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Towards recycling of ionic liquids in fiber spinning process –Carbohydrate transformation products in aqueous ionic liquid solutions studied by liquid chromatography/quadrupole time-of-flight mass spectrometry

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ABSTRACT

New technologies for the production of man-made cellulose fibers are being developed to produce fibers sustainably for various textile applications. The Ioncell® process uses an ionic liquid in which cellulose is dissolved to form a spinning solution. This spinning solution is spun into an aqueous coagulation bath using dry-jet wet spinning technology to produce Ioncell fibres. In order to develop a sustainable and economically viable process, the ionic liquid must be efficiently recycled in the process. Organic compounds resulting from degradation reactions of the cellulosic materials used for fiber production might accumulate in the ionic liquid over time and reduce its dissolution power. This study aimed to tentatively identify the main carbohydrate transformation products from aqueous ionic liquid solution. In addition to the actual coagulation bath sample, carbohydrate transformation reactions were studied using model samples. The main monomeric carbohydrate constituents of a hardwood pulp, glucose and xylose, were mixed with an ionic liquid and water and heated to 90 °C for 8 h to accelerate the transformation reactions. Most of the original monosaccharides were converted into other compounds, so that after the heat treatment only 11 wt% of the glucose and 1.1 wt% of the xylose remained. The liquid chromatography/time-of-flight mass spectrometry analyses revealed that both the spin bath sample and model samples contained mainly hydroxycarboxylic acids and carboxylic acids. The superbase of ionic liquid catalyzed the alkaline transformation reactions of carbohydrates.

1. Introduction

Ioncell® is a cellulose processing technology to produce man-made cellulose fibers for textile and technical applications. This technology utilizes protic superbase ionic liquids (ILs) such as 1,5-diazabicyclo [4.3.0]non-5-enium acetate ([DBNH][OAc] or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate ([mTBDH][OAc]) as cellulose solvents [1]. ILs have important role in current glycoscience due to their dissolution power, environmentally benign nature, and recyclability among other features [2]. In the Ioncell® process, the fibers are regenerated in an aqueous coagulation bath. In a continuous process, the IL needs to be recovered from the coagulation bath and reused in the process for cellulose dissolution. Recycling of IL is impeded by the fact that part of the IL molecules degrades in an aqueous environment [3]. Also, organic impurities from cellulosic materials may accumulate in the coagulation bath, and these impurities can affect the dissolution ability of IL in the continuous process. While the organic impurities in the coagulation bath of the Ioncell® process have not yet been studied, organic degradation products from viscose coagulation baths have been reported in the literature [4]. Most of these products are carboxylic acids derived from monosaccharide degradation [4,5]. Generally, monosaccharide degradation products have been characterized using gas chromatographic (GC) techniques, GC-FID, and GC-MS after trimethylsilylation [4,6].

The use of liquid chromatographic (LC) techniques for the characterization of organic compounds from IL/water mixtures would be feasible since no extraction with organic solvents or derivatization is needed, unlike in the case of GC. Identification of the organic

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compounds in the IL/water mixtures is, however, a difficult task. The amount of these compounds in the spinning bath is likely to be very low, and the IL, which is abundant in the sample matrix, may interfere with the analysis. This is true especially if carboxylic acids are analyzed in the presence of either [DBNH][OAc] or [mTBDH][OAc], both of which contain acetic acid. Chromatographic separation of low amounts of carboxylic acids from a matrix containing acetic acid is a challenge. In our preliminary tests, ion chromatography (IC) with Dionex PA-22 column was tested for a mixture of lactic acid and acetic acid (the concentration of acetic acid was a thousand times higher compared to lactic acid), but no satisfactory separation between the two components was achieved, as expected. Removal of acetic acid from the samples by solid-phase extraction could also be an option, but the structural similarity to other organic acids complicates this approach. Due to the above-mentioned challenges, the optimal method should be insensitive to acetic acid but highly sensitive to other carboxylic acids. Negative mode electrospray ionization MS (ESI-MS) yields a weak signal for acetic acid [7]; therefore, MS in negative mode is the optimal detection method in this case.

Ion exclusion chromatography with H-type cation exchange resin has been commonly used for the separation of organic acids, monosaccharides, alcohols, and sugar degradation products from various sample matrices (food, biomass, etc.). With these types of columns, the acids are separated in their protonated form, and thus, dilute sulfuric acid is commonly used as a mobile phase. The disadvantage of sulfuric acid is its non-volatility, which prohibits its use with mass spectrometry (MS). Nevertheless, ion exclusion columns have been successfully coupled to MS by substituting the sulfuric acid with volatile acids such as acetic or formic acids [7–9].

This study aimed to tentatively identify possible organic contaminants (cellulose-/pulp-based) in the [mTBDH][OAc] containing spin bath solution. Identification of the major organic contaminants is crucial since they may accumulate in the IL when the IL is recycled and eventually reduce the solvation capacity of the IL. Since the amounts of organic contaminants in the spin bath solution were expected to be low, the solution was concentrated by thin film evaporation and batch distillation before the analysis. In addition, the degradation of the main hardwood pulp compounds cellulose and xylan, as well as their monosaccharides glucose and xylose in [mTBDH][OAc] at elevated temperature and reaction time was investigated using model experiments. Liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-qTOF-MS) was used for the separation and identification of the organic contaminants from the challenging IL-containing sample matrix.

2. Experimental

2.1. Materials

D-Xylose and D-glucose were purchased from Sigma-Aldrich (Germany). Pre-hydrolyzed kraft birch pulp sample was provided by Stora Enso (Enocell mill, Finland). mTBD superbase was from BOC Sciences (USA), and equimolar IL was prepared by mixing stoichiometric amounts of base and glacial acetic acid in a glass reactor. Birch xylan was extracted from sawdust from a sawmill with pressurized hot-water extraction [10]. The extract was concentrated by ultrafiltration [11]. The concentrated extract was ethanol precipitated, pressure filtered to remove ethanol, and dried. The sample was dissolved in water and further purified by eluting through XAD7HP adsorbent, concentrated by heating under nitrogen flow, and again ethanol precipitated. The precipitate was collected and dried in a vacuum oven to produce a xylan sample for the experiments. Details of the procedure can be found in the supplementary file S1. All other reagents and standard compounds were from Sigma-Aldrich, Merck, or VWR Prolabo.

2.2. Acceleration of carbohydrate transformation reactions in [mTBDH][OAc]

The main hardwood polysaccharide constituents (D-glucose, D-xylose), birch xylan, and birch pulp were mixed with [mTBDH][OAc] and water so that the carbohydrate consisted of 5 %, ionic liquid 90 %, and water 5 % (wt%). The mixtures were heated to 90 °C in an oven, and the elevated temperature was maintained for 8 h to accelerate the transformation reactions. After the heat treatment, the samples were cooled down to room temperature and stored in a refrigerator.

2.3. Concentration of the spin bath solution

The water removal from the aqueous ionic liquid solution from the spin bath and concentration of the carbohydrate transformation products were performed in three stages. Firstly, a pilot-scale agitated thin-film evaporation system by UIC GmbH, was used to lower the water content to approximately 50 mass-%. Secondly, the pre-concentrated ionic liquid was re-treated using the agitated thin film evaporation system to a water content of 3.2 mass-%. Lastly, reduced-pressure batch distillation (distillation pressure 1.6 mbar) was used to concentrate the carbohydrate transformation products. According to analysis of the distillate fractions (95 mass-% of the initial batch) and the bottom product (5 mass-% of the initial batch), it was evident that carbohydrate transformation products were enriched to a high degree in the bottom flask.

2.4. Liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-qTOF-MS)

The major carbohydrate transformation products were identified with LC-MS. Agilent 1260 HPLC system was coupled to Agilent 6350 Accurate-Mass Q-TOF mass spectrometer. An ion exclusion column (Phenomenex Rezex ROA H^+ (300 × 7.8 mm) was selected since most of the degradation products were assumed to be acidic. The eluent used was 0.5 % formic acid, and the flow rate was 0.5 ml/min. The column was heated to 55 °C. The Q-TOF parameters used were as follows: gas temperature (N_2) 300 °C, fragmentor voltage 75 V, and capillary voltage 3000 V. A scan range m/z from 50 to 1100 was selected. All the samples and standards were diluted with 0.5 % formic acid. The concentration of reference compounds was between 1 and 10 mg/l. The model samples and concentrated spin bath sample were diluted to around 1:3 or 1:4 (w/v). Since formic acid and acetic acid could not be detected with the LC-MS setup described above, the analysis was done with LC-UV (UV at 210 nm) using similar chromatographic conditions except that the eluent was changed to 0.0025 M sulfuric acid.

2.5. Size-exclusion chromatography (SEC)

The degradation of pulp samples was monitored with SEC system consisting of Dionex Ultimate 3000 HPLC module, Shodex RI (RI-101) detector, and Viscotek/Malvern SEC/MALS 20 multi-angle light-scattering (MALS) detector. The columns used were Agilent PLgel MIXED-A (x 4), and the flow rate was 0.75 ml/min. The pulp samples were dissolved in DMAc/LiCl eluent (final composition 0.9 % LiCl in DMAc) using a solvent exchange procedure (water/acetone/DMAc) [12]. The injection volume was 100 µl. Detector constants (MALS and DRI) were determined using a narrow polystyrene sample with M_w of 96 000 g/mol and $Đ$ 1.04 [13]. The $\partial n/\partial c$ value of 0.136 ml/g was used for celluloses in 0.9 % LiCl in DMAc [12].

Molar mass distributions of hemicellulose model samples were determined using Agilent 1100 HPLC system equipped with ultraviolet (UV) and refractive index (RI) detectors. The columns used were Polymer Standards Service MCX 300 × 8 mm (three columns with pore sizes of 100 Å, 500 Å, 1000 Å). The flow rate was 0.7 ml/min, and the injection volume was 50 µl. The samples were dissolved in eluent (0.1 M

NaOH) at a concentration of 2 mg/ml. The calibration curve was accomplished with polystyrene sulfonate standards (1000–29800 g/mol), ascorbic acid (176 g/mol), and NaCl (58 g/mol). Samples and standards were filtered with 0.2 μm syringe filters before analysis.

2.6. High-performance anion-exchange chromatography with pulse-amperometric detection (HPAEC-PAD)

The monosaccharide content in glucose and xylose model samples was analyzed using Dionex ICS-5000 HPAEC-PAD. The column used was Dionex CarboPac PA20, and the flow rate was 0.38 ml/min. Water was used as eluent, and 0.1 M NaOH was added post-column before the PAD detector. The calibration curve was constructed using monosaccharide solutions covering the concentration range from 1 mg/l to 50 mg/l. All the samples were filtered with 0.2 μm syringe filters.

3. Results and discussion

3.1. Degradation of pulp and hemicelluloses

The molar mass distribution of hardwood pulp was determined for an untreated sample and a sample heat-treated in IL to test whether the treatment caused degradation of the polysaccharides. As seen in Fig. 1 A, only minor differences can be observed in the case of birch pulp. The overlay of the two distributions reveals, however, changes in the low-molar-mass region. Even dissolving pulps commonly contain a few percentages of hemicelluloses, and these hemicelluloses are assumed to elute at the low-molar-mass side of the distribution. Since cellulose is expected to be more resistant in ILs, the differences observed in the low-molar-mass region might originate from the partial degradation of hemicelluloses (xylans in the case of hardwood).

In addition to the pulp, the possible effect of heat treatment in the presence of IL and water on hardwood hemicellulose, birch xylan, was investigated. Birch xylan degraded considerably during heat treatment (Fig. 1 B). The weight-average molar mass (M_w) of birch xylan decreased from 2200 g/mol to 660 g/mol. Since the IL [mTBDH][OAc] creates alkaline conditions in the presence of water, the reduction of molar masses is likely due to alkaline hydrolysis and alkaline peeling reactions. In the alkaline peeling reaction, monosaccharides are released from the reducing end of the polysaccharide chain. The peeling reaction is initialized by a keto-enol tautomerization reaction that opens the hemiacetal at the reducing end of the polysaccharide into an aldehyde, and as a result, a monomer is removed from the polysaccharide backbone by β-alkoxy elimination [14,15]. Due to the amorphous nature of hemicelluloses, they are more prone to alkaline peeling compared to cellulose [16]. The heat-treated glucose and xylose samples were also analyzed by SEC, and the results showed that the compounds both having molar masses lower than the mass of the monosaccharides, as well as compounds having higher molar masses than the mass of the monosaccharides, were present indicating the occurrence of both degradation and condensation reactions in IL (chromatograms not shown). Ion exclusion chromatography coupled to qTOF-MS was employed for a more detailed investigation of these compounds.

3.2. Tentative identification of carbohydrate transformation products in IL/water mixtures

Based on the existing literature on carbohydrate degradation/transformation in alkaline conditions, acidic compounds were expected to form from carbohydrates in IL/water mixtures. The list of compounds found in the LC-qTOF-MS analysis is presented in Table 1 and the extracted ion chromatograms (EICs) for major organic compounds found in the concentrated spin bath solution are given in Fig. 2. It should be noted here that the identification of compounds was based on the *m/z* values and retention time comparison between the standard compounds and peaks observed from the samples. Since it was likely that the samples contained isomers and compounds that are not fully resolved in the ion exclusion column, the identification suffers from a certain

Table 1
Identified organic degradation products of glucose and xylose in [mTBDH][OAc] and concentrated [mTBDH][OAc] spin bath solution identified by LC-MS.

	Formula	Glucose	Xylose	Spin bath solution
Formic acid[a]	CH_2O_2	x	x	x
Glyoxal	$C_2H_2O_2$			x
Glycolic acid	$C_2H_4O_3$	x	x	x
Methylglyoxal	$C_3H_4O_2$	x	x	x
Hydroxyacetone	$C_3H_6O_2$	x	x	x
Pyruvic acid	$C_3H_4O_3$	x	x	x
Lactic acid	$C_3H_6O_3$	x	x	x
Glyceraldehyde	$C_3H_6O_3$		x	x
Malonic acid	$C_3H_4O_4$		x	x
Glyceric acid	$C_3H_6O_4$	x		
Tartronic acid	$C_3H_4O_5$	x	x	x
2-Hydroxybutanoic acid	$C_4H_8O_3$			x
Maleic acid	$C_4H_4O_4$		x	
Succinic acid	$C_4H_6O_4$	x	x	x
Malic acid	$C_4H_6O_5$	x	x	x
Erythronic acid	$C_4H_8O_5$	x	x	
Glutaric acid	$C_5H_8O_4$		x	
2-Deoxy-d-arabinose	$C_5H_{10}O_4$	x		x
α/β-Ketoglutaric acid	$C_5H_6O_5$	x	x	x
Xylonic acid/Arabinonic acid	$C_5H_{10}O_6$	x	x	
Catechol	$C_6H_6O_2$		x	
Adipic acid	$C_6H_{10}O_4$			x
Tricarballylic acid	$C_6H_8O_6$			x
D-glucuronic acid	$C_6H_{10}O_7$	x		
Gluconic acid	$C_6H_{12}O_7$	x		

[a] Detected by LC-UV.

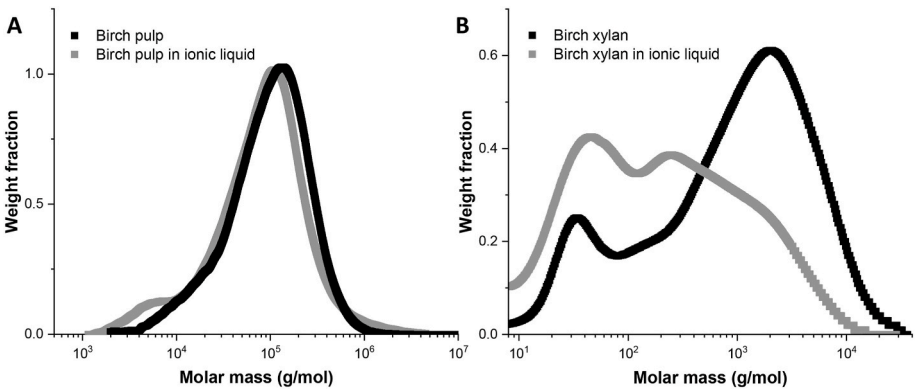

Fig. 1. Molar mass distributions for birch pulp (A) and birch xylan (B) and their counterparts heat-treated in presence of ionic liquid and water.

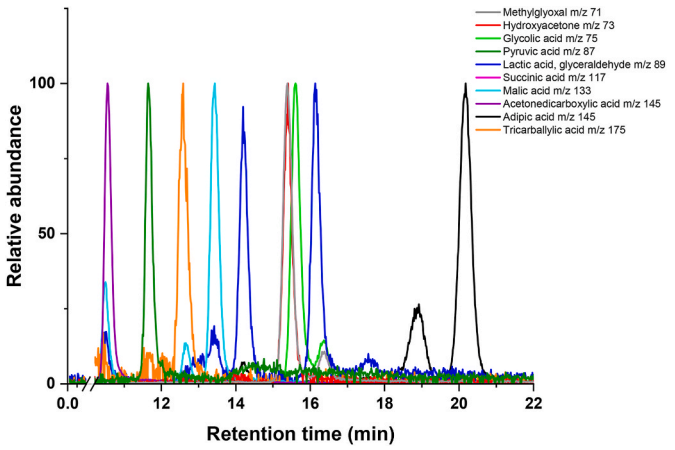

Fig. 2. Extracted ion chromatograms (EICs) for the major organic compounds found in the concentrated spin bath sample. Methylglyoxal, hydroxyacetone, and succinic acid elute at the same retention time of 15.4 min. Lactic acid and glyceraldehyde have the same chemical formula, but their retention times differ from each other (glyceraldehyde 14.2 min and lactic acid 16.1 min).

uncertainty. Verification of the peak identification would require tandem MS. Due to the presence of various compounds, several transformation mechanisms likely occur in the IL/water mixtures. The prevailing mechanisms are summarized in the following paragraphs. The IL [mTBDH][OAc] creates alkaline conditions in the presence of water, which promotes alkaline degradation of polysaccharides and monosaccharides. The content of monosaccharides in heat-treated IL solutions was determined with HPAEC-PAD. After this treatment, only 15 wt % of glucose and 1.1 wt % of the xylose employed could be detected. Thus, the majority of the monosaccharides were transformed into other compounds in the IL.

3.3. *Compounds having ≤4 carbon atoms*

Compounds having fewer than 5 carbon atoms (xylose) or 6 carbon atoms (glucose) can be formed as direct cleavage products of the monosaccharide intermediates and by subsequent reactions of the cleaved carbonyl compounds formed. Formic acid was found in our glucose and xylose model samples as well as in the spin bath sample. Also, the amount of acetic acid was slightly increased in monosaccharide model samples from the initial amount originating from IL, suggesting the formation of acetic acid during heat-treatment. The formation of these low-molar-mass acids from the monosaccharides in alkaline conditions has been extensively discussed in literature. Degradation is assumed to begin with the isomerization of the monosaccharide to an α-dicarbonyl intermediate by loss of water and followed by benzilic acid-type rearrangement to produce acidic degradation products [17]. It was stated that saccharinic acids are formed from monosaccharides in alkaline media by benzilic acid rearrangement of the corresponding deoxyuloses [18]. The presence of saccharinic acids (glucoisosaccharinic acid and xyloisosaccharinic acid) could not be verified due to a lack of standard compounds. The same applies to deoxyuloses. The presence of deoxyuloses could not be verified in this study, but LC-qTOF-MS analyses suggested the presence of $C_6H_{10}O_5$ in both the monosaccharide model samples as well as in the concentrated spin bath sample, evidencing the presence of these compounds. Low molar mass acids have been proposed to form from the deoxyuloses. Formic acid can form by hydrolytic α-dicarbonyl cleavage of 3-deoxy-D-*erythro*-hexos-2-ulose. Acetic acid can form by hydrolytic α-dicarbonyl cleavage of 1-deoxy--D-*erythro*-hexo-2,3-diulose [19] or β-dicarbonyl cleavage of 1-deoxy--hexo-2,4-diulose [20]. Additionally, the amount of formic acid has been observed to correlate with the amounts of hydroxyacetone and methylglyoxal [18]. Both carbonyl compounds were tentatively identified in the glucose and xylose model samples as well as in the concentrated spin bath solution. These compounds are possible precursors for acetaldehyde, which is an intermediate of acetic acid. In addition to methylglyoxal, glyoxal was found from the spin bath sample. Glyoxal, glyceraldehyde, and glycolaldehyde are products of retro-aldol reactions formed from C5 and C6 monosaccharides. Glyoxal is known to derive from biomass by oxidation via glycolaldehyde [21].

All the heat-treated model samples turned dark brown in the oven (Fig. 3). The IL [mTBDH][OAc] itself has a light yellowish color, so it was obvious that carbohydrates were responsible for the discoloration. As already mentioned, methylglyoxal was found in all the samples studied, as well as pyruvic acid, which is formed from methylglyoxal by oxidation. Methylglyoxal is known to form from glucose via its 2,3-enol form and fragmentation of 3-deoxyglucosone [22]. Alternatively, methylglyoxal has been proposed to form from glucose and xylose via the Maillard reaction. Model reactions between these monosaccharides and lysine are the most studied [22–25]. In the model studies with xylose, 4-hydroxy-5-methyl-3(*2H*)-furanone (HMFO) was identified as an intermediate, which then transformed to 2-hydroxy-3,4-dioxo-pentanal and further decomposed to dicarbonyl compounds, namely methylglyoxal and diacetyl. Methylglyoxal can also be formed from 1-deoxyxylosone (1-DX). Dicarbonyl compounds methylglyoxal and diacetyl can polymerize to brown or colorless polymers with or without amines. Methylglyoxal derived from HMFO has been found to contribute significantly to the browning in the model systems [22,24,25]. Thus, methylglyoxal might have caused the brownish color of our IL model samples. The superbase mTBD used here is known to hydrolyze to 1-[3-(methylammoniopropyl]-1,3-diazinan-2-one (H-mTBD-1) and 1-[3-ammoniopropyl]-3-methyl-1,3-diazinan-2-one (H-mTBD-2) to some extent [3], and these amines might contribute to the discoloration reactions. Nitrogen-containing higher-molar-mass compounds were also observed in the LC-qTOF-MS analysis, which might indicate the presence of polymerized (brown) compounds. In addition, SEC analysis of heat-treated monosaccharides indicated the presence of compounds with a higher molar mass than the mass of glucose or xylose.

Glycolic acid was present in all studied samples, and it has been reported to be one of the major acids found in the model studies on carbohydrate degradation in alkaline conditions [7,17,26,27]. Glycolic acid can be formed by oxidation of glycolaldehyde, but also from glyoxal via the intermolecular Cannizzaro reaction, and when hydrogen peroxide reacts with hydroxymethyl glyoxal [18,28]. The formation of hydroxymethyl glyoxal could not be verified in this study due to the lack of a standard compound. Glucose model sample, however, contained

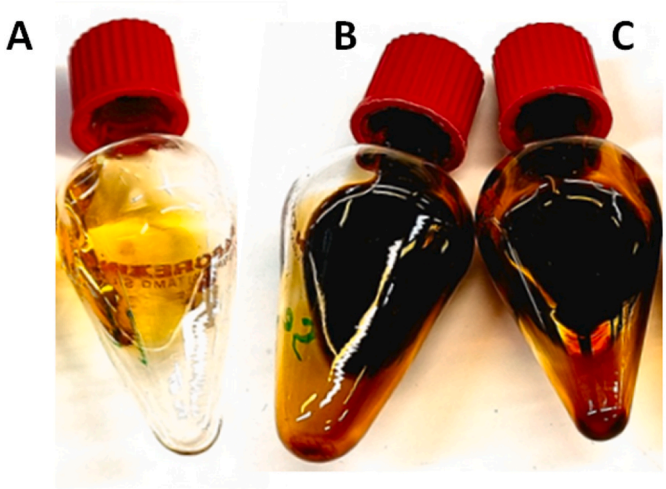

Fig. 3. Model samples containing ionic liquid after heat-treatment. Ionic liquid and water (A), ionic liquid, water, and xylose (B), and ionic liquid, water, and glucose (C). See Experimental section for further details on the model samples.

several peaks indicating the presence of $C_3H_4O_3$, and thus, the existence of hydroxymethyl glyoxal in the glucose model sample cannot be completely ruled out.

Both model samples, as well as spin bath sample, likely contained hydroxyacetone. Hydroxyacetone has been reported to form from the Amadori rearrangement product of ^{13}C-labelled glucose via β-cleavage. Similarly, glyceraldehyde forms from glucose Amadori rearrangement product via retroaldolization in neutral or alkaline conditions [29]. Hydroxyacetone can be oxidized to methylglyoxal, which can be oxidized further to pyruvic acid [18]. Like hydroxyacetone, pyruvic acid was also found in both glucose and xylose model samples, as well as in the spin bath sample.

Several mechanisms have been proposed for the formation of lactic acid from monosaccharides in alkaline conditions. Lactic acid can be formed from methylglyoxal via the Cannizaro reaction or by direct oxidation of lactaldehyde [18]. The formation of lactic acid from pentoses and hexoses can also be explained by oxidative α-dicarbonyl cleavage of 1-deoxy-3,4-diuloses [20]. In addition, lactic acid can be formed from fructose via dihydroxyacetone [30]. Other C3 acids, namely malonic acid, glyceric acid, and tartronic acid were also tentatively detected. Glyceric acid was found from glucose and xylose model samples. It can be formed from the oxidation of glyceraldehyde or by the intermolecular Cannizzaro reaction of hydroxymethylglyoxal. Similarly, tartronic acid is an oxidation product of glyceraldehyde, and dihydroxyacetone and glyceric acid are formed as intermediates [18]. Glyceraldehyde was found in xylose model sample and the spin bath sample. Formation of malonic acid from biomass is reported in the literature [7,31] but the reaction mechanism of malonic acid is less discussed. Malonic acid was detected in model studies, in which the role of lignin in the alkaline degradation of biomass was investigated using acetovanillone and methyl β-D-glucopyranoside as model compounds. The acetovanillone-induced formation of methanol from β-D-glucopyranoside was suggested. This pathway might then produce malonic acid [31].

2-Hydroxybutanoic acid, maleic acid, succinic acid, malic acid, and erythronic acid are C4 acids, which were tentatively detected in the IL containing samples. 2-Hydroxybutanoic acid was found after treatment of cotton cellulose with 3 M NaOH at 260 °C [27]. It has also been reported that 2-hydroxybutanoic acid has been found in the black liquor from Kraft pulping of wood [32] and has been confirmed to form especially from arabinoxylans [33]. Maleic acid was detected only in the xylose model sample. Maleic acid can be formed by oxidation of furfural, which might explain its formation from xylose [34]. Furfural, however, was not detected in the samples (neither with MS nor UV), which was not surprising since furfural is formed from C5 monosaccharides under acidic conditions. Maleic acid can transform to malic acid in the presence of water [34]. Malic acid was detected in all the samples. Oxidative α-dicarbonyl cleavage was proposed for the formation of erythronic acid from deoxyuloses [18,20]. Succinic acid has been reported to form from cellulosic biomass in alkaline conditions [7,17,35]. Free radicals are formed during monosaccharide degradation, and it has been postulated that succinic acid forms by recombination of free radicals [36]. The formation of main degradation products (according to our best knowledge) is summarized in Fig. 4.

3.4. Compounds having 5 or 6 carbon atoms

Several compounds having 5 or 6 carbon atoms were detected in the monosaccharide model samples. Some of them could not be verified due to the lack of standard compounds. LC-qTOF-MS analysis suggested the presence of $C_5H_8O_4$, which could be xylo-isosaccharinic acid-1,4-lactone (XISAL). In the case of the xylose model sample, however, the identified $C_5H_8O_4$ compound was likely glutaric acid based on the retention time of the glutaric acid standard compound. α-Dicarbonyl cleavage of 3-

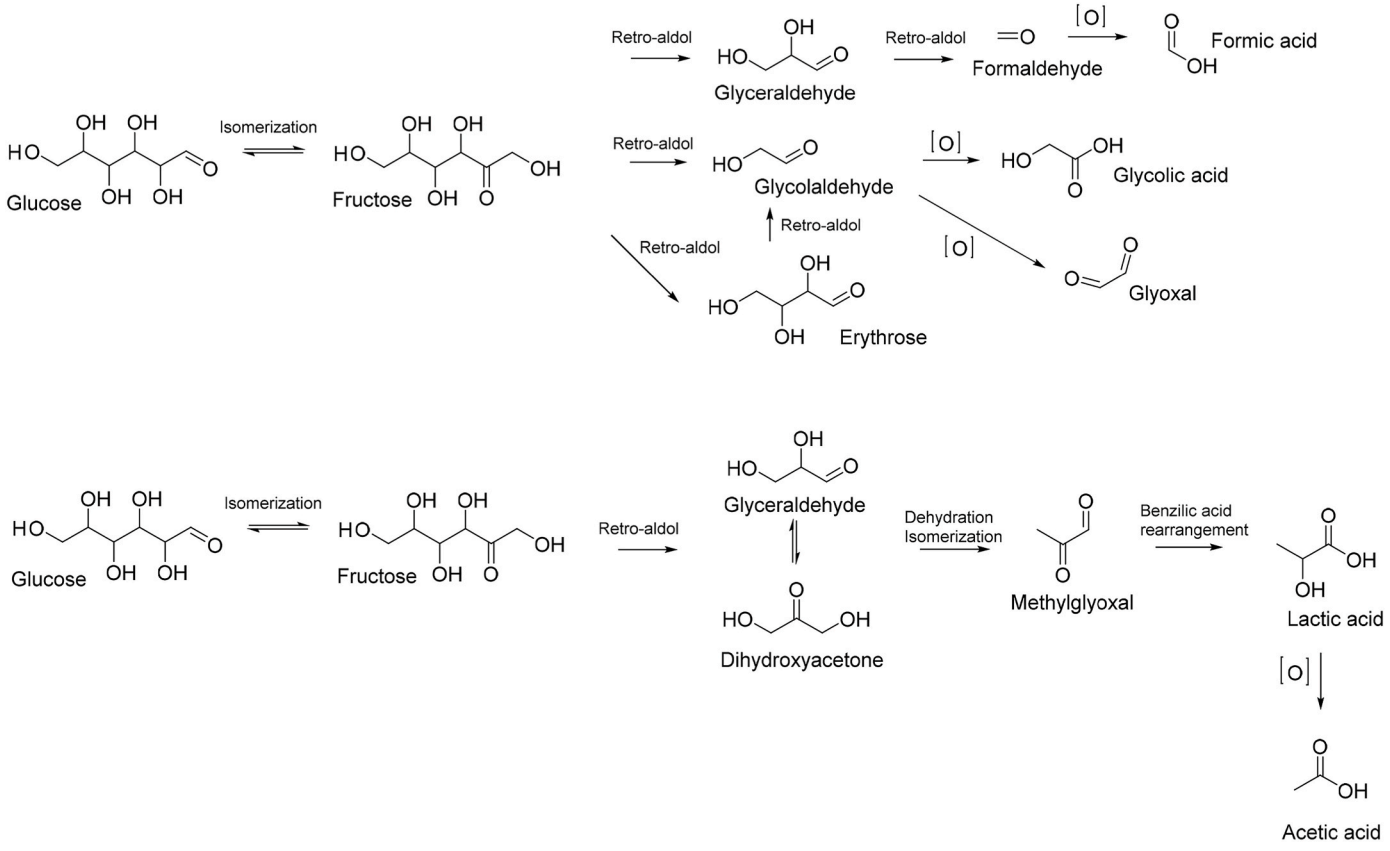

Fig. 4. Formation of main monosaccharide degradation products in alkaline conditions.

deoxy-D-*erythro*-hexos-2-ulose yields formic acid and 2-deoxy-D-arabinose [18] the latter of which was found in glucose model sample and the concentrated spin bath sample. Very likely, all samples also contained ketoglutaric acid (α and/or β; only β-ketoglutaric standard was run as reference).

Xylonic acid and/or arabinonic acid (only xylonic acid standard was analyzed, and thus the presence of arabinonic acid cannot be verified) were found in both xylose and glucose model samples. Pentoses (xylose, arabinose) are known to form from glucose by selective C–C bond cleavage in the presence of weak Brønsted acids [37]. Xylose was also reported to form from glucose in the hydrothermal reaction when NaOH was used as an alkaline catalyst. Xylose is then further transformed to formic and glycolic acids via formaldehyde and glyceraldehyde [38]. In our case, $C_5H_{10}O_5$ structures were detected in the glucose model sample, indicating the transformation of glucose into pentose structures. According to our findings, some amount of xylose was partially oxidized to xylonic acid and/or arabinonic acid.

As revealed by the HPAEC-PAD analysis, xylose and glucose model samples contained some amounts of original monosaccharides that were not transformed into other compounds. Thus, $C_6H_{12}O_6$ compounds were also detected from the glucose model sample and $C_5H_{10}O_5$ from the xylose model sample in the LC-qTOF-MS analysis. The presence of deoxypentonic and deoxyhexonic acids could not be verified. In terms of C6 acids, adipic acid and tricarballylic acid were detected from the spin bath sample. Both acids have been found to form from biomass after acidic pretreatment [7,39] but fewer studies have reported that these structures may form in alkaline conditions. Adipic acid has been proposed to form from glucose via glucaric acid [40] but it can also form from cellulosic materials under alkaline conditions [35]. D-glucuronic acid was likely present in the glucose model sample. Oxidation of the C-6 hydroxyl group of glucose has been reported to occur with various mechanisms [18,41]. The glucose oxidation product, gluconic acid, was present in the glucose model sample.

The xylose model sample contained a $C_6H_6O_2$ compound, which was identified as catechol. Catechol has been reported to form from glucose and xylose in alkaline conditions (NaOH) at 96 °C [42]. Catechol, in addition to other phenolic compounds, cyclopentanones, and hydroquinones, has been reported to form from cellulosic biomass through a thermochemical liquefaction route in which the biomass conversion is facilitated at high temperature (300 °C) in the presence of an alkaline catalyst. It was demonstrated that two four-carbon compounds, biacetyl and acetoin, act as precursors for aromatic components during thermochemical liquefaction. From these two precursors, biacetyl can be formed from glucose via a retro-aldol reaction. In addition, biacetyl has been found to form from erythrose or glyceraldehyde [43].

LC-qTOF-MS analyses revealed the presence of higher-molar-mass compounds (≥C7), but these compounds were not identified. Many of the higher-molar-mass compounds contained nitrogen, indicating the presence of structures that were formed from both carbohydrates and IL. In addition, chromophores containing aromatic and quinoid structures were likely formed both in the model samples and in the spin bath sample.

4. Conclusions

To date, a limited amount of knowledge on the carbohydrate degradation/transformation products in ionic liquids is available in the literature. In this study, the two most prevalent monosaccharide constituents present in hardwood pulp, glucose and xylose, were heat-treated in the presence of [mTBDH][OAc] and water to accelerate the transformation of carbohydrates to other compounds. In addition, coagulation (spin) bath solution from an Ioncell® cellulose spinning process was collected and concentrated using thin film evaporation and batch distillation. Organic compounds from both the model samples as well as concentrated spin bath solution were tentatively identified using LC-qTOF MS analysis (identification based on the retention times and *m/z* values). Most of the degradation products were hydroxycarboxylic acids and other carboxylic acids. In addition, glyoxal, methylglyoxal, hydroxyacetone, glyceraldehyde, 2-deoxy-D-arabinose, and catechol were tentatively identified. All these compounds can be expected to form from carbohydrates in alkaline conditions. Thus, it can be concluded that IL [mTBDH][OAc] catalyzes the carbohydrate transformation reactions in the presence of water. The identification of the most important organic carbohydrate transformation products in IL is important for the development of fiber spinning and solvent recovery processes. Degradation products from the cellulosic raw material used for the fiber production accumulate in the IL over time. At the latest, when a concentration is reached at which the dissolving capacity of the recycled IL or spinnability of the solution is impaired, these degradation products must be removed from the system. Analytical methodology for detection of these products is crucial also when developing the IL purification strategies.

CRediT authorship contribution statement

Leena Pitkänen: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Monika Tuominen:** Writing – review & editing, Investigation. **Behnaz Asadzadeh:** Writing – review & editing, Methodology, Investigation. **Petri Uusi-Kyyny:** Writing – review & editing, Methodology, Investigation. **Kalle Kaipanen:** Writing – review & editing, Resources. **Petri Kilpeläinen:** Writing – review & editing, Resources. **Michael Hummel:** Writing – review & editing, Conceptualization. **Herbert Sixta:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2025.109808.

Data availability

Data will be made available on request.

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