



# A review on the pretreatment of lignocellulose for high-value chemicals



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## ABSTRACT

Pretreatment is an important process to transform lignocellulosic biomass to high-value chemicals. This process potentially provides economic sustainability, which is challenged by energy crisis and environmental pollution. Pretreatment is mainly applied to improve the digestibility of cellulose by increasing enzyme accessibility. Different lignocellulosic biomasses require various pretreatment processes and conditions depending on process configurations selected for subsequent hydrolysis and fermentation steps. In this article, studies on the pretreatment of lignocellulose for high-value chemicals were reviewed. The relative advantages of various pretreatment processes, including physical, chemical, physicochemical, and biological methods, were also assessed in economic perspectives. Existing problems and development potential were also discussed. This review provides a theoretical basis for future research on lignocellulosic biomass for chemical applications.

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## 1. Introduction

With the rapid development of our society, the current environmental, economic and social concerns regarding sustainability energy have pushed researchers toward finding new cleaner, renewable and sustainable energy resource [1,2]. As we all know that fossil fuels are commonly used nonrenewable and can cause negative effects on the environment with posing new risks to humans [3,4], which can no longer satisfied the demand of various chemicals for us. However, in contrast to fossil fuels, lignocelluloses which commonly obtained from four major source (forest residues (woods, branches, foliage, etc.), agricultural residues (corn stover, rice straw, etc.), energy crops (switch grass, yellow poplar, etc.), and cellulosic waste (such as municipal solid waste and food waste) is an abundant and cost-effective renewable resource with production of  $15\text{--}17 \times 10^{10}$  Mt. annually [5–10]. And most of it can be converted into various different forms high-value chemicals such as ethanol fuels, bio-oil, acids, saccharides, phenols, aldehydes, xylitol, and cellulose acetate, which is correlated with sustainability and low-carbon life (Fig. 1) [11–18]. It has a good application prospect for alleviating energy and environmental deterioration to improve economic and social sustainability. However, majority lignocellulosic biomasses are discarded or combusted directly up to now, which not only be wasted, but also cause pollution to environment [5, 19]. United Nations Conference on Environment and Development (UNCED) predicted that the utilization of biomass resource may reach half of the total resource usage in the world by 2050 [20].

Biomass is the most logical carbon-based feedstock obtained from living organisms such as plants, animals, and microorganisms [10]. Among biomasses, lignocellulose is the most common, which is composed of various polysaccharide celluloses, hemicelluloses, phenol-aldehyde polymer lignin, and soluble polar and non-polar substances. Because of its complex structure, the conversion technology of lignocelluloses materials to energy is costly and ineffective up to now [21–25]. Besides, the compositions of various lignocelluloses are different, it is necessary to understand the structure of it to design suitable pretreatment, which can be improve the effectiveness of lignocellulose usage and reduce its costs [26,27]. Current studies on pretreatment mainly focus on identifying, evaluating, developing, and demonstrating potential approaches for subsequent enzymatic hydrolysis that requires short bioconversion period and low enzyme concentration [28]. Few review articles [1,2,21,22,28–32] have summarized and analyzed various

lignocellulose pretreatment processes to present recommendations for future development. This review also provides a valuable reference on synthesis of cellulose acetate, cellulosic ethanol, and other similar materials.

## 2. Structure of lignocellulose

Lignocelluloses mainly consist of 40–50% cellulose, 25–30% hemicellulose, 15–20% lignin, and traces of pectin, nitrogen compounds, and inorganic ingredients [33,34]. Cellulose, which is a linear syndiotactic (alternating spatial arrangement of the side chains) polymer of glucose linked together by  $\beta$ -(1 → 4)-glycosidic bonds, is the most abundant polymer on earth, has many beneficial properties such as biocompatibility, stereoregularity, hydrophilicity, and reactive hydroxyl groups. This polymer is insoluble in water unless at high temperature or with the presence of certain catalyst. Its distinct polymer chains in orderly bundled arrangement and highly crystalline structure cause its stable properties, and its structure determines the framework of cell wall. Hemicellulose is a mixture composed of different polysaccharides, including straight and branched chain ones, to connect different numbers of acetyl and methyl. This polysaccharide has a low degree of polymerization, and without crystalline regions, so it is relatively easily degraded into monosaccharides, such as arabinose, xylose, galactose, fucose, mannose, dextrose, or glucuronide. Lignin is a complex hydrophobic, cross-linked aromatic polymer that interferes with the hydrolysis process. It has a three-dimensional heterogeneous polycrystalline reticulated polymer, which belongs to polyphenolic compounds. Such polymer is formed by phenyl propane structural units via ether linkages and carbon-carbon bond connection, and it lacks regularity and orderliness of the repeating units [35–38] (Fig. 2). The high crystallization zone; different binding forces between cellulose, hemicellulose, and lignin molecules; high degree of polymerization; pore structure on the surface of cellulose; and overwrite protection effect by lignin and hemicellulose determine that the cell walls are stable and difficult to be degraded, as shown in Table 1. Cellulose, hemicellulose, and lignin form the plant cell wall with a highly ordered crystal structure, so the degradation of any class of ingredients will be subjected to the constraints of other ingredients. Thus, lignocellulose must be pretreated to degrade the network structure of lignin and improve the efficiency of cellulose utilization [39–41]. Moreover, reducing the lignin matrix content is in

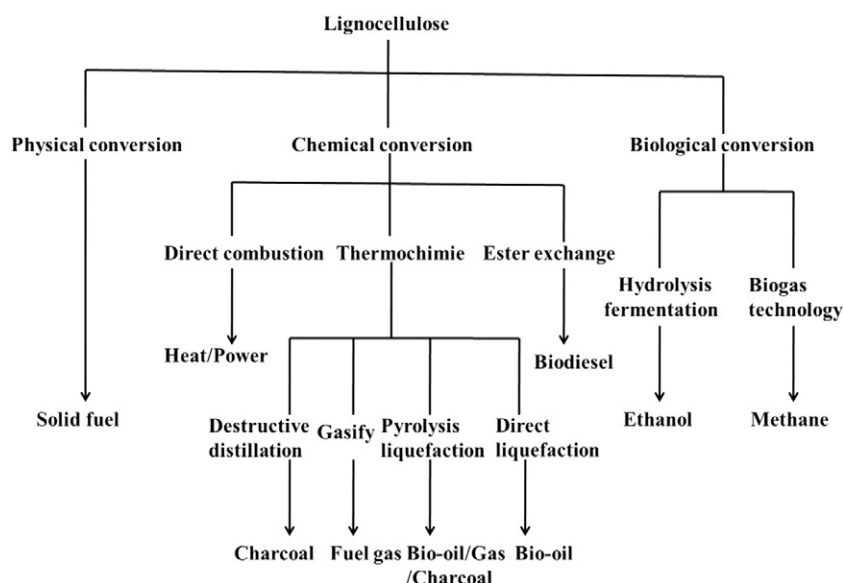


Fig. 1. Different forms of energy obtained through different pretreatment methods.

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