



Review

Bio-based products from xylan: A review

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ABSTRACT

Obtaining chemicals and materials in sustainable ways is of growing importance. A potential source of sustainable chemicals and materials is lignocellulosic biomass residues generated as waste from agriculture. Hemicellulose which is a large component in lignocellulosic biomass residues, provides many potential applications such as the generation of chemicals, packaging materials, drug delivery and biomedical applications. This review deals with the various techniques which can be used for the extraction of hemicellulose from biomass residues, purification and some potential applications of the extracted hemicellulose. The methods that have been used to further produce chemicals from extracted hemicellulose as well as their applications are discussed.

1. Introduction

There is an estimated 5 billion tons of biomass residues produced globally from the agriculture sector every year (www.unep.org). There is no systematic tracking of the amount of agricultural residue produced and amounts reported are estimated based on the yield of crop harvested (Smil, 1999). Post harvesting, waste residue is often transported to dump sites to decompose and/or be burned. However, dumping either requires land to be especially set aside or be dumped at landfills which also require space that would normally be used for household waste disposal. In either case while these residues decompose they would still take up space that could be used for other purposes. Burning of agricultural waste on the other hand generates unnecessary carbon dioxide and often leads to the release of chemicals such as polycyclic aromatic hydrocarbons and dioxins (Burning Agricultural Waste: A Source of Dioxins, 2017 Burning Agricultural Waste: A Source of Dioxins).

Nonetheless, this waste may prove both useful and profitable; for example, the global agricultural waste is estimated to have the same energy value as 1.2 billion tons of oil, which is a quarter of the world oil production (Smil, 1999). Also, agricultural waste residues are a valuable source of carbohydrates and can therefore be considered as a viable feed stock from which bio-based materials can be developed. The latter valorization of agricultural waste is preferred because it is relatively greener and extends the life-cycle of crops. However, this often requires thorough washing and pre-treatment of agricultural source to maximise properties of resultant bio-based products. Unfortunately during the washing and pre-treatment process, chemical composition of the agricultural feedstock gets affected depending on the type of

method employed. This review deals with an in-depth account of lignocellulose, a bio-based product, as well as different pre-treatment techniques that can be employed for the extraction of hemicellulose from lignocellulose. The conversion of hemicellulose (especially the xylan fractions) into value-added bio-based products (biocomposites and hydrogels) and chemicals is also described.

2. Lignocellulosic biomass

Lignocellulose biomass is a plant material derived from common plants such as softwoods, hardwoods and grasses. Fig. 1 shows an illustration of lignocellulosic biomass, and as can be seen, it is mainly comprised of three polymers namely lignin, cellulose and hemicellulose (Lee, 1997). Other constituents that make up a smaller part of the biomass are pectin, protein, wax and extractives (Kumar, Barrett, Delwiche, & Stroeve, 2009). The amounts of each of the constituents present vary in plants from species to species and can also vary with the age of the plant (Kumar et al., 2009; Verardi, Ricca, De Bari, & Calabrò, 2012). Cellulose forms microfibrils which are held together by hemicellulose and lignin by a combination of hydrogen and covalent bonds (Lee, 1997). Table 1 shows the amounts of cellulose, hemicellulose and lignin found in various types of lignocellulosic biomass. From this table, it can be seen that cellulose is the most abundant polymer in the lignocellulosic biomass.

2.1. Cellulose

Cellulose is the most abundant polymer in lignocellulosic biomass

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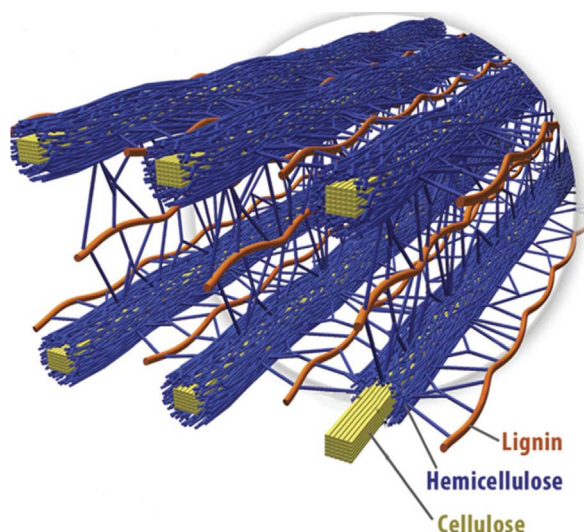


Fig. 1. Illustration of lignocellulosic biomass (Brandt, Grasvik, Hallett, & Welton, 2013).

Table 1

Amount of cellulose, hemicellulose and lignin in various types of lignocellulosic biomass (Isikgor & Becer, 2015).

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Harwood			
Poplar	50.8–53.3	26.2–28.7	15.5–16.3
Oak	40.4	35.9	24.1
Eucalyptus	54.1	18.4	21.5
Softwood			
Pine	42.0–50.0	24.0–27.0	20.0
Douglas fir	44.0	11.0	27.0
Spruce	45.5	22.9	27.9
Agricultural waste			
Wheat straw	35.0–39.0	23.0–30.0	12.0–16.0
Barley hull	34.0	36.0	13.8–19.0
Barely straw	36.0–43.0	24.0–33.0	6.3–9.8
Rice straw	29.2–34.7	23.0–25.9	17.0–19.0
Rice husks	28.7–35.6	12.0–29.3	15.4–20.0
Oat straw	31.0–35.0	20.0–26.0	10.0–15.0
Ray straw	36.2–47.0	19.0–24.5	9.9–24.0
Corn cob	33.7–41.2	31.9–36.0	6.1–15.9
Corn stalks	35.0–39.6	16.8–35.0	7.0–18.4
Sugarcane bagasse	25.0–45.0	28.0–32.0	15.0–25.0
Sorghum straw	32.0–35.0	24.0–27.0	15.0–21.0
Grasses			
Grasses	25.0–40.0	25.0–50.0	10.0–30.0
Switchgrass	36.0–40.0	25.0–50.0	15.0–20.0

constituting 30–50%, as can be seen in Table 1, of the biomass and is dependent on the plant species as well as age (Limayem & Rieke, 2012). It consists of D-glucose units which are joined via β -1,4 glycosidic linkage (Mussatto & Teixeira, 2010). Each repeating glucose unit is rotated 180° to its neighbouring glucose unit (Ten & Vermerris, 2013). There are both hydrogen bonding and van der Waal forces present in cellulose chains.

Although there are amorphous regions of cellulose, hydrogen bonding leads to the chains being parallel to each other, resulting in crystalline regions (Limayem & Rieke, 2012). Cross-linkage of the cellulose chains through hydrogen bonding produces the microfibrils as shown in Fig. 1 (Agbor, Cicek, Sparling, Berlin, & Levin, 2011). The degree of polymerisation of cellulose can range from 10000 to 15000 monomer units (Agbor et al., 2011).

2.2. Lignin

Lignin makes up between 10 and 20% of the lignocellulosic biomass depending on the species (Limayem & Rieke, 2012). It is made up of

phenylpropane units that are held together by various types of linkages, and is closely bound to hemicellulose and cellulose and acts as the glue that holds them together (Fig. 1). These characteristics place lignin as a provider of the structural integrity and rigidity of lignocellulosic biomass, as well as help in preventing the swelling of lignocellulosic biomass (Maurya, Singla, & Negi, 2015). Lignin is hydrophobic and consequently prevents water from entering cell walls; thus protecting the cellulose and hemicellulose (Mokhothu & John, 2015). Furthermore, it is extremely resistant to chemical and enzymatic degradation and is responsible for protecting the lignocellulosic biomass from bacterial attack (Isikgor & Becer, 2015; Mussatto & Teixeira, 2010).

2.3. Hemicellulose

Hemicellulose make up between 15 and 35% of lignocellulosic biomass (Limayem & Rieke, 2012). Unlike cellulose, the various types of hemicelluloses are non-crystalline, have shorter chains and are branched (Cunha & Gandini, 2010; Mussatto & Teixeira, 2010). Similar to cellulose, hemicelluloses are made up of 1,4 linked β -D-pyranol residues such as glucose, mannose and xylose, in which the oxygen in position 4 is of equatorial orientation (Rose, 2003). The amount of and types of branching (functional groups) varies depending on the source of the feedstock (Limayem & Rieke, 2012). Hemicellulose is a heteropolymer made up of monosaccharides such as pentose, hexoses, acetylated sugars and uronic acids. The various types can vary widely with different plants and is sometimes used to classify the plant order (Mussatto & Teixeira, 2010). Some forms of hemicellulose starts to dissolve in water at a temperature of 150 °C and its solubility increase in the order of galactose, arabinose, glucose, xylose and mannose; these are various sugars which are either pentose sugars or hexose sugars (Hendriks & Zeeman, 2009). The most abundant hemicellulose type is xylan, although its composition varies among species (Limayem & Rieke, 2012).

There are three main sub-groups of hemicelluloses that have a backbone of 1-4 linked β -D- pyranose (hemiacetal sugars) residues; namely mannans, xylans and xyloglucans. The sugars that constitute most various hemicelluloses structure are shown in Fig. 2.

2.3.1. Mannan

Mannans are hemicellulose which are composed of a backbone made up of mannose units (Moreira, 2008). There are four subgroups of mannans; namely linear mannan, glucomannans, galactomannans and galactoglucomannans (Yildiz & Oner, 2014). The homopolymer that is linear mannan, consists solely of mannose residues and can be found in the endosperm of some plant species such as the ivory nut and Leguminosae (Petkowicz, Reicher, Chanzy, Taravel, & Vuong, 2001; Rose, 2003).

2.3.1.1. Galactomannans. The general structure of galactomannans is

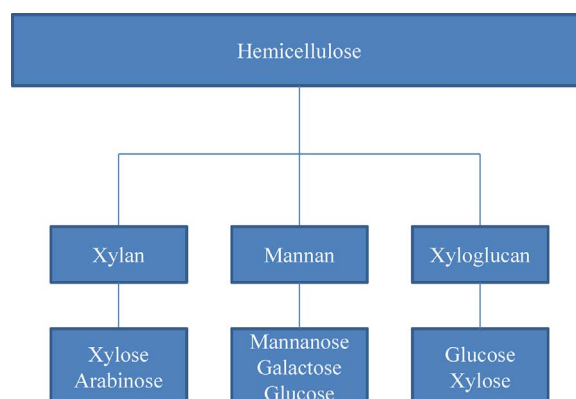


Fig. 2. Flow diagram of the sugars that make up the various hemicelluloses.

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