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Pyrolysis behaviors of four O-acetyl-preserved hemicelluloses isolated from hardwoods and softwoods

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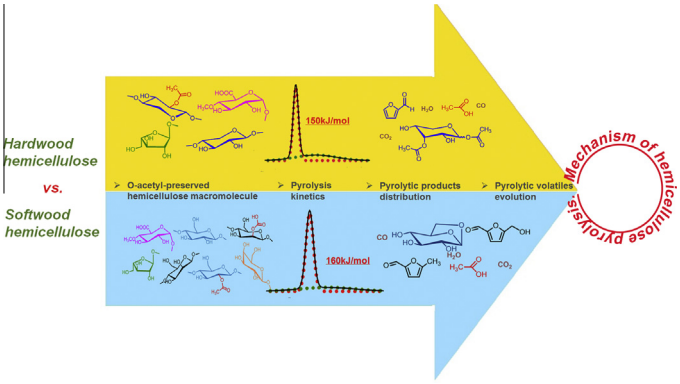
HIGHLIGHTS

- O-acetyl-preserved hemicelluloses were isolated successfully from woody biomass.
- Pyrolysis of hardwood hemicellulose with high content of O-acetyl yield more acids.
- Hydroxymethyl in softwood hemicellulose leads to HMF and anhydro sugars formation.
- DG-DAEM showed softwood hemicellulose pyrolysis having higher activation energy.

GRAPHICAL ABSTRACT



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ABSTRACT

The pyrolysis mechanisms of O-acetyl-preserved hemicelluloses isolated from both hardwoods and softwoods have been investigated. Their chemical structures, pyrolysis kinetics, pyrolytic product distributions, and pyrolytic gaseous evolutions have been systematically studied. Hardwood hemicellulose was mainly composed of 4-O-methyl-D-glucurono-D-xylan and had high contents of O-acetyl and uronic acid units, whereas softwood hemicelluloses were composed of D-galacto-D-gluco-D-mannan and L-arabino-4-O-methyl-D-glucurono-D-xylan. A double-Gaussian distributed activation energy model has been introduced to simulate the pyrolysis kinetics. Hardwood hemicellulose pyrolysis showed lower activation energies than softwood hemicellulose pyrolysis. Hardwood hemicellulose pyrolysis mainly yielded furfural and acids, whereas for softwood hemicellulose pyrolysis, 5-hydroxymethylfurfural and anhydro sugars were typical products. The evolution behaviors of H_2O, CO_2, CO, and acids from the pyrolyzes of the four hemicelluloses are discussed.

1. Introduction

Fast pyrolysis has been developed as a promising technology for converting biomass into biofuel and bio-based chemicals [1–3]. As the most abundant component in lignocellulosic biomass, cellulose has a regular and ordered structure derived from the polymerization of β-D-glucose units. The pyrolysis mechanism of cellulose has been extensively studied. In contrast to cellulose, hemicellulose is composed of heteropolysaccharide and has a more complicated structure. The monosaccharide units comprising hemicellulose include pentoses (xylose and arabinose) and hexoses (glucose, mannose, and galactose), as well as some other low content saccharides,

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such as rhamnose and fucose. The sugar residues in the hemicellulose backbone are highly substituted with O-acetyl groups, uronic acid moieties, and other saccharide residues, and some parts of the lignin structure are also covalently bonded with hemicellulose. Hemicelluloses from various kinds of biomass show great differences in their degree of polymerization, monosaccharide constitution, and degree of branching [4]. The backbone of hardwood hemicellulose is mainly composed of xylose units connected through β-1,4-glucosidic bonds, whereas that of softwood hemicellulose consists of mannose and glucose units. Generally, hardwood hemicellulose has a higher degree of O-acetyl substitution than softwood hemicellulose; about half of the xylose units in hardwood hemicellulose are acetylated [5]. Compared to cellulose, fewer studies have been focused on the pyrolysis mechanism of hemicellulose due to its irregular and branched structure.

Model compounds used in hemicellulose pyrolysis mechanistic studies can be classified into three types: (1) Hemicellulose-based monosaccharides, such as xylose, mannose, arabinose, and galactose. Räisänen et al. [6] proved that the pyrolytic product distributions from hexose and pentose were very different by using a pyrolyzer coupled with a gas chromatography–mass spectrometry set-up (Py–GC/MS). Wang et al. [7] found that the dissociation of the additional hydroxymethyl group in hexose was associated with a high energy barrier, and that all of the monosaccharide units in hemicellulose were easily ring-opened and cracked, leading to the formation of 1-hydroxy-2-propanone, furanone, and other small molecules. (2) Commercially available xylan, e.g. beechwood xylan, mainly composed of xylose and arabinose units. Xylan is one of the main polysaccharide components of hemicellulose, and is usually found in hardwood, herbage, and cereals in the forms of glucuronoxylan, arabinoxylan, arabinoglucuronoxylan, etc. [8], whereas the main polysaccharide in softwood hemicellulose is galactoglucomannan [9]. Yang et al. [10] indicated that xylan mainly decomposed in the range 220–315 °C and showed maximum weight loss rate at 268 °C. Cai et al. [11] studied the kinetics of xylan pyrolysis by using a distributed activation energy model (DAEM), and found that its mean activation energy was about 178 kJ/mol, much lower than that for cellulose pyrolysis. (3) Hemicellulose samples directly extracted from biomass. Although this type of hemicellulose has the most similar structure as the natural form, the isolation process is extremely complex. The amorphous structure of hemicellulose is subject to change under various extraction conditions, and the extracted hemicellulose yield is very low. The most popular method for hemicellulose isolation is to use an alkali solution (usually NaOH or KOH) to extract it from delignified holocellulose. However, alkali could damage the O-acetyl groups, as well as ester and ether bonds, and hence the resulting hemicellulose usually has a low degree of branching [12]. The alkali solution might also introduce extra alkali metal into the sample. Patwardhan et al. [13] isolated hemicellulose from switchgrass by using alkali solution, and subsequently used it as a model compound for a study of the pyrolytic product distribution. The results showed that the content of acetic acid was very low. It has been shown that hemicellulose isolated by extraction with dimethyl sulfoxide (DMSO) retains its O-acetyl groups. This implies less damage to the structure, and so the hemicellulose isolated in this way is closer to the natural form and more suitable for use as a model compound [14,15].

Previous studies on the hemicellulose pyrolysis mechanism have typically used a single model compound as a representative of the natural material. However, as mentioned above, hemicelluloses from different biomass sources may differ greatly, especially between hardwoods and softwoods. In this study, four O-acetyl-preserved hemicellulose samples have been isolated from *Eucalyptus saligna* (ES), *Fraxinus mandshurica* (FM), *Pinus sylvestris* (PS), and *Tsuga chinensis* (TC) by extraction with DMSO. ES and FM are hardwoods, whereas PS and TC are softwoods. The hemicellulose samples isolated from them were designated as ESH, FMH, PSH, and TCH, respectively. The obtained hemicellulose samples were subsequently used as model compounds for structure characterization and studies of the pyrolysis mechanism. This study provides systematic information on the relationship between hemicellulose structure and its pyrolysis characteristics.

2. Material and methods

2.1. Isolation of hemicellulose

Four biomass samples, ES, FM, PS and TC, were obtained from a local timber mill (Zhejiang province, China). All four of these biomass sources are widely distributed in China. Before extraction, all of the biomass samples were dried, ground, and sieved (40–60 mesh).

The method used in this study was an improved process based on that described in previous studies [14,16]. A flowchart of the process is shown in Fig. 1S. The raw biomass was first dried at 60 °C for more than 16 h, and then subjected to soxhlet extraction with toluene/ethanol (2:1, v/v) for 8 h to remove extractives. The dewaxed samples were immediately delignified with sodium chlorite (1.3 wt%) for 3 h with stirring. The delignification process was repeated three times to completely remove lignin from the biomass. The filtered holocellulose was further extracted with DMSO at 70 °C for 5 h. Subsequently, the filtrate was diluted with four times its volume of ethanol, and then a little concentrated hydrochloric acid (less than 1 mL of per liter of ethanol/DMSO solution) was added to precipitate the crude hemicellulose. This was purified by washing with ethanol and lyophilization (−0.1 MPa, −50 °C, Freezone, LABCONCO, USA) prior to pyrolysis studies.

2.2. Structural characterization of hemicellulose

The ultimate analysis of the four hemicellulose samples was carried out on a Vario MICRO Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). The molecular weight distributions were measured at 50 °C on a PL GPC 50Plus (Varian Polymer Laboratories, UK). Hemicellulose samples were dissolved in pure water, and the concentrations were about 2 mg/mL. 0.1 mol/L sodium nitrate solution was used as eluent and kept at a flow rate of 0.8 mL/min. The obtained relative molecular weight was calibrated with polyethylene oxide standards.

The neutral sugars of the hemicellulose samples were released by stepwise hydrolysis in 72% H_2SO_4 for 3 h at 20 °C and subsequently in 1 mol/L H_2SO_4 for 1.5 h at 100 °C. The obtained sugar solution was treated with $Ba(OH)_2$ until neutral pH was reached, precipitating SO_4^{2-} to avoid its influence on the following measurements. The neutral sugars were quantitatively analyzed on a Dionex Ultimate 3000 high-performance liquid chromatography (HPLC) apparatus (Dionex Corporation, USA) equipped with a Shodex SP0810 sugar column (Showa Denko Kabushiki-gaisha, Japan). The total uronic acid content was determined according to the method proposed by Blumenkrantz and Asboe-Hansen [17]. The total uronic acid content was analyzed by means of a Shimadzu UV-3150 spectrophotometer (Shimadzu Corporation, Japan) at a wavelength of 520 nm.

The functional groups present in the hemicellulose structure were identified by Fourier-transform infrared spectroscopy (FTIR). The spectra were recorded on a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific Corporation, USA) in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}; each spectrum was accumulated from 36 scans. Solution-state ^1H NMR, ^{13}C NMR,