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## Review article

# Pretreatment processes for lignocellulosic biomass conversion to biofuels and bioproducts



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## ABSTRACT

Lignocellulosic materials, such as forestry, agricultural and agroindustrial residues, are among the most important sources of biomass for the production of fuels, chemicals and materials. However there are physical and chemical barriers in the lignin–carbohydrate supramolecular structure that render most plant cell wall components almost completely unavailable for conversion into commercial products. Thus successful conversion strategies must lead to the disruption of this structure and result in partial or total separation of the lignocellulosic components, increasing the accessibility of cellulose, hemicelluloses and lignins. It must also minimize the formation of by-products. Each pretreatment technology has its own characteristics and is usually applied to a specific source of carbohydrates and lignins. A general overview of the most important pretreatment methods for the production of platform chemicals and fermentable sugars are given in this paper.

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## 1. Introduction

Lignocellulosic biomass - such as sugarcane bagasse and straw, corn stover, cotton stalks, wheat straw, rice straw, rice husk, and wood chips - are widely available at a relatively low cost and are good raw materials for the production of fuels, chemicals and materials because of their heterogeneous chemical composition [1,2]. Generally, lignocellulosic biomass is composed of cellulose, hemicelluloses, and lignin, as well as small amounts of extractives (see Fig. 1) [3\*\*]. Cellulose and hemicellulose are chain polysaccharides and can be converted into fermentable sugars and a wide variety of other products [4]. Lignin is strongly intermeshed and bonded with polysaccharide structures through covalent or non-covalent bonds and is a potential source of high value-added aromatic products [5].

A consistent analysis of pretreatment methods - processes that are required to overcome the recalcitrance attributed to the structural characteristics of lignocellulosic materials - is fundamental [4,6,7]. It must render polysaccharides easily accessible to

chemicals and enzymes since this process determines the type and yield of the final products, the choice and efficiency of the subsequent transformation steps and other facts that make pretreatment responsible for the highest cost of the global project [1,2,3\*\*].

## 2. Pretreatment processes and platform chemicals

Pretreatment processes generate chemical intermediates for several industrial sectors such as food, paper and timber and fibers: They may be petroleum substitutes or have new functionalities or better properties than the ones that are traditionally manufactured such as: (i) Liquid hydrocarbon fuels [2,8] and chemicals like furfural [9], 5-hydroxymethylfurfural (HMF) [10], 2,5-furandicarboxylic acid (FDCA) [11],  $\gamma$ -valerolactone (GVL) [12,13], polymers [14,15] and organic acids [16–20] from hemicellulose and cellulose carbohydrates; (ii) Thermal and electrical energy, diesel fuel, carbon fiber, adhesives, additives, dispersants and aromatics from phenolic lignin compounds [21,22,23,24\*,25,26]; (iii) Biogas [27,28].

## 3. Sources of lignocellulosic materials

Cellulose is a linear chain of  $\beta$ -1,4 linked D-glucose units, has a large number of hydroxyl groups along its backbone and forms

Abbreviations: AFEX, Ammonia fibre expansion; FDCA, 2,5-furandicarboxylic acid; GVL,  $\gamma$ -valerolactone; HMF, 5-hydroxymethyl; SPORL, sulfite pretreatment to overcome recalcitrance of lignocellulose; THF, tetrahydrofuran.

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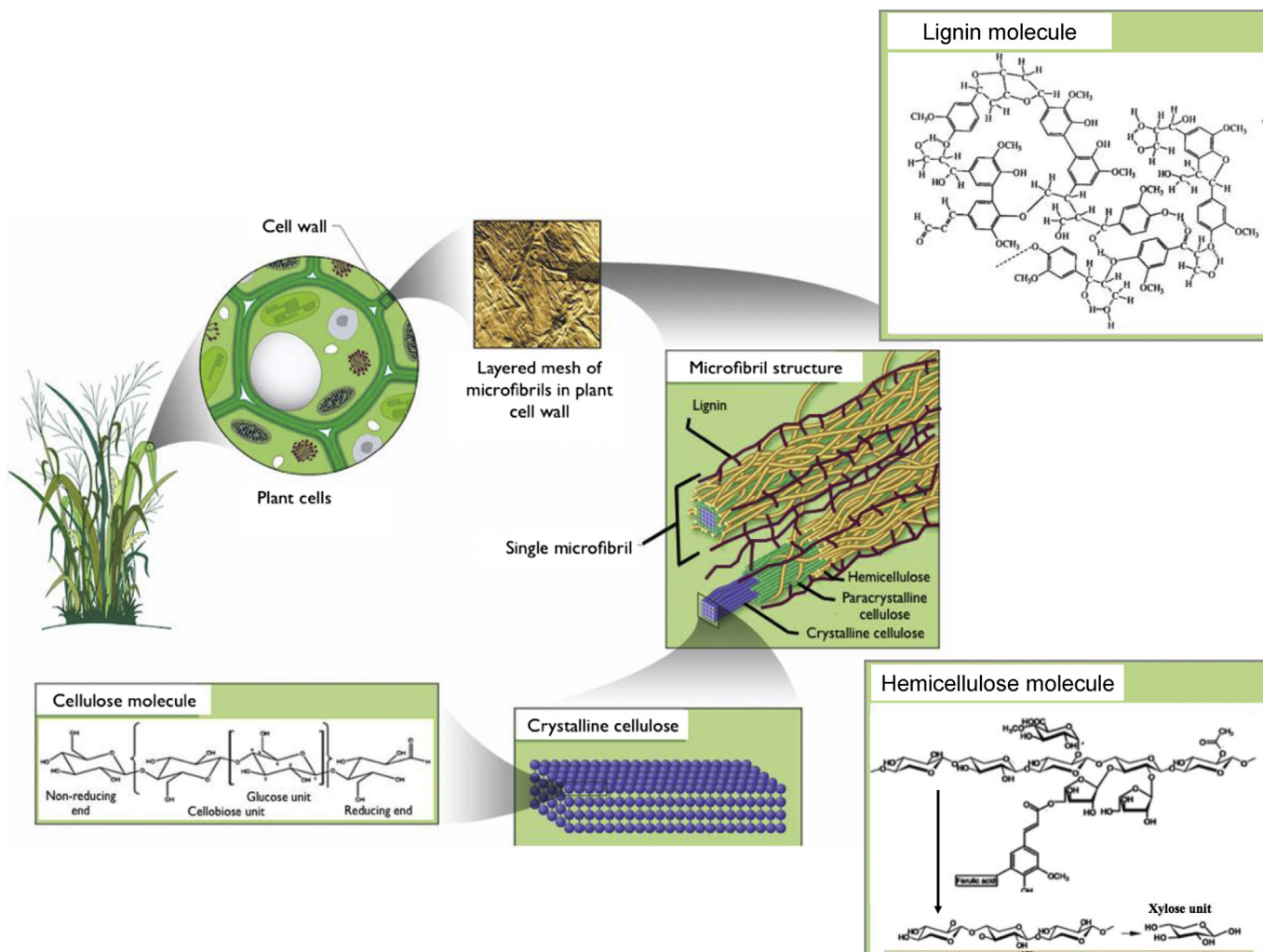


Fig. 1. Lignocellulosic Structure [62].

well-ordered hydrogen and van der Waals bonding networks that are responsible for its compact crystalline structure [29–31]. Hemicelluloses are heteropolymers (xylan, mannan, galactan, and arabinan, glucuronic acid, acetyl groups and uronic acids) and contain  $\beta$ -D-xylopyranosyl residues linked by 1,4 glycosidic bonds [32]. Lignin is formed from the oxidative coupling of *p*-hydroxycinnamyl alcohol monolignols, especially *p*-hydroxycinnamyl, coniferyl and sinapyl alcohols and linkages, such as  $\beta$ -0-4,  $\beta$ -5,  $\beta$ - $\beta$ , 5-5, and 4-0-5, among these components [24\*]. Generally, ester and ether linkages between hydroxyl groups of polysaccharides and  $\alpha$ -carbanol of phenylpropane subunits in lignin are the major connections in woods. In grasses, ferulic and *p*-coumaric acids are likely to form inter-molecular ester-ether bridges between hemicelluloses and lignin [30,33].

The relative proportion and composition of cellulose, hemicellulose and lignin and the types of bonds that they form vary with the biomass, the part of the plant material, the time of harvest and how it was cultivated [5]. Thus it is not possible to generally apply the same pretreatment technology to different fractions or type of biomass nor rely on the same operating conditions [34].

Softwoods contain more mannose in their hemicelluloses, fibers that are longer, denser and stronger than hardwoods, agricultural residues and grasses and more lignin than those three types of vegetables [3\*, 35\*]. Hardwoods contain more lignin and a more heterogeneous hemicellulose (which contains xylan, mannose,

glucose and rhamnose) than agricultural residues and grasses [36]. Those two types of biomasses have a larger proportion of hemicelluloses formed of xylose and a lignin with a more diversified composition than the hardwoods, followed by softwoods [32,37]. The concentrations of hemicellulose, cellulose and lignin of agricultural residues and of grasses are similar, however the accessibility of the fibers of grasses is larger and favors the reduction of the digestibility of these biomasses under conditions of low severity [33,38\*]. Thus softwoods require more severe conditions to reduce their recalcitrance, followed by hardwoods, agricultural residues and grasses [3\*\*,39,40].

The identification of the lignocellulosic structures that respond in the same way to a pretreatment allows them to be treated simultaneously in the same reactor on a longer term. Hopefully this will result in a reduction of the respective price which represents about 35–45% of their current costs of ethanol production [41,42]. It is worth to note that the average price of the mixture should be cheaper than that of a single type of biomass and should also flexibilize the demands for raw materials adjusting it to periods of greater availability and avoiding price speculation by suppliers as well as increasing the advantages of scale in producing bioproducts or biofuels [35\*,40,43,34]. For instance, the decrystallization of chains from the cellulose surface has been evaluated by molecular simulation in different solvents (it is spontaneous in water and ionic liquids), because they affect the forces that govern cellulose

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