



Thermal degradation behavior and kinetic analysis of spruce glucomannan and its methylated derivatives



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ABSTRACT

The thermal degradation behavior and kinetics of spruce glucomannan (SGM) and its methylated derivatives were investigated using thermogravimetric analysis to characterize its temperature-dependent changes for use in specific applications. The results were compared with those obtained for commercial konjac glucomannan (KGM). The SGM and the KGM exhibited two overlapping peaks from 200 to 375 °C, which correspond to the intensive devolatilization of more than 59% of the total weight. Differences in the pyrolysis-product distributions and thermal stabilities appeared as a result of the different chemical compositions and molecular weights of the two GMs. The Friedman and Flynn-Wall-Ozawa isoconversional methods and the Coats–Redfern were adopted to determine the kinetic triplet of the intensive devolatilization region. Both GMs can be modeled using a complex mechanism that involves both a Dn-type and an Fn-type reaction. The comparative study of partially methylated GM indicated higher homogeneity and thermal resistance for the material with the higher degree of substitution.

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1. Introduction

Hemicelluloses are structural carbohydrates of plant cell walls that, in close association with cellulose and lignin, form the lignocellulosic biomass. Hemicelluloses generally occur as heteropolysaccharides, in which their main building units are hexoses (D-glucose, D-mannose and D-galactose) and pentoses (D-xylose and L-arabinose). Small amounts of deoxyhexoses (L-rhamnose and L-fucose) and uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid) are also present. Hemicelluloses have a lower degree of polymerization (DP) and are more easily hydrolyzed and less thermally stable than cellulose. An understanding of their pyrolytic behavior is of paramount importance in improving process fundamentals and designing effective biomass-conversion technologies, such as the torrefaction process, which is carried out at the typical degradation temperature of hemicelluloses (Branca, Di Blasi, Mango, & Hrablay, 2013; Chaouch, Pétrissans, Pétrissans, & Gérardin, 2010). In general, in

thermochemical conversion technologies, pyrolysis plays a key role in determining the reaction kinetics, and it is therefore critical to reactor design and the determination of product distribution, composition and properties (Raveendran, Ganesh, & Khilar, 1995). Pyrolysis studies are also essential to implementing new biomass-conversion technologies, such as low-temperature carbonization and chemical production from solid fuels (Seo, Park, Hwang, & Yu, 2010). A significant number of studies are available concerning the pyrolysis of xylan from hardwood hemicelluloses (Bilbao, Millera, & Arauzo, 1989; Di Blasi & Lanzetta, 1997; Shen, Gu, & Bridgwater, 2010). In contrast, no study is available regarding the thermal behavior, thermal degradation kinetics and products of pyrolysis of softwood glucomannan, which is the main component of softwood hemicellulose.

The thermal and kinetic aspects of solid state decomposition reactions are complex (Yang, Miranda, & Roy, 2001) and involve a large number of parameters to investigate. Thermogravimetric analysis (TGA) is one of the most widely used techniques to assess the thermal and kinetic behavior of carbohydrate polymers, allowing the determination of parameters such as the kinetic triplet, which includes (Nelson David, Hallen Richard, & Theander, 1988) the apparent activation energy, the reaction mechanism ($f(\alpha)$) and the pre-exponential factor (A) (Akbar, Iqbal, Massey, & Masih, 2012; Iqbal, Massey, Akbar, Ashraf, & Masih, 2013; Moriana, Vilaplana, Karlsson, & Ribes-Greus, 2011; Yao, Wu, Lei, Guo, & Xu, 2008;

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Zohuriaan & Shokrolahi, 2004); the thermal stability and the distribution of pyrolysis products (Ramajo-Escalera, Espina, García, Sosa-Arno, & Nebra, 2006; Wilson, Yang, Blasiak, John, & Mhilu, 2011); and the proximate analysis data, including the calorific value (García, Pizarro, Lavín, & Bueno, 2013).

There are other technologies related to thermal processing that also require the superior materials characterization offered by TGA to predict their temperature dependence and to solve the drawbacks related to their temperature sensitivity. Biomass can be processed by extrusion, injection and compression molding to design sustainable materials as an alternative to synthetic polymers. To do this, knowledge of the thermal degradation kinetics and behavior is of practical relevance for understanding and predicting the thermal resistance and degradation of materials to be used for specific applications (Aggarwal, Dollimore, & Heon, 1997). Among all the hemicellulose components, hexoses are known to be less susceptible to hydrolysis and dehydration reactions than pentoses (Akbar et al., 2012). Therefore, glucomannan is thermally more stable than xylan (C. Ramos-Sánchez, Rey, L. Rodríguez, Martín-Gil, & Martín-Gil, 1988). This property, together with other properties, such as its viscosity (Xue Jiao He, Amadou, & Qin, 2012) and renewability (Kohyama, Kim, Shibuya, Nishinari, & Tsutsumi, 1992), render glucomannan carbohydrates as one of the most interesting hemicellulose polymers to be applied in materials science. In this sense, several approaches have been reported in the literature with interesting results. Cheng, Abd Karim, and Seow (2008) made emulsion films from carboxymethyl cellulose and deacetylated konjac glucomannan (KGM) with a higher barrier and mechanical efficiency. Mikkonen et al. (2010) studied the thermal properties of films based on KGM and spruce galactoglucomannans with cellulose nanowhiskers. Enomoto-Rogers, Ohmomo, and Iwata (2013) used KGM as a thermoplastic and evaluated differences in its thermal stability as a function of the degree of acetylation (DS_{Ac}), showing an improvement with increasing DS_{Ac} of the KGM.

In this study, spruce glucomannan (SGM) was selected for thermal assessment from among the other potential hemicellulose polymers because no detailed study has previously been conducted to determine its thermal degradation behavior and kinetics. The scope of this work includes the development of an appropriate methodology for gathering suitable information regarding the pyrolysis-product distribution, heating value, thermal stability and kinetic triplet of a glucomannan polymer. These parameters are useful in understanding and predicting the thermal behavior of glucomannan to define its potential for use in bioenergy or as a material that is resistant enough to be processed using conventional thermal technologies and/or to have a competitive service life. SGM was extracted from softwood and was later modified *via* methylation to obtain various degree of substitution (DS). The influence of the DS value on the thermal behavior was also explored, and all results were compared with those of a well-established commercial KGM (Kohyama et al., 1992).

2. Experimental

2.1. Materials

Spruce (*Picea abies*) wood chips were obtained from the Södra Cell Värö mill in Sweden. The wood chips were cut into 1 cm wide pieces and mechanically milled into 20-mesh powders. The food-additive-grade KGM with a molecular mass of 1000 kDa that was used in this study was purchased from Hubei Konson Konjac Gum Co., Ltd., China. All chemicals were of high purity and were purchased from Fluka, Aldrich or Merck. Analytical reactions were carried out in 1 mL or 5 mL V-vials in a heating block with an

evaporating unit that was obtained from Barkey GmbH & Co. KG, Germany.

2.2. Extraction of SGM

The method used for SGM extraction was based on the method developed by Zhang, Li, Lindstroem, Stepan, and Gatenholm (2013). Wood powders were mixed with acetone and allowed to stand overnight to remove the extractives. After the acetone was filtered off, the wood powders were delignified using HOAc and $NaClO_2$ for 7 h to obtain holocellulose. The holocellulose was then added to a NaOH/ H_3BO_3 (17.5/4.0%) solution in a polyethylene bottle and shaken overnight under an N_2 atmosphere. The solution was filtered out, and Fehling solution was added to the solution until no further precipitation of the copper complex was observed. The precipitates were then dissolved in HCl, washed and subsequently re-precipitated using 70%, 96% and, finally, pure ethanol, followed by freeze drying. To purify the SGM, the materials were dissolved in water and dialyzed (molecular weight cut off (MWCO): 3.5 kDa). The yield of isolated SGM was 6.7% with respect to the starting wood powders. The average molecular weight (M_w) of the SGM was determined to be 10 kDa using alkaline size-exclusion chromatography (SEC).

2.3. Carbohydrate and linkage analysis of SGM and KGM

The carbohydrate compositions of the SGM and KGM were determined following the standard procedures for the Tappi test method T222 om-06 (2006) using a High-Performance Anion-Exchange Chromatograph (HPAEC-PAD, Dionex, Sunnyvale, CA, USA) for mono-sugar quantification directly following the acid hydrolysis.

The glycosyl linkage analysis was performed at the Complex Carbohydrate Research Center (The University of Georgia) according to the method described by York, Darvill, McNeil, Stevenson, and Albersheim (1986). The samples were permethylated, depolymerized, reduced and acetylated, and the resultant partially methylated alditol acetates (PMAAs) were analyzed *via* gas chromatography–mass spectrometry (GC–MS).

2.4. Preparation of partially methylated glucomannans with different DS values

The KGM and SGM were well dissolved in H_2O and DMSO, respectively. The methylation of the KGM was performed in H_2O with NaOH/MeI, while the SGM was methylated in DMSO with Li-dimsyl/MeI, both at room temperature. The reactions were carried out under nitrogen. The partially methylated samples were isolated *via* dialysis (MWCO: 3.5 kDa) and freeze dried. Partially methylated spruce glucomannan (MeSGM) and partially methylated konjac glucomannan (MeKGM) were obtained. The definition of the DS is the average number of substituted OH groups per anhydroglucose unit (Kato, Kawaguchi, & Mizuno, 1973), which can take values between 0 and 3. The base 1.6 M Li dimsyl ($CH_3SOCH_2^- Li^+$) was freshly prepared, and NaOH was freshly finely pulverized. The methylation conditions are summarized in Table 1. The molar compositions of the various MeSGM and MeKGM samples were determined *via* GLC after hydrolysis, reduction and acetylation according to the method followed in previous studies (Adden, Niedner, Mueller, & Mischnick, 2006; Voiges, Adden, Rinken, & Mischnick, 2012). The DS values were obtained *via* gas chromatography. MeSGM1, MeSGM2 and MeKGM1, along with the SGM and KGM, were used to study the effects of methylation modification on the thermal degradation behavior and kinetics.

For the quantitative measurement of alditol acetates obtained from partially methylated GMs *via* gas liquid chromatography

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