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Sugars and sugar derivatives in ionic liquid media obtained from lignocellulosic biomass: Comparison of capillary electrophoresis and chromatographic analysis

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ABSTRACT

Processing of woody lignocellulosic biomass, under heating in combination with ionic liquids (ILs) was studied in order to obtain simple (fermentable) sugars. Due to the new environmental challenges, finding greener ways to produce platform chemicals and/or bio-fuels has become a popular research area. Various industrial, pilot or laboratory scale technologies for the depolymerization or fractionation of lignocellulosic polysaccharides to monomers are known. One of the new, interesting, methods is to utilize ILs in biomass pre-treatment procedures with an aim to bypass other pre-treatment methods. Furthermore, in order even to initiate studies whether ILs can contribute to catalytic depolymerization, there has to be a robust way to analyze the IL-treated lignocellulosics. This is a major issue since woody samples that contain any salts such as ILs can indeed be quite challenging from the analytic point of view. The applied capillary electrophoresis was found to be an excellent analytical method providing substantial improvements compared to the earlier used chromatographic methods.

In this work it was demonstrated that application of ILs, at elevated temperatures, contributes to hydrolysis and depolymerization of lignocellulose. The effect is time and temperature dependent: in harsh conditions sugars degrade but too low processing temperatures or short treatment times result in no meaningful effect. The formation of the degradation products of the monosaccharides is a good indicator of the harshness of the applied chemical conditions. Evidently, furfural and 5-(hydroxymethyl)furfural formed in rather short treatment times.

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1. Introduction

1.1. Utilization possibilities of lignocellulosic biomass

A lot of lignocellulosic biomass is not currently used for making wood products or pulp; in fact, for such fractions as residues from forestry or agriculture, straw and various energy crops other uses need to be found. These resources could tentatively be utilized in biorefinery processes where the aim would be to depolymerize the polysaccharides (cellulose and hemicelluloses) in lignocellulosic biomass to monosaccharides, which could then be further converted to alcohols, acids, or biopolymers (through chemical and enzymatic catalysis, or conventional fermentation process). Alcohols and acids produced in this way could also serve as platform chemicals in the production of liquid fuels, other chemicals, and bio-based polymers [1].

Both mono- and polysaccharides, obtained from biomass (and especially from wood) create an interesting new field for generating new products and research topics with relatively high expectations. Some high-value products utilizing biomass-derived mono- or polysaccharides (or new forest-based biorefinery type techniques in manufacturing processes) have already been successfully developed and commercialized (e.g. xylitol, furfural and various lignin-, cellulose- or hemicellulose-based products) [2–5]. Biodegradable films (e.g. derived from xylans and mannans) and other products, which are expected to be able – at least to some extent – to compete with plastics in future, are also under development [5–7].

Considering e.g. the bioethanol process, to achieve a high yield of sugar the lignocellulose is typically pre-treated thermochemically before enzymes are added [8]. Existing technology for pre-treatment of lignocellulose include acid-based methods, which

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may involve the utilization of catalysts such as sulfuric acid and sulfur dioxide, steam explosion and hydro-thermolysis, and alkaline methods, such as ammonia fiber explosion (AFEX) [8]. The method and conditions for biomass pre-treatment need to be selected on the basis of the recalcitrance of the feedstock. For example, acid hydrolysis serves as an appropriate option for more recalcitrant types of lignocellulose, such as softwood [8]. Pre-treatment with acid hydrolysis efficiently degrades the hemicelluloses and facilitates enzymatic attack on cellulose.

Apart from the conventional pre-treatment methods discussed above, there are also emerging technologies, such as treatment of lignocellulose with ionic liquids. High efficiency for the solvation of cellulose, lignin, and even wood has been proved in an increasing range of ionic liquids based on many different concepts, including those of dialkyl imidazolium derivates [9] and organic super-base derived approaches [10]. Utilization of various ionic liquid (IL) treatments, in combination with heat [10–14], have proven to dissociate wood polysaccharides to monosaccharides quite well. However, despite the efficient solvent properties of some ionic liquids (ILs), wood is not soluble in ionic liquids under mild dissolution conditions (e.g. 80 °C, 18 h) [11] – instead, usually in the IL treatment of wood, non-fibrous pulp is obtained, while lignin is not efficiently separated and wood components are selectively precipitated. Mechanical treatments, e.g. the pulverization degree of the sawdust, affect the lignin linkages and solubilization of wood [11]. Application of heat, microwaves, as well as ultrasound all contribute to the degradation/depolymerization of lignocellulosic material. Concerning temperature, 150 °C alone is apparently able to initiate the degradation of polysaccharides. Furthermore, it is important to keep in mind that also some ionic liquids, e.g. 1-ethyl-3-methylimidazolium chloride (EmimCl) and 1-butyl-3-methylimidazolium chloride (BmimCl), are starting to degrade at 150 °C [16–18] and, in addition, more stable ILs are not effective for treatment of lignocellulosic materials [15]. 1-ethyl-3-methylimidazolium acetate (EmimOAc) starts to decompose even earlier, i.e. at 120 °C.

1.2. Analysis methods

Chromatographic analytical methods are generally based on the derivatization of analytes to produce sensitive means of detection by UV–vis or even fluorescence spectroscopy. Neutral sugars have also been analyzed by HPLC using evaporative light-scattering (ELSD), refractive-index (RID) and pulsed-amperometric detectors (PAD). Since in capillary electrophoresis (CE) analysis, one has to overcome the extreme conditions required for the ionization of the carbohydrates and their low sensitivity to absorb UV light [19], some novel CE methods have been developed. One strategy is to add chromophores to the background electrolytes (BGEs) for indirect detection. Many suitable co-ions have been reported earlier, and several derivatization techniques have been devised. ILs were shown to be suitable BGE additives for the CE analysis of neutral carbohydrates [19]. CE method requires no derivatization, and only dilution is needed for the preparation of the samples. Adding ILs to BGEs serves therefore a dual function. First, ILs act as chromophores due to their absorbance of UV light, enabling indirect detection. Secondly, ILs interact selectively with the analytes to facilitate their separation.

Conventionally, when analyzing sugars or other carbohydrates in wood, paper and pulp sample with chromatographic methods, pre-treatment of sample is often needed: the sample is most often exposed either to acid hydrolysis, acid methanolysis or enzymatic hydrolysis, followed by derivatization/silylation prior to analysis. When acid hydrolysis, acid methanolysis, and enzymatic hydrolysis were compared in terms of depolymerization and analyzed by means of gas chromatography (GC) using both HP-1 and HP-5 capillary columns and FID (flame ionization detector) as well as MSD (mass spectrometric detector), HPAEC–PAD (high-performance anion-exchange chromatography with pulsed amperometric detection), and HPAEC-Borate (high-performance borate-complex anion-exchange chromatography with spectrophotometric detection) techniques for subsequent analysis of the released monosaccharides, the acid methanolysis method was proven to be a better method than the acid hydrolysis method for the samples containing xylan and uronic acid [20]. Acid hydrolysis was shown to be a requirement for crystalline polysaccharide depolymerization, but the strong acid conditions evidently led to degradation of labile sugars. Acid methanolysis combined with GC analysis was proven to be a convenient method for obtaining the sugar unit composition and amount of non-crystalline polysaccharides in lignocellulosic biomass [20]. However, the highest degree of recovery was observed for bleached chemical pulp samples, when the enzymatic and acid hydrolysis methods were used. The plant methanolyzates were not suitable as such for an analysis on an HPAEC–PAD system [20]. For analysis of the total amount of sugar units (including cellulose, other non-crystalline hemicelluloses, and pectins), a combination of the methanolysis and hydrolysis methods is recommended [20–22].

When conventional analysis methods cannot be used, for example, due to the toleration limits exceeding contents of salts (e.g. ILs or molten salts) in the samples, the recommendations given above will be of little value; namely the traditional GC and HPLC columns made for carbohydrate analysis do not tolerate much over 50 ppm of salts. Some reliability problems have been observed by the methods, using GC even in the case of a quantitative determination of monosaccharides in IL-containing samples when very diluted sample concentrations were used. Alternative analysis methods are under development, and particularly capillary electrophoresis seems to be the analysis method of choice in the future. The presence of high concentration salt solutions (ion character of ILs) results in analytical challenges in traditional columns [23,24]. This issue is particularly important if the utilized ILs are water-soluble and otherwise soluble in similar solvents as analytes such as monosaccharides, like it is the case in the work presented here.

1.3. General information about wood composition

5-HMF is the degradation product of hexoses (e.g. glucose (Glc), fructose (Fru), galactose (Gal), mannose (Man), rhamnose (Rha)), while furfural is the degradation product of pentoses (e.g. arabinose (Ara) and xylose (Xyl); and because hexoses are more common in woody biomass than pentoses in terms of the building blocks of the polysaccharides. Namely, hardwoods and softwoods contain, respectively, 35–50% and 35–45% of cellulose, 30–35% and 25–30% of hemicelluloses as well as 20–25% of lignin (in percentage of the dry wood solids), and in addition, the content of extractives is less than 5% for both [20,22,25]. The total amount of polymeric sugars is 60–85% of the dry wood solids. As cellulose consists of the hexose (glucose) units/monomeric building blocks, and the fraction of cellulose dominates over the share of the hemicelluloses in wood composition, there are indeed more hexoses than pentoses. The amounts of the hemicelluloses (building units of which are hexoses, pentoses, deoxyhexoses, and uronic acids) vary in the following way (in percentage of the dry wood mass): 15–20% galactoglucomannans in softwoods, 2–5% glucomannans in hardwoods, 7–10% arabinoglucuronoxylans in softwoods, 5–35% arabinogalactans in larch wood, and 15–30% glucuronoxylans in hardwoods [25,26]. The softwood hemicelluloses – galactoglucomannans and arabinogalactans – contain more hexoses than pentoses as their building blocks (despite the name, Gal is the main building block in arabinogalactans, and Glc and Man are the main building blocks in galactoglucomannans). However, the xylans that

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