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Quantitative solid state NMR analysis of residues from acid hydrolysis of loblolly pine wood

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ABSTRACT

The composition of solid residues from hydrolysis reactions of loblolly pine wood with dilute mineral acids is analyzed by ^{13}C Cross Polarization Magic Angle Spinning (CP MAS) NMR spectroscopy. Using this method, the carbohydrate and lignin fractions are quantified in less than 3 h as compared to over a day using wet chemical methods. In addition to the quantitative information, ^{13}C CP MAS NMR spectroscopy provides information on the formation of additional extractives and pseudo lignin from the carbohydrates. Being a non-destructive technique, NMR spectroscopy provides unambiguous evidence of the presence of side reactions and products, which is a clear advantage over the wet chemical analytical methods. Quantitative results from NMR spectroscopy and proximate analysis are compared for the residues from hydrolysis of loblolly pine wood under 13 different conditions; samples were treated either at 150 °C or 200 °C in the presence of various acids (HCl, H_2SO_4, H_3PO_4, HNO_3 and TFA) or water. The lignin content determined by both methods differed on averaged by 2.9 wt% resulting in a standard deviation of 3.5 wt%. It is shown that solid degradation products are formed from saccharide precursors under harsh reaction conditions. These degradation reactions limit the total possible yield of monosaccharides from any subsequent reaction.

1. Introduction

The development of production routes for fuels and chemicals from alternative resources (e.g. coal, gas and biomass) is one of the great scientific challenges of the 21st century. Biomass is a particularly interesting resource because it is CO_2 neutral and renewable. Consequently, a growing number of researchers is investigating potential routes for its utilization (Corma et al., 2007; Huber et al., 2006; Valenzuela et al., 2006). Among the variety of feedstocks that have been considered for biofuel production, lignocellulosic biomass is particularly attractive because it is available in large quantities and non-edible.

A variety of approaches exists for processing biorenewable feedstocks, including gasification, pyrolysis and depolymerization by hydrolysis. The advantage of hydrolysis is that it provides well defined platform molecules (e.g. monosaccharides and products thereof), in some cases at very high yield (Werpy and Petersen, 2004; Wyman et al., 2005). Hydrolysis can be catalyzed by conventional acids, bases or enzymes (Sjöström, 1999). The lignin fraction of biomass can be processed with base catalysts, whereas acids catalyze the hydrolysis of the glycosidic bonds in carbohydrates (cellulose and hemicellulose) to form oligo- and monosaccharides. Specific enzymes exist for hydrolysis of either fraction.

Acid catalyzed hydrolysis of lignocellulosic biomass has been studied extensively since the 1920s (Sherrard and Blanco, 1923). In recent years, increasing attention has been focused on acid hydrolysis of various types of lignocellulosic biomass such as corn stover and switchgrass (Esteghlalian et al., 1997), and various wood species (Taherzadeh et al., 1997). In addition to hydrolysis, several acid catalyzed side reactions occur under typical processing conditions. Most importantly, hexoses and pentoses are dehydrated to HMF and furfural, respectively (Antal et al., 1990).

To improve the conversion and selectivity in acid catalyzed hydrolysis reactions, it is important to know the products and intermediates that are formed in this process. Analyses of both the liquid and solid phase products have been reported. Water-soluble products have been determined largely by chromatographic methods (Marzialetti et al., 2008; Yang and Wyman, 2004). For the solid residue, wet chemical methods similar to analysis of the raw material for determination of major constituents (carbohydrates, lignin, extractives and ash) are commonly used (Bura et al., 2002). For example, the Klason lignin content is determined as the insoluble residue after treatment with 72% H_2SO_4 (Sjöström, 1999).

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However, these techniques are not designed for the analysis of samples containing products that are different from the constituents of the original biomass and may, therefore, not be suitable for analyzing fractions that have already undergone chemical modifications. In addition, they are laborious and time-consuming.

Spectroscopic techniques like IR (Meder et al., 1999) and NMR (Bardet et al., 2004; Kogel-Knabner, 1997; Liitiä et al., 2003; Maunu, 2002; Sievers et al., 2009; Wikberg and Maunu, 2004) spectroscopy have been used to investigate the composition of wood-based samples. In particular, solid state ^{13}C NMR spectroscopy has been successfully applied for the qualitative characterization of wood (Liitiä et al., 2003; Maunu, 2002; Wikberg and Maunu, 2004) and wood products (Bardet et al., 2004; Maunu, 2002; Sievers et al., 2009). Valuable studies were published on changes in the composition of wood products (Bardet et al., 1997) as well as on the crystallinity of the cellulose fraction in wood (Liitiä et al., 2003; Wickholm et al., 2001). Controversial results were obtained on the interactions between different fractions of wood suggesting separated phases (Bardet et al., 1997) and an intimate proximity of the different fractions (Ahvazi and Argyropoulos, 1999). Quantitative ^{13}C MAS NMR studies are demanding for several reasons. The presence of paramagnetic nuclei in the ash fraction can dramatically lower the sensitivity of adjacent carbon nuclei (Keeler and Maciel, 2003). Moreover, in most cases the use of cross polarization (CP) is necessary to obtain an acceptable signal-to-noise ratio in a reasonable instrument time (Maunu, 2002). This pulse sequence results in a different spectroscopic sensitivity for particular carbon nuclei depending on their chemical environment (Laws et al., 2002). However, quantitative information can still be obtained when care is taken to use appropriate methods (Conte et al., 2004; Love et al., 1992).

In this study, the washed residues from acid hydrolysis of loblolly pine wood using different dilute mineral acids are investigated by ^{13}C CP MAS NMR spectroscopy and proximate analysis. Chemical transformations of the insoluble parts of pine wood are studied, and a method for quantification of the residue is presented.

2. Experimental

2.1. Materials

Loblolly pine wood was harvested near Oglethorpe, GA. The logs were debarked, chipped and milled. For the hydrolysis experiments, the $-25 + 60$ mesh fraction was used. The samples were stored in a freezer until used. Cellulose was purchased from Sigma–Aldrich (fibrous, medium, Catalogue No. C6288). The lignin samples were prepared by treating loblolly pine wood with a 72% H_2SO_4 solution (vide infra) (TAPPI method T 222 om-98). Sulfuric acid (95–97%, Sigma–Aldrich, St. Louis, MO), trifluoroacetic acid (TFA) (99.9%, EMD, Gibbstown, NJ), nitric acid (70%, Sigma–Aldrich, St. Louis, MO), phosphoric acid (85%, Acros Organic, Morris Plains, NJ), and hydrochloric acid (36.5–38.0%, BDH, Poole, United Kingdom) were used without further purification.

2.2. Thermogravimetric analysis

The moisture content of loblolly pine wood was determined by heating 17 mg of loblolly pine wood in a STA Thermogravimetric Analyzer (Netszch, Selb, Germany) under a mixture of nitrogen and air. The mass loss observed between 25 and 105 °C was assigned to moisture in the wood. The moisture content measurement was repeated every 2–3 months to assess changes in the solids over time and did not deviate appreciably from the original results.

2.3. Proximate analysis

The concentrations of extractives, ash, lignin and carbohydrates in loblolly pine wood and the residues from the acid hydrolysis experiments were determined following the TAPPI methods T 211 om-93, T 264 cm-97, T 222 om-98 and T 249 cm-00 with the exception that the amount of residue available required smaller sample sizes than suggested in the standard procedures. Before analysis, all samples were dried overnight at 105 °C. The ash content was determined as the mass of the residue after heating the sample in air to 525 °C for 2 h (T 211 om-93). The extractives content was measured as the mass loss by Soxhlet extraction in dichloromethane for 24 cycles (T 264 cm-97). The lignin content was determined as the residue from hydrolysis in a 72% H_2SO_4 solution after filtration and drying (T 222 om-98). The concentrations of carbohydrates (e.g. glucose, arabinose, galactose, xylose and mannose in cellulose and hemicellulose) were measured after acid hydrolysis of the samples as described for the determination of the lignin content (T 249 cm-00). The liquid product obtained from this treatment was filtered and analyzed using High-Performance Anion-Exchange Chromatography with pulsed amperometric detector (HPAEC-PAD, Dionex, Sunnyvale, CA) with a CarboPac PA10 column.

2.4. Acid hydrolysis

For the hydrolysis experiments, aqueous stock solutions of the acids (sulfuric, phosphoric, nitric, trifluoroacetic and hydrochloric acid) were prepared prior to the experiment at room temperature by adding the acids to distilled water until the desired pH (usually 1.65; for TFA also 0.95 and 2.23) was reached. The pH of the stock solutions was measured using a Fischer Scientific AP50 electrode. The hydrolysis experiments were performed in batches consisting of 10 g of wood and 82.82 ml of aqueous acid solution. This corresponds to a liquid to solid ratio of 9 when the moisture in the wood is taken into account. The experiments were conducted in a 300 ml Parr autoclave reactor using Teflon liner to prevent corrosion of the reactor. The mixture of reactants was stirred at 170 rpm. The system was heated to the reaction temperature within 35 min (for reactions at 120 and 150 °C) or 50 min (for reactions at 200 °C). After 60 min at the reaction temperature, the heater was removed and the reactor was cooled to room temperature within 90 min with the aid of an ice bath. Experimental conditions of the individual reactions are given in Table 1. After the reaction, the solid and liquid reaction products were separated by filtration and the solid residue was washed with distilled water until the wash was clear. The washed residue was dried at 105 °C for 16 h. Soluble products yields were determined according to the following equation:

$$Y = \frac{m_{\mathrm{wood,dry}} - m_{\mathrm{residue}}}{m_{\mathrm{wood,dry}}} \cdot 100 \qquad (1)$$

where Y is the soluble products yield, $m_{\mathrm{wood,dry}}$ is the mass of the wood feedstock without its moisture content and m_{residue} is the mass of the residue after drying for 16 h.

2.5. ^{13}C CP MAS NMR spectroscopy

For solid state MAS NMR measurements, the samples were pressed into 7 mm zirconia rotors and spun at 5 kHz. The measurements were conducted on a Bruker Avance 300 spectrometer (Bruker BioSpin, Rheinstetten, Germany) with a resonance frequency of 75.48 MHz for ^{13}C. The signal-to-noise ratio was enhanced by applying cross polarization (Laws et al., 2002). The contact time was 1 ms. The spectra were recorded as the sum of 2400 scans and calibrated using the methine carbon atoms of adamantane as an external standard ($\delta = 29.47$ ppm). The spectra of treated and