xylonic acid, PHA, PHB etc. Subjecting the sugar under acid process via chemical route leads to sugar dehydration, thus producing furfural and formic acid.

Sugar oligomers, especially xylooligosaccharides, are made up of xylose units. The biomolecule is produced via chemical, enzymatic or combination of both processes. These sugar oligomers have been reported to possess distinct biological activity such as antioxidant, anticancer, antimicrobial etc. (Karp et al. 2021).

Lignin-based products

Bio-oil is a product from pyrolysis or liquefaction of lignocellulosic biomass. Pyrolysis involves heating lignocellulosic biomass at atmospheric pressure and in an inert environment. Besides bio-oil, pyrolysis produces other products such as bio-char and gas. Lignin bio-oil can be generated using various techniques such as fast pyrolysis, oxidative degradation, and heterogeneous catalyst conversion among others.

Carbon fibre is commonly produced with polyacrylonitrile as precursor. It is a lightweight material and has excellent mechanical properties. Carbon fibre can also be produced from lignin, thus reducing the manufacturing cost.

Polyurethane can be produced from lignin by modifying the surface of lignin through esterification or etherification process. Vanillin can also be obtained from lignin by oxidation process and it is used for various applications in food and cosmetic industries.

LIGNOCELLULOSIC BIOMASS VALORISATION FOR CIRCULAR ECONOMY

Circular economy is a concept in which every resource is used in a closed loop and waste is minimised and valorised. The goal is to manufacture value-added products using zero waste biorefinery approach, that is comparable to the fossil-based refinery. Hence, introducing lignocellulosic biomass as a feedstock is an effective resource management. It can maximise the value of lignocellulosic biomass and minimising the waste loss within the entire value chain (Clark et al. 2016). Lignocellulosic biomass valorisation could be implemented in the framework of circular economy concept by converting the biomass into various intermediate products via integration of suitable and cost effective processing techniques followed by transformation into value-added end products. At the end of each product's cycle, it is retrieved, reused and recycled into the value chain. Highly integrated biomass strategy is needed to ensure maximum resource utilisation and energy efficiency whilst minimising environment impact.

CONCLUSIONS

The valorisation of lignocellulosic biomass is essential for the production of value-added products from sustainable source, ranging from biofuels, industrial bioproducts to biochemicals. Lignocellulosic biomass is an effective feedstock for biorefinery in order to capitalise the biomass value to its fullest extent. Ultimately, suitable process integration is important to enhance the efficiency and cost effectiveness in the production of value-added products from the conversion of lignocellulosic biomass.

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Climate change issue has resulted in a considerable push from authorities and society to shift dependency from fossil fuels to renewable biomass. Lignocellulosic biomass is a sustainable bioresource and can be an alternative to fossil fuels. Lignocellulosic biomass from renewable feedstock can be used for production of various biofuels, bio-based products and bio-based chemicals. This article aims to give a brief overview on the valorisation of lignocellulosic biomass for energy generation and production of value-added products.

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