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CELLULOSE VALORIZATION IN IONIC LIQUIDS

November 2011

KATHOLIEKE UNIVERSITEIT
LEUVEN

Arenberg Doctoral School of Science, Engineering & Technology
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Igor IGNATYEV

Dissertation presented in
partial fulfilment of the
requirements for the degree
of Doctor of Bioengineering

November 2011

Doctoraatsproefschrift nr. 996 aan de faculteit Bio-ingenieurswetenschappen van de K.U.Leuven

CELLULOSE VALORIZATION IN IONIC LIQUIDS

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Dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Bioengineering

November 2011

ISBN 978-90-8826-212-8
D/2011/11.109/45

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Acknowledgements

First, I am gratefully indebted to my promoter Prof. Dr. Dirk de Vos for teaching, helping, motivating and inspiring me throughout my PhD studies at K.U.Leuven. He showed me the beauty of the scientific research.

I would like to thank Prof. Dr. Koen Binnemans for co-supervising my research.

I also thank very much my dear mother Docent Dr. Lidia Ignatyeva, Mikhail, and all other family members for their trust, hope and support.

I also thank my colleagues: Charlie, Pascal, Sabina, Johan, Stef, Dirk, Bart, Paolo, Loon, Roman, Annelies, Jan, Tamas, Elena, Titus, Lieve, Pieter, José, Sree and all others for their support, presence and advises.

Hilda, Lieve, Ines and Birgit helped me a lot with administrative issues.

I am grateful to new friends I have met Leuven: Wim, Lucas, Stéphane, Karel, Liviu, Dimitri, Dorin and Florin.

Financial support by K.U.Leuven (project IDO/05/005 and CECAT grant) and the PhD fellowship (DBOF) from the Leuven Arenberg Doctoral School are gratefully acknowledged. I would like also to thank IoLiTec (Denzlingen, Germany) for their support.

Igor Ignatyev

List of Publications

- **I.A. Ignatyev**, C.V. Doorslaer, P.G.N. Mertens, K. Binnemans, D.E. De Vos, *ChemSusChem*, **2010**, *3*, 91.

- **I.A. Ignatyev**, C.V. Doorslaer, P.G.N. Mertens, K. Binnemans, D.E. De Vos, *Green Chem.*, **2010**, *12*, 1790.

- **I.A. Ignatyev**, P.G.N. Mertens, K. Binnemans, D.E. De Vos, *Holzforschung*, **2011**, in press.

Curriculum Vitae

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Abstract

Cellulose and some other polysaccharides can be used, in principle, as renewable sources of valuable chemicals and energy. However, many classical solvents cannot be used as reaction media for processing of these biopolymers. Relatively recently a new class of solvents, ionic liquids, has been discovered as suitable solvents for different types of biopolymers. For instance, the ionic liquid 1-butyl-3-methylimidazolium chloride can dissolve up to 25 wt. % of cellulose. This discovery has opened new perspectives for cellulose valorization. In this dissertation, different approaches for valorization of cellulose and of some other biochemicals are studied.

The first approach was the reductive splitting of cellulose in the presence of hydrogen gas. Initial experiments were performed with model substrates. The study was started with the hydrogenolysis of the ketal 1,1-diethoxycyclohexane in solvent-free systems (since this ketal is not soluble in the ionic liquids of interest) over heterogeneous metal catalysts. Secondly, cellobiose was split and reduced in 1-butyl-3-methylimidazolium chloride in the presence of the homogeneous precatalyst $HRuCl(CO)(PPh_3)_3$. For the splitting of cellulose itself in 1-butyl-3-methylimidazolium chloride the combination of the heterogeneous metal catalyst Rh/C and the homogeneous precatalyst $HRuCl(CO)(PPh_3)_3$ proved to be the best choice. One of the possible roles of the ruthenium compound is to enhance the transfer of hydrogen molecules from the atmosphere inside the reactor into the reaction mixture. Cellulose could be fully converted under relatively mild conditions to sorbitol as the dominant product, in 74 % yield.

The second approach was the production of alkylglycosides out of cellulose in the presence of an acidic catalyst in 1-butyl-3-methylimidazolium chloride. The substrate was alkylated by the primary alcohols *n*-butanol and *n*-octanol. The acidic resin Amberlyst 15DRY proved to be the optimum acidic catalyst: it catalyzes the hydrolysis of the β (1→4) links in the polymeric chain of cellulose as

well as the alkylation of the hydroxyl groups at the C1 position of the glucose intermediate. Cellulose was fully converted under mild conditions. In the reaction with *n*-butanol the obtained yield of butylglycosides was 86 %. The possibility of transalkylation was also studied.

The third approach was the production of α-D-glucose pentaacetate out of cellulose in 1-butyl-3-methylimidazolium chloride. The transformation comprised two steps: first a hydrolysis reaction, catalyzed by the acid catalyst Amberlyst 15DRY, and secondly an acetylation reaction. The product yield was 70 %. α-D-Glucose pentaacetate could be quantitatively isolated by simple liquid – liquid extraction from the ionic liquid to dibutyl ether. The solvent and the catalyst were successfully recycled and reused.

In the fourth part, new ways towards the hydrolysis of cellulose and xylan in ionic liquids have been studied. Cellulose hydrolysis was carried out in 1-butyl-3-methylimidazolium chloride with α-D-glucose as the major product in 45 % yield. This reaction was performed in the presence of the solid acid catalyst Smopex-101, which can be recycled without significant loss of activity, in contrast with the reference catalyst Amberlyst 15DRY. Xylan was hydrolyzed in 1-ethyl-3-methylimidazolium chloride in the presence of *para*-toluenesulfonic acid to xylose, with a yield of 42 %. Up to 84 % yield of furfural was obtained after dehydration of xylan in the presence of tungstophosphoric acid in the same solvent. A one-pot conversion of cellulose and xylan into alkylhexosides and alkylpentosides respectively was also performed.

Samenvatting

Cellulose en bepaalde andere polysachariden kunnen worden gebruikt als een hernieuwbare bron van waardevolle chemicaliën en energie. De klassieke solventen kunnen meestal niet gebruikt worden als reactiemedia voor de verwerking van deze biopolymeren. Ionische vloeistoffen zijn onlangs ontdekt als geschikte oplosmiddelen voor deze biopolymeren. De ionische vloeistof 1-butyl-3-methylimidazolium chloride kan tot 25 gewichtsprocent cellulose oplossen. Deze ontdekking heeft nieuwe perspectieven gecreëerd voor de valorisatie van cellulose. In dit proefschrift worden verschillende procedures voor valorisatie van cellulose en van een aantal andere biochemicaliën bestudeerd.

De eerste procedure is de reductieve splitsing van cellulose in de aanwezigheid van waterstofgas. Initiële experimenten werden uitgevoerd met modelcomponenten. Het onderzoek werd gestart met hydrogenolyse van 1,1-diethoxycyclohexaan in solventvrije systemen (aangezien dit ketaal niet oplosbaar is in de relevante ionische vloeistoffen) over heterogene katalysatoren. Vervolgens werd cellobiose gesplitst en gereduceerd in 1-butyl-3-methylimidazolium chloride in aanwezigheid van de homogene prekatalysator $HRuCl(CO)(PPh_3)_3$. Voor de splitsing van cellulose in 1-butyl-3-methylimidazolium chloride was de combinatie van de heterogene metaalkatalysator Rh/C en de homogene prekatalysator $HRuCl(CO)(PPh_3)_3$ de beste keuze. Eén van de mogelijke rollen van $HRuCl(CO)(PPh_3)_3$ is het verbeteren van de overdracht van de waterstofmoleculen uit de atmosfeer in de reactor naar het reactiemengsel. Cellulose kan volledig worden omgezet onder relatief milde omstandigheden tot sorbitol als het dominante product, in 74 % opbrengst.

De tweede procedure was de productie van alkylglycosiden uit cellulose in de aanwezigheid van een zure katalysator in 1-butyl-3-methylimidazolium chloride. Het substraat werd gealkyleerd door de primaire alcoholen *n*-butanol en *n*-octanol. Amberlyst 15DRY bleek

de optimale katalysator te zijn: over deze katalysator gebeurt de hydrolyse van de β(1→4) bindingen in polymeermoleculen van cellulose en de alkylering van de hydroxylgroepen op de C1 positie van de glucose tussenproduct. Cellulose werd volledig omgezet onder milde omstandigheden. In de reactie met *n*-butanol bedroeg de verkregen opbrengst van butylglycosiden 86 %. De mogelijkheid van transalkylering werd ook bestudeerd.

De derde methode is de productie van α-D-glucose penta-acetaat uit cellulose in 1-butyl-3-methylimidazolium chloride. De transformatie gebeurt in twee stappen: de eerste is de hydrolyse gekatalyseerd door Amberlyst 15DRY, en de tweede is acetylering. De opbrengst was 70 %. α-D-glucose penta-acetaat kan kwantitatief worden geïsoleerd door eenvoudige vloeistof - vloeistof extractie van de ionische vloeistof naar dibutylether. Het solvent en de katalysator werden succesvol gerecycleerd en hergebruikt.

In het vierde deel, werden nieuwe methodes voor de hydrolyse van cellulose en xylaan in ionische vloeistoffen bestudeerd. De hydrolyse van cellulose werd uitgevoerd in 1-butyl-3-methylimidazolium chloride, en α-D-glucose was het belangrijkste product met 45 % opbrengst. Deze reactie werd uitgevoerd in de aanwezigheid van de heterogene katalysator Smopex-101 met Brønsted-zure functionele groepen, die kan worden herbruikt zonder een significant activiteitsverlies, in tegenstelling tot de standaardkatalysator Amberlyst 15DRY. Xylaan werd gehydrolyseerd in 1-ethyl-3-methylimidazolium chloride in de aanwezigheid van para-tolueensulfonzuur naar xylose, met een opbrengst van 42 %. Furfural werd verkregen na dehydratatie van xylaan in de aanwezigheid van tungstofosforzuur in hetzelfde solvent met een maximale opbrengst van 84 %. Tenslotte werd ook de één-pot conversie van cellulose en xylaan naar respectievelijk alkylhexosiden en alkylpentosiden uitgevoerd.

List of Abbreviations

A – allyl

OAc – acetate

Bu – *n*-butyl

BGF – butylglucofuranoside

BGP – butylglucopyranoside

BX – butylxyloside

Et – ethyl

CA – cellulose acetate

Cl – chloride

DP –degree of polymerization

DS – degree of substitution

GPAc – α-D-glucose pentaacetate

HMF – hydroxymethylfurfural

IL –ionic liquid

Im – imidazolium

Me – methyl

NMR – nuclear magnetic resonance spectroscopy

Oct – *n*-octyl

OGF – octylglucofuranoside

OGP – octylglucopyranosides

OX - octylxyloside

OTf – trifluoromethanesulfonate (triflate)

Pr – *n*-propyl

Py – pyridinium

(*R*)-Tol-BINAP – (*R*)-(+)-2,2'-Bis(di-p-tolylphosphino)-1,1'-binaphthyl

$scCO_2$ – supercritical CO_2

Tf – trifluoromethanesulfonyl

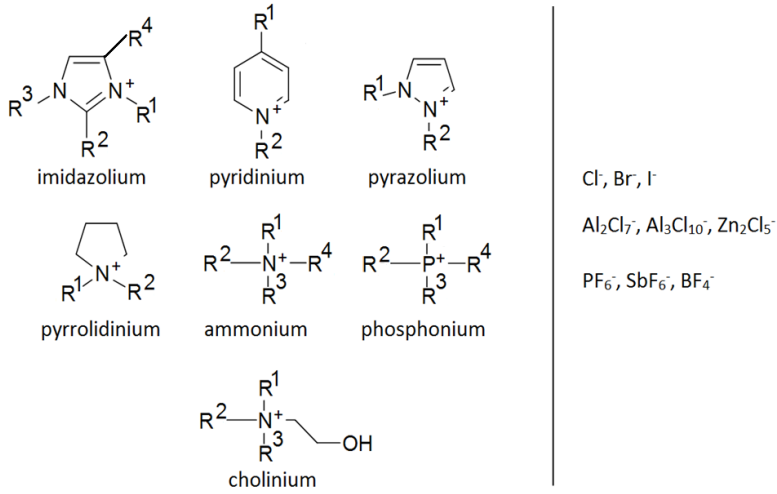
1 Introduction

1.1 Introduction to Ionic Liquids

Ionic liquids (ILs) are generally defined as solvents consisting entirely of ions with melting points below 100 °C. Many authors consider a 1914 paper by Walden[1] on ethylammonium nitrate as the first report on ionic liquids. However, the protic ionic liquid ethylammonium nitrate does not entirely consist of ions. There is also a significant fraction of neutral species at room temperature,[2] and it is not a genuine ionic liquid according to the definition given above. Intense research activities in the field of ionic liquids did not start before the end of the 1990s.

A typical ionic liquid consists of an organic cation and an inorganic anion. Ionic liquids differ from molecular solvents by their unique ionic character and consequently by their unique structure and organization. Their properties can be easily tuned by variations of cation and anion.[3] Coulombic interactions are the dominant interactions between the ions; however such interactions as H-bonding, π-π stacking, van der Waals interaction etc. are present as well in ionic liquids.[4] It has also been proposed that on mesoscopic scale, ionic liquids are capable to form supramolecular structures e.g. using H-bonding.[4-6]

Asymmetry of the cation contributes to a lowering of the melting point and consequently to lowering of the viscosity, the latter being a very important solvent property. Ionic liquids with asymmetrical, “ugly” cations have lower melting points than their analogues with symmetric, “beautiful” cations. For example, ILs with the “ugly” 1-butyl-3-methylimidazolium cation melt at significantly lower temperatures (by about 100 °C) than the analogous salts of the “prettier”, more symmetric 1-butylpyridinium cation.[7] One of the aspects of attractiveness of ILs is their non-toxicity in most of the cases. [8] However, some ILs are highly toxic.[9] Commonly used cations and anions are presented in Scheme 1.1.



Scheme 1.1. *Main cations and anions of ionic liquids.*

It is possible to design ILs with specific physicochemical properties like viscosity, polarity, density, acidity. This tuneability turns them into attractive reaction media:[10-13]

- ILs can dissolve a large range of various organic and inorganic materials. They can dissolve polar and nonpolar species, behave as polar or nonpolar solvents;
- ILs are often composed of weakly coordinating anions, so they have the potential to be highly polar yet weakly coordinating solvents;
- ILs can form biphasic systems with classical solvents, and they exhibit low interface tension which allows them to adapt to the second solvent;
- ILs have an extremely low vapor pressure, so they are not volatile;
- ILs have a wide temperature range of the liquid state (from -80 till 350 °C);
- ILs can have acidic and superacidic properties;

- ILs often have large electrochemical windows, so they can be used as solvents in electrochemical synthesis and as electrolytes for electrodeposition of metals.

It is worth to mention that the physicochemical properties of ILs can be dramatically influenced by impurities and additives such as water, halides and co-solvents.[14] Water is molecularly dispersed at low concentrations ($[H_2O] < 2$ M) in 1-alkyl-3-methylimidazolium ILs. However, at higher concentrations small water aggregates form a well-defined hydrogen-bonded network which dramatically influences the physicochemical properties of the resulting IL.[15-17] For instance, the solubility of carbohydrates substantially decreases in the presense of water.[17] It is very difficult to avoid contamination of ionic liquids by water because all known ionic liquids are hygroscopic. Some of them mix with water in all compositions, while others saturate it and then form two layers.[18]

Ionic liquids can be synthesized relatively easily. The three most common ways to prepare them are:[12, 19-21]

- an exchange reaction of a halide (X) of an organic cation A^+ with a silver salt of a suitable anion B^-; the silver halide precipitates during the course of reaction:

$$AgB + A^+X^- \rightarrow A^+B^- + AgX \downarrow;$$

- reaction between a metal halide MX_n and a quaternary ammonium salt:

$$[\equiv N^+\text{-alkyl}]X + MX_n \rightarrow [\equiv N^+\text{-alkyl}][MX_{n+1}]^-$$

- ion-exchange reaction on ion-exchange resins or clays.

Another interesting approach is the *in-situ* preparation of ionic liquids in reaction vessels.[22] In this case the corresponding trialkylammonium halide and the metal halide (e.g. trimethylamine hydrochloride and aluminium trichloride) are mixed and the ionic liquid is formed directly.

1.2 Examples of Applications of Ionic Liquids in Catalysis

1.2.1 Introduction

Ionic liquids started to attract attention as media for catalytic reactions around a quarter of a century ago. The use of an ionic liquid as solvent for a Friedel–Crafts acylation was reported in 1986.[23] However, only recently these solvents have started to be applied in a wide range of catalytic processes.

The large number of possible cation and anion combinations for the design of ILs creates a great opportunity for "tuning" their properties. Therefore, a huge number of designer and task-specific ILs have been synthesized.[24, 25] This allows to control not only reactions in ILs, but also solvent – solute interactions in biphasic systems.[26] Ionic liquids can act either as (i) solvent, (ii) solvent and catalyst or co-catalyst, (iii) solvent and support, (iv) solvent and ligand.[4]

Processes performed after the end of a reaction, e.g. isolation of the catalyst, are always of a high practical importance. Clearly, ILs have a lot of interesting applications in the field of homogeneous catalysis. They are used in biphasic catalysis when the catalyst is soluble in one phase and the substrate and product are soluble in the other,[27] or when the catalyst is immobilized, allowing the extraction/distillation of the organic product while the IL/catalyst system can be reused. Immobilization of ILs on solid inorganic supports has been developed in order to minimize the required amount of often expensive ILs in continuous-flow-operated fixed-bed processes.[4] Similar possibilities exist for heterogeneous catalysts and biocatalysts as well, e.g. processes involving nanoparticulate metal catalysts. ILs have been particularly effective in covering the charged layer on the surface of the colloids, preventing the aggregation and resulting in stabilization of the system.[28] By changing the composition of the ionic liquid, the stability, size, and solubility and other properties of nanoparticles can be specifically tuned.[29]

The same properties that make ILs effective solvents also makes them interesting liquids for studies involving sonochemistry, acoustic cavitation, and sonoluminescence. Recent research on using ultrasound to accelerate chemical reactions conducted in ILs have found them, in combination with catalysts, to be a versatile solution in several applications.[30]

Some examples showing important applications of ionic liquids in catalysis are further described.

1.2.2 Friedel–Crafts Alkylation and Acetylation

High concentrations of $[Al_2Cl_7]^-$ in acidic chloroaluminate(III) ILs result in suitable solvents-catalysts for electrophilic aromatic substitutions.[31] The first catalytic process with an IL was the Friedel–Crafts acylation of benzene carried out in the [EtMeIm][Cl]–$AlCl_3$ ionic liquid (Scheme 1.2).[23] Acetylation of anthracene gave valuable diacetylated products.[32] It was shown that after initial monoacetylation, disproportionation to diacetylanthracenes and anthracene occurred presumably due to the presence of a Brønsted superacid in the system. The range of substrates was further extended when the acylation of a variety of substituted indoles was reported.[33] For some of the products formed, it was claimed that acylation in the chloroaluminate(III) ionic liquid was the best available synthesis method.

Scheme 1.2 *Friedel-Crafts acylation of benzene.*

Akzo-Nobel developed cheap ionic liquids based on triethylamine hydrochloride and aluminium chloride ($2AlCl_3$ + $[HNMe_3][Cl]$ ⇆ $[HNMe_3][Al_2Cl_7]$). These ILs were successfully applied for the alkylation of benzene with 1-dodecene, an example of a

Friedel-Crafts alkylation.[34] It appeared that higher yields of 2-dodecylbenzene were obtained in the IL (46 %) compared to the conventional process catalyzed by HF (20 %).[35] One of the advantages of operating the reaction in ILs is that alkylbenzenes are poorly miscible with the ILs, thus leading to spontaneous product segregation and preventing further alkylation of alkylbenzenes. Overalkylation is very typical for reactions in classical solvents since the alkylated aromatic hydrocarbons are more reactive than the starting material.

1.2.3 Diels-Alder Reaction

The choice of solvent significantly affects the rate and selectivity of the Diels-Alder reaction, which is catalyzed by Lewis acids (Scheme 1.3).[36] In this reaction, ionic liquids act both as solvent and catalyst for this reaction.

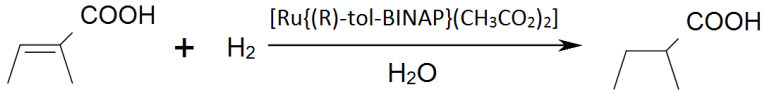
Scheme 1.3. *Diels-Alder reaction between 1,3-butadiene and ethene.*

Seddon *et al.* have initiated the investigation of the Diels-Alder reaction in imidazolium ILs.[37] The zinc-containing ionic liquids MX-$ZnCl_2$ (MX = 1-butyl-3-methylimidazolium chloride or 1-ethyl-3-methylimidazolium bromide) were described as novel reaction media, as well as Lewis acid catalysts for the highly regioselective Diels–Alder reaction of myrcene with acrolein.[38] Application of imidazolium ionic liquids with such anions as lactate, salicylate,[39] and camphorsulfonate [40] as the medium in the Diels-Alder reaction has also been reported. Caffeine was reported as a natural, cheap source of the xanthinium salt, which was used with bismuth(III) triflate for the preparation of a reusable catalytic system for the Diels-Alder reaction.[41] Recently the combination of imidazolium and pyridinium ionic liquids with erbium(III) triflate has been presented as

a very effective catalytic system for the reaction between various dienes and dienophiles.[42] Phosphonium and ammonium ILs are also being employed in Diels-Alder reactions, but less often. These cations are cheaper than imidazolium and their manufacture is cheaper and less energy-consuming. In the group of phosphonium ILs, the phosphonium tosylates were investigated as solvents for the Diels-Alder reaction of cyclopentadiene or isoprene with various dienophiles in the absence of metal catalysts.[43] Catalytic systems consisting of the ionic liquid trihexyltetradecyl bis(trifluoromethylsulfonyl)imide and metal catalysts have been reported as highly effective and possibly reusable in the synthesis of functionalized norbornenes via Diels-Alder reactions.[44]

1.2.4 Hydrogenation Reactions

Ionic liquids can be used as solvents for a wide range of platinum group metal catalyzed hydrogenation reactions. Chauvin *et al.* used Osborne's catalyst, [Rh(norbornadiene)PPh_3][PF_6] for the hydrogenation of 1-pentene in both hexafluoroantimonate and hexafluorophosphate−containing ionic liquids.[45] The hydrogenation rates were significantly higher than in acetone. The results for reactions using [BuMeIm][BF_4] were significantly poorer due to the presence of catalyst-deactivating chloride anions remaining from the synthesis of the ionic liquid. The separation of the product from the reaction mixture was simple and the catalyst-containing ionic liquid solution could be recycled. Dupont *et al.* demonstrated partial hydrogenation of benzene to cyclohexene in [BuMeIm][PF_6] in the presence of Ru nanoparticles. In most of classical systems, this reaction proceeds further to cyclohexane formation.[46]



Scheme 1.4. *[Ru{(R)-tol-BINAP}(CH_3CO_2)$_2$]-catalyzed hydrogenations of tiglic acid.*

Jessop *et al.* have studied the selectivities of the [Ru{(R)-tol-BINAP}$(CH_3CO_2)_2$]-catalyzed hydrogenations of *trans*-2,3-dimethylacrylic acid (tiglic acid) (Scheme 1.4) and 2-phenylacrylic acid (atropic acid) in a variety of ionic liquids.[47] The interesting feature of these substrates is that the enantioselectivity of the hydrogenation of tiglic acid is negatively dependent on the hydrogen concentration (higher selectivity at low concentration), whereas that of atropic acid is positively dependent (higher selectivity at high concentration).

For tiglic acid, it was found that the selectivities increased in the order {[BuMeIm][PF_6]/*i*-PrOH} < [BuMeIm][OTf] < [BuMeIm][BF_4] = [MeBuPy][BF_4] = {[BuMeIm][PF_6]/toluene} < [BuMeIm][PF_6] = [PrMeMeIm][Tf_2N] < [EtMeIm][Tf_2N] at 5 bars. For atropic acid, the selectivities were increased in the order {[BuMeIm][PF_6]/toluene} < [BuMeIm][BF_4] < [EtMeIm][OTf] < [BuMeIm][PF_6] = [EtMeIm][Tf_2N] < {[BuMeIm][PF_6]/*i*-PrOH} < [PrMeMeIm][Tf_2N] at 50 bars.

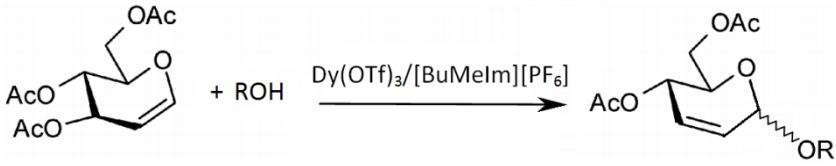
The trend for tiglic acid is determined by the anion effect as reported for the solubility of hydrogen gas.[48] In case of atropic acid, for which maintenance of the highest possible hydrogen concentration is essential to maintain the selectivity, this dependence is more complex. The rate of hydrogen transfer to the ionic liquid presumably becomes important and consequently other properties, such as viscosity, begin to play a role.

The hydrogenation of but-2-yne-1,4-diol in the presence of the catalyst [Rh(η^4-C_7H_8)(PPh_3)$_2$][BF_4] demonstrates the possibility of using a thermally controlled ionic liquid–water biphasic or homogeneous system for catalysis.[49] [OctMeIm][BF_4] forms biphasic systems with water at room temperature, but is fully miscible at the reaction temperature of 80 °C. This phenomenon has a great practical value. First, there is no interface for the reagent to cross, and secondly water substantially reduces the viscosity of the ionic liquids at 80 °C. On cooling to room temperature after the end of the reaction, two phases reform, with the ionic liquid phase containing the catalyst and the aqueous phase containing a mixture of 2-butene-

1,4-diol and butane-1,4-diol products that can simply be removed by decantation without catalyst contamination.

1.2.5 Glycosylation in Ionic Liquids

Recent reports have highlighted the potential of ionic liquids to be used as reaction media for glycosylation reactions.[50] Toshima *et al.* reported that the glycosidations of glucopyranosyl fluorides with alcohols in ionic liquids and in the presence of protic acid led under mild conditions to 54–91 % yields of glycosides. [51] The stereoselectivity of the glycosidation was significantly affected by the ionic liquid employed. The reactivity of glycosyl trichloroacetimidates and diethyl phosphites with alcohols in the presence and absence of Lewis acids has also recently been reported with such ILs as [BuMeIm][PF_6] and [HexMeIm][NTf_2].[51, 52] These reactions provide *ca.* 70 % yields of corresponding glycosides or disaccharides. Yadav *et al.* have performed glycosylations of D-glycals with a variety of alcohols, phenols, and hydroxy α-amino acids in the presence of 5 mol. % dysprosium(III) triflate immobilized in [BuMeIm][PF_6] (Scheme 1.5).[53]



Scheme 1.5. *Glycosylation of 3,4,6-tri-O-acetyl-D-glucal with alcohol.*

The corresponding 2,3-unsaturated glycopyranosides were produced in excellent yields with high α-selectivity. The catalyst immobilized in ionic liquids could be reused without loss of activity.

1.3 Catalytic Processing of Cellulose in Ionic Liquids

1.3.1 Introduction

Cellulose, the most abundant biopolymer on earth, consists of β-(1→4)-linked glycosidic units. It is a large volume renewable resource used in industry (paper, fibers, polymers, textile, and food sectors). Natural cellulose is highly crystalloid and contains strong intra- and intermolecular hydrogen bonding and van der Waals interactions between the polymer molecules. Therefore, it forms three-dimensional gels in its solutions. Cellulose is soluble in conventional solvents only under extreme conditions,[54] which is the main obstacle to the more extensive development of its use. The search for new solvents for dissolving and processing cellulose has attracted increasing attention.[55]

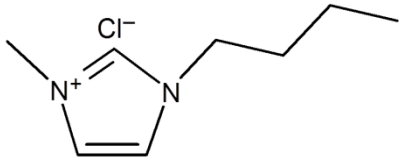
Traditional solvents for cellulose are based on polar organic solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, 1,3-dimethyl-2-imidazolidinone or dimethyl sulfoxide with addition of charged compounds such as $[NBu_4][F]$ or LiCl. These solvents have serious drawbacks: toxicity, high cost, low dissolving capacity, difficult recycling and thermal instability in process conditions.[56] Consequently, processing cellulose is often complex, inefficient, and often economically unprofitable.

Recent research has revealed the potential of ionic liquids as solvents for the dissolution and processing of cellulose. More than 20 different ILs have been reported to be able to dissolve cellulose.[4] Low viscosity contributes a lot to the process of dissolution; prolongation of the dissolution times does not necessarily increase solubility.[57-59] Elevated temperatures can improve the solubility, but if they are too high, it can lead to thermal degradation of the dissolved biopolymer.[60-62] Cellulose can be easily precipitated by adding sufficient amounts of water, ethanol or acetone.[54] The regeneration of cellulose from its ionic liquids solutions results in amorphous cellulose.[63]

The solubility of cellulose in ILs can be significantly improved by microwave radiation. For instance, the solubility of cellulose with a DP of 1000 in [BuMeIm][Cl] could be increased by 150 %.[64] This can be explained by the fact that microwaves provide internal heating and consequently more efficient breakdown of the hydrogen bond network of polymer molecules. Excessive microwave heating can also lead to thermal degradation of the biopolymer.[56]

Optimal cations for cellulose dissolution are based on the methylimidazolium and methylpyridinium cations, with allyl, ethyl, or butyl side chains. It is interesting to mention, that even numbers of carbon atoms in the side chain result in better cellulose dissolution in the series C2 to C20 compared with odd numbers.[65] The maximum dissolution power is reached with the C4 side chain.[56] A double bond containing side chain reduces the viscosity of the IL. The same effect is observed if one of the alkyl chain carbon atoms is replaced by an oxygen atom, even if those ILs are not suitable for cellulose dissolution.[66, 67]

Optimal anions for cellulose dissolution are chloride, acetate, and formate. Chloride anions are capable of interaction with the hydroxyl groups of the cellulose molecules due to their optimal radius, which allows them to interfere with the 3D-network of hydroxyl groups between and inside cellulose molecules.[68] The cation of the ionic liquid is also involved in the dissolution process, although the anion has the major contribution.[4] The oxygen and hydrogen atoms of the cellulose form electron donor−electron acceptor complexes with the charged species of the IL. It has been suggested that this occurs primarily between the C6 and C3 hydroxyl groups of surrounding cellulose chains.[69] This interaction results in the separation of the hydroxyl groups of the different cellulose chains and contributes to the dissolution of the cellulose in the ionic liquid.[56, 70] 1-Butyl-3-methylimidazolium chloride (Scheme 1.6) can dissolve up to 25 wt. % of cellulose.[71].



Scheme 1.6. *Structural formula of the IL [BuMeIm][Cl].*

1-Butyl-3-methylimidazolium chloride forms slightly yellowish crystals at room temperature. This solvent is very hydrophilic.[72] X-ray crystallographic analysis has revealed the presence of a hydrogen-bonding network involving the chloride anion, the ring, and the hydrogen atoms of the *n*-butyl chain. The imidazolium rings form a sheet-type supramolecular structure.[73] The melting point of anhydrous [BuMeIm][Cl] is *ca.* 65 °C;[74] the onset temperature of thermal decomposition is *ca.* 160 °C.[75]

[BuMeIm][Cl] is a commercially available product, produced at a multi-ton scale by BASF. It can be synthesized by alkylating 1-methylimidazole with 1-chlorobutane.[76]

Another very efficient ionic liquid solvent for cellulose is 1-ethyl-3-methylimidazolium acetate ([EtMeIm][OAc]), which can dissolve up to 12 wt. % of this biopolymer.[77] As could be expected these two ionic liquids are currently the most effective solvents for the (chemical) processing of cellulose. However, the acetate anion of [EtMeIm][OAc] may neutralize acidic catalysts.[78] Since acid-catalyzed hydrolysis is a step of most of the processes studied in this work, [BuMeIm][Cl] was mostly used in our experiments.

Heinze *et al.* [79] studied interactions of IL cations with cellooligomers with DPs from 6 to 10. NMR analysis showed that 1-ethyl-3-methylimidazolium acetate forms a covalent bond between the C1 carbon of the glycosidic unit and the C2 atom of the imidazolium cation. This suggestion was based on the fact that the C1 carbon signal of the glycosidic unit disappears after dissolution in 1-ethyl-3-methylimidazolium acetate. Ebner *et al.* confirmed this conclusion by means of ^{13}C-isotopic labeling and fluorescence

labeling experiments which indicated the irreversible formation of a covalent bond between the C2 carbon of 1-alkyl-3-methyl-imidazolium ILs and the reducing end of cellulose.[80] However, such bond is not formed when the same oligomer is dissolved in 1-ethyl-3-methylimidazolium chloride.[79] It was suggested that formation of this covalent bond is catalyzed by bases. One explanation for this phenomenon can be found in possible residual imidazole impurities in [BuMeIm][Ac], as opposed to a possible base-free [EtMeIm][Cl]. Another reason for this phenomenon can be a stronger hydrogen-bond network between the ions of [EtMeIm][Cl].[79]

The main industrial source of cellulose remains of course wood, and the classical environmentally detrimental sulfate process is still widely used for extracting cellulose from it.[58, 81] IL-based processes can become a "green" alternative. Some ILs are capable of dissolving lignin, another major component of wood.[81, 82] Sun *et al.* dissolved wood powder in [EtMeIm][OAc] and in [BuMeIm][Cl] and partially separated lignin by using a reconstitution mixture of acetone and water.[81] Lignin can easily stay dissolved in this mixture, while cellulose dissolved in the IL is being precipitated. This method can be possibly improved by using cholinium-based ionic liquids, the cholinium alkanoates, in the delignification process, as these ILs are good solvents for lignin and poor solvents for cellulose.[83]

1.3.2 Cellulose Hydrolysis in Ionic Liquids

So far, the heterogeneous hydrolysis of cellulose into sugars in water has been investigated using a range of solid acid catalysts. Shimizu *et al.*[84] and Tian *et al.*[85] reported the hydrolysis of cellobiose and cellulose by heteropolyacids. Hara *et al.* reported that amorphous carbon bearing -SO_3H, -COOH and -OH groups exhibits higher hydrolysis activity (10 % of glucose yield) at 90 °C for 3 h.[86-88] Onda investigated solid acid catalysts for the hydrolysis of cellulose with β-1,4-glycosidic bonds into glucose, finding that a sulfonated activated-carbon catalyst exhibits a remarkably high yield of glucose (40.5 %)

and a selectivity higher than 90 % at 150 °C for 24 h.[89] The layered transition metal oxide $HNbMoO_6$ was reported to be active in cellulose hydrolysis.[90] The total yield of products (glucose and cellobiose) was estimated to be 8.5 % in the hydrolysis of cellulose.

Alternatively, ionic liquids can be used as reaction media, which usually provides efficient dissolution of cellulose and consequently makes the reaction homogeneous.[77, 91-94] When the cellulose structure is unfolded in an ionic liquid, the depolymerization becomes rather easy, and can be conducted in moderate conditions.[78] Li *et al.* reported a 77 % yield of total reducing sugars after cellulose hydrolysis in [BuMeIm][Cl] in the presence of H_2SO_4.[62] Schüth *et al.*[94] successfully used the sulfonated resin Amberlyst 15DRY, a solid acid catalyst, for hydrolysis of cellulose in [BuMeIm][Cl].

1.3.3 Reductive Splitting of Cellulose in Ionic Liquids in the Presence of Hydrogen

Another novel interesting example of cellulose valorization is its conversion into polyols. This process can be catalyzed by metal catalysts, e.g. by transition metal nanoparticles which are attracting nowadays a widespread attention.[95] Nanoparticle-based catalytic systems exhibit high catalytic activities and often higher selectivity when compared with conventional heterogeneous catalysts. The particle size and surface structure are the most important factors dominating the catalytic selectivity of metal nanoparticle-based catalysts.[96] Yan *et al.* reported cellobiose conversion into sorbitol by using a Ru nanocatalyst in an aqueous solution,[97] and it was also observed that cellulose can be converted into hexitols under hydrothermal and hydrogen conditions over transition-metal catalysts in supercritical water.[98, 99] High yields (>90 %) of hexitols after cellulose hydrolytic hydrogenation in the presence of Ru-loaded zeolites and trace amounts of mineral acid were reported by Sels et *al*.[100] Jacobs et *al.* reached full conversion of ball-milled cellulose in

water at 190 °C under H_2 pressure into hexitols in the presence of $H_4SiW_{12}O_{40}$ and Ru/C.[101] However, the poor solubility of cellulose still hinders these catalytic processes.

To assist the solubility, ionic liquids are starting to be used as a solvent in cellulose pretreatment and transformation.[97] In addition, the ionic liquid species can stabilize transition-metal nanoparticles to sustain their small size, their high surface area, and to inhibit nanoparticle leaching.[102] Zhu *et al.* have reported 93 % yield of sorbitol after cellulose splitting in the ionic liquid trihexyltetradecylphosphonium dodecylbenzene sulfonate in the presence of Ru nanoparticles and 1-(4'-(4''-(2'''-boronobenzyl)piperazinyl)-2'-butenyl)-3-*n*-butylimidazolium chloride.[103]

1.3.4 Cellulose Acetylation in Ionic Liquids

The synthesis of cellulose acetate (CA) was first reported by Schuetzenberger in 1865 and performed on industrial scale for the first time in 1900.[104] Cellulose acetate is still one of the most important commercial cellulose derivatives, and it is applied in coatings, films, membranes, in textile, and by the tobacco industry. The classical way to produce CA industrially is heterogeneous acetylation of cellulose with excess of acetic anhydride (10–40 % above the amount needed for cellulose triacetate formation) in the presence of sulfuric or perchloric acid as catalyst.[105] This heterogeneous process has serious drawbacks. The most important disadvantage is that the direct preparation of mono- and di-substituted cellulose acetates is not possible. Cellulose diacetates with DS's from 2.2 to 2.7 are more commercially valuable than cellulose triacetates (DS 2.8-3.0), and the first ones are obtained industrially via a two-stage heterogeneous process. This process is very complicated and energy consuming.[106] During the past two decades, alternative procedures for acetylation of cellulose under homogeneous reaction conditions have been reported. The main

advantages of the homogeneous cellulose derivatization are the following:[107]

- easy control of the DS by adjusting the reaction time, temperature, and molar ratio of derivatizing agent to cellulose;
- negligible degradation of cellulose during the reaction;
- possibility to introduce functional groups.

In 1982 Diamantoglou *et al.* showed a pathway to synthesize cellulose acetate homogeneously in DMA/LiCl in the presence of acid catalysts, such as methanesulfonic acid, perchloric acid, formic acid and sulfuric acid, and finally form cellulose acetate fibers.[108] However, this solvent system has some drawbacks, such as the need for expensive reagents, the complex cellulose dissolution process, drastic conditions, and difficult solvent recycling. This process has not widely been applied because of the difficult recycling strategy of the solvent system.

Ionic liquids can be a good alternative since they can easily be recycled and reused after the product has been isolated by simple precipitation by addition of an excess of water. Moreover, for acetylation of cellulose in ILs, in general no catalyst is required.[109, 110] In 2005, Abbott *et al.* reported cellulose and monosaccharides acetylation in a zinc-based ionic liquid with Lewis acid properties.[111] Kosan *et al.* have recently studied preparation and subsequent shaping of cellulose acetates with low DS's (0.06 – 1.4) in [BuMeIm][Cl].[109] Yan *et al.* have observed formation of cellulose acetates with DS's from 0.4 to 3.0 in 1-allyl-3-methylimidazolium chloride.[110] Reactions were performed in relatively highly concentrated cellulose solutions.

1.3.5 Degradation of Cellulose and of Some Other Carbohydrates in Ionic Liquids

Ionic liquids act in carbohydrate breakdown as solvents, agents for reducing the crystallinity of cellulose, catalysts etc.[112-118]

Decomposition of cellulose using dicationic imidazolium chloride or bromide was reported to produce levoglucosenone and other anhydrosugars at 180 °C, but the product yields were low.[112] Thermal decomposition of cellulose in [BuMeIm][Cl] with the aid of nucleophiles such as 2,4-dinitrophenylhydrazine has been patented by BASF.[114] The aim was here to decrease the degree of polymerisation of cellulose. Another BASF patent describes the degradation of cellulose by heating in the acidic ionic liquid [BuMeIm][HSO_4], with the optional presence of water.[115] A patent on the production of 2,5-bis(hydroxymethyl)furan describes the efficient pyrolysis of carbohydrates such as sugar, cellulose or starch, followed by hydrogenation in [BuMeIm][Cl].[116] Another patent describes bio-oil production via microwave-assisted cracking of biomass dissolved in [BuMeIm][Cl].[117] After irradiation with microwave radiation for 5–30 min, the bio-oil was separated from the ionic liquid by supercritical fluid extraction.

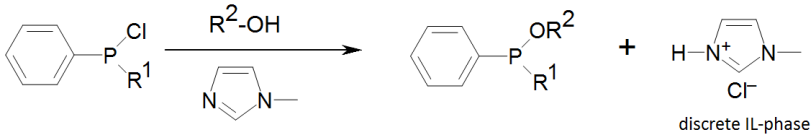
A variety of ILs, including [AMeIm][Cl], have been reported to be used in partially dissolving lignocellulose for anaerobic reaction at 150–300 °C to give various products including pyrolysis oil, levoglucosenone, levulonic acid, levulinic acid, hydroxymethylfurfural, furfural or 2-methylfurfural in good yields.[113]

1.4 Industrial Applications of Ionic Liquids

A significant demand for ionic liquids has given rise to appearance of many commercial suppliers (e.g. Merck, BASF, Sigma-Aldrich, IoLiTec). Nevertheless, the prices of ionic liquids in general in comparison with conventional solvents remain high. However, the cost analysis made for the large-scale production of imidazolium-

based ionic liquids with the chloride anion showed that these ILs cost about 1.5 € for 1 kg.[119] Consequently, virtually complete solvent recovery will make e.g. biomass processing with ionic liquids in principle economically feasible. Another difficulty is that changing of an established industrial process is not easy even if it can be more profitable in the long term.[4] Some established commercial applications of ionic liquids are further presented.

BASIL Process. BASIL = **B**iphasic **A**cid **S**cavenging utilizing **I**onic **L**iquids. The BASIL process is used for the production of the generic photoinitiator precursor alkoxyphenylphosphines. Previously triethylamine was used to scavenge the acid that was formed in the course of the reaction, but this made the reaction mixture difficult to handle as the waste by-product, triethylammonium chloride formed a dense insoluble paste. Replacement of triethylamine with 1-methylimidazole results in the formation of 1-methylimidazolium chloride, an IL, which phase-separates from of the reaction mixture (Scheme 1.7).



Scheme 1.7. *The BASIL ™ process.*

This new process uses a much smaller reactor than the initial process. The space-time yield is increased from 8 kg m^{-3} h^{-1} to 690000 kg m^{-3} h^{-1}, and the yield increased from 50 % to 98 %. 1-Methylimidazole is recycled, via base decomposition of 1-*H*-3-methylimidazolium chloride, in a proprietary process.[120] The reaction is now carried out at a multi-ton scale, proving that handling large quantities of ionic liquids is practical. This process won the ECN Innovation Award in 2004.[121]

Dimersol and Difasol Processes. The Dimersol process consists of the dimerization of alkenes, typically propene (Dimersol-G) or butenes (Dimersol-X) to the more valuable branched hexenes and

octenes. The dimerization reaction is catalyzed by a cationic nickel complex of the general form $[R_3PNiCH_2R]AlCl_4$ and is commonly operated under solventless conditions. However, it has been found that the catalyst shows greater activity when it is dissolved in undesirable aromatic or halogenated hydrocarbons.[122] The use of chloroaluminate ionic liquids as solvents for these nickel-catalyzed dimerization reactions has been developed and tested by IFP (France).[123] The reaction can be performed in a biphasic system between –15 °C and 5 °C, as the products form a separate secondary phase, which can be easily separated, and the catalyst remains selectively dissolved in the primary ionic liquid phase. Activity and selectivity of catalyst are much higher than in both solvent-free and conventional solvent-based systems. This process has been patented and can be applied in existing chemical plants.[124]

IoLiTec. IoLiTec is a SME company specializing in marketing ionic liquids and developing new applications for them. They have developed an efficient technology to clean expensive and sensitive surfaces using ionic liquids as antistatic cleaning agents. Dilute aqueous sodium chloride solutions are traditionally used as the wetting agent for brushes in this process; replacing these solutions with an ionic liquid significantly improves the efficiency of cleaning.[121]

1.5 Existing Processes of Starch Valorization

Starch is quite widely spread in nature. This carbohydrate is produced by plants to store energy and usually exists in the form of small granules. Starch is a mixture of two glucose polymers: linear amylose and branched amylopectin.[125]

Starch and cellulose are very similar polysaccharides. However, in starch, glycosidic units are oriented in the same direction, and in cellulose, each successive unit is rotated 180° around the axis of the polymer backbone chain, relative to the last repeat unit. This

difference makes starch a significantly less inert material than cellulose. Starch is soluble in convenient solvents.[125] Existing techniques of starch processing are quite interesting for this study, since they can be similar with possible processes for cellulose valorization.

One of typical ways of starch valorization is acid hydrolysis. This process is conducted in aqueous suspensions in the presence of various acid catalysts including mineral acids,[126] zeolites [127] and enzymes.[128] Hydrolysis products vary from oligomers [126] till glucose,[126, 127] depending on the exact method used. Glucose can be further hydrogenated into sorbitol in the presence of metal catalyst in a one-pot process as described by Jacobs *et al*.[127]

Another interesting way of starch valorization is conversion into alkylglycosides, which can be used as biodegradable surfactants. Throckmorton *et al.* synthesized various biodegradable surfactants by reacting starch derived glycol and glycerol glycosides with ethylene oxide, propylene oxide, and long chain lipophilic materials.[129]

1.6 Separation Techniques

The low volatility of ILs product separation and recovery from ionic liquids a difficult task.[130] Volatile products can be isolated by so-called back-distillation.[131] Although water and classical organic solvents can be in some cases effective in extracting reaction products from ILs,[132, 130] this approach is not always suitable for isolation of products of biomass conversion.[133] To overcome this limitation, a “green” nonpolar solvent, supercritical CO_2 ($scCO_2$), can be used. The principle of product recovery in this case is based on the solubility of $scCO_2$ in the IL (controlled by pressure) to transfer organic products to the $scCO_2$-rich phase, and the insolubility of IL in $scCO_2$. A high efficiency of supercritical CO_2 extraction in isolation of nonpolar natural products has been already demonstrated.[133] One of excellent examples is $scCO_2$ extraction of bio-oil performed by Rout *et al.*[134]

On the other hand, both polar and nonpolar products [135] and catalysts [136] can be isolated from IL by pressure-driven nanofiltration. In this case, reaction product is isolated from solvent over a membrane by means of a pressure gradient.[137] Van Doorslaer *et al.* have shown an efficient isolation of pelargonic acid and monomethyl azelate from IL.[135]

1.7 Outline of This Thesis

The scope of this PhD thesis is to investigate new ways of cellulose catalytic transformation into valuable chemical which can be used e.g. as surfactants or precursors of biofuels exploiting the unique propert of ionic liquids to sollubilize cellulose under relatively mild conditions.

The first part of this dissertation is an **introduction (chapter 1)**, which is a concise survey of literature on ionic liquids, catalysis in ionic liquids, and cellulose dissolution in ionic liquids in the context of the research made.

Chapter 2 shows the results of performed experiments on cellulose hydrocracking in the presence of both homogeneous and heterogeneous catalysts. Cellulose was fully converted in [BuMeIm][Cl] in the presence of the heterogeneous metal catalyst Rh/C and the homogeneous precatalyst $HRuCl(CO)(PPh_3)_3$. The conditions applied led to a high yield of the sugar alcohol sorbitol.

Chapter 3 describes the production of alkylglycosides from cellulose in the presence of the acidic catalyst Amberlyst 15DRY in [BuMeIm][Cl]. *n*-Butanol and *n*-octanol are used as alkylating agents for direct alkylation. Moreover, synthesis of dodecylhexosides via cross-alkylation was also investigated.

Chapter 4 deals with the production of α-D-glucose pentaacetate from cellulose in 1-butyl-3-methylimidazolium chloride. The transformation of cellulose into the glucose ester α-D-glucose

pentaacetate was carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride under mild reaction conditions. Besides an optimization of the reaction conditions, a way of quantitative product isolation and recycling of catalyst and solvent were studied.

Chapter 5 describes hydrolysis and subsequent reactions, mainly alkylation, of cellulose and xylan in the presence of acid catalysts. A recyclable heterogeneous catalyst, an alternative for the reference catalyst Amberlyst 15DRY, for cellulose hydrolysis was found.

The final part of the thesis (**chapter 6**) gives the conclusions and an outlook for future work.

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2 Reductive Splitting of Cellulose in the Ionic Liquid 1-Butyl-3-Methylimidazolium Chloride

The depolymerization of cellulose is carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride in the presence of hydrogen gas. First, the ketal 1,1-diethoxycyclohexane and cellobiose were used as model substrates. For the depolymerization of cellulose itself, the combination of a heterogeneous metal catalyst and a homogeneous ruthenium catalyst proved effective. One of the possible roles of the ruthenium compound is to enhance the transfer of hydrogen to the metallic surface. The cellulose is fully converted under relatively mild conditions, with sorbitol as the dominant product in 51–74 % yield.

2.1 Introduction

Chemocatalytic depolymerization of cellulose to simple building blocks is of great current interest, but only a limited number of approaches are available. A first approach, exemplified by the work of Fukuoka and co-workers, employs aqueous conditions and solid bifunctional catalysts, for example, platinum and ruthenium on different acidic supports, for the conversion of cellulose into sugar alcohols.[1-3] The maximal yield of alcohols achieved was 31 % (25 % sorbitol, 6 % mannitol). A principal problem is that efficient access of the water-insoluble cellulose to the solid acid surface is not easy. In the mechanism proposed by Fukuoka, molecular hydrogen is split on the metallic surface, followed by spillover of protons to the support surface, and this facilitates the acetal splitting.[4, 5] In parallel, there has been a search for innovative solvent types that can dissolve the cellulose. For example, hot water (244 °C) can be used to convert cellulose into various alcohols, even without added acids. On the other hand, ionic liquids are also promising reaction media, in view of the unique property of some chloride-containing ionic liquids to break the hydrogen bonds and dissolve the cellulose chains at a molecular level.[6-12] For example, 1-butyl-3-methylimidazolium

chloride ([BuMeIm][Cl]) can dissolve up to 25 wt. % of cellulose, even if at these concentrations the viscosity is too high to allow further catalytic processing.[13, 14] The solubility of cellulose in ionic liquids has already been exploited in various applications, such as the derivatization of the cellulose chains,[15-27] or the production of composite materials containing, besides cellulose, other constituents such as carbon nanotubes or inorganic materials.[28-32]

Recent studies have also demonstrated that cellulose can be hydrolyzed in ionic liquids with dissolved or solid acids as the catalyst.[33-35] Various mineral acids, such as HCl,[33-35] organic acids such as CF_3SO_3H,[35] or even sulfonic acid resins, have proven effective.[36, 37] A detailed study of the kinetics has shown that depending on the pK_a of the acids, the formation of reducing sugars can be favored in comparison to their degradation, and glucose yields as high as 50 % have been reported.[33-35] However, prolonged reaction results in further conversion of the sugars, for example, to 5-hydroxymethylfurfural (HMF), and in the presence of suitable catalysts such as metal chlorides, this can by itself be a promising pathway to valorization of cellulose and other carbohydrate polymers.[38-40] It is indeed known that monomeric sugars such as glucose or fructose can be efficiently dehydrated to 5-hydroxymethylfurfural in ionic liquids.[41-46]

As an alternative approach, it is worthwhile to investigate whether cellulose can be converted in a one-pot process to reduced compounds, such as sorbitol or other sugar alcohols.[47] This indeed constitutes an alternative way to suppress side reactions of the glucose. Besides a two-step cellulose conversion via glucose, one could also envisage direct hydrogenolysis of the acetal functions in the molecularly dissolved cellulose. There are several reports, in the open literature and in the patent literature, on the direct hydrogenolysis of acetals and ketals, without intermediacy of the free carbonyl compound.[48-51] Herein, we demonstrate that a combination of a heterogeneous Pt or Rh catalyst and a homogeneous Ru catalyst can completely convert cellulose to a sorbitol/glucose mixture in 1-

butyl-3-methyl imidazolium chloride ([BuMeIm][Cl]) as the solvent under relatively soft conditions.

2.2 Experimental

1-Butyl-3-methylimidazolium chloride (99 %) and 1-ethyl-2,3-dimethylimidazolium bromide (99 %) were obtained from IoLiTec Ionic Liquids Technologies GmbH. The cellulose used was Avicel PH 101 (DP 215–240). Carbonylchlorohydridotris-(triphenylphosphine)ruthenium(II) was from Sigma–Aldrich. Platinum on carbon (0.5 wt. %) was obtained from the Engelhard Corporation. Rhodium on carbon (5 wt. %), ruthenium on carbon (5 wt. %), and palladium on carbon (5 wt. %) were obtained from Johnson Matthey. Other chemicals were from commercial suppliers and were used as received.

In a typical reaction, cellulose (0.05 g), Pt/C (0.033 g), $HRuCl(CO)(PPh_3)_3$ (0.033 g), water (3 µL), and [BuMeIm][Cl] (1 g) were loaded in a single-cylinder stainless steel reactor (10 mL) or in a TOP-multireactor (10×2 mL). The reaction mixture was stirred, pressurized with H_2 to 3.5 MPa at room temperature, and subsequently heated at 110 °C for 48 h. After reaction samples were derivatized using MSTFA (*N*-(trimethylsilyl)-*N*-methyltrifluoroacetamide) they were injected onto a 30 m HP-1 column in a GC (HP 5890) or a GC-MS (Agilent 6890 GC and 5973 MS) instrument. Typically, a *ca.* fourfold excess of MSTFA with respect to -OH groups was added to 0.3 mL of sample mixed with 0.3 mL of pyridine, and the mixture was stirred for 3 h at 80 °C. Derivatized compounds were then extracted into 0.6 mL of dibutylether and analyzed. The procedure was verified and made quantitative using known amounts of reference compounds such as glucose, sorbitol, mannitol, xylose, xylitol, erythritol, threitol, and others. All the product yields mentioned in the text were determined chromatographically and calculated from peak areas of corresponding reaction products. The water content of the ionic

liquids was determined with a coulometric Karl-Fischer titrator (Mettler Toledo DL39) and anhydrous methanol as the solvent. Each sample was at least 0.1 g, and triplicate measurements were performed on each sample. The pH was measured by using pH indicator strips (Macherey–Nagel), before analysis, samples were dissolved in distilled water.

2.3 Results and Discussion

Initially, reductive splitting of ionic-liquid-dissolved cellulose was approached as a hydrogenolysis of an acetal, for which several methods have been reported.[48-54] In order to investigate the effectiveness of reported catalysts for acetal or ketal hydrogenolysis, 1,1-diethoxycyclohexane was selected as the reference compound. While this compound is not soluble in [BuMeIm][Cl], it is a liquid at room temperature and thus can even be hydrogenolyzed in solvent-free conditions. As a mixture of Pt and Rh catalysts has been reported as being most effective for ketal hydrogenolysis,[54] these catalysts were applied to the hydrogenolysis of 1,1-diethoxycyclohexane. Attempts to hydrogenolyze this substrate in the absence of Lewis acids gave no result. In the presence of a Lewis-acidic promoter hydrogenolysis was conducted successfully. $BF_3{\cdot}Et_2O$ and $AlCl_3$ were tested, and the former was found to be more effective. Neat 1,1-diethoxycyclohexane (0.5 mL) was hydrogenolyzed successfully by using a combination of the heterogeneous catalysts Rh/C (0.003 g; 5 wt. %) and Pt/C (0.007 g; 0.5 wt. %) in the presence of the Lewis acid $BF_3{\cdot}Et_2O$ (0.5 mL) at 20 °C under 2 MPa of hydrogen gas during 7 h. The only product was ethoxycyclohexane, which was obtained in 100 % yield, together with ethanol.

The next compound chosen for investigation was cellobiose. Cellobiose consists of two glucose molecules linked in a β(1→4) bond, and thus represents a dimeric model for the cellulose polymer. Cellobiose is well-soluble in [BuMeIm][Cl]; cellobiose and its reaction products were easily and unequivocally quantified by GC and GC–MS

after derivatization with a silylating agent. Our initial approach to apply the same conditions in [BuMeIm][Cl] as for the ketal hydrogenolysis in conventional media was not fruitful, even when a range of conditions were tested. A representative result is shown in Table 2.1 (entry 1): while some glucose was obtained by hydrolysis of the cellobiose, the glucose did not react further to sorbitol, despite the presence of metal catalysts and a hydrogen pressure of 3.5 MPa in the vessel. More than a half of the initial substrate remained unreacted. Some of the glucose was transformed to levoglucosan and 5-hydroxymethylfurfural, which are typical glucose degradation products. This highlights that in certain conditions, the hydrogenation in the ionic liquid medium is problematic, as will be explained below. Much better results were obtained when the heterogeneous catalysts were replaced by a homogeneous catalyst precursor, that is, $HRuCl(CO)(PPh_3)_3$ (Table 2.1, entry 2). Such ruthenium hydride compounds have been reported in literature as hydrogenolysis catalysts for fructose and glucose,[55, 56] for example in *N*-methyl-2-pyrrolidinone. In the presence of $HRuCl(CO)(PPh_3)_3$ and KOH, and in [BuMeIm][Cl] as the solvent, cellobiose conversion was almost complete, with sorbitol as a major product. Minor amounts of C4-polyols and C5-polyols were also recovered, originating from the hydrogenolysis of glucose, as reported by Andrews and Klaeren.[55] The role of hydroxide ions in these reactions is manifold: basicity promotes the retro-aldol cleavage that results in fragmentation of the sugar molecules; but the base is also reported to promote coordination of the sugar molecules to ruthenium as alcoholates, and bases are known to facilitate the heterolytic formation of hydrides from dihydrogen on ruthenium complexes. The latter effect has not only been reported for hydrogenation in conventional solvents;[57] it is known that addition of bases promotes hydrogenations in ionic liquids as well.[58-60]

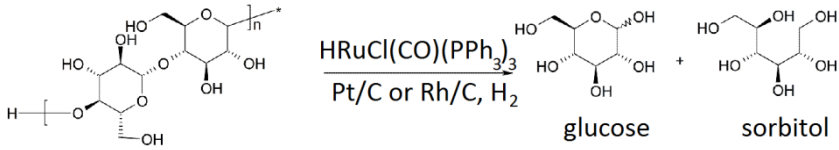
Table 2.1. Hydrogenation of cellobiose in [BuMeIm][Cl].

Entry	Catalyst	Amount of product in final mixture, %	Total conversion, %	Yield of hydrogenated product, %
1[a]	0.002 g Rh/C (5 wt. %) 0.0006 g Pt/C (0.5 wt. %)	52 dimers 10 glucose 21 levoglucosan 17 HMF	48	0
2[b]	0.01 g $HRuCl(CO)(PPh_3)_3$	10 dimers 6 glucose 43 sorbitol 24 C6-alcohols 17 C4-alcohols	90	76

[a] Reaction conditions: cellobiose (0.0416 g), solvent (0.7 g of [BuMeIm][Cl]), 150 °C, hydrogen (3.5 MPa, measured at 25 °C), 15 h.
[b] Reaction conditions: cellobiose (0.01 g), solvent (1 g of [BuMeIm][Cl]), KOH (0.0072 g), 150 °C, hydrogen (3.5 MPa, measured at 25 °C), 24 h.

Eventually, cellulose was applied as the reagent in the form of the microcrystalline commercial product Avicel. As reported, [BuMeIm][Cl] proved very effective in dissolving cellulose.[6-12] In a first attempt, we used the mixture of heterogeneous catalysts that was effective for ketal hydrogenolysis, that is, Rh/C and Pt/C, together with the Lewis acid BF_3 (Table 2.2, entry 1). However, in these conditions, the initial substrate remained unreacted, so no monomeric products with 6 or less carbon atoms or dimers were detected at all, confirming that selective depolymerization of cellulose is a nontrivial task. Attention therefore turned to the homogeneous catalyst $HRuCl(CO)(PPh_3)_3$, in combination with the base KOH, in the same ratio as applied for cellobiose. After extended reaction times, a modest conversion (20 %) was obtained, with surprisingly glucose, rather than hydrogenolysis or hydrogenation products, as the principal reaction product (Table 2.2, entry 2). This indicates that hydrolysis of the β-1,4 chain is the initial reaction, even if water was not intentionally added to the mixture. Minor contamination of [BuMeIm][Cl] by water should always be taken into account; Karl–Fischer titration showed that the level of contamination was *ca.* 0.1 wt. %. The cellulose that is used as a reagent may contain some additional water (typically 4–7 wt. % based on cellulose).[61] As the hydrolysis reaction is expected to be

counteracted by base, the ratio base/Ru complex was lowered, which resulted in a strong increase of the conversion to 72 % (Table 2.2, entry 3). Addition of a minute amount of water (0.25 wt. %) to provide a stoichiometric amount smoothly raised the conversion to *ca.* 100 %, without compromising the dissolution of the cellulose.[61] However, in these conditions only a minor fraction of the hexoses was hydrogenated, and glucose was still the major product (Table 2.2, entry 4). In order to increase the hydrogenation rate, 0.5 wt. % Pt/C was added as a second, heterogeneous hydrogenation catalyst. Pt/C has been reported to be even more active for glucose hydrogenation than the widely used Ru/C.[62, 63] This gave good results (Table 2.2, entry 5; Scheme 2.1): the cellulose was fully converted to predominantly C6-compounds, and within the C6-fraction, sorbitol was the main compound. A reaction time of 48 h appeared to be optimal. At shorter times, the conversion of the cellulose was incomplete, with only 26 % conversion of cellulose to C6-compounds after 24 h. Reaction times longer than 48 h resulted in progressive deterioration of the selectivity, with formation of shorter polyols and other side products. Note that for the 48 h reaction, formation of the epimeric compound mannitol, which is possible under both acidic [4, 5] and basic [55] conditions, did not occur to a detectable extent. This is expected, because pH measurements of the reaction mixtures showed that they are essentially neutral.



Scheme 2.1. *Splitting of cellulose with formation of glucose and sorbitol.*

Control experiments confirmed that each component of the catalytic reaction mixture, that is, hydrogen, $HRuCl(CO)(PPh_3)_3$, Pt/C, and water, was necessary for a high conversion of cellulose (Table 2.3). For example, no hydrogenation products were detected when the

hydrogen atmosphere was replaced by argon, confirming that the reducing equivalents originated from the supplied molecular hydrogen, and not from another source (Table 2.3, entry 1 *vs.* Table 2.2, entry 5). In the absence of the ruthenium complex, not only the hydrogenation rate but also the rate of the hydrolysis was much suppressed, suggesting that the ruthenium species may facilitate the cellulose depolymerization by complexation to alcohol or diol moieties in the substrate (Table 2.3, entry 2).[64] In the complete absence of KOH, both conversion and polyol yield were much lower (entry 3). This is not unexpected, because one of roles of KOH is to activate the ruthenium compound (see above).[57-60] Disaccharide compounds, such as cellobiose, only rarely appeared in the chromatograms, and then usually in low or very low concentrations.

Table 2.2. Stepwise optimization of cellulose hydrogenation in [BuMeIm][Cl].[a]

Entry	Catalyst	Co-catalyst, additive	Time, h	Cellulose converted to dimers and smaller molecules, %	Amount of product in final mixture, %	Yield of hydrogenated product, %
1	0.0006 g Rh/C (5 wt. %) 0.0014 g Pt/C (0.5 wt%)	0.1 mL $BF_3{\cdot}Et_2O$	48	0	no products detected	0
2	0.01 g $HRuCl(CO)(PPh_3)_3$	0.0072 g KOH	96	20	10 dimers 78 glucose 2 sorbitol 6 levoglucosan 4 HMF	0.4
3	0.033 g $HRuCl(CO)(PPh_3)_3$	0.0017 g KOH	48	72	9 dimers 58 glucose 21 other C6-sugars 11 sorbitol	7
4	0.033 g $HRuCl(CO)(PPh_3)_3$	0.0017 g KOH 3 µL H_2O	48	100	1 dimers 76 glucose 20 other C6-sugars 3 sorbitol	3
5	0.033 g Pt/C (0.5 wt. %) 0.033 g $HRuCl(CO)(PPh_3)_3$	0.0017 g KOH 3 µL H_2O	48	100	51 sorbitol 49 glucose	51

[a] Reaction conditions (except for entry 1): cellulose (0.05 g), solvent (1 g of [BuMeIm][Cl]), temperature (150 °C), hydrogen (3.5 MPa, measured at 25 °C).
[b] Reaction conditions: 0.01 g of cellulose was treated in 0.6 g of [BuMeIm][Cl] at 110 °C under of hydrogen (3.5 MPa, measured at 25 °C).

This shows that the first steps in the depolymerization of cellulose are slower than the eventual hydrolysis of the oligomers. In principle, Ru may be coordinated by a carbene formed from the imidazolium cation.[65] This possibility was investigated by performing a reaction in 1-ethyl-2,3-dimethylimidazolium bromide (Table 2.3, entry 4). While not all bromide-based ionic liquids are suitable for cellulose dissolution,[16, 66] the use of this particular ionic liquid resulted in a complete dissolution of the cellulose reactant. The cation in 1-ethyl-2,3-dimethylimidazolium bromide cannot be transformed to a carbene; yet similar results were obtained in the reaction of cellulose as in [BuMeIm][Cl].

The important role of the homogeneous ruthenium compound was confirmed by reactions of either cellulose or glucose in the presence of only Pt/C in the ionic liquid (Table 2.3, entry 2, and Table 2.4, entry 2). Not only when cellulose was the substrate, but also starting from glucose, the hydrogenation yield on Pt/C in [BuMeIm][Cl] was essentially zero, even under a hydrogen pressure of 3.5 MPa (Table 2.4, entry 2). To rationalize this result, one must realize that the solubility of hydrogen in many ionic liquids is generally much lower than in convenient solvents.[67, 68] Thus, for many reported hydrogenations in ionic liquids, it is the low mole fraction of the substrate or product, rather than the high mole fraction of the ionic liquid itself, that is responsible for the hydrogen dissolution. In the present case, it is unlikely that the dissolved cellulose would generate a sufficient hydrogen dissolution in the ionic liquid for keeping Pt/C active. Consequently, Pt/C, which in water is the most active reported glucose hydrogenation catalyst,[62, 63] loses its activity when employed in [BuMeIm][Cl] at high temperature.

For the sake of comparison, Ru/C was also tested (Table 2.4, entry 3). Activity preservation in the ionic liquid is much better for Ru/C than for Pt/C, implying that Ru/C is less sensitive to the strongly decreased hydrogen concentration in the ionic liquid. However, the

glucose hydrogenation is still incomplete after 24 h, and some hydrogenolysis compounds were detected. In this context, and in view of the results of Tables 2.3 and 2.4, the ruthenium complex acts as a hydrogen transport agent in the ionic liquid via formation of hydride compounds, supplying a metal catalyst such as Pt/C with hydrogen. When the ruthenium phosphine compound is replaced with another ruthenium compound that less readily forms hydrides, such as $RuCl_3$, no products are formed (Table 2.3, entry 5). The same observation is made when the ruthenium compound is replaced by a Lewis acid such as lanthanum(III) triflate (Table 2.3, entry 6).

This indicates that the role of the ruthenium compound is not just to act as a Lewis acid. Just like the ruthenium complex seems to be unique in the catalytic mixture, the nature of the metal catalyst is important as well. Not only 0.5 wt. % Pt/C, but also 5 wt. % Rh/C can be used; this resulted in a significant increase of the sorbitol yield up to 74 %, with almost no detectable degradation products (Table 2.3, entry 7). By contrast, when Pd/C was used as a replacement for Pt/C, a very low conversion of cellulose was observed (Table 2.3, entry 8). This suggests that the presence of a heterogeneous catalyst can modify the activity of the homogeneous catalyst, or even deactivate it, as seems the case here when the homogeneous Ru catalyst was combined with Pd/C. Finally, sorbitol is also obtained when Ru/C is employed as the heterogeneous catalyst, either alone, or in combination with $HRuCl(CO)(PPh_3)_3$ (Table 2.3, entries 9 and 10). However, the reaction is considerably less selective than when $HRuCl(CO)(PPh_3)_3$ and Rh/C are combined, and a lower overall yield of C6-polyols is obtained (14–20 %). This agrees with literature data that metallic Ru is a highly selective catalyst for glucose hydrogenation when the conditions are carefully controlled;[63, 69] however, in some conditions, for example, at higher temperature, hydrogenolytic degradation of the products can occur.[70]

Table 2.3. Conversion of cellulose under various conditions.[a]

Entry	Catalyst	Cellulose converted to dimers and smaller molecules, %	Amount of product in final mixture, %	Yield of hydrogenated product, %	Remarks
1[b]	0.033 g $HRuCl(CO)(PPh_3)_3$ 0.033 g Pt/C (0.5 wt. %)	0.4	100 glucose	0	H_2 replaced by Ar.
2	0.033 g Pt/C (0.5 wt. %)	0.3	86 glucose 14 levoglucosan	0	$HRuCl(CO)(PPh_3)_3$ omitted.
3[c]	0.033 g $HRuCl(CO)(PPh_3)_3$ 0.033 g Pt/C (0.5 wt. %)	19	19 glucose 25 other C6-sugars 22 sorbitol 16 C5-sugars 4 C5-alcohols 11 levoglucosan 3 C4-alcohols	5.4	KOH omitted.
4[d]	0.033 g $HRuCl(CO)(PPh_3)_3$ Pt/C (0.5 wt. %)	100	37 glucose 30 other C6-sugars 33 sorbitol	33	Reaction performed in $[EtMe_2Im][Br]$.
5	0.0085 g $RuCl_3$ Pt/C (0.033 g; 0.5 wt. %)	0	no product detected	0	$HRuCl(CO)(PPh_3)_3$ replaced by $RuCl_3$.
6	0.024 g $LaTf_3$ 0.033 g Pt/C (0.5 wt. %)	1.3	100 glucose	0	$HRuCl(CO)(PPh_3)_3$ replaced by $LaTf_3$.
7	0.033 g $HRuCl(CO)(PPh_3)_3$ 0.038 g Rh/C (5 wt. %)	100	26 glucose 74 sorbitol	74	Pt/C replaced by Rh/C.
8	0.0388 g $HRuCl(CO)(PPh_3)_3$ 0.038 g Pd/C (5 wt. %)	1.6	15 glucose 42 other C6-sugars 15 sorbitol 8 C5-sugars 12 C5-alcohols 8 C4-alcohols	0.6	Pt/C replaced by Pd/C.
9	0.033 g $HRuCl(CO)(PPh_3)_3$ 0.019 g Ru/C (5 wt. %)	100	10 sorbitol 10 mannitol 40 C6-sugars 29 levoglucosan 11 C4-alcohols	31	Pt/C replaced by Ru/C.
10	0.019 g Ru/C (5 wt. %)	100	12 sorbitol 2 mannitol 25 C6-sugars 38 levoglucosan 16 C4-alcohols	34	Pt/C replaced by Ru/C, and $HRuCl(CO)(PPh_3)_3$ omitted.

[a] Reaction conditions: cellulose (0.05 g), solvent (1 g [BuMeIm][Cl], except entry 4), co-catalysts (3 µL H_2O, 0.0017 g KOH, except entry 3), temperature (150 °C), hydrogen (3.5 MPa, measured at 25 °C, except entry 1), 48 h.
[b] Reaction conducted under 0.8 MPa of Ar.
[c] KOH was omitted.
[d] Solvent 1 g of 1-ethyl-2,3-dimethylimidazolium bromide, co-catalyst KOH (0.0072 g), 24 h.

Table 2.4. Attempted hydrogenation of glucose in [BuMeIm][Cl].[a]

Entry	Catalyst	Amount of product in final mixture, %	Total conversion, %	Yield of hydrogenated product, %
1	$HRuCl(CO)(PPh_3)_3$	14 glucose 74 sorbitol 12 C4-alcohols	86	64
2	Pt/C (0.5 wt. %)	74 glucose 13 HMF 13 levoglucosan	26	0
3	Ru/C (5 wt. %)	43 glucose 29 sorbitol 5 mannitol 7 C5-products 16 C4-products	57	45

[a] Reaction conditions: 0.05 g of glucose, solvent (1 g of [BuMeIm][Cl]), 0.037 g of catalyst, co-catalysts (3 mL of H_2O, 0.0017 g KOH), 150 °C, hydrogen (3.5 MPa, measured at 25 °C), 24 h.

2.4 Conclusions

The results clearly prove that when the cellulose structure is unfolded in an ionic liquid, the depolymerization becomes rather easy, and can be conducted in moderate conditions. As no acid was added in the present experiments, higher temperatures (150 °C) were needed than in reports on acid-catalyzed cellulose hydrolysis in ionic liquids; for example, in a study using [EtMeIm][Cl] and liquid acids the standard reaction temperature was only 90 °C.[35] The fact that no acid addition is required allows to efficiently avoid the degradation of hexose monomers to hydroxymethylfurfural or levoglucosan, and as the hydrogenation to sugar alcohols proceeds in the same pot, the cellulose can practically be converted fully into a useful glucose and sugar alcohol mixture. However, the low hydrogen solubility in ionic liquids is problematic for the consecutive hydrogenation, and the combination of cellulose solvation with sufficient hydrogen dissolution is a future target for ionic liquid selection or design. For separating the reaction products from the ionic liquid containing the homogeneous catalyst, pressure-driven nanofiltration could be a promising technique. It has indeed been shown that nanofiltration is one of the few techniques that is able to separate ionic liquids from polar reaction products.[71] Additionally, larger residual cellulose oligomers and a homogeneous catalyst with

a high molecular mass, such as the Ru complex used in the present study, may also be withheld by a membrane with a sufficiently small molecular mass cutoff.

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3 Cellulose Conversion into Alkylglycosides in the Ionic Liquid 1-Butyl-3-Methylimidazolium Chloride

The conversion of cellulose into alkylglycosides is carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride in the presence of an acidic catalyst. Primary alcohols like *n*-butanol and *n*-octanol were used as alkylating reagents. The acidic resin Amberlyst 15DRY proved the optimum heterogeneous catalyst: it catalyzes the hydrolysis of the β-1,4 links in the cellulose polymeric chain as well as the alkylation of the hydroxyl groups at the C1 position of the glucose intermediate. The cellulose was fully converted under mild conditions; in a reaction with butanol, the obtained yield of butylglucopyranoside isomers was 86 %.

3.1 Introduction

Alkylglycosides are a class of biodegradable nonionic surfactants with a broad application scope, *e.g.* in the cosmetic, detergency, food and pharmaceutical industries.[1] One of their interesting features is their ability to form liquid crystals.[2] The conventional alkylglycoside synthesis was first described by E. Fischer as the formation of a glycoside by the reaction of an aldose or ketose with an alcohol in the presence of acid species,[3a] and since then numerous homogeneous and heterogeneous catalysts have been proposed and applied for their synthesis.[3-6] Typical drawbacks of this reaction, such as the necessity for functional group protection and deprotection,[6] or the formation of oligomeric species, can be avoided using specific heterogeneous acidic catalysts like sulfonated resins,[7] acid clays [8] and zeolites.[9-10]

Ionic liquids, and in particular chloride-containing ones, can be suitable solvents for cellulose. They disrupt the hydrogen bonds and dissolve the cellulose chains at the molecular level.[11] For instance, 1-butyl-3-methylimidazolium chloride ([BuMeIm][Cl]) can dissolve up to 25 wt. % of cellulose.[12] There are already multiple examples of

successful cellulose transformations in ionic liquids, such as derivatization of the cellulose chains,[13] or production of composite materials containing besides cellulose also carbon nanotubes or inorganic materials.[14] Cellulose hydrolysis was successfully conducted in the ionic liquid 1-butyl-3-methylimidazolium chloride with glucose as the major product in the presence of homogeneous acids, or of the solid acidic catalyst Amberlyst 15DRY.[15] However, prolongation of the reaction time can cause pyrolysis of glucose, and when homogeneous acids are used, a ceiling yield of 50 % is reached at which hexose degradation starts to decrease the overall process yield.[15b]

It is worthwhile to investigate whether glucose, formed through acid hydrolysis of cellulose, can be further transformed in a one-pot process into more stable compounds like alkylglycosides. We have recently reported that addition of hydrogenation catalysts allows to convert in one pot the intermediately formed glucose into polyols, but the poor solubility of hydrogen in [BuMeIm][Cl] is a serious handicap for efficient hydrogenation.[16] This urged us to consider hexose acetalization as an alternative reaction. Not only this allows to use the most abundant carbohydrate source available for alkylglycoside production; the alkylation may in addition suppress the undesirable pyrolysis of glucose. There is an apparent compatibility between hydrolysis and alkylation reactions as they both require acid catalysis. In this work, we demonstrate an effective one-pot transformation of cellulose in the presence of Amberlyst 15DRY to butylglucopyranosides and octylglucopyranosides in 1-butyl-3-methylimidazolium chloride as the solvent under relatively mild conditions.

3.2 Experimental

1-Butyl-3-methylimidazolium chloride (99 %), ethyltributylphosphonium diethyl phosphate (>95 %) and tetrabutylphosphonium chloride (>95 %) were obtained from IoLiTec

Ionic Liquids Technologies GmbH. 1-Ethyl-3-methylimidazolium diethyl phosphate (≥98.0 % (HPLC/T)), 1-ethyl-3-methylimidazolium acetate (97 %) were obtained from Sigma-Aldrich. The cellulose used was Avicel PH 101 (DP 215–240). α-D-glucopyranoside (min 98 %), butyl α-D-glucopyranoside and butyl β-D-glucopyranoside (min 98 %) were obtained from Carbosynth Limited. Amberlyst 15DRY was purchased from Sigma-Aldrich. The H-β zeolite was a commercial sample from the PQ corporation (CP 811 BL-25). The H-MCM-22 was prepared in house based on a literature recipe.[17] Other chemicals were from commercial suppliers and were used as received. In a typical experiment, cellulose (0.05 g) was dissolved in [BuMeIm][Cl] (1 g) in a sealed glass vial (10 mL) at 110 °C with continuous stirring for 15 min. Then, the vessel was opened, and Amberlyst 15DRY (0.01 g), alcohol (0.3 mL of *n*-butanol or 0.5 mL of *n*-octanol), water (20 µL) added. After sealing, reaction mixture was stirred and heated at 110 °C for maximum 24 h. For reactions with methanol and ethanol, 10 mL stainless steel batch pressure reactors were employed under 8 bars of argon. After reaction, samples were derivatized using MSTFA (*N*-(trimethylsilyl)-*N*-methyltrifluoroacetamide) and injected onto a 30 m HP-1 column in a GC (HP 5890) or a GC-MS (Agilent 6890 GC and 5973 MS) instrument. Typically, a *ca.* fourfold excess of MSTFA with respect to the –OH groups was added to a 0.3 mL of sample mixed with 0.3 mL of pyridine, and the mixture was stirred for 3 h at 80 °C. Derivatized compounds were then extracted into 0.5 mL of dibutylether and analyzed. The procedure was verified and made quantitative using known amounts of reference compounds such as glucose, butyl α-D-glucopyranoside, butyl β-D-glucopyranoside, and others. All the product yields mentioned in the text were determined chromatographically and calculated from peak areas of corresponding reaction products. The water content of the ionic liquids was determined with a coulometric Karl-Fischer titrator (Mettler Toledo DL39) and anhydrous methanol as the solvent. Each sample was at least 0.1 g, and triplicate measurements were performed on each sample.

3.3 Results and Discussion

In a first phase, glucose was used as a substrate for the alkylation in ionic liquids. Multiple interesting procedures for glucose alkylation have been reported.[7-10] In order to investigate the effect of the ionic liquid solvent on the alkylation, we performed alkylation reactions with or without [BuMeIm][Cl] in *n*-butanol, without adding any other solvent. All catalysts tested, including Amberlyst 15DRY, showed significant activity for butylation of glucose at 90°C (Table 3.1, entries 1-4).

Table 3.1. Initial experiments with glucose.[a]

Entry	Solvent	*n*-Butanol, mL	Catalyst	Yield of α-BGP, %	Yield of β-BGP, %
1	-	1	Hβ–zeolite (0.01 g)	45	30
2	1 g [BuMeIm][Cl]	0.3	*p*TSA (0.005 g)	31	26
3	-	1	Amberlyst 15DRY (0.01 g)	48	32
4	1 g [BuMeIm][Cl]	0.3	Amberlyst 15DRY (0.01 g)	17	10

[a] Reaction conditions: glucose (0.01 g), 90 °C, 4 h.

The main products were butyl-α-D-glucopyranoside (α-BGP) and butyl β-D-glucopyranoside (β-BGP). Yields in the presence of [BuMeIm][Cl] are considerably lower than in pure BuOH, and a big part of glucose remains unreacted. This is simply a thermodynamic and kinetic consequence of the threefold lower *n*-BuOH concentration when the reaction was carried out in the presence of the ionic liquid. Nevertheless, the result in the presence of *para*-toluenesulfonic acid shows that a >50 % yield of butylglucosides can be achieved easily, even in an ionic liquid (Table 3.1, entry 2).

As a step-up towards cellulose, cellobiose was investigated as a reaction substrate, in view of its molecular structure intermediate between glucose and cellulose. This compound consists of two glucose units linked by a β(1→4) bond, and thus represents a dimeric model for the cellulose polymer. Just like glucose, cellobiose is readily soluble in [BuMeIm][Cl]. In the reaction with this dimeric substrate,

the acid catalyst should be capable not only of alkylation but also of hydrolysis of the β(1→4) bond. This also implies that some water should be available in the reaction medium. Minor contamination of the hydrophilic [BuMeIm][Cl] by water is hard to avoid; Karl–Fischer titration showed that the level of contamination was *ca.* 0.1 wt. % of water. To ensure that an at least stoichiometric amount of water is available, 20 µl of water was added per g of ionic liquid. We applied Amberlyst 15DRY, a catalyst previously reported to hydrolyze cellulose in [BuMeIm][Cl].[15a] Cellobiose (0.05 g) was successfully hydrolyzed and butylated by using 0.01 g of Amberlyst 15DRY and 0.3 mL of *n*-butanol in 1 g of water-enriched [BuMeIm][Cl] at 110 °C for 24 h. α-BGP and β-BGP were obtained with yields of 43 % and 24 % respectively. By-products were glucose (31 %) and levoglucosan (2 %). The detection of the latter product indicates that in certain conditions alkylation in the presence of an acidic catalyst can lead to degradation reactions, as will be demonstrated below. 110 °C has previously been reported as an optimal temperature for glucose butylation.[9-10]

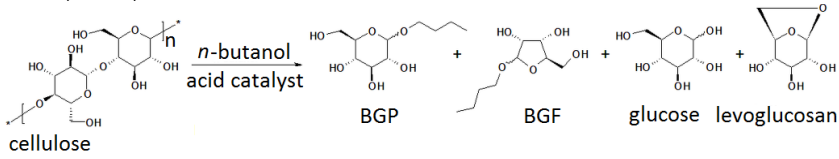
Next, cellulose, the principal compound under investigation, was applied in the form of the microcrystalline commercial product Avicel. The cellulose reagent may contain some additional water which can be consumed in the hydrolysis (typically 4–7 wt. % based on cellulose).[18] In our first attempt, H-β zeolite (Si/Al = 13) and H-MCM-22 zeolite (Si/Al = 30) were applied besides Amberlyst 15DRY [7c] for reactions with *n*-butanol. The zeolite materials that were chosen are both strong heterogeneous acids with excellent transport properties, due to the small crystal size, in the case of H-β, or due to the flaky morphology, in the case of H-MCM-22. Amberlyst 15DRY is macroporous Brønsted acid resin. Moreover, zeolites like H-β [9] have been reported to be suitable catalysts for alkylation of monomeric carbohydrates. However, when the zeolites were tested, no products of cellulose depolymerization were detected at all, not even after a 24 h reaction time (Table 3.2, entries 1 and 2). Significantly better results were obtained with Amberlyst 15DRY (Table 3.2, entry 3). This

suggests that the dissolved polymer chains can only interact with well-accessible acid sites in macropores.

Table 3.2. Initial experiments with cellulose.

Entry	Catalyst	Yield of α-BGP, %	Yield of β-BGP, %	Yield of BGF, %	Yield of glucose, %	Yield of levoglucosan, %	Total conversion of cellulose, %
1	H-β-zeolite (0.01 g)	0	0	0	0	0	0
2	H-MCM-22 (0.01 g)	0	0	0	0	0	0
3	Amberlyst 15DRY (0.01 g)	29	16	5	10	7	67

[a] Reaction conditions: cellulose (0.05 g), 1 g of [BuMeIm][Cl], 20 µl of water, 0.3 of mL *n*-butanol, 110 °C, 24 h.



Scheme 3.1. *Splitting of cellulose with formation of α-BGP, β-BGP, glucose and levoglucosan.*

Detailed product identification by comparison with reference compounds, by comparison with results of reported reactions and by GC-MS identification showed that the major product was BGP in its α- and β-forms, with the α-anomer as the dominant product. A smaller amount of butylglucofuranosides (BGF) was also detected, as well as of glucose (Table 3.2, entry 3, Scheme 3.1). Levoglucosan, a pyrolysis product, has been also identified. It is worth to note that pyrolysis of glucose and similar compounds can also lead to dehydrated compounds such as furans; [15] however, these were not detected here by means of GC or GC-MS.

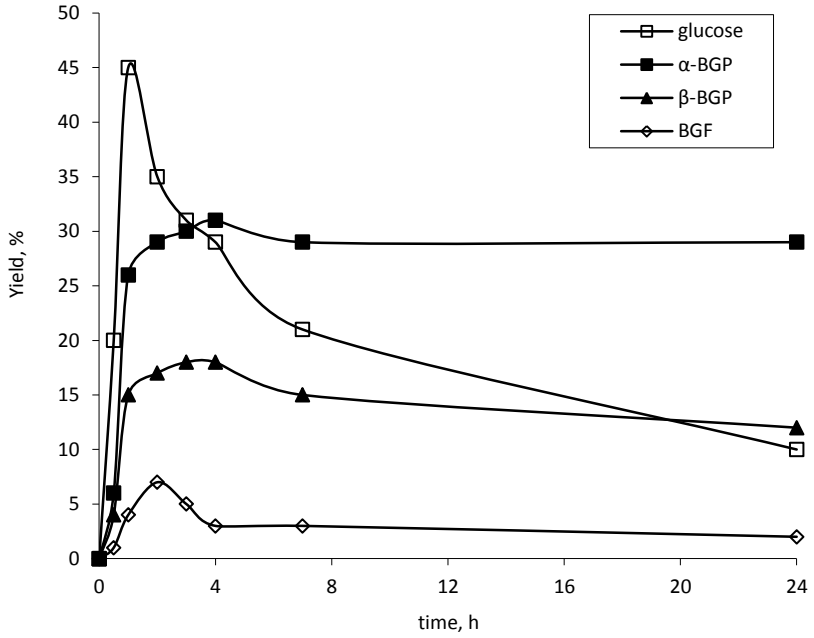


Figure 3.1 *Run profile of reaction between cellulose (0.05 g) and n-butanol (0.3 mL) in [BuMeIm][Cl] (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.*

Figure 3.1 shows that glucose is the major primary product of the reaction. At 110 °C and in the conditions specified, its concentration passes through a maximum at 1 h and then decreases with time. The total yield of alkylated carbohydrates is more or less constant in the 2 h – 4 h time interval. The BGPs are the major products, and in this fraction, α-BGP is dominant. However, the selectivity slowly changes. The α-BGP/β-BGP ratio increases from 1.5 at the first sampling point, to 1.7 at maximal product yield, and eventually evolves towards 2 at long reaction times. Between reaction times of 2 h and 4 h, the furanosides are gradually isomerized into pyranosides. α-BGP is indeed thermodynamically more stable than β-BGP and the BGFs. This variation of the α-BGP over β-BGP ratio early in the reaction has also been reported by Moreau for the alkylation of D-glucose with *n*-butanol. [10] Remarkably, in a zeolite-catalyzed, solventless reaction of glucose, β-

BGP is the kinetically favored product, and the initial α-BGP/β-BGP ratio is as low as 0.5. Only at over 90 % conversion, the α/β ratio stabilizes at ~ 2, which is close to the value observed in the ionic liquid mediated reaction. This suggests that the ionic liquid facilitates the β-BGP to α-BGP conversion in the alkylglycoside fraction.

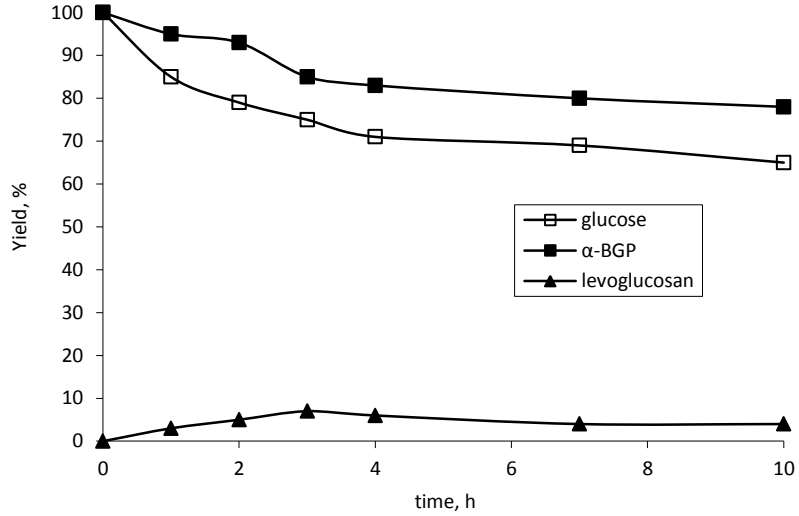


Figure 3.2 *Stability of a mixture of glucose and α-BGP in [BuMeIm][Cl] (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.*

While attempting to reach the equilibrium by extending the reaction time up to 24 h, it was observed that the product yield starts to decrease slowly. In order to understand this phenomenon, pure α-BGP and glucose were dissolved in [BuMeIm][Cl] in the presence of the acid resin, and the mixture composition was monitored versus time. This showed clearly that at 110 °C, α-BGP is more resistant to acidic hydrolysis caused by Amberlyst 15DRY than glucose, as is shown in Figure 3.2. Especially initially, the concentration of glucose falls faster than that of α-BGP.

We observed that under the same conditions but without the acidic catalyst, concentrations of glucose and α-BGP remained virtually unchanged during the same periods of time.

Table 3.3. Attempts to maximize conversion of cellulose.[a]

Entry	Solvent	Co-reagent	Yield of α-BGP, %	Yield of β-BGP, %	Yield of BGF, %	Yield of glucose, %	Yield of levoglucosan, %	Total yield of butylated products
1	1 g [BuMeIm][Cl]	-	29	16	5	10	7	50
2[b]	1 g [BuMeIm][Cl]	-	53	30	3	9	6	85
3[b]	1 g [BuMeIm][Cl]	3 μL H_2O	61	25	0	11	4	86
4[c]	1 g [BuMeIm][Cl]	-	37	20	13	18	12	70
5[d]	1 g [BuMeIm][Cl]	-	33	16	12	27	12	61
6[e]	1 g [BuMeIm][Cl]	-	28	12	11	15	8	51
7[f]	1 g [BuMeIm][Cl]	-	24	10	9	18	9	43
8	1 g [EtMeIm][Et_2PO_4]	-	0	0	0	0	0	0
9	1 g [EtMeIm][AcO]	-	0	0	0	0	0	0
10	1 g [EtMeIm][AcO]	4 μL H_2O	0	0	0	0	0	0
11	1 g [Bu_3PEt][Et_2PO_4]	-	12	12	0	19	5	24
12	1 g [Bu_3PEt][Et_2PO_4]	4 μL H_2O	14	14	0	22	0	28
13	1 g [Bu_4P][Cl]	-	0	0	0	0	0	0
14	1 g [Bu_4P][Cl]	4 μL H_2O	0	0	0	0	0	0

[a] Reaction conditions: 0.05 g of cellulose, 0.3 mL of *n*-butanol, 0.01 g of Amberlyst 15DRY, 110 °C, 24 h.
[b] After 4 h, 1.2 mL of n-butanol was added to the reaction mixture.
[c] 95 % of the Amberlyst 15DRY particles were removed after 4 h.
[d] 70 % of the Amberlyst 15DRY particles were removed after 4 h.
[e] 95 % of the Amberlyst 15DRY particles were removed after 2 h.
[f] 70 % of the Amberlyst 15DRY particles were removed after 2 h.

The fact that even the α-BGP concentration decreases is likely due to the dynamic nature of the equilibrium between glucose and α-BGP: as glucose starts to disappear, the equilibrium shifts to glucose and α-BGP is transformed back into glucose, even in the presence of butanol.

In order to maximize the yield of butylated products two approaches were used. First, it was attempted to shift the equilibrium via the law of mass action. This was achieved by adding an additional volume of *n*-butanol after some time of cellulose hydrolysis, when the extra solvent does no longer cause precipitation of the polymeric material (Table 3.3, entries 2 – 3). Indeed, addition of a large excess of butanol right from the start could impede smooth cellulose dissolution. In a second approach, part of the Amberlyst 15DRY particles were removed after some reaction time. It was speculated that the amount of acid catalyst required for the hydrolysis may be higher than the amount needed for the alkylation (Table 3.3, entries 4 – 7). Particularly the first approach was successful in raising the alkylglycoside yield, and using an overall BuOH to carbohydrate ratio of 50, the yield climbed up to 86 %. Remark that this is much higher than the *ca.* 50 % maximal yield of glucose from cellulose that is obtained when no secondary reaction is performed in the same pot.[15b] The same experiment was also performed on a five-fold increased scale, with otherwise identical ratios of reactants and ionic liquid solvent. A summed 84 % maximal yield of alkylated compounds was retrieved, using the same overall 50:1 ratio of butanol to carbohydrate monomeric units. Regarding the partial removal of the acid catalyst, the best effect was noted when 95 % of the particles were removed after 4 h (Table 3.3, entries 4-5), with finally a yield of 70 % butylated products at the relatively low molar BuOH to the glucose monomer ratio of 10. Such a procedure constitutes a compromise between a sufficient catalyst exposure to allow smooth hydrolysis and alkylation, and on the other hand, prevention of acid-catalyzed degradation late in the reaction.

It was also tried to use alternative ionic liquids that dissolve

cellulose, such as 1-ethyl-3-methylimidazolium diethylphosphate, 1-ethyl-3-methylimidazolium acetate, ethyltributylphosphonium diethylphosphate or tetrabutylphosphonium chloride (Table 3.3, entries 8 – 14). Note that some of these ILs are considerably more hydrophobic than [BuMeIm][Cl]. Therefore, these ionic liquid solvents were also tested with addition of an amount of water that is stoichiometric with respect to the cellulose. Only in ethyltributylphosphonium diethylphosphate some cellulose conversion was observed (Table 3.3, entries 11-12). Using other anions than chloride can be very detrimental for acid-catalyzed cellulose hydrolysis, since some anions that have been reported as suitable for cellulose dissolution, e.g. acetate, may actually act as a buffer and consequently quench the acidity of the resin. This could account for the lack of activity in the presence of 1-ethyl-3-methylimidazolium acetate. One of the factors contributing to the suitability of ethyltributylphosphonium diethylphosphate could be the asymmetric nature of its cation, which decreases the viscosity of the medium and thus increases diffusivities and reaction rates.[19]

While the addition of a minute amount of water (0.25 or 0.33 wt. %) did not hinder the dissolution of the cellulose, it had no significant effect in this type of reaction (Table 3.3, entries 2, 10, 12, 14). None of the assessed alternative ILs matched the performance of [BuMeIm][Cl].

Besides *n*-butanol, also *n*-octanol was used as an alkylating agent. Using the same 10 to 1 molar ratio of alcohol with respect to the carbohydrate monomer, a similar kinetic profile was observed. Figure 3.3 shows that α-OGP (octylglucopyranoside) is the major product of the reaction already after 30 min. Its concentration passes through a maximum at 4 h and then decreases with time. Again, the β-isomer and the furanosides are the prevalent by-products. By analogy with the alkylation with butanol, the predominance of α-OGP can be explained by its higher thermodynamic stability in comparison with β-OGP and OGF (octylglucofuranoside).[20] Control experiments

showed that α-OGP is again more resistant to acidic degradation caused by Amberlyst 15DRY than the intermediate glucose. Reaction between 0.05 g of cellulose and 0.5 mL of *n*-octanol in 1 g of ethyltributylphosphonium diethyl phosphate, in the presence of 0.01 g of Amberlyst 15DRY at 110 °C during 24 h gave the following product yields: 20 % of α-OGP, 5 % of β-OGP, 22 % of glucose and 5 % of levoglucosan. This confirms that the ionic liquid choice in this reaction is not limited to just [BuMeIm][Cl].

In solvent-free systems, the rate of glucose alkylation decreases with increasing length of alcohol alkyl chain.[21] This is due to the decreasing solubility of glucose in more apolar solvents. We have observed a different situation when cellulose, dissolved in [BuMeIm][Cl] is the carbohydrate source: octylation is initially faster than butylation. On the other hand, using shorter alcohols negatively affected the reaction. Thus, when methanol or ethanol were applied in the same molar ratio with respect to the carbohydrate monomers, the cellulose was not visibly dissolved, and no products of etherification or hydrolysis could be detected. It seems that the short alcohols compete more successfully than the cellulose for the hydrogen bond formation with the chloride anions. As the chain length of the alcohol reagent increases, its hydrogen bond donor capacity decreases, and this allows a better solvation of the cellulose by the ionic liquid and a faster reaction.

However, a too long alkyl chain, as in 1-dodecanol, again decreases the product yields. Thus, no products were obtained from a 24 h reaction of cellulose and *n*-dodecanol in [BuMeIm][Cl] at 110 °C, even if a visually homogeneous reaction mixture was formed. Apparently, [BuMeIm][Cl] is not a suitable solvent to affect the reaction between dissolved glucose and *n*-dodecanol, which have widely different polarities.

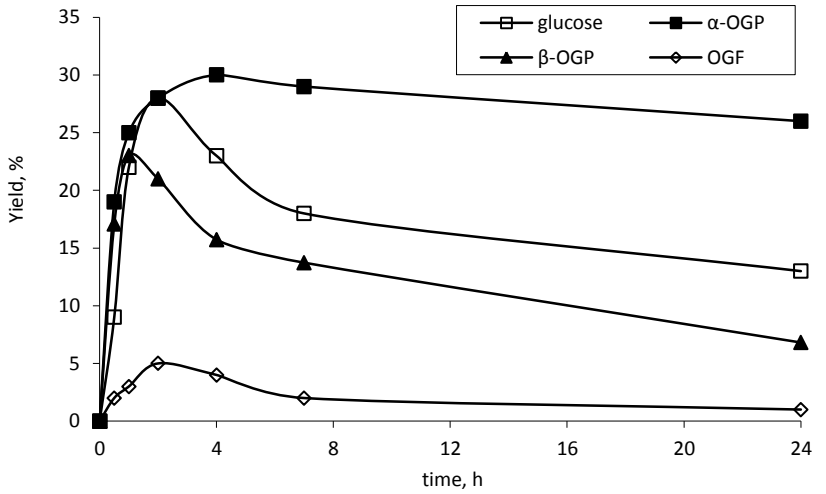


Figure 3.3. *Run profile of reaction between cellulose (0.05 g) and n-octanol (0.5 mL) in [BuMeIm][Cl] (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.*

Table 3.4. Transalkylation of α-BGP with *n*-octanol.[a]

Entry	Amberlyst 15DRY amount, g	Yield of α-OGP, %	Yield of β-OGP, %	Yield of OGF, %	Yield of glucose, %	Yield of BGF, %	Yield of BGP, %	Yield of levoglucosan, %	Total yield of octylated compounds, %
1	0.0200	38	21	5	15	6	5	10	64
2	0.0105	30	10	4	12	4	10	8	44
3	0.001	6	4	8	0	0	80	0	18
4	0	0	0	3	0	0	90	0	10

[a] Reaction conditions: α-BGP (0.05 g), 1 g of [BuMeIm][Cl], 0.5 mL of *n*-octanol, 110 °C, 24 h.

In an alternative approach to prepare the long-chain alkylglycosides, it was attempted to perform a transalkylation, starting from a short-chain alkylglycoside. That this transalkylation can easily be performed in an ionic liquid is evident from the data in Table 3.4: reaction of α-BGP and *n*-octanol gave up to 64 % yield of octylated compounds within 24 h. The acidic catalyst concentration required for this transalkylation is similar to the amount of catalyst typically used in the cellulose depolymerization, i.e. at least 10 mg of catalyst per g of ionic liquid (entries 1 to 4). In order to synthesize

dodecylglucosides, a reaction was performed using 0.05 g of cellulose, 0.3 mL of *n*-butanol, 0.01 g of Amberlyst 15DRY and 20 µL of water in 1 g of [BuMeIm][Cl]. After 2 h of stirring at 110 °C, 0.611 g of *n*-dodecanol was added. After another 2 h at 110°C, *n*-butanol was evaporated from the reaction mixture in a rotary evaporator, and an extra portion of 0.611 g of *n*-dodecanol was added. As is shown on Figure 3.4, equilibrium was apparently reached after 10 h. At this point, the yield of DGP is 45 % (29 % α-DGP and 16 % β-DGP), with the α-glucopyranoside isomers dominating over the β-isomers during the whole course of the reaction. This proves that hydrolysis followed by transalkylation is a viable route in forming the long-chain alkylglycosides from cellulose.

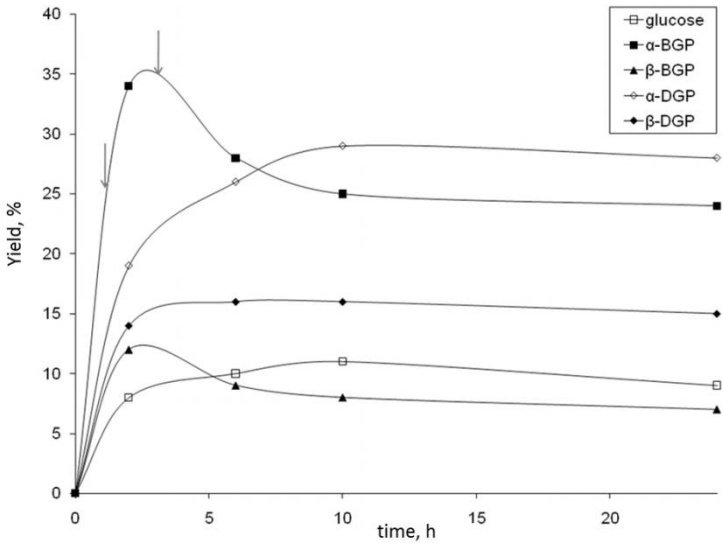


Figure 3.4 *Run profile of reaction between cellulose (0.05 g), n-butanol (0.3 mL) and subsequently n-dodecanol (two loads of 0.611 g, indicated by arrows) in [BuMeIm][Cl] (1 g) in the presence of Amberlyst 15DRY (0.01 g) at 110 °C.*

3.4 Conclusions

The results prove that when the cellulose structure is unfolded in an ionic liquid, the depolymerization becomes rather easy, and can be

carried out in moderate conditions. Two ionic liquids were identified that allow to dissolve the cellulose and to perform the acid-catalyzed hydrolysis and alkylation. While the use of an acid catalyst could cause degradation of the formed hexoses, it was demonstrated here that this problem can be alleviated by in situ conversion of the glucose to alkylglycosides. When an excess of the alcohol was offered, or when part of the acid catalyst was removed during the alkylation phase, the yield of alkylglycoside could be maximized. The direct synthesis of alkyl glycosides with longer chains, such as dodecylglycopyranosides, is less easy, but can be achieved via transalkylation. The reaction products are nonpolar compounds and consequently can be isolated by supercritical extraction with carbon dioxide.[22] This techniques has been already successfully used for isolation of surfactants.[23]

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4 Synthesis of Glucose Esters from Cellulose in Ionic Liquids

The transformation of cellulose into the glucose ester α-D-glucose pentaacetate was carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride under mild reaction conditions. The reaction comprises two steps: the first involves a hydrolysis reaction, yielding α-D-glucose and glucose oligomers; only after some time, the acetylating reagent acetic anhydride is added. Under optimized conditions and using the acidic resin Amberlyst 15DRY as a hydrolysis catalyst, a 70 % yield of α-D-glucose pentaacetate was obtained. This product could be quantitatively isolated by simple liquid – liquid extraction, which allowed easy recycling of the ionic liquid and catalyst.

4.1 Introduction

As a major constituent of wood, straw, grass and crop residues [1] cellulose is the most abundant biopolymer on the planet.[2] Transformation of this renewable resource into base and high-value chemicals may be a profitable process for the chemical industry.[3-5] Its very rigid structure and consequently its difficult dissolution and chemical processing remain however a scientific and technological challenge.[6, 7]

In contrast with classical organic solvents, which need often extreme conditions to solubilize cellulose, some ionic liquids display a high cellulose solubility even at moderate temperatures.[8] In particular, chloride- or acetate-based ionic liquids efficiently dissolve cellulose due to their ability to disrupt the three-dimensional hydrogen bond network of cellulose.[8-15] For example, 1-butyl-3-methylimidazolium chloride ([BuMeIm][Cl]) and 1-ethyl-3-methylimidazolium acetate ([EtMeIm][AcO]) can dissolve up to respectively 25 [11] and 12 [12] wt. % of cellulose. As could be expected these two ionic liquids are currently the most effective solvents for the (chemical) processing of this biopolymer.[11, 12, 15-17]

Various cellulose transformation processes in ILs have been reported,[17-28] e.g., acid-catalyzed dehydration into 5-hydroxymethylfurfural,[29] conversion into levulinic acid,[22] production of magnetically active cellulose fibres,[24] and transformation of cellulose into alkylglucosides in [BuMeIm][Cl] in the presence of Amberlyst 15DRY.[18, 27] Also derivatisation reactions of cellulose have been reported before,[21, 30-40] such as acetylation, which leads to formation of the valuable product cellulose acetate.[30-32, 35, 38, 40] Synthesis of monomeric acetylated species from cellulose can however also be of high practical interest. Cellulose hydrolysis was successfully performed in [BuMeIm][Cl] with glucose as the major product in the presence of Amberlyst 15DRY and other acidic catalysts.[23, 25, 41] Glucose acetylation in ILs, applying acetic anhydride as the acetylating reagent, has also been reported.[30] This prompted us to consider an alternative cellulose transformation pathway, namely the direct one-pot conversion into α-D-glucose pentaacetate (GPAc). GPAc is a valuable compound with multiple applications, such as the activation of percompounds, like H_2O_2 and sodium percarbonate,[42] which are applied in bleaching,[43] disinfection and cold-sterilization processes.[44] GPAc is also known to promote insulin synthesis and release.[45] Moreover, this glucose ester can be easily separated from the reaction mixture by liquid – liquid extraction.[46] This is a big advantage since the isolation of classical cellulose hydrolysis products such as glucose and sorbitol from the ionic liquid, is often problematic due to their higher polarity.[18, 19, 27]

In this chapter a mild transformation of cellulose into α-D-glucose pentaacetate in [BuMeIm][Cl], with Amberlyst 15DRY as acidic catalyst will be demonstrated.

4.2 Experimental Section

4.2.1 Materials

1-Butyl-3-methylimidazolium chloride (99 %) was obtained from Ionic Liquids Technologies GmbH (IoLiTec). 1-Butyl-3-methylimidazolium acetate (≥95%), α-D-glucose pentaacetate, β-D-glucose pentaacetate, cellulose (Avicel PH 101; DP 215–240), Nafion SAC-13 and Amberlyst 15DRY were purchased from Sigma-Aldrich. Smopex-101 was purchased from Alfa Aesar GmbH & Co KG. $HNbMoO_6$ was prepared in-house based on a literature recipe:[47] $LiNbMoO_6$ was prepared by calcination of a stoichiometric mixture of Li_2CO_3, Nb_2O_5, and MoO_3 at 580 °C. After 12 h of calcination a grinding was performed; then calcination was restarted for another 12 h. Then a proton-exchange reaction towards $HNbMoO_6$ was carried out by shaking $LiNbMoO_6$ in 1 M HNO_3 at room temperature for 1 week. Afterwards the product was washed with distilled water and dried in air at 70 °C. Other chemicals were obtained from commercial suppliers and were used as received.

4.2.2 Typical Reaction Procedure

Reactions were performed in sealed glass vials (10 mL) with continuous stirring. In a typical reaction, 0.05 g cellulose was hydrolyzed in 1 g of 1-butyl-3-methylimidazolium chloride for 4 h at 110 °C in the presence of Amberlyst 15DRY (0.005 g) and 20 µL water. Next, Amberlyst 15DRY particles were removed from a fraction of the reaction mixture (0.1 mL), and the resulting mixture was acetylated with 0.17 mL of acetic anhydride at 100 °C for 16 h.

4.2.3 Separation of Reaction Product and IL/Catalyst Recycling

Amberlyst 15DRY particles were removed from the IL and regenerated by washing with 95-97 % sulfuric acid according to a

procedure described elsewhere.[41] The IL phase was stirred with *n*-Bu_2O in a 1:5 volume ratio at 80 °C for 1 h. In this way the product was nearly quantitatively extracted into the ether phase. The remaining 1 mL of IL and the regenerated catalyst were then reused for a second transformation of cellulose into GPAc under the conditions described in paragraph 4.2.2.

4.2.4 Analysis

Prior to GC and GC-MS analysis glucose and similar compounds with free hydroxyl groups were silylated using *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA). Typically, a four-fold excess of MSTFA with respect to the hydroxyl groups was added to 0.1 mL of reaction mixture. This was mixed with 0.3 mL of pyridine, and stirred for 3 h at 80 °C. The silylated compounds were then extracted into 0.5 mL of dibutylether. The extraction procedure was optimized and confirmed to be quantitative using known amounts of reference compounds such as glucose, α-D-glucose pentaacetate, β-D-glucose pentaacetate, levoglucosan, hydroxymethylfurfural, and cellobiose. All the product yields mentioned in the text were determined chromatographically and calculated from peak areas of corresponding reaction products. Quantitative and qualitative gas chromatography analyses were performed using a 30 m HP-1 column in a GC (HP 5890) or a GC-MS (Agilent 6890 GC and 5973 MS) instrument.

The depolymerization of cellulose was followed by gel-permeation chromatography of the tricarbanilate derivatives of the cellulose samples. Dried isolated cellulose (≤0.005 g) was derivatized with phenylisocyanate (0.1 mL) in dimethyl sulfoxide (1 mL) at 70 °C, resulting in cellulose tricarbanilates, which are readily soluble in tetrahydrofuran.[48] The gel-permeation chromatography analysis was carried out at 35 °C with a Shimadzu HPLC LC10 instrument. For the detection of the derivates a UV-Vis detector at 236 nm was used. The system was calibrated with polystyrene standards.

The water content of the ionic liquids was determined with a coulometric Karl-Fischer titrator (Mettler Toledo DL39) and anhydrous methanol as the solvent. Each sample was at least 0.1 g, and triplicate measurements were performed on each sample. The level of water contamination of 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate was found to be *ca.* 0.1 wt. %.

The concentration of H^+-cations, released from Amberlyst 15DRY beads, was detected by titration with 0.0001 M NaOH with a Metrohm 848 Titrino Plus autotitrator.

4.3 Results and Discussion

4.3.1 Peracetylation of Glucose in Ionic Liquids

In order to tackle the transformation of cellulose into the glucose ester α-D-glucose pentaacetate (GPAc), the acetylation of glucose was investigated first. Since cellulose hydrolysis was successfully performed before in [BuMeIm][Cl],[23, 25, 41] this ionic liquid was selected for the valorization of cellulose into glucose esters. Based on the good results in literature acetic anhydride (Ac_2O) was chosen as acetylating agent.[30, 31, 35, 40]

In a first experiment $3.1 \cdot 10^{-4}$ mol glucose was dissolved in 1 g of [BuMeIm][Cl], together with varying amounts of acetic anhydride. The acetylation of the hydroxyl groups of cellulose does not require a catalyst.[30, 40, 46, 49] Figure 4.1 shows that if $1.7 \cdot 10^{-3}$ mol of Ac_2O (a close-to-stoichiometric amount with respect to the hydroxyl groups of glucose) was employed the conversion of glucose increased till 100 %. However, apart from the desired product GPAc (60 % yield), also a significant fraction of the glucose diacetate (GDAc, 7 % yield) and triacetate (GTAc 33 % yield) were obtained. The presence of incompletely acetylated glucose molecules in case of a close-to-stoichiometric ratio of hydroxyl groups of glucose/acetic anhydride was reported before.[42] Increasing the amount of Ac_2O further to

$3.4 \cdot 10^{-3}$ mol resulted in a 100 % yield of GPAc. In practice, this amounts to an acetic anhydride to glucose ratio of at least 11 which is needed to attain nearly full acetylation of the glucose molecule.

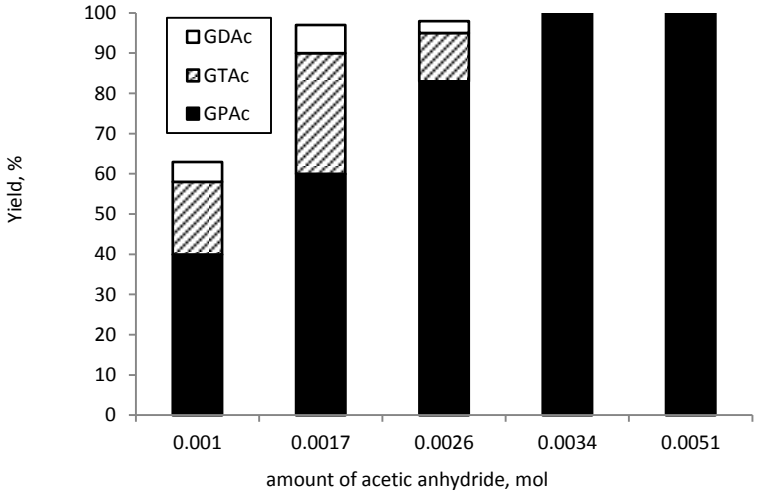


Figure 4.1. *Influence of amount of Ac_2O on the glucose acetylation (Reaction conditions: $3.1 \cdot 10^{-4}$ mol (0.056 g) glucose, 1 g of [BuMeIm][Cl], 100 °C, 4 h).*

4.3.2 Synthesis of GPAc from Cellobiose

With the glucose acetylation explored, the transformation of cellobiose into GPAc was studied. A series of acidic catalysts were chosen and tested in the hydrolysis of cellobiose in the ionic liquid medium. The sulfonated resin Amberlyst 15DRY possesses strong acidic properties and has been reported as catalyst for efficient cellulose hydrolysis.[23] Silica-supported Nafion SAC-13 was selected in view of its high recyclability in a similar process.[50] Smopex-101, a fiber based on polyethylene grafted with styrene and sulfonated with chlorosulfonic acid, has been claimed to be a more effective catalyst than Amberlyst 15DRY due to the presence of stronger Brønsted acid sites.[51, 52] $HNbMoO_6$ is an exfoliated nanosheet material with strong acid properties, which has been relatively recently reported as a promising solid acid catalyst for saccharide hydrolysis.[53] In Figure

4.2, it can be seen that in the catalyst-free reaction system the glucose yield is near to zero due to a very low conversion of the initial substrate. Introducing 0.01 g of Nafion SAC-13 into the reaction mixture did not improve the glucose yield much (5 %). The activities of $HNbMoO_6$ and Smopex-101 were significantly higher with glucose yields of 20 % and 60 % respectively. However, the highest yield of glucose was observed in the presence of Amberlyst 15DRY. The low activity of Nafion SAC-13 as an acid catalyst can be ascribed to its relatively low content of acid sites: Amberlyst 15DRY has an acid amount of 4.7 meq H^+g^{-1} *vs.* 0.12 meq H^+g^{-1} for Nafion SAC-13 (data provided by the supplier). $HNbMoO_6$ has a layered structure;[53] possibly, in the relatively viscous ionic liquid medium the intercalation of molecules between the sheets proceeds less well than e.g. in water, and this may decrease the access of the cellobiose reactants to the active sites.

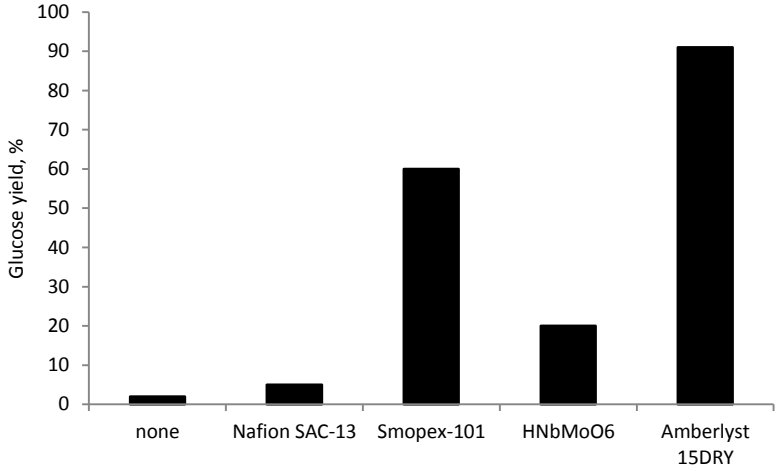


Figure 4.2. *Influence of acidic catalyst on the cellobiose hydrolysis (Reaction conditions: 1.55·10^{-4} mol (0.053 g) cellobiose, 0.01 g of catalyst, 1 g [BuMeIm][Cl], 20 µL of H_2O, 110 °C, 4 h).*

As Amberlyst 15DRY showed the highest activity it was used for production of GPAc from cellobiose. After the hydrolysis Amberlyst 15DRY particles were removed from the reaction mixture. For the

subsequent acetylation a fraction of this mixture (0.1 mL), containing about $3.1 \cdot 10^{-5}$ mol of glucosidic units, was mixed with $1.7 \cdot 10^{-3}$ mol of Ac_2O. Note that a large excess of acetic anhydride was added, as this gave the best results in the acetylation of glucose. Despite the large excess of acetylating agent, after 4 h at 100 °C only 12 % yield of GPAc was obtained. It was hypothesized that this low yield was caused by the degradation of GPAc under strong acidic conditions, as such a degradation has been reported before.[23] Since leaching of protons from the Amberlyst 15DRY particles has been proposed before,[41] some protons may remain in the solution even after removal of the polymeric catalyst particles. In order to investigate this influence of the acid on the GPAc instability, the hydrolysis of cellobiose was performed under the same reaction conditions but with a lowered amount of Amberlyst 15DRY (0.005 g). Although this led to a slightly lower glucose yield of 85 % after the hydrolysis step, a 95 % yield of GPAc was obtained after the second step. The lower amount of catalyst probably leads to less proton leaching, resulting in an environment in which GPAc is more stable. This will be examined in more detail with cellulose as the substrate.

4.3.3 Synthesis of GPAc from Cellulose

Evaluation of decomposition of GPAc

Next, the hydrolysis and acetylation of the principal substrate, i.e. cellulose, were investigated. In a first experiment, 0.05 g of cellulose in 1 g of [BuMeIm][Cl] was reacted with 20 µL of H_2O in the presence of 0.01 g of Amberlyst 15DRY. As shown in Table 4.1 (Entry 1), after 4 h at 110 °C, a 40 % yield of glucose was attained. Subsequent acetylation of a 0.1 mL fraction with a large excess of Ac_2O ($1.7 \cdot 10^{-3}$ mol) did only yield 2 % GPAc after 7 h (Entry 2). This yield is based on the amount of glucose monomers initially present in the cellulose substrate. This low yield is in line with the low yields of GPAc obtained from cellobiose with the same amount of catalyst and may be due to fast degradation of GPAc under the applied acidic reaction

conditions. The presence of typical degradation products such as 5-hydroxymethylfurfural and levoglucosan in the product pool supports this hypothesis.[54] In order to check whether acetic acid, which could be formed from Ac_2O, contributes to the GPAc decomposition side reaction, *n*-BuOAc was used as an acetylating agent under the same conditions (Entry 3). Indeed, *n*-BuOAc would only release butanol as a by-product of the acylation instead of a carboxylic acid. However, this ester turns out to be insufficiently reactive to perform a transacylation, and no GPAc was obtained.

Table 4.1. Cellulose transformation into GPAc.

Entry	Step	T, °C	Reactant	Time, h	Product yields, %
1	1[a]	110	20 µL H_2O	4	4 levoglucosan 40 glucose 7 other C6 – sugars 1 dimers of C6 – sugars
2	2[b]	100	$1.7 \cdot 10^{-3}$ mol Ac_2O	7	5 hydroxymethylfurfural 2 GPAc
3	2[b]	100	$1.7 \cdot 10^{-3}$ mol *n*-BuOAc	7	2 levoglucosan 15 glucose

[a] Hydrolysis conditions: 0.05 g of cellulose ($3.1 \cdot 10^{-4}$ mol glucosidic units), 1 g of [BuMeIm][Cl], 0.01 g Amberlyst 15DRY
[b] Acetylation: 0.1 mL of the reaction mixture of entry 1 was taken, and catalyst particles were removed prior to the acetylation reaction.

To confirm the hypothesis of GPAc degradation, two control experiments were conducted. In a first experiment, $3 \cdot 10^{-4}$ mol of GPAc was dissolved in 1 g of [BuMeIm][Cl] and reacted at 100 °C in the presence of 0.01 g Amberlyst 15DRY and 20 µL H_2O. Figure 4.3 illustrates the fast degradation of GPAc under the employed conditions, with only 15 % of the GPAc remaining after 2 h. After 7 h no GPAc can be detected anymore. Note that the GPAc decomposition does not necessarily proceed via glucose as an intermediate, but rather involves direct formation of anhydride compounds via elimination of acetyl groups, which results in the formation of acetic anhydride and acetic acid.[55] The combined yield of GPAc and hydroxymethylfurfural and levoglucosan is well below

100 %, which is probably due to the formation of light degradation products that were not quantified in the GC analysis.[54] Secondly, an experiment with glucose was carried out under identical conditions. The evolution of glucose in time when reacted at 100 °C is also presented in Figure 4.3. It seems that glucose is substantially more stable than GPAc, even if it eventually also forms degradation products like levoglucosan or hydroxymethylfurfural.

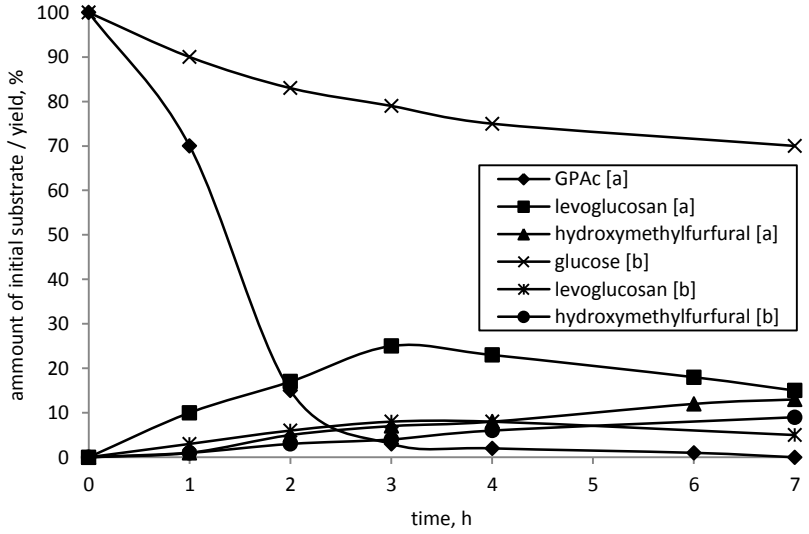


Figure 4.3. *Decomposition of GPAc [a] and glucose [b] (Reaction condition: $3.1 \cdot 10^{-4}$ mol GPAc [a] or glucose [b], 0.01 g of Amberlyst 15DRY, 1 g of [BuMeIm][Cl], 20 µL of H_2O, 100 °C, 4 h).*

In order to prove that the degradation is acid-catalyzed, control experiments were also conducted in absence of the acidic catalyst. Figure 4.4 illustrates that the concentration of both GPAc and glucose remained almost unchanged after 6 h. Only minor amounts of levoglucosan (3 % after GPAc degradation and 1 % after glucose degradation) were detected in both cases.

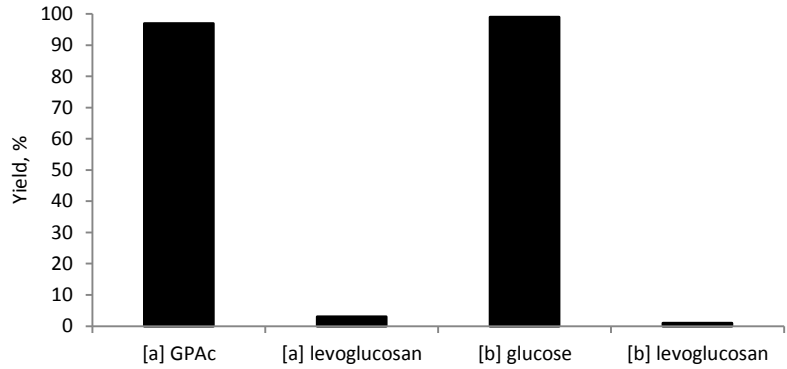


Figure 4.4. *Decomposition of GPAc [a] and glucose [b] under acid-free conditions (Reaction condition: $3.1 \cdot 10^{-4}$ mol GPAc [a] or glucose [b], 1 g of [BuMeIm][Cl], 20 µL of H_2O, 100 °C, 6 h).*

Influence of amount of Amberlyst 15DRY

Since the acid catalyst causes degradation of GPAc, it was important to optimize the amount of this catalyst in order to prevent excessive product degradation, but without affecting the hydrolysis yield too much. Therefore, three hydrolysis experiments were performed with lower amounts of Amberlyst 15DRY. In Table 4.2, the results of these experiments are compared with the ones for 0.01 g of catalyst. In absence of a catalyst (Table 4.2, entry 1), most of the initial substrate remained unreacted, and only a minor amount of glucose was detected after cellulose hydrolysis. Lowering the amount of catalyst from 0.01 g till 0.005 g did not affect the product distribution after hydrolysis much, with respectively 40 % and 36 % glucose yields (Entry 2-3). Further reducing the amount of Amberlyst 15DRY, however, led to a significant decrease in glucose yield (Entry 4).

Table 4.2. Cellulose hydrolysis/acetylation in the presence of various amounts of Amberlyst 15DRY.

Entry	Catalyst	Product yield, % after step 1[a]	GPAc yield, % after step 2[b]
1	-	3 glucose	-
2	0.01 g Amberlyst 15DRY	4 levoglucosan 40 glucose 7 other C6 – sugars 1 dimers of C6 – sugars	10
3	0.005 g Amberlyst 15DRY	1 levoglucosan 36 glucose 2 other C6 – sugars 8 dimers of C6 – sugars	70
4	0.003 g Amberlyst 15DRY	19 glucose 12 dimers of C6 – sugars	15

[a] Hydrolysis conditions: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) of cellulose, 20 µL of H_2O, 1 g of [BuMeIm][Cl], 110 °C, 4 h.
[b] Acetylation conditions: 0.1 mL (one tenth) of the reaction mixture after hydrolysis (with catalyst particles removed), $1.7 \cdot 10^{-3}$ mol (0.17 mL) of Ac_2O, 100 °C, 16 h.

In a second step, Amberlyst 15DRY particles were removed and 0.1 mL of the reaction mixtures (*ca.* $3.09 \cdot 10^{-5}$ mol of glucosidic units), was acetylated with an excess of Ac_2O under the same conditions as in the preliminary experiment with 0.01 g (Table 4.1, entry 2). While in the case of 0.01 g of catalyst, the GPAc yield was only 10 %, a yield of 70 % was reached with 0.005 g after 16 h of acetylation. The difference in GPAc yield can be explained by the higher concentration of leached protons for the reaction solution with 0.01 g of catalyst compared to the one starting with only 0.005 g of catalyst, which makes it more acidic and thus more active for the degradation of GPAc and glucose. It has been observed before that the amount of leached protons in the reaction solution is proportional with the amount of catalyst.[41] The result with 0.003 g catalyst confirmed this hypothesis. Although the hydrolysis was far from optimal with this amount, still a larger amount of GPAc was formed than with 0.01 g Amberlyst 15DRY. Probably decomposition of GPAc and glucose hardly takes place at this low catalyst concentration.

Screening of acidic catalysts

After optimizing the catalyst amount, the performance of some alternative acid catalysts, which were also evaluated in the cellobiose

hydrolysis, was assessed: Nafion SAC-13, Smopex-101 and $HNbMoO_6$ (Table 4.3). The optimized reaction conditions for Amberlyst 15DRY were employed: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) cellulose, 0.005 g of acid catalyst, 1 g of [BuMeIm][Cl], 110 °C, 4 h. Application of these three catalysts gave no satisfactory results compared to Amberlyst 15DRY. While a 70 % GPAc yield was attained in the presence of Amberlyst 15DRY (Entry 4), only 1 % of GPAc and 3 % of glucose were reached with Nafion SAC-13 (Entry 1). In the presence of the other catalysts, even no acetylated glucose was formed at all (Entries 2-3).

The poor results obtained for the cellulose transformation into GPAc with these three other acidic catalysts are in line with the observations for cellobiose. Again, the low acidity and potentially hindered diffusion due to the polymeric structure of cellulose explain the lack in activity for respectively Nafion SAC-13 and $HNbMoO_6$.[52, 53] Smopex, on the other hand probably has a too high acidity compared to Amberlyst 15DRY.[52] Moreover, it is practically impossible to separate the catalytic fibers of Smopex-101 from the ionic liquid based product mixture. Thus, while the hydrolysis of cellulose is efficiently catalyzed in the presence of Smopex-101 (cfr. the relatively good hydrolysis results with cellobiose), the too strong acidity and the problematic removal from the reaction mixture likely contribute to the decomposition of GPAc.

Table 4.3. Screening of acidic catalysts for transformation of cellulose to GPAc [a]

Entry	Catalyst	Product yields, %
1	0.005 g Nafion SAC-13	3 glucose 1 GPAc
2	0.005 g Smopex-101	11 hydroxymethylfurfural
3	0.005 g HNbMoO6	2 glucose
4	0.005 g Amberlyst 15DRY	70 GPAc

[a] Hydrolysis conditions: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) cellulose, 1 g of [BuMeIm][Cl], 20 µL of H_2O, 110 °C, 4 h.
[b] Acetylation conditions: 0.1 mL (one tenth) of the reaction mixture after hydrolysis (with as many as possible catalyst particles removed), $1.7 \cdot 10^{-3}$ mol (0.17 mL) of Ac_2O, 100 °C, 16 h.

Evolution of GPAc yield in time

In order to find an optimal duration of the acetylation, the reaction course was followed as a function of time in optimal conditions. In these experiments 0.1 mL of mixture **A**, containing *ca.* $3.09 \cdot 10^{-5}$ mol of glucosidic units, was acetylated with $1.7 \cdot 10^{-3}$ mol of acetic anhydride at 100 °C. Mixture **A** is the product mixture, obtained after hydrolysis of 0.05 g of cellulose in 1 g of [BuMeIm][Cl] in presence of 0.005 g of Amberlyst 15DRY at 110 °C for 4 h. Catalytic beads were removed prior to acetylation. Figure 4.5 illustrates that a maximum yield of GPAc is attained after 16 h reaction time. Upon prolonging the reaction time, the GPAc yield started to decrease again. More insight in this reaction course will be provided below.

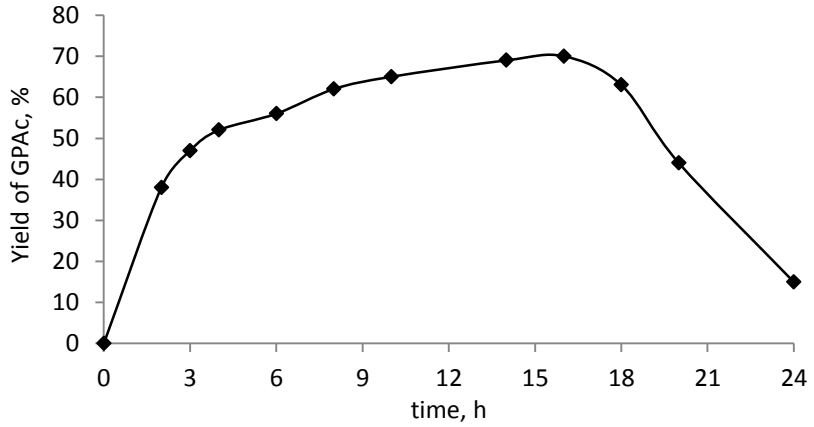


Figure 4.5. *Progress of the acetylation yield after the hydrolysis step (Reaction conditions: 0.1 mL of mixture* ***A****,* $1.7 \cdot 10^{-3}$ *mol* Ac_2O*, 100 °C).*

Influence of other reaction parameters

Since it was shown for the glucose acetylation that the amount of acetic anhydride has a significant influence on the yield of GPAc, the influence of the acetylating agent amount was also investigated for the cellulose transformation into glucose esters. One can conclude from Table 4.4, that a too small amount of Ac_2O decreased the acetylation degree of the glucose derivatives (Table 4.4, entries 1

– 2). Apart from GPAc, also glucose triacetate and diacetate were detected, as was the case for the glucose acetylation. $1.7 \cdot 10^{-3}$ mol seems to be the optimal amount of acetylation agent (Table 4.4, entry 3). In contrast with glucose acetylation, also a too high excess of Ac_2O decreased the GPAc yields (Table 4.4, entries 4 – 5). This has been previously reported by Zhang *et al.* for a similar ionic liquid, 1-allyl-3-methylimidazolium chloride.[13] This effect can be explained by the fact that at the moment of the Ac_2O addition, the depolymerization of the cellulose is not yet complete, as is evidenced by the detection of dimeric compounds after the first stage. If a too large excess of Ac_2O is added after the first stage, it could compromise the solubility of the remaining cellulose fragments and glucose oligomers in the IL.

Table 4.4 Influence of the acetylation agent.[a]

Entry	Acetylating agent	Yield, %
1	$4.9 \cdot 10^{-4}$ mol Ac_2O	17 GPAc 8 glucose triacetate 5 glucose diacetate
2	$9.8 \cdot 10^{-4}$ mol Ac_2O	35 GPAc 5 glucose triacetate
3	$1.7 \cdot 10^{-3}$ mol Ac_2O	70 GPAc
4	$3 \cdot 10^{-3}$ mol Ac_2O	40 GPAc
5	$1 \cdot 10^{-2}$ mol Ac_2O	31 GPAc
6	$1.7 \cdot 10^{-3}$ mol propanoic anhydride	65 GPAc

[a] Reaction conditions: 0.1 mL of mixture A (hydrolysis mixture; cfr paragraph 'Evolution of GPAc yield in time'), 100 °C, 16 h.

After optimizing the amount of Ac_2O, also an acetylation experiment was performed with propanoic anhydride (Table 4.4, entry 6); a 65 % yield of α-D-glucose pentapropanoate was obtained after mixing 0.1 mL of mixture **A** with $1.7 \cdot 10^{-3}$ mol of propanoic anhydride at 100 °C for 16 h.

In order to assess the temperature effect on the hydrolysis and acetylation, these reactions were performed at different temperatures. First, the hydrolysis of 0.05 g of cellulose was conducted in 1 g of [BuMeIm][Cl] during 4 h at 100 °C in the presence

of 0.005 g of Amberlyst 15DRY (Table 4.5, entry 1). The temperature of 100 °C was chosen since hydrolysis of cellulose in [BuMeIm][Cl] at this temperature has been previously reported in literature.[23] At 100 °C a glucose yield of 20 % was seen (Table 4.5, entry 1). Increasing the temperature to 110 °C resulted however in a higher glucose yield (36 %; Table 4.5, entry 2). Secondly, the acetylation of 0.1 mL of mixture **A** was compared at 85 °C and 100 °C. The yield of GPAc at 85 °C is significantly lower (34 %) than at 100 °C (70 %) (Table 4.5, entry 3-4). The lower yield at 85 °C could may be explained by a lower rate constant according to the Arrhenius equation and also by the higher viscosity of the IL at this temperature.[56]

Table 4.5. Influence of temperature on the hydrolysis and acetylation of cellulose.[a]

Entry	Reaction step	T, °C	Yield, %
1	Hydrolysis[a]	100	20 glucose 1 dimers of C6 – sugars
2	Hydrolysis[a]	110	1 levoglucosan 36 glucose 2 other C6 – sugars 8 dimers of C6 – sugars
3	Acetylation[b]	85	34 GPAc
4	Acetylation[b]	100	70 GPAc

[a] Hydrolysis conditions: 0.05 g of cellulose, 0.005 g of Amberlyst 15DRY, 1 g of [BuMeIm][Cl], 20 µL H_2O, 4 h.
[b] Acetylation conditions: 0.1 mL of hydrolysis mixture (with catalyst particles removed), $1.7 \cdot 10^{-3}$ mol Ac_2O, 16 h.

As an alternative solvent, the IL [EtMeIm][AcO] was also applied, as it has as well good cellulose dissolution properties: it can dissolve up to 12 wt. % of cellulose at 100 °C.[12] Moreover, it might show a better compatibility with the Ac_2O than [BuMeIm][Cl], in view of its acetate anion. Experiments with [EtMeIm][AcO] were conducted under optimized conditions: i) hydrolysis conditions: 0.05 g cellulose, 0.005 g Amberlyst 15DRY, 1 g of [EtMeIm][Ac_2O], 20 µL H_2O, 110 °C, 4 h; ii) acetylation conditions: 0.1 mL of hydrolysis mixture (with major part of catalyst particles removed), $1.7 \cdot 10^{-3}$ mol

Ac_2O, 100 °C, 16 h. However, none of our attempts led to detectable levels of product formation, undoubtedly due to neutralization of the acidity of Amberlyst 15DRY by the acetate anion of this IL.

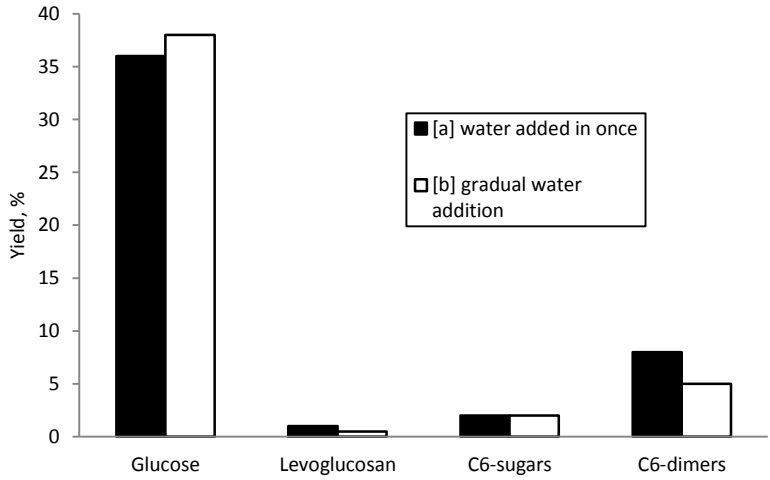


Figure 4.6. *Influence of the gradual addition of water on cellulose hydrolysis ([a] Reaction conditions: 0.05 g of cellulose, 0.005 g of Amberlyst 15DRY, 1 g of [BuMeIm][Cl], 20 µL of H_2O, 110 °C, 4 h. [b] 20 µL H_2O was added gradually by portions of 5 µL after each hour for 4 h, the first portion was added at t = 0 h).*

Gradual water addition during cellulose hydrolysis in IL has been reported as a possibility to increase the glucose yield.[57] This urged us to apply this technique for improving the cellulose conversion into GPAc. Instead of adding the 20 µL of H_2O all at once, it was added gradually by portions of 5 µL after each hour for 4 h. The first portion was added at the beginning of the reaction. As is presented in Figure 4.6, the product distribution after hydrolysis (0.5 % levoglucosan, 38 % glucose, 2 % other C6 – sugars, 5 % dimers of C6 – sugars) is, however, very similar to the one obtained without gradual water addition. As expected, also after acetylation no higher GPAc yield could be reached.

Separation of reaction products and IL/catalyst recycling

To demonstrate the recycling of the [BuMeIm][Cl] and the catalyst, the GPAc formed in the first reaction run needed to be removed first. Control experiments with purchased GPAc showed that dibutylether was suited for the isolation of the product by simple extraction. In these experiments, a known amount of GPAc was dissolved in the IL phase, which was then stirred with *n*-Bu_2O in a 1:5 volume ratio at 80 °C for 1 h. In this way the GPAc was nearly quantitatively extracted into the ether phase. Thus, after performing the cellulose hydrolysis and acetylation under optimal conditions, the GPAc was isolated with dibutylether. The remaining 1 mL IL was then reused for a second transformation of cellulose into GPAc under identical conditions. Note that the catalyst particles should be washed with H_2SO_4 solution before reuse, due to the release of its H_3O^+ content.[41] Titrating the ionic liquid phase after removal of Amberlyst 15DRY particles revealed that after 4 h of stirring at 110 °C 80 % of H^+-cations is released into [BuMeIm][Cl]. Because of this, we added only 0.001 g (20 % of the standard amount of 0.005 g) of Amberlyst 15DRY into the recycled IL. As is shown in Figure 4.7, only a small decrease in GPAc yield was observed after the first recycle. While after the first reaction cycle a 70 % GPAc yield was attained, 65 % yield could be obtained with the recycled Amberlyst 15DRY/[BuMeIm][Cl] system.

Keeping in mind that the product could be separated successfully with dibutylether, the acetylation step was tried in a biphasic system of [BuMeIm][Cl] and the ether solvent. A fraction (0.1 mL) of the hydrolysis reaction mixture was therefore mixed with 0.17 mL Ac_2O and 0.5 mL of Bu_2O. However, stirring this mixture for 16 h at 100 °C led to only 25 % yield of GPAc (Figure 4.7). Apparently, the biphasic system was not as efficient as the monophasic system for the acetylation, probably due to extraction of Ac_2O to Bu_2O. Indeed, with the glucose and its oligomers in the IL phase and the acetic anhydride in the ether phase, the Ac_2O is not available for the acetylation of the intermediates.

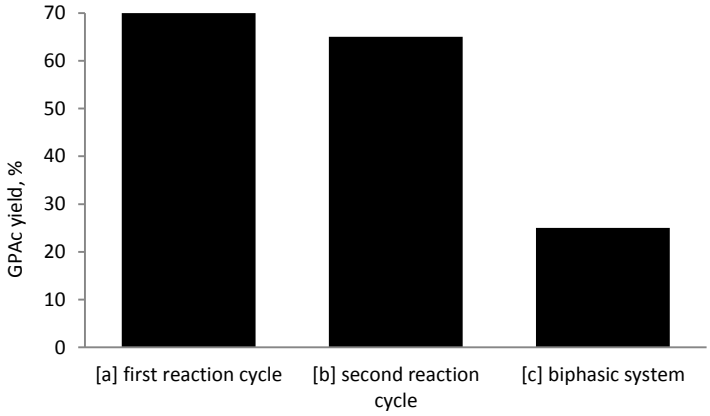


Figure 4.7. *Amberlyst 15 DRY and [BuMeIm][Cl] recycling experiment. ([a] Hydrolysis conditions: 0.05 g of cellulose, 0.005 g of Amberlyst 15DRY, 1 g of [BuMeIm][Cl], 110 °C, 4 h. Acetylation conditions: 0.1 mL of hydrolysis reaction mixture (with catalyst particles removed) $1.7 \cdot 10^{-3}$ mol Ac_2O, 100 °C, 16 h. [b] 0.001 g of recycled Amberlyst 15DRY and 1 g recycled [BuMeIm][Cl]. [c] 0.5 mL of Bu_2O was added as a second phase during acetylation).*

Mechanism of the formation of glucose esters from cellulose

Finally, the mechanism of glucose ester formation starting from cellulose will be discussed. This reaction typically consists out of two steps: 1) hydrolysis of the cellulose with formation of glucose and oligomeric species 2) acetylation of the hydrolysis products. The rate determining step hereby is the first step, as the acetylation of the hydroxyl groups proceeds relatively fast.[49] Hydrolysis of the β(1→4) links in the cellulose molecules occurs more slowly as was proven by gel permeation chromatography. With this technique the extent of cellulose depolymerization degree was evaluated at different time intervals of the hydrolysis reaction. The chromatograms are presented in Figure 4.8. After 1 h of hydrolysis only a small fraction of the cellulose is converted into oligomeric species. Although a small peak appeared after 1 h, a large peak,

representing a compound with a degree of polymerization (DP) close to that of the original substrate (DP 215–240), was still present. This large peak nearly disappeared after 2.5 h, but a distinct group of peaks with lower MW (oligomeric species) could be observed.

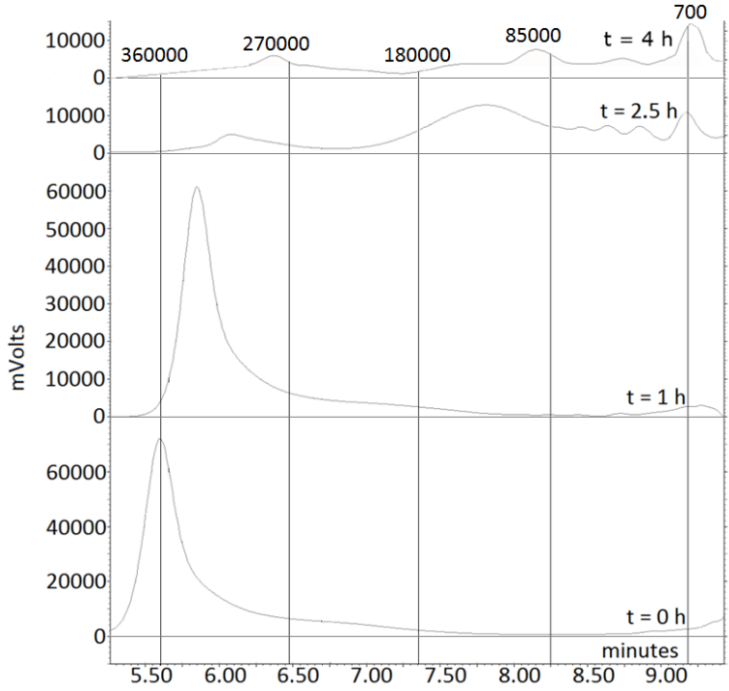
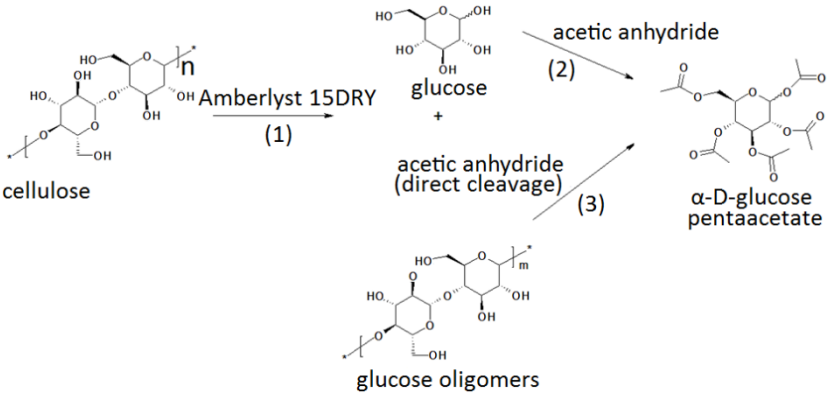


Figure 4.8. *Gel-permeation chromatograms of cellulose hydrolysis (Reaction conditions: 0.05 g of cellulose, 1 g of [BuMeIm][Cl], 0.001 g of Amberlyst 15DRY, numbers on top of the figure (360000, 270000 etc.) indicate weight average molecular weight).*

After 4 h the peaks of oligomeric species were still visible, which means that hydrolysis was incomplete after the first (hydrolytic) step. As GPAc is the only end product of the optimized cellulose transformation, it can be concluded that the depolymerization still continues during the second step. In the course of the acetylation step, the β(1→4) links in acetylated oligomeric molecules are probably being directly cleaved by AcOH rather than by water. In order to confirm this hypothesis, the direct acetylation of

cellobiose has been investigated. No hydrolysis conditions were applied first. This acetylation of $1.55 \cdot 10^{-4}$ mol of cellobiose, with $1.7 \cdot 10^{-2}$ mol Ac_2O in 1 g of [BuMeIm][Cl] was performed at 100 °C. After 16 h a GPAc yield of 23 % was reached. Detection of a significant amount of GPAc upon cellobiose acetylation in the absence of extra added water confirms our hypothesis.



Scheme 4.1. *Cellulose hydrolysis (1) and subsequent formation of GPAc via acetylation of glucose (2) or direct cleavage of the glucose oligomers (3).*

The reaction proceeds stereoselectively as the α-anomer is much more stable than the β-anomer due to the anomeric effect.[58] Thus, the α-anomer is almost exclusively formed (Scheme 4.1, Table 4.3, entry 3). This is in good agreement with the data previously reported in literature.[58, 59] The stereoconfiguration was confirmed by GC and GC-MS using commercial samples of α-D-glucose pentaacetate and β-D-glucose pentaacetate.

4.4 Conclusions

In this work an efficient transformation of cellulose into glucose esters in an ionic liquid medium was demonstrated. A 70 % yield of α-D-glucose pentaacetate could be reached in the presence of an acidic catalyst. By keeping the concentration of this catalyst low,

degradation of the glucose ester could be minimized. This cellulose transformation typically involves two steps: after hydrolysis of the polymer a consecutive reaction with acetic anhydride takes place, in which glucose is acetylated and oligomers are being directly cleaved by AcOH/Ac_2O. This results in selective formation of GPAc, which can be easily isolated by extraction. Both IL and catalyst could be recycled after reaction.

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5 Hydrolysis and Consecutive Reactions of Cellulose and Xylan in Ionic Liquids in the Presence of Alternative Acid Catalysts

Abstract

Cellulose and xylan were successfully transformed into valuable monomeric products via hydrolysis and consecutive reactions. Cellulose hydrolysis was carried out in the ionic liquid 1-butyl-3-methylimidazolium chloride leading to a glucose yield of 45 %. The reaction was performed in the presence of the heterogeneous acid catalyst Smopex-101, which could be recycled after reaction. Xylan hydrolysis in 1-ethyl-3-methylimidazolium chloride in the presence of *para*-toluenesulfonic acid resulted in a yield of 42 % for xylose. Dehydration of xylan in the presence of tungstophosphoric acid led up to a yield of 84 % for furfural. The one-pot conversion of cellulose and xylan into respectively alkylhexosides and alkylpentosides was also performed. In the case of *n*-butanol the yields of butylglucopyranoside and butylxyloside isomers were 64 and 45 %, respectively.

5.1 Introduction

Polysaccharides are quite abundant in nature and are considered as promising renewable resources for a range of valuable chemicals and biofuels.[1-5] Cellulose is the most abundant biopolymer on earth.[6] In nature, it occurs in combination with hemicelluloses, such as xylan, and together they form the principle carbohydrate components of biomass.[7, 8] Cellulose is a polysaccharide, consisting of a linear chain of several hundreds to over ten thousand β(1→4) linked D-glucosidic units.[8, 9] A large number of oxygen and hydroxyl groups are present in these chains, which results in a three-dimensional network through hydrogen bonding (Figure 5.1). This makes cellulose a relatively inert material.[8, 10] Xylan consists of a α(1→4) linked D-xylose backbone and can be substituted by different side groups such as L-arabinose, D-galactose, acetyl, feruloyl, *para*-coumaroyl, and

glucuronic acid residues (Figure 5.2).[11] Since xylan contains only two hydrogen atoms at C5, rather than an extra hydroxymethyl substituent, it is unable to form a stable hydrogen bonded network,[12] which explains its higher reactivity.[13]

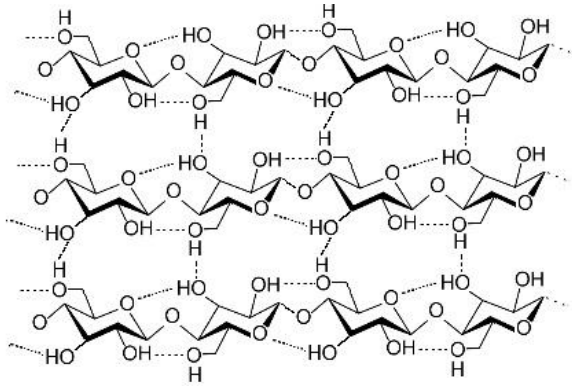


Figure 5.1 *Structure of cellulose.*

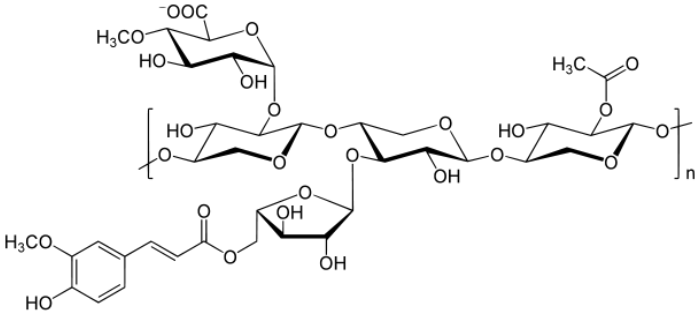


Figure 5.2 *Structure of xylan.*

Valorization of these carbohydrate-based polysaccharides is of a high practical interest.[4, 5, 14] However, extreme conditions are required to solubilize cellulose in classical organic solvents due to its rigid structure.[2, 3, 15, 16] On contrary, some ionic liquids (ILs) display a good dissolution behavior for cellulose, even at mild conditions.[17-22] These ionic solvents have therefore frequently been employed as reaction medium for the transformation of this biopolymer.[2, 18, 20-24]

Seddon *et al.* and Zhao *et al.* have shown that ionic liquids are efficient media for the acidic hydrolysis of cellulose towards monomeric glucose units.[25, 26] Rinaldi *et al.* reported the cellulose hydrolysis in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BuMeIm][Cl]) in the presence of the solid acid catalyst Amberlyst 15DRY.[2] While at first it was assumed that this catalyst was heterogeneous, it appeared later on that Amberlyst 15DRY was homogeneous to some extent due to gradual H^+-release from the catalyst beads into solution. Before reuse the beads needed to be regenerated by sulfuric acid.[27] As previously reported by our group, the formed glucose could be further transformed in a one-pot process into alkylhexosides in the presence of Amberlyst 15DRY.[28, 29] Thus, it would be worthwhile to search for a heterogeneous alternative for this catalyst, which can efficiently catalyze both the cellulose hydrolysis and the production of alkylhexosides.

In contrast with cellulose, xylan can be dissolved in conventional solvents,[30] but application of an ionic liquid as a solvent for its processing is of a high practical importance since in nature xylan predominantly occurs in lignocellulosic complexes in wood.[7] Classical pretreatments of wood such as acid hydrolysis, steam explosion, alkaline hydrolysis and ammonia fiber explosion are environmentally unfavorable and inefficient.[31] This pretreatment of lignocellulosic biomass can generally be performed more mildly in ionic liquids. For example, Nakamura *et al.* have reported wood dissolution in the ionic liquid 1-ethyl-3-methylimidazolium chloride ([EtMeIm][Cl]).[32] For a deeper insight into this topic, the reader is referred to an excellent review by Doherty *et al.*[33] Moreover, xylan hydrolysis in the presence of methanesulfonic acid in the ionic liquid [EtMeIm][Cl] was reported by Seddon *et al.*[34] This urged us to investigate this reaction more in detail and to perform subsequently the synthesis of alkylxylosides, analogous to the synthesis of alkylglycosides.[28, 29] Furthermore, xylan is much more susceptible to pyrolysis and dehydration than cellulose,[35-37] and a typical product of this reaction, namely furfural[38] has many applications in base and

intermediate chemistry, plastics, pharmaceutical and agrochemical industries.[39] The transformation of xylan into furfural has already been performed in dimethylsulfoxide (DMSO).[38] However, the rather low yields and the toxicity of this solvent remain a major disadvantage. Keeping all this in mind, it would be worthwhile to investigate the application of ionic liquids in this process.

Summarizing, ionic liquids will be applied as alternative reaction media for the hydrolysis of cellulose and xylan, xylan dehydration, and one-pot production of alkylhexosides and alkylpentosides out of respectively cellulose and xylan. In case of cellulose, a heterogeneous alternative for the existing acidic catalysts will be implemented.

5.2 Experimental Section

5.2.1 Materials

1-Butyl-3-methylimidazolium chloride (99 %) and 1-ethyl-3-methylimidazolium chloride (≥98 %) were obtained from Ionic Liquids Technologies GmbH (IoLiTec). Cellulose (Avicel PH 101; DP 215-240), xylan from birch wood (90 % xylose), Nafion SAC-13 (silica-supported acidic catalyst resin), Amberlyst 15DRY (cation exchange resin based on a styrene-divinylbenzene matrix), tungstophosphoric acid ($H_3[P(W_3O_{10})_4]\cdot xH_2O$, heteropolyacid) were obtained from Sigma-Aldrich. Smopex-101 (a fiber based on polyethylene grafted with styrene and sulfonated with chlorosulfonic acid [40]) was purchased from Alfa Aesar GmbH & Co KG. Other chemicals were obtained from commercial suppliers and were used as received.

5.2.2 Typical Reaction Procedures

Reactions were typically performed in sealed glass vials (10 mL) with continuous stirring.

Cellulose hydrolysis: 0.05 g of cellulose was dissolved in 1 g of [BuMeIm][Cl] and stirred in the presence of 0.01-0.015 g of Smopex-101 and 20 µL of water at 110 °C for 2-24 h.

Catalyst leaching test: First cellulose hydrolysis was performed in the presence of Smopex-101 (for the procedure, see cellulose hydrolysis). After 2 h, the catalyst was removed, and the reaction was restarted in absence of the catalyst. In order to remove the catalyst, the reaction mixture was dissolved in *n*-butanol at 100 °C, and the catalyst fibers were separated using filter paper. Finally, *n*-butanol was removed from the reaction mixture in a rotary evaporator.

Cellulose conversion into alkylglycosides: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) of cellulose and $3.3 \cdot 10^{-3}$ mol of alcohol were introduced in the glass vial, together with 0.01 g of Smopex-101 and 20 µL of water. The reaction mixture was stirred at 110 °C for 0.5-24 h.

Xylan hydrolysis: 0.025 g of xylan, 0.005-0.015 g of *para*-toluenesulfonic acid and 20 µL of water were dissolved in 1 g of [EtMeIm][Cl]. This mixture was stirred at 80-100 °C for 30 min-4 h.

Xylan dehydration: 0.025 g of xylan was dehydrated in 1 g of [EtMeIm][Cl] in the presence of 0.02 g of tungstophosphoric acid and 20 µL of water at 140 °C; samples were taken at times from 30 min to 4 h.

Xylan conversion into alkylxylosides: reactions between 0.025 g ($1.88 \cdot 10^{-4}$ mol xylosidic units) of xylan and $3.3 \cdot 10^{-3}$ mol of alcohol were performed in the presence of 0.01 g of *para*-toluenesulfonic acid and 20 µL of water at 90 °C and lasted from 30 min to 24 h.

5.2.3 Analysis

Prior to GC and GC-MS analysis glucose, xylose and similar compounds were silylated using *N*-methyl-*N*-(trimethylsilyl)

trifluoroacetamide (MSTFA). Typically, a four-fold excess of MSTFA with respect to the hydroxyl groups was added to 0.1 mL of reaction mixture. This was mixed with 0.3 mL of pyridine and stirred for 3 h at 80 °C. The silylated compounds were then extracted with 0.5 mL of dibutylether. The extraction procedure was optimized and confirmed to be quantitative using known amounts of reference compounds such as glucose, xylose, furfural and others. All the product yields mentioned in the text were determined chromatographically and calculated from peak areas of corresponding reaction products. Quantitative and qualitative gas chromatography analyses were performed using a GC (HP 5890) equipped with a 30 m HP-1 column or a GC-MS (Agilent 6890 GC and 5973 MS) with a 30 m HP-5MS column.

The water content of the ionic liquids was determined with a coulometric Karl-Fischer titrator (Mettler Toledo DL39) and anhydrous methanol as the solvent. Each sample was at least 0.1 g, and triplicate measurements were performed on each sample. The level of water contamination of 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium chloride was found to be *ca.* 0.1 wt. %.

5.3 Results and Discussion

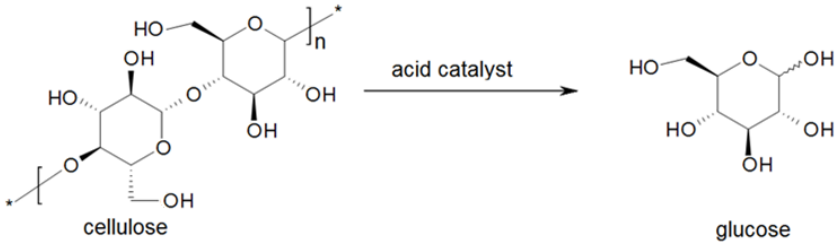
5.3.1 Cellulose Transformation into Alkylglycosides

Before addressing the cellulose conversion into alkylglycosides, the hydrolysis of cellulose, the first step of the one pot alkylglycoside synthesis,[28] was optimized.

5.3.1.1 Cellulose Hydrolysis

Optimization of reaction conditions

[BuMeIm][Cl] was used as the solvent, since cellulose hydrolysis (Scheme 5.1) has already successfully been performed in this ionic liquid.[2, 27] Because it has been proven that the employed catalyst Amberlyst 15DRY is homogeneous to a large extent,[27] the performance of the solid acid Smopex-101 as a heterogeneous alternative for this catalyst was investigated.



Scheme 5.2. *Cellulose Hydrolysis.*

Two experiments were conducted with these catalysts under equal conditions: 0.05 g of cellulose was dissolved in 1 g of [BuMeIm][Cl] and was hydrolyzed in the presence of 0.01 g of acid catalyst at 110 °C. The glucose yields in function of time are presented in Figure 5.3. One can conclude from these data that the evolution of the glucose yield is similar in both cases and reaches a maximum at 4 h. Smopex-101 showed a slightly higher activity than Amberlyst 15DRY. These two catalyst have similar amounts of acid content (4.7 and 3.4 meq H^+g^{-1} for Amberlyst 15DRY and Smopex-101 respectively, (data provided by suppliers)). However, Amberlyst 15DRY has a macroporous structure which possibly makes its acid sites less accessible.[41] Prolongation of the reaction time caused in both cases excessive dehydration of glucose. This has been observed before for glucose under these acidic conditions.[2]

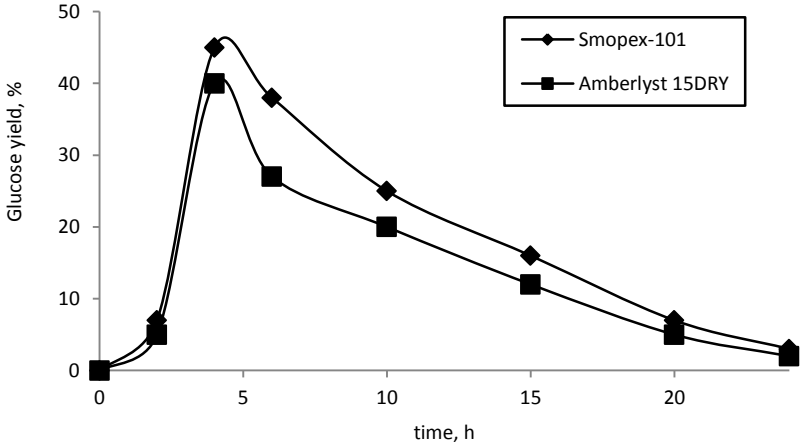


Figure 5.4 *Evolution of glucose yield in time during cellulose hydrolysis (Reaction conditions: 0.05 g of cellulose, 1 g of [BuMeIm][Cl], 0.01 g of catalyst, 20 µL of water, 110 °C).*

Detailed description of all the detected products can be found in Table 5.1. It appears from these data that during the whole reaction, the total yield of reducing sugars is also higher in the presence of Smopex-101. Note that at longer reaction times (more than 4 h) more dehydration products (levoglucosan, hydroxymethylfurfural (HMF)[42, 43]) were detected with Smopex-101. This is probably due to faster thermal dehydration of the hydrolysis products in the presence of the latter catalyst due to its higher acidic activity.[40]

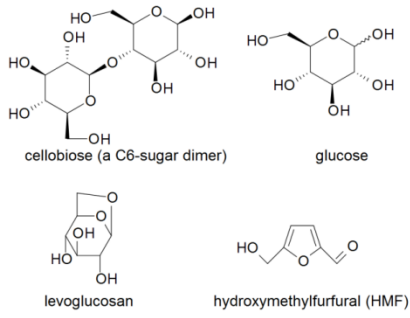


Figure 5.5. *Main products and byproducts of acid-catalyzed hydrolysis of cellulose.*

Table 5.1. Product distribution of cellulose hydrolysis.[a]

Entry	Time, h	Product yields in the presence of Smopex-101, %	Product yields in the presence of Amberlyst 15DRY, %
1	2	1 other C6-sugars 7 glucose 6 dimers of C6-sugars	1 other C6-sugars 5 glucose
2	4	4 levoglucosan 45 glucose 3 other C6-sugars 16 dimers of C6-sugars	2 levoglucosan 40 glucose 1 other C6-sugars 1 dimers of C6-sugars
3	6	3 HMF 5 levoglucosan 3 other C6-sugars 38 glucose 6 dimers of C6-sugars	1 HMF 3 levoglucosan 27 glucose 2 other C6-sugars
4	10	5 HMF 2 levoglucosan 1 other C6-sugars 25 glucose 3 dimers of C6-sugars	2 HMF 20 glucose 1 other C6-sugars
5	15	6 HMF 3 levoglucosan 1 other C6-sugars 16 glucose 2 dimers of C6-sugars	4 HMF 12 glucose 1 other C6-sugars
6	20	3 HMF 2 levoglucosan 7 glucose 1 dimers of C6-sugars	2 HMF 5 glucose
7	24	1 HMF 3 glucose 1 other C6-sugars 1 dimers of C6-sugars	1 HMF 2 glucose

[a] Reaction conditions: 0.05 g of cellulose, 1 g of BuMeImCl, 0.01 g of acidic catalyst, 20 μL of water, 110 °C.

Next, the influence of the amount of catalyst on the cellulose hydrolysis was evaluated (Table 5.2). Here, on one hand, enough catalyst is needed to stimulate the hydrolysis. On the other hand, too high acidity can cause dehydration of glucose.[2] Two hydrolysis

experiments were performed with varying amounts of Smopex-101. In Table 5.2, the results of these experiments are compared with the one for 0.01 g of catalyst (Entry 2). Reducing the amount of Smopex-101 from 0.01 g to 0.005 g led to a lower glucose yield presumably due to the lowered hydrolysis efficiency. When a higher amount (0.015 g) of Smopex-101 was used, the total yield of reducing sugars was relatively high, but still lower than for 0.01 g. This is probably caused by the dehydration of the formed hydrolysis products, since a higher amount of levoglucosan was detected after reaction in the presence of 0.015 g of Smopex-101.

Table 5.2. Cellulose hydrolysis in the presence of various amounts of Smopex-101. [a]

Entry	Amount of Smopex-101, g	Product, %	Sum of detected products, %
1	0.005	1 other C6-sugars 16 glucose 2 dimers of C6-sugars	19
2	0.01	2 levoglucosan 45 glucose 3 other C6-sugars 16 dimers of C6-sugars	66
3	0.015	5 levoglucosan 33 glucose 1 dimers of C6-sugars	39

[a] Reaction conditions: 0.05 g of cellulose, 1 g of [BuMeIm][Cl], 20 µL of water, 4 h, 110 °C.

The gradual water addition during cellulose hydrolysis in ILs has been reported as a possibility to increase the glucose yield.[44] Therefore, this technique was also investigated for our reaction system. 0.05 g of cellulose and 0.01 g of Smopex-101 were added to 1 g of [BuMeIm][Cl] and reacted for 4 h at 110 °C. Instead of adding all the water at once, portions of 5 µL were added each hour (4 portions in total, first portion at t = 0). After 4 h the following product yields were observed: 1 % levoglucosan, 42 % glucose, 4 % other C6-sugars, and 18 % of dimeric C6-sugars. These yields are very similar to the ones, reached without gradual water addition (Table 5.2, entry 2). Note that the addition of a higher amount of water (120 µl, 6 portions of 20 µl) had a detrimental effect on the hydrolysis

efficiency. After 4 h of reaction, following product yields were observed: 1 % levoglucosan, 20 % glucose, 2 % other C6-sugars, and 2 % of dimeric products. Too much water in the reaction system, presumably results in a lower cellulose solubility and consequently low conversion of the initial substrate, explaining the lower product yields.

Evaluation of heterogeneity and recyclability of Smopex-101

In order to investigate the heterogeneity of Smopex-101, a catalyst leaching test was performed. After 2 h of cellulose hydrolysis in the presence of 0.01 g of Smopex-101, the catalyst was removed and the reaction was continued for another 13 h. As can be seen in Figure 5.6, the glucose yield did not increase further after removal of the catalyst. On the contrary, if the catalyst stayed in the reaction mixture the glucose yield increased from 7 % at 2 h to 45 % at 4 h. This is a solid proof that no active catalyst leaches into the reaction solution. One of possible reasons of Smopex-101 stability is the absence of swelling by water and other solvents, which occurs for Amberlyst 15DRY.[41] Note that in absence of the catalyst also no dehydration of glucose is observed at longer reaction times.

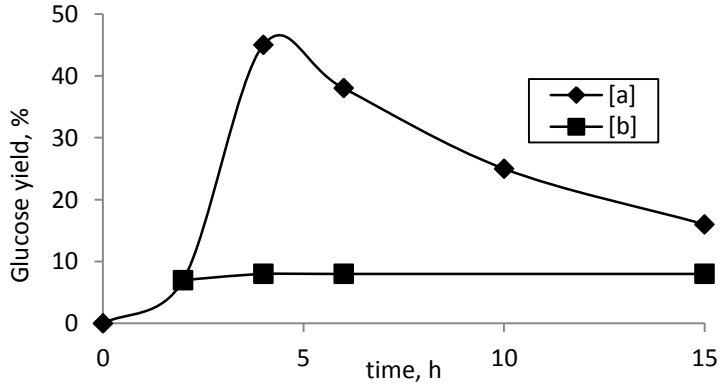


Figure 5.6 *Catalyst leaching test with Smopex-101 ([a] Reaction conditions: 0.05 g of cellulose, 0.01 g of Smopex-101, 1 g of [BuMeIm][Cl], 20 µL of water, 110 °C. [b] Smopex-101 was removed after 2 h of reaction).*

After checking the heterogeneity, a catalyst recycling experiment was performed. The isolated fibers of Smopex-101 were washed with distilled water, dried under air and reused again under the same reaction conditions. In Figure 5.7, the product yields for the first and second reaction cycle are illustrated. One can conclude from Figure 5.7 that the catalytic activity was only slightly lower upon recycling. Glucose yields of 45 and 40 % were obtained for the original and the recycled catalyst respectively. It was reported before that Smopex-101 fibers can be isolated and reused without substantial loss of activity.[45, 46] No regeneration is needed before a reuse.

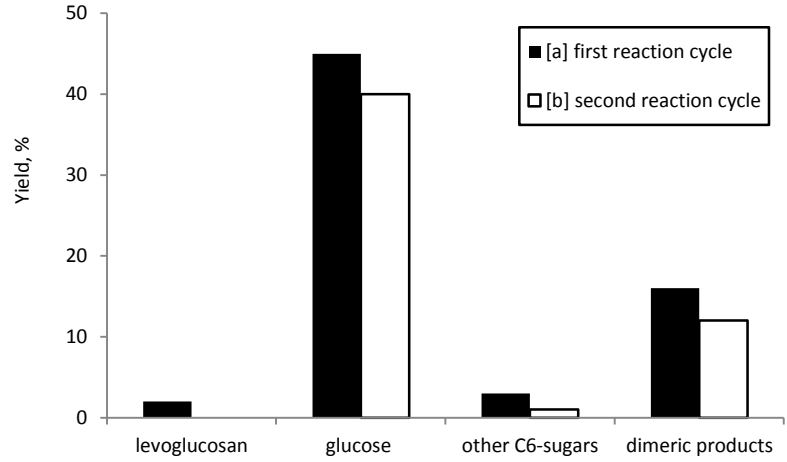
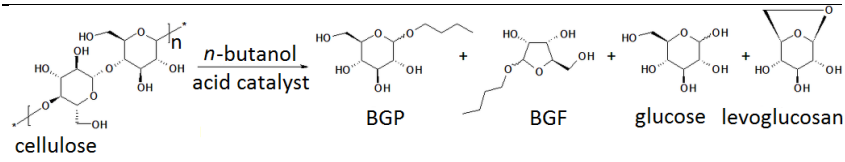


Figure 5.7 *Smopex-101 recycling experiment ([a] Reaction conditions: 0.05 g of cellulose, 1 g of [BuMeIm][Cl], 0.01 g of Smopex-101, 20 µL of water, 4 h, 110 °C.[b] Recycled Smopex-101 was used).*

5.3.1.2 Cellulose conversion into Alkylglycosides

We have recently reported the synthesis of alkylhexosides out of cellulose (Scheme 5.2) in the presence of Amberlyst 15DRY.[28]



Scheme 5.2. *Splitting of cellulose with formation of α-BGP, β-BGP, glucose and levoglucosan.*

The higher activity of Smopex-101 for the cellulose hydrolysis reaction, urged us to apply Smopex-101 as the catalyst for the one pot transformation towards alkylglycosides. Moreover, since it appeared that Amberlyst 15DRY does not really behave as a heterogeneous catalyst, Smopex-101 could form a good alternative for this reaction. To compare both catalysts, an experiment under analogous conditions as for Amberlyst 15DRY was carried out. The results with Smopex-101 are presented in Figure 5.9 and Figure 5.10, for *n*-butanol and *n*-octanol respectively. For comparison, also the results with *n*-butanol for Amberlyst 15DRY were added (Figure 5.6).

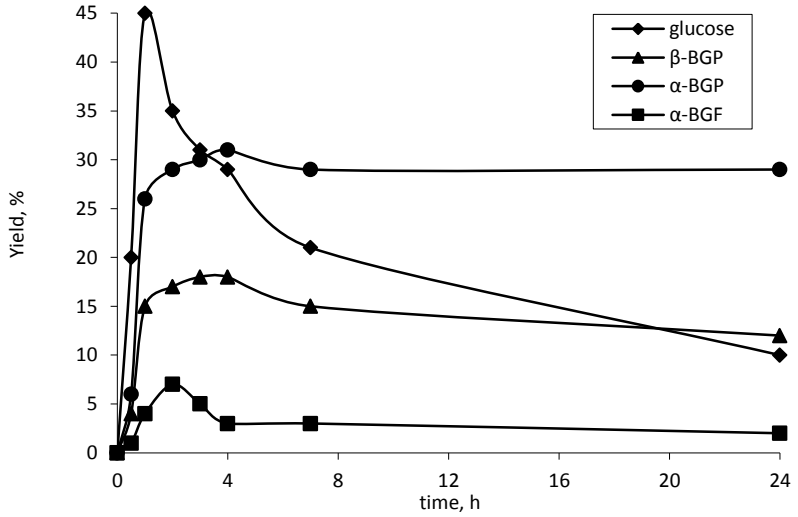


Figure 5.8 *Run profile of reaction between cellulose and n-butanol (Reaction conditions: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) of cellulose, $3.3 \cdot 10^{-3}$ mol n-BuOH, 1 g of [BuMeIm][Cl], 20 µL of water, 0.01 g of Amberlyst 15DRY, 110 °C).*

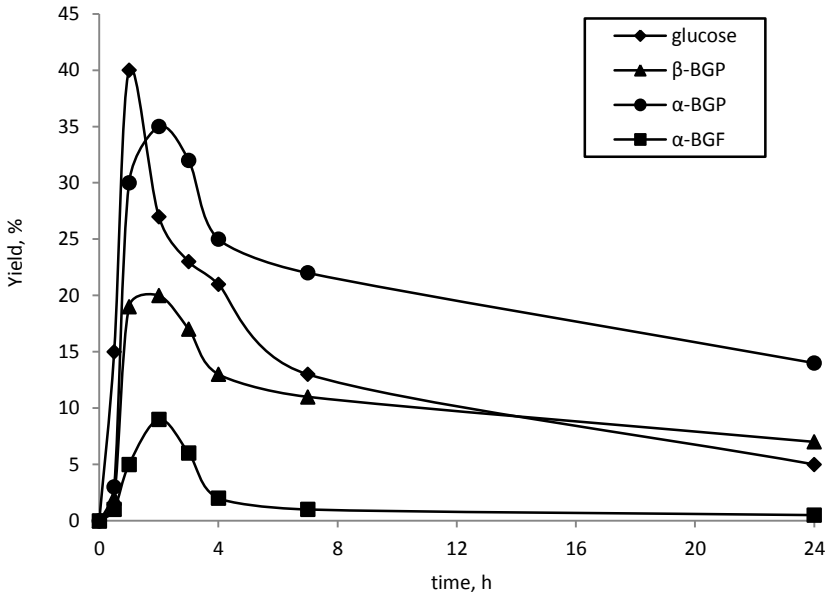


Figure 5.9 *Run profile of reaction between cellulose and n-butanol (Reaction conditions: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) of cellulose, $3.3 \cdot 10^{-3}$ mol n-BuOH, 1 g of [BuMeIm][Cl], 20 µL of water, 0.01 g of Smopex-101, 110 °C).*

As can be seen in Figures 5.8 and 5.9 the evolution of the glucose yield in time is similar for both catalysts.[28] The glucose yield passes through a maximum at 1 h and then decreased with time as it is being converted into butylated compounds. In case of Smopex-101, the yields of butylated compounds were maximal at 2 h: 35 % of α-butylglucopyranoside (α-BGP), 20 % of β- butylglucopyranoside (β-BGP), and 9 % of butylglucofuranoside (BGF). In the presence of Amberlyst 15DRY maximal yields were also obtained after 2 h, however they were lower than with Smopex-101: 29 % of α-BGP, 17 % of β-BGP, and 7 % of BGF. Butylglucopyranosides (BGPs) form in both cases the main products with α-BGP as the dominating form. The selectivity towards α-BGP even increases further in time. In case of Smopex-101 the α-BGP to β-BGP ratio increases from 1.5 at 30 min to 1.75 at 2 h, and eventually evolves towards 2 at longer reaction times. β-BGP and BGF are presumably isomerized in time into α-BGP,

which is thermodynamically more stable.[47] Prolongation of the reaction time leads to decreased yields of all four products. This decrease is more pronounced compared to the reaction with Amberlyst 15DRY, probably caused by the higher acidity of Smopex-101 resulting in more dehydration of the formed products.[28]

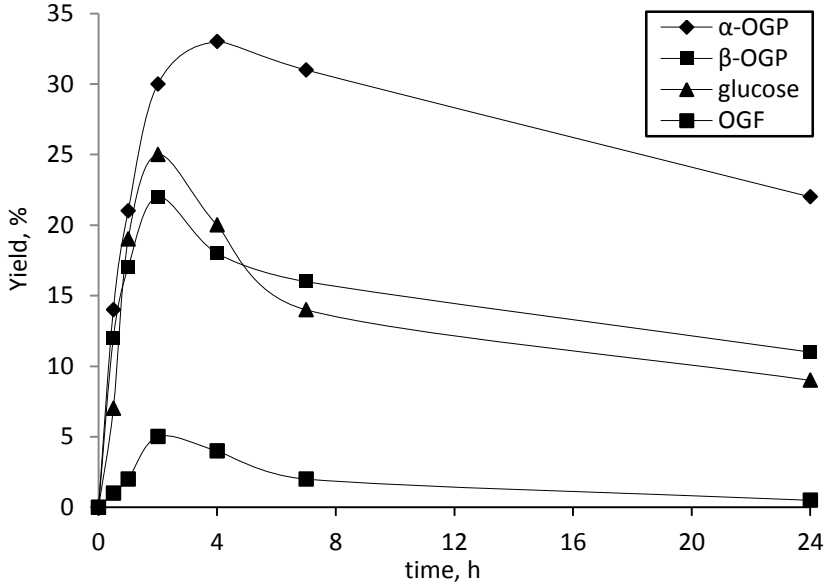


Figure 5.10 *Run profile of reaction between cellulose and n-octanol (Reaction conditions: 0.05 g ($3.1 \cdot 10^{-4}$ mol glucosidic units) of cellulose, $3.3 \cdot 10^{-3}$ mol n-octanol, 1 g of [BuMeIm][Cl], 20 µL of water, 0.01 g of Smopex-101, 110 °C).*

Comparison of Figure 5.10 with Figure 3.3 of chapter 3 shows us that the kinetic profile of the reaction with *n*-octanol is also very similar for both catalysts. Figure 5.10 shows that in the presence of Smopex-101, α-octylglucopyranoside (α-OGP) was the major product after 30 min. Its yield passed through a maximum at 4 h (33 % yield) and then decreased in time. α-OGP remained the major product during the whole course of the reaction presumably because it is more thermodynamically stable than β-octylglucopyranoside (β-OGP) and octylglucofuranoside (OGF).[48] As well as for the butylation,

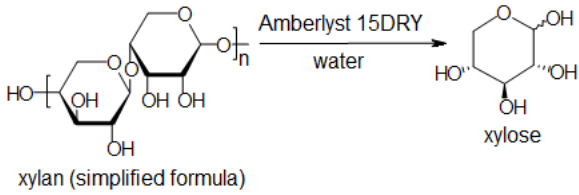
prolongation of the reaction time led to thermal degradation of all four products.[28]

Remarkably, the total yields of butylated and octylated compound are comparable (Figures 5.9 and 5.10). In solvent-free systems however, the rate of glucose alkylation drops significantly with increasing length of alcohol alkyl chain due to decreasing solubility of glucose in more apolar alcohols.[49] In [BuMeIm][Cl] this phenomenon was not observed. This is probably a result of the changing solubility of cellulose in the presence of alcohols with a different chain length: as the alkyl chain length of the alcohol increases, its hydrogen-bond-donor capacity decreases, allowing a better cellulose solubility in [BuMeIm][Cl].[28] Maximal yields of butylglucosides (64 %) and octylglucosides (57 %) are higher than those obtained in the presence of Amberlyst 15DRY (butylglucosides: 53 %, octylglucosides: 54 %)[28] presumably due to the more efficient hydrolysis of cellulose in the presence of Smopex-101.

5.3.2 Xylan Hydrolysis and Consecutive reactions

5.3.2.1 Xylan Hydrolysis

Since [EtMeIm][Cl] has been reported as an efficient medium for xylan hydrolysis, [34] this IL was also employed here. In a first series of experiments, a screening of catalysts was made. Therefore, 0.025 g of xylan was dissolved in 1 g of [EtMeIm][Cl] and hydrolyzed for 1 h at 90 °C in the presence of 0.01 g catalyst and 20 µL of water. Three catalysts were investigated: the solid acid catalysts Amberlyst 15DRY and Smopex-101, as well as the homogeneous catalyst *para*-toluenesulfonic acid hydrate (*p*TSA).



Scheme 5.3. *Xylan hydrolysis.*

After 1 h, relatively low yields of xylose were detected in case of Amberlyst 15DRY (10 %) and Smopex-101 (5 %) (Table 5.3, entries 1-2). Fukaya *et al.* reported that compared to cellulose higher temperatures are needed to dissolve xylan in ILs.[23] This lower solubility of xylan is a result of the lower hydroxyl group density in xylan.[23, 50] Indeed, based on the findings for cellulose, the interaction between the hydroxyl groups of the polymer and the IL is crucial for its dissolution.[14] The lower solubility of xylan probably causes unsatisfactory contact between the polymeric molecules and the acidic sites of solid catalysts. Note that after 1 h probably not enough protons have been leached from Amberlyst 15DRY particles into the reaction mixture, since this leaching process is gradual.[27] This hypothesis was confirmed by the results obtained for the homogeneous catalyst *p*TSA. This catalyst, which also possesses sulfonic acid groups, readily dissolves in the polar ionic liquid, resulting in a better contact between substrate and catalyst.[51] This better contact results in a higher xylose yield of 42 % (Table 5.3, entry 3). The yield of furfural, which is a typical product of xylose dehydration,[38] is also higher in case of *p*TSA application.

Table 5.3. Screening of catalysts for the xylan hydrolysis.[a]

Entry	Catalyst	Products, %
1	Amberlyst 15DRY	7 furfural 10 xylose
2	Smopex-101	5 furfural 5 xylose
3	*p*TSA·H_2O	13 furfural 42 xylose

[a] Reaction conditions: 0.025 g of xylan, 1 g of [EtMeIm][Cl], 0.01 g of catalyst, 20 µL of H_2O, 90 °C, 1 h.

In order to optimize the time of hydrolysis, a series of kinetic experiments has been conducted in the presence of 0.01 g of *p*TSA and 20 µL of water at 90 °C. One can conclude from Figure 5.11, that 1 h is the optimal reaction time, with a xylose and furfural yield of 42 % and 15 % respectively. Prolongation of the reaction led to a decrease of the xylose yield presumably due to the acid-catalyzed dehydration of xylose. This dehydration has also been observed for glucose and GPAc in the previous chapter. Note that the presence of furfural, a typical dehydration product, is a first confirmation of this hypothesis.[38]

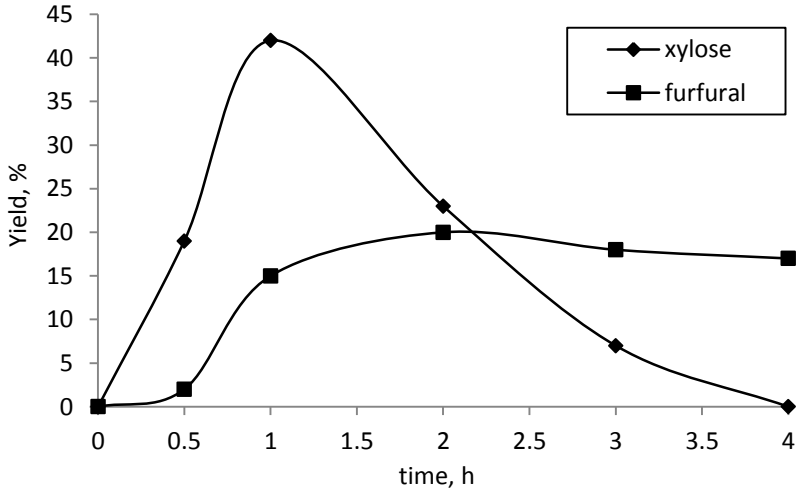


Figure 5.11 *Xylan hydrolysis (Reaction conditions: 0.025 g of xylan, 1 g of [EtMeIm][Cl], 0.01 g of pTSA, 20 µL of water, 90 °C).*

In line with results for cellulose and glucose, two control experiments were conducted to evaluate this acid-catalyzed dehydration of xylose (Figure 5.12). In a first experiment, $1.7 \cdot 10^{-4}$ mol of xylose was dissolved in 1 g of [EtMeIm][Cl] and reacted at 90 °C in the presence of 0.01 g of *p*TSA and 20 µL of water. Under these acidic conditions, xylose is unstable as is clear from Figure 5.12. After 5 h, only 4 % of xylose was still present and after 6 h no xylose could be found at all. Again the typical dehydration product furfural was

detected.[38] The combined yield of xylose and furfural does not reach 100 %. This was also the case for the glucose and GPAc degradation (Chapter 4), and again the formation of light dehydration products such as pyruvaldehyde, formic acid, and lactic acid,[52] which are hard to be analyzed by the GC procedure employed, is probably the underlying reason.[42] In a second experiment, in absence of the acid catalyst the concentration of xylose remained almost unchanged after 6 h. Only minor amounts of furfural could be detected.

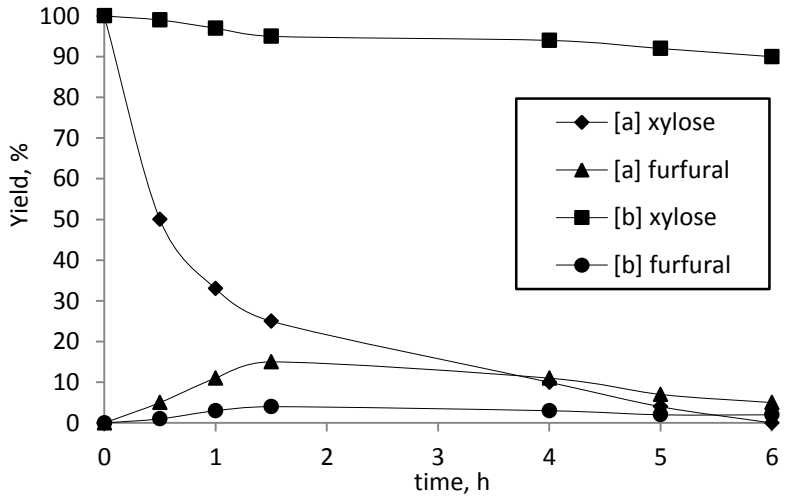


Figure 5.12 *Xylose dehydration ([a] Reaction conditions: 0.028 g of xylose, 1 g of [EtMeIm][Cl], 0.01 g of pTSA, 20 µL of water, 90 °C. [b] No acid catalyst added).*

As it was found that the acid catalyst causes dehydration of xylose, it was important to find an optimal amount for *p*TSA in order to maximize the product yield. Note that the reaction time was reduced to 1 h to prevent too much dehydration of the product. In Table 5.4, the hydrolysis results with varying amount of *p*TSA are presented.

Table 5.4. Xylan hydrolysis in the presence of various amounts of *p*TSA. [a]

Entry	Amount of *p*TSA, g	Product, %	Sum of detected products, %
1	0.005	20 xylose 5 furfural	25
2	0.01	42 xylose 13 furfural	59
3	0.015	25 xylose 20 furfural	45

[a] Reaction conditions: 0.025 g of xylan, 1 g of [EtMeIm][Cl], 20 µL of water, 1 h, 90 °C.

If the reaction was conducted with 0.005 g of *p*TSA, the hydrolysis proceeded not efficiently and resulted in a low xylose yield (20 %). The dehydration side reaction was also suppressed in this case, which is clear from the low amount of furfural (5 % yield) in the reaction mixture. It means that a big part of the initial substrate remains unreacted under these conditions. Although 0.01 g of catalyst resulted in more dehydration, the hydrolysis reaction was also accelerated, leading to a 46 % xylose yield. Although one would expect that further increasing the amount of *p*TSA (0.015 g) would lead to higher xylose yields, only a 20 % yield was observed caused by excessive dehydration (20 % furfural yield) with this higher amount of catalyst. Thus, one can conclude that 0.01 g is the optimal amount of *p*TSA.

After optimizing the amount of *p*TSA, the temperature effect on the reaction was assessed (Table 5.5). Xylan was hydrolyzed in the presence of 0.01 g of *p*TSA at 80, 90 and 100 °C. Hydrolysis at 80 °C led to a lower yield of xylose (20 %) than at 90 °C (42 %) (Entries 1-2). The lower yield at 80 °C could be explained by the lower rate constant according to the Arrhenius equation and also by the higher viscosity of the IL at this temperature.[53] Increasing of the temperature to 100 °C also resulted in a lower yield, despite the lower viscosity (Entry 3). Presumably, the dehydration becomes more significant at 100 °C. An increased yield of furfural (13 % at 90 °C; 20 % at 100 °C) supports this hypothesis.

Table 5.5. Influence of temperature on the hydrolysis of xylan.[a]

Entry	T, °C	Products, %
1	80	21 xylose 10 furfural
2	90	42 xylose 13 furfural
3	100	30 xylose 20 furfural

[a] Reaction conditions: 0.025 g of xylan, 1 g of [EtMeIm][Cl], 0.01 g of *p*TSA, 20 µL of water, 1 h.

Finally, the gradual water addition technique has been applied for xylan hydrolysis.[44] Therefore, starting from the beginning of the reaction water portions of 5 µL were added each 15 min (4 portions in total). For the gradual water addition, a 43 % xylose and 12 % furfural yield were detected after 1 h. In Figure 5.13, a comparison is made with the reaction where all the water was added at once. Thus, as was the case for cellulose, gradual water addition did not improve the yields of hydrolysis products.[44]

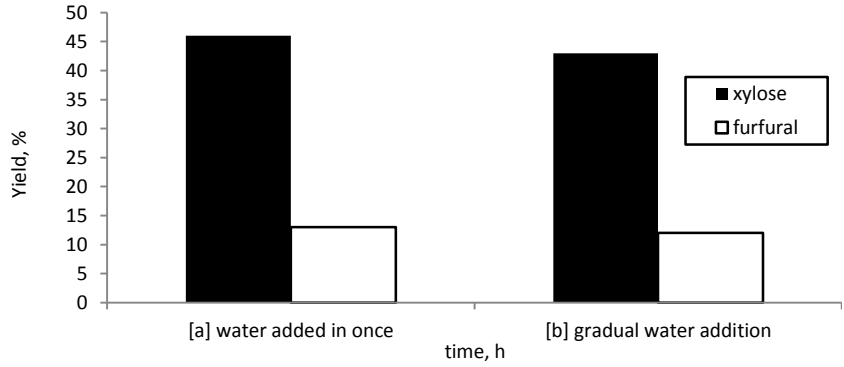


Figure 5.13 *Influence of the gradual addition of water on xylan hydrolysis ([a] Reaction conditions: 0.025 g of xylan, 0.01 g of pTSA, 1 g of [EtMeIm][Cl], 20 µL of water, 90 °C, 1 h. [b] 20 µL of water was added gradually by portions of 5 µL each 15 min for 1 h, the first portion was added at t = 0 h).*

5.3.2.2 Xylan Dehydration into Furfural

Tungstophosphoric acid (TPA) has been reported as a very efficient catalyst for xylose dehydration into furfural in DMSO at 140 °C.[38] This urged us to evaluate the activity of this catalyst in the xylan dehydration. Figure 5.14 illustrates the furfural yield in time, in [EtMeIm][Cl] as ionic liquid. After 2 h a 84 % yield of furfural was reached. In DMSO, the maximal yield of furfural (60 %) starting from xylose was only reached after 6 h.[38] Prolongation of the reaction time led to lower furfural yields, due to the further degradation of furfural by dehydration.[34] This was observed both in [EtMeIm][Cl] [34] and in DMSO.[38]

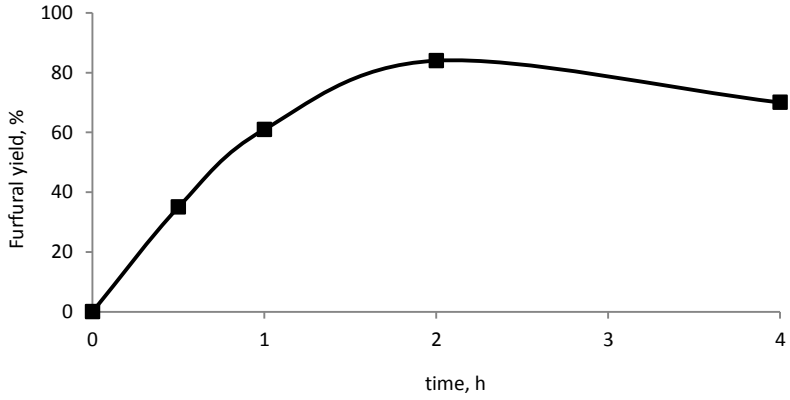
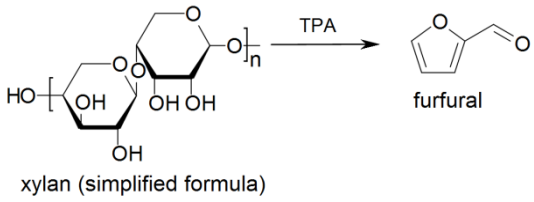


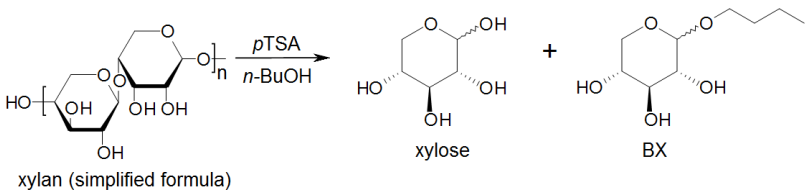
Figure 5.14 *Xylan dehydration into furfural (Reaction conditions: 1 g of [EtMeIm][Cl], 0.025 g of xylan, 0.02 g of TPA, 20 µL of water, 140 °C).*



Scheme 5.4. *Xylan dehydration in the presence of TPA.*

5.3.2.3 Xylan Conversion into Alkylxylosides

Synthesis of butylxylosides and octylxylosides starting from xylan was also assessed, analogous to the synthesis of alkylglycosides (paragraph 5.3.1.2). Therefore 0.025 g ($1.88 \cdot 10^{-4}$ mol of xylosidic units) of xylan was reacted with $3.3 \cdot 10^{-3}$ mol of alcohol in 1 g of [EtMeIm][Cl] in the presence of 0.01 g of *p*TSA at 90 °C. The kinetic profiles for *n*-butanol and *n*-octanol are presented in Figures 5.15 and 5.16 respectively. The kinetic profile of the reaction with *n*-BuOH shows that after 2 h a maximal combined butylated compounds yield of 45 % was reached. After this reaction time, the product distribution did not change significantly anymore. By analogy with the synthesis of alkylglycosides, the predominance of α-alkylxylosides during the whole course of the reaction can be explained by their higher thermodynamic stability in comparison with β-alkylxylosides.[48] Moreover, alkylxylosides seem to be, analogous to the alkylglycosides, relatively stable against dehydration.[28] Presumably, the lower solubility of xylose and alkylxylosides in the presence of *n*-butanol contributes to this higher stability. It seems that the hydroxyl groups of *n*-butanol successfully compete with xylose for the hydrogen bond formation with the chloride anions of [EtMeIm][Cl]. This could maybe lead to aggregation of xylose molecules through hydrogen bonding between them, which can suppress their degradation.



Scheme 5.5. *Splitting of xylan with formation of α-BX, β-BX, and xylose.*

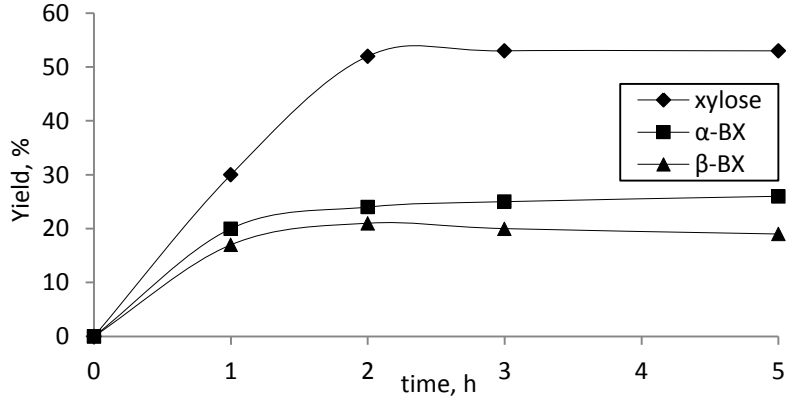


Figure 5.15 *Run profile of reaction between xylan and n-butanol (Reaction conditions: 0.025 g (1.88·10^{-4} mol xylosidic units) of xylan, 3.3·10^{-3} mol n-butanol, 1 g of [EtMeIm][Cl], 0.01 g of pTSA, 20 µL of water, 90 °C).*

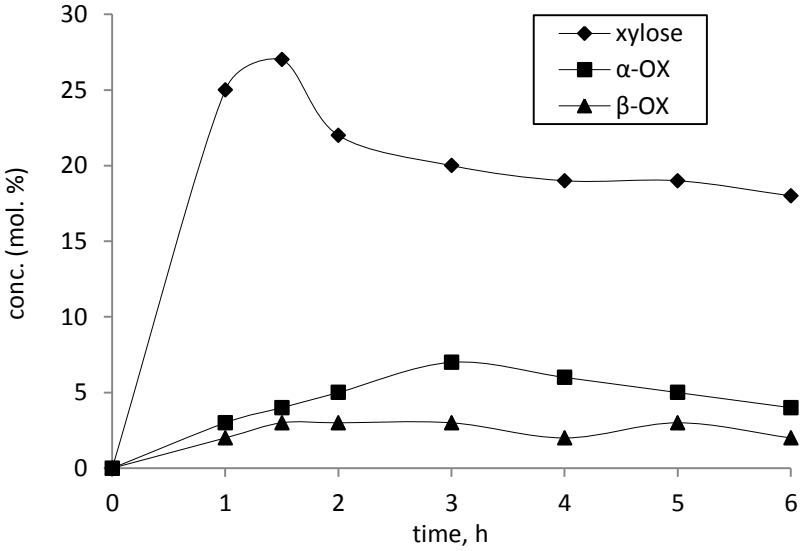


Figure 5.16 *Run profile of reaction between xylan and n-octanol (Reaction conditions: 0.025 g (1.88·10^{-4} mol xylosidic units) of xylan, 3.3·10^{-3} mol n-octanol, 1 g of [EtMeIm][Cl], 0.01 g of pTSA, 20 µL of water, 90 °C).*

In case of octylation the concentration of xylose is maximized at 1.5 h. The yields of α-octylxyloside (α-OX) and β-octylxyloside (β-OX) are significantly lower (maximal total yield is 10 % at 3 h). Again, the α-anomer predominates over the β-anomer. In contrast with the cellulose conversion into alkylglycosides, there is a big difference between the yields of butylated and octylated compounds in this case. A possible reason for the lower yields of octylated compounds is that *n*-octanol is significantly less soluble in [EtMeIm][Cl] than *n*-butanol, because of the decreased length of the alkyl chain on the imidazolium cation for [EtMeIm][Cl] in comparison with [BuMeIm][Cl] [54, 55] This could explain why this difference was not observed in [BuMeIm][Cl].

5.4 Conclusions

In this work, Smopex-101 has been demonstrated as an efficient heterogeneous acidic catalyst for cellulose hydrolysis in the ionic liquid 1-butyl-3-methylimidazolium chloride. In the presence of 0.01 g of the catalyst a 45 % yield of glucose could be reached after 4 h. Longer reaction times and a larger amount of Smopex-101 led to more glucose dehydration, resulting in decreased yields. The Smopex-101 catalyst could be recycled without significant loss in activity. Moreover, this catalyst was also found to be active for the further conversion into alkylglycosides. In a reaction with *n*-butanol, a 64 % yield of butylglucopyranoside was achieved. Both for the cellulose hydrolysis and the transformation into alkylglycosides Smopex showed a higher activity than the reference catalyst Amberlyst 15DRY.

Xylan was successfully hydrolyzed and converted into alkylxylosides in the presence of *para*-toluene sulfonic acid. The hydrolysis reaction resulted in a 42 % yield of xylose after 1 h. Again, dehydration became more significant at longer reaction times. A reaction between xylan and *n*-butanol led to a 45 % yield of

butylxyloside in the presence of the same catalyst. Finally, furfural production via xylan dehydration has also been performed. Tungstophosphoric acid displayed a high activity for the reaction, with a furfural yield of 84 % after only 2 h.

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6 Conclusions and Further Perspectives

6.1 General Conclusions

Ionic liquids (ILs) are being transformed now from a laboratory curiosity into industrially relevant products with promising applications. This is evident from the large number of patents and industrial processes involving these solvents. One of the most important advantages of ILs is that they are mostly “green” solvents. Some of them are toxic, but their high tuning capability allows the creation of environmentally friendly ionic liquids suitable for various chemical technological processes. Introduction of ionic liquids into industrial processes creates many new interesting opportunities. For instance, almost all the classical solvents are not suitable for cellulose dissolution and further valorization under mild conditions, but some ionic liquids are suitable for this purpose, and this opens new opportunities for biomass conversion. Finding of new efficient and creative ways of biomass conversion is an important challenge of modern science and technology.

In this work, four different ways of cellulose valorization mostly in the ionic liquid 1-butyl-3-methylimidazolium chloride have been investigated:

1. reductive splitting of cellulose in the presence of hydrogen gas,
2. cellulose conversion into alkylglycosides,
3. transformation of cellulose into α-D-glucose pentaacetate,
4. cellulose hydrolysis.

The results of our experiments prove that when cellulose is dissolved in an ionic liquid, which makes its chains more accessible to chemical transformations, the depolymerization becomes rather easy, and can be carried out under moderate reaction conditions.

6.1 Reductive Splitting of Cellulose in the Ionic Liquid 1-Butyl-3-Methylimidazolium Chloride

As no acid addition is required, the acid-catalyzed pyrolysis of hexose monomers to hydroxymethylfurfural or levoglucosan is avoided. The hydrogenation to sugar alcohols proceeds in the same pot, and cellulose is fully converted into a mixture of glucose and sorbitol. Low solubility of hydrogen gas in ionic liquids is problematic for the consecutive hydrogenation, but this problem is solved by application of hydrogen transport agents or by using a catalyst, active at low concentrations of hydrogen.

6.2 Cellulose Conversion into Alkylglycosides in the Ionic Liquid 1-Butyl-3-Methylimidazolium Chloride

Two ionic liquids were identified to enable the dissolution of cellulose and to perform the hydrolysis and alkylation in the presence of the acidic catalyst Amberlyst 15DRY: 1-butyl-3-methylimidazolium chloride and ethyltributyl-phosphonium diethyl phosphate. While the use of an acid catalyst could cause degradation of the formed hexoses, it is demonstrated in this work that this problem can be alleviated by *in situ* conversion of the glucose to alkylglycosides. When an excess of the alcohol was added, or when part of the acid catalyst was removed during the alkylation phase, the yield of alkylglycoside was maximized. The direct synthesis of alkyl glycosides with longer chains, such as dodecylglycopyranosides, is more difficult, but can be achieved via transalkylation.

6.3 Synthesis of Glucose Esters from Cellulose in Ionic Liquids

The efficient transformation of cellulose into glucose esters in an ionic liquid medium was demonstrated. A 70 % yield of α-D-glucose pentaacetate could be reached in the presence of an acidic catalyst. By keeping the amount and the acidity of this catalyst low, the acid-

catalyzed thermal decomposition of the glucose ester could be minimized. This cellulose transformation typically involves two steps: after hydrolysis of the polymer, a consecutive reaction with acetic anhydride takes place, in which glucose is acetylated and oligomers are being directly cleaved. This results in selective GPAc formation, which can be easily isolated by extraction. Both ionic liquid and catalyst could be recycled after reaction.

6.4 Hydrolysis and Consecutive Reactions of Cellulose and Xylan in Ionic Liquids in the Presence of Alternative Acid Catalysts

In this work, Smopex-101 has been demonstrated as an efficient heterogeneous acidic catalyst for cellulose hydrolysis in the ionic liquid 1-butyl-3-methylimidazolium chloride. In the presence of 0.01 g of the catalyst, a 45 % yield of glucose could be reached after 4 h. Longer reaction times and a larger amount of Smopex-101 led to more glucose dehydration, resulting in decreased yields. The smopex-101 catalyst could be recycled without significant loss in activity. Moreover, this catalyst was also found to be active for the further conversion into alkylglycosides. In a reaction with *n*-butanol, a 64 % yield of butylglucopyranoside was achieved. Both for the cellulose hydrolysis and the transformation into alkylglycosides, Smopex-101 showed a higher activity than the reference catalyst Amberlyst 15DRY.

Xylan was successfully hydrolyzed and converted into alkylxylosides in the presence of *para*-toluenesulfonic acid. The hydrolysis reaction resulted in a 42 % yield of xylose after 1 hour. Again, dehydration became more significant at longer reaction times. A reaction between xylan and *n*-butanol led to a 45 % yield of butylxyloside in the presence of the same catalyst. Finally, furfural production via xylan dehydration has also been performed. Tungstophosphoric acid displayed a high activity for the reaction, with a furfural yield of 84 % after only 2 hours.

6.5 Further Perspectives

The solubility of hydrogen gas in ionic liquids is a problem for cellulose hydrocracking, and the combination of cellulose solvation with sufficient hydrogen dissolution is a future target for ionic liquid selection and design. Another way to solve this problem is the design of a hydrogenation catalyst, preferably a heterogeneous one, which would be highly active and selective at low hydrogen concentrations in ionic liquids.

For separation of both nonpolar and polar products like glucose and sorbitol from ionic liquids pressure-driven nanofiltration is a promising technique. It has indeed been shown that nanofiltration is one of the few techniques that is able to separate ionic liquids from polar reaction products.[1] Additionally, larger residual cellulose oligomers and a homogeneous catalyst with a high molecular mass, such as the Ru complex used in one of parts of the present study, may also be withheld by a membrane with a sufficiently small molecular mass cutoff. Moreover, nanofiltration can be coupled with catalysis in order to increase product yield in a membrane reactor.[2] In such a hybrid process, product is continuously removed from the reaction mixture, while catalyst remains there. It increases the reaction conversion by shifting the equilibrium. Membrane-reactor technology is not yet widely used commercially, however it certainly has a bright future.[3]

Nonpolar reaction products such as alkylhexosides and alkylpentosides may be isolated from the ionic liquid by supercritical antisolvent precipitation with carbon dioxide.[4] It has indeed been shown, that nonpolar natural products can be isolated by this technique[5-7], including detergents.[7] Development of product isolation techniques, increase of demand for ILs and consequent decrease of price can make application of ILs for industrial scale biomass conversion possible.

It was demonstrated that the relatively high melting points of chloride based ILs (above 70 °C for [BuMeIm][Cl]) could be a technical

drawback and possibly limit their practical application in cellulose processing or homogeneous cellulose derivatization.[8] Moreover, in case of possible commercialization it can increase energy consumption. So, design of new functionalized ionic liquids for cellulose dissolution and processing with lower melting points can improve in principle the efficiency of the studied processes.[8]

It has been recently reported that organic electrolyte solutions, which contain small molar fractions of IL, can instantaneously dissolve large amounts of cellulose.[9] It is one of the examples of effects of ILs as additives.[10] Cellulose processing in such systems can be very promising and creates new perspectives for commercialization. However, further research is needed since these effects of ILs are not fully understood.[10, 11]

6.6 References

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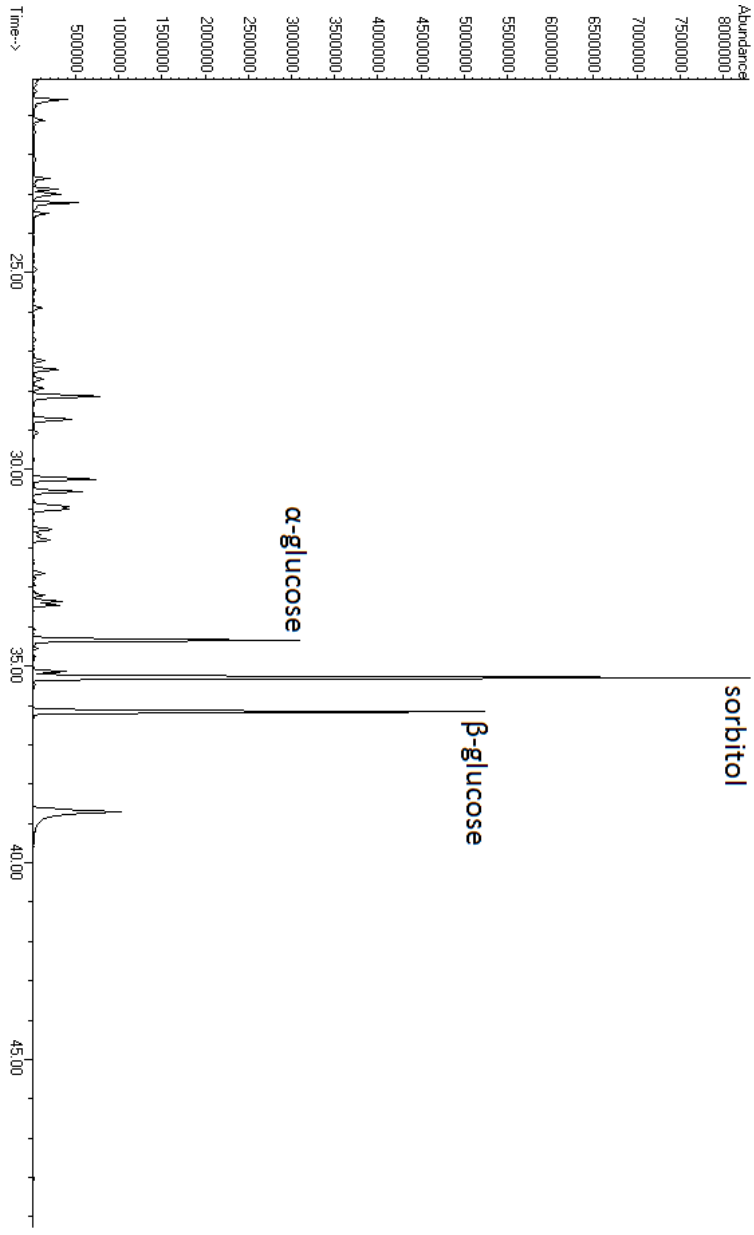
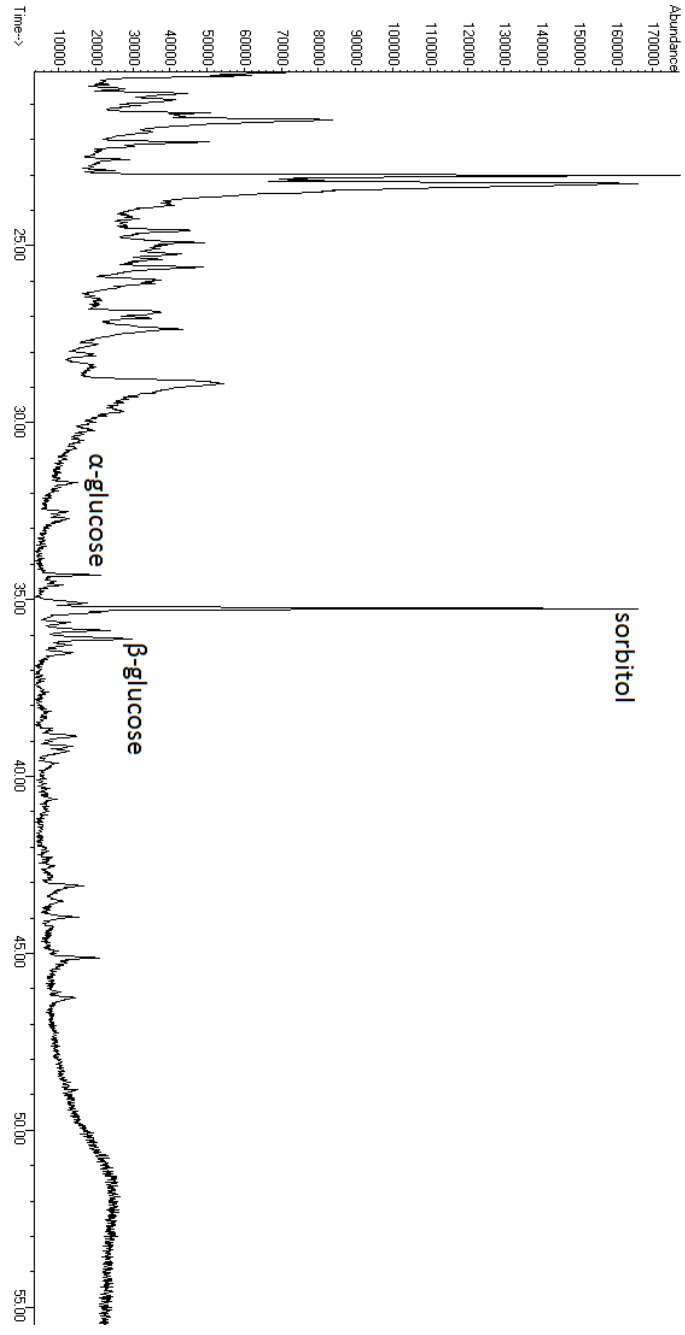
Appendix

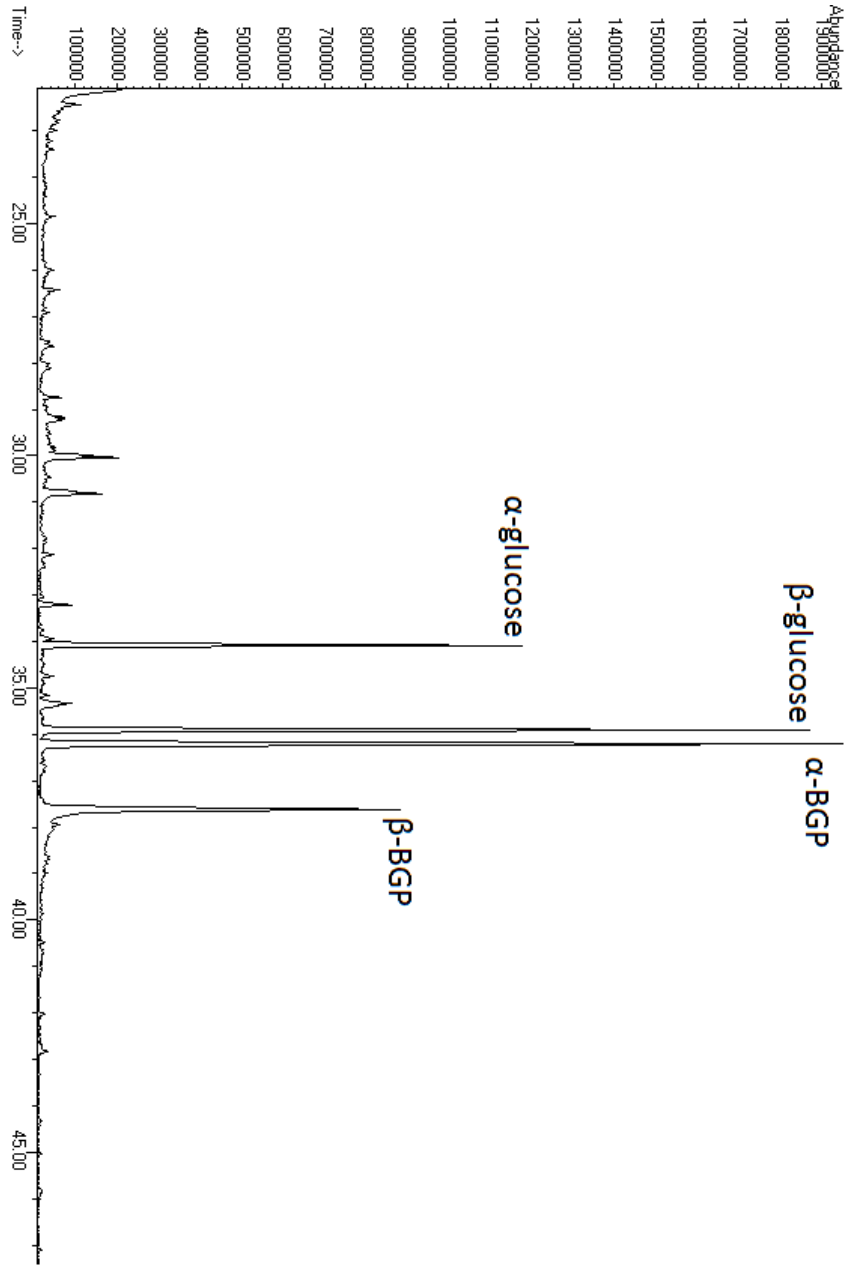
1. Chromatogram of reaction mixture after reductive splitting of cellulose over Pt/C (Table 2.2, entry 5)



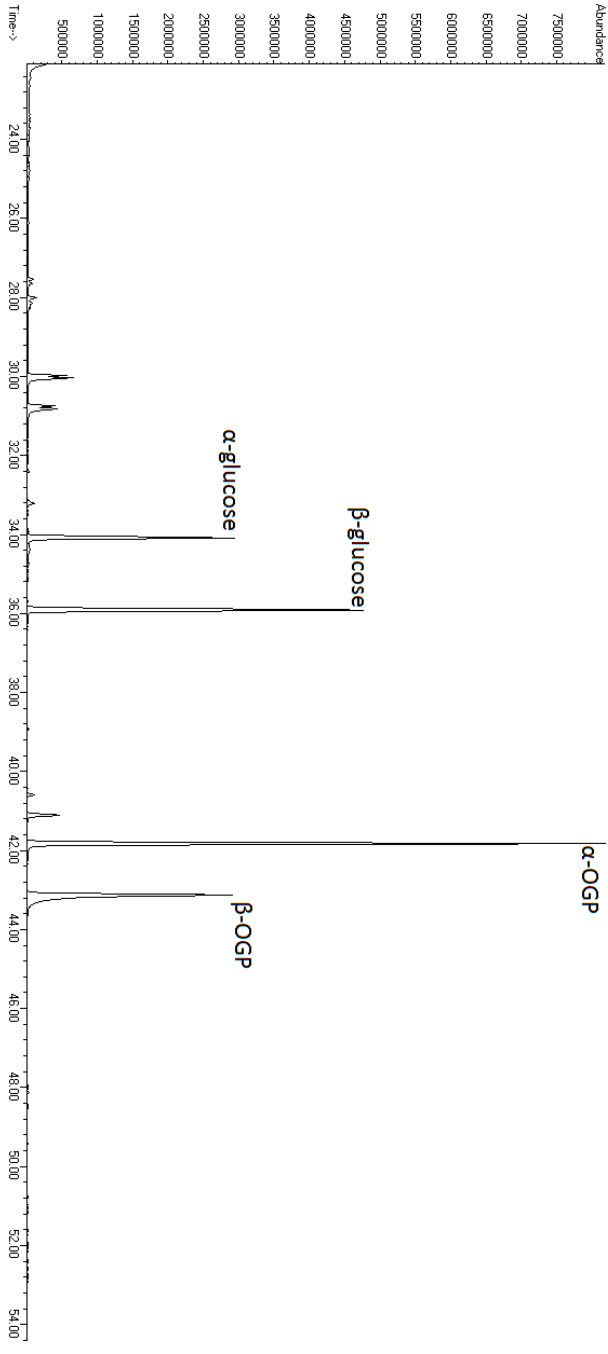
2. Chromatogram of reaction mixture after reductive splitting of cellulose over Rh/C (Table 2.3, entry 7)



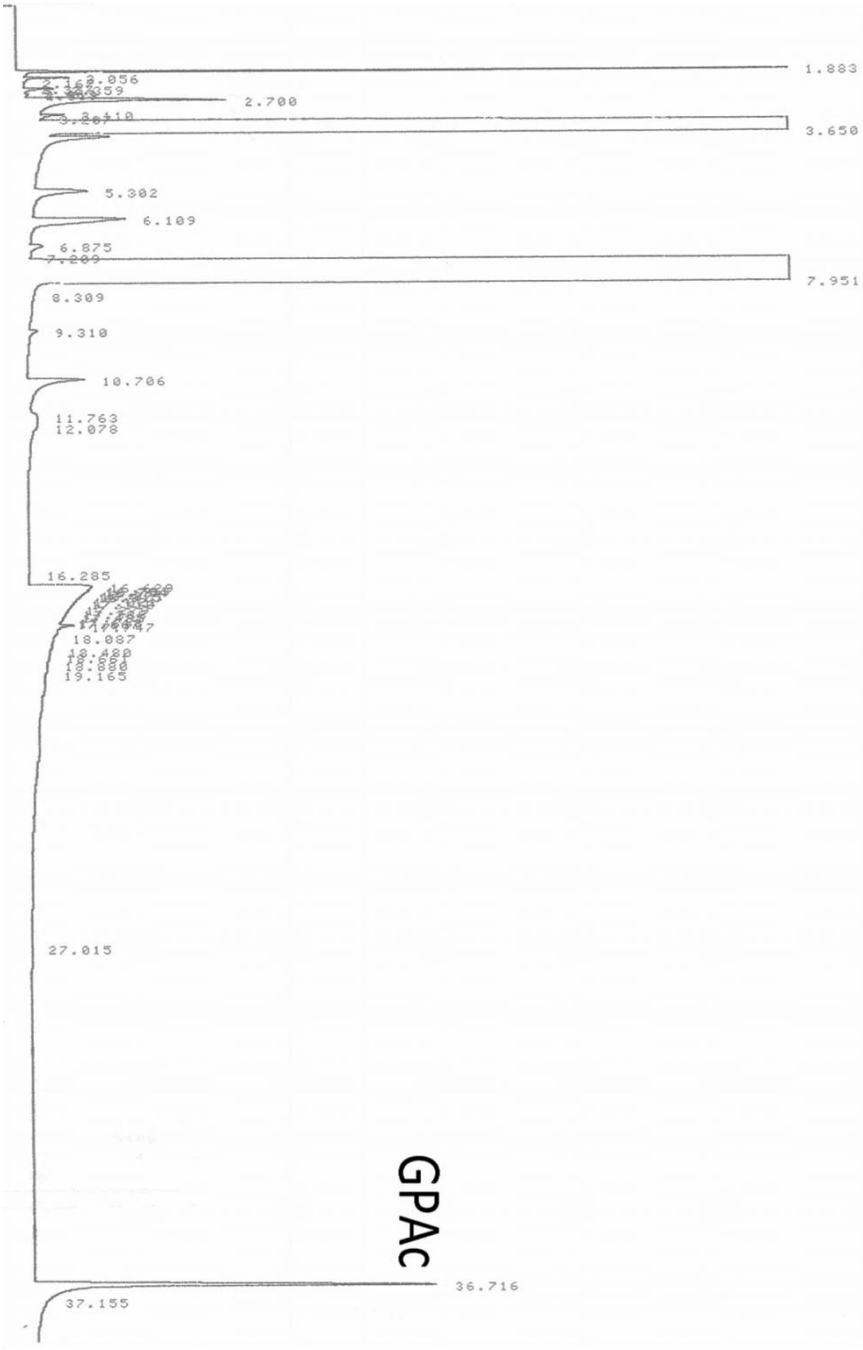
3. Chromatogram of reaction mixture after cellulose conversion into butylglycosides (Table 3.2, entry 3)



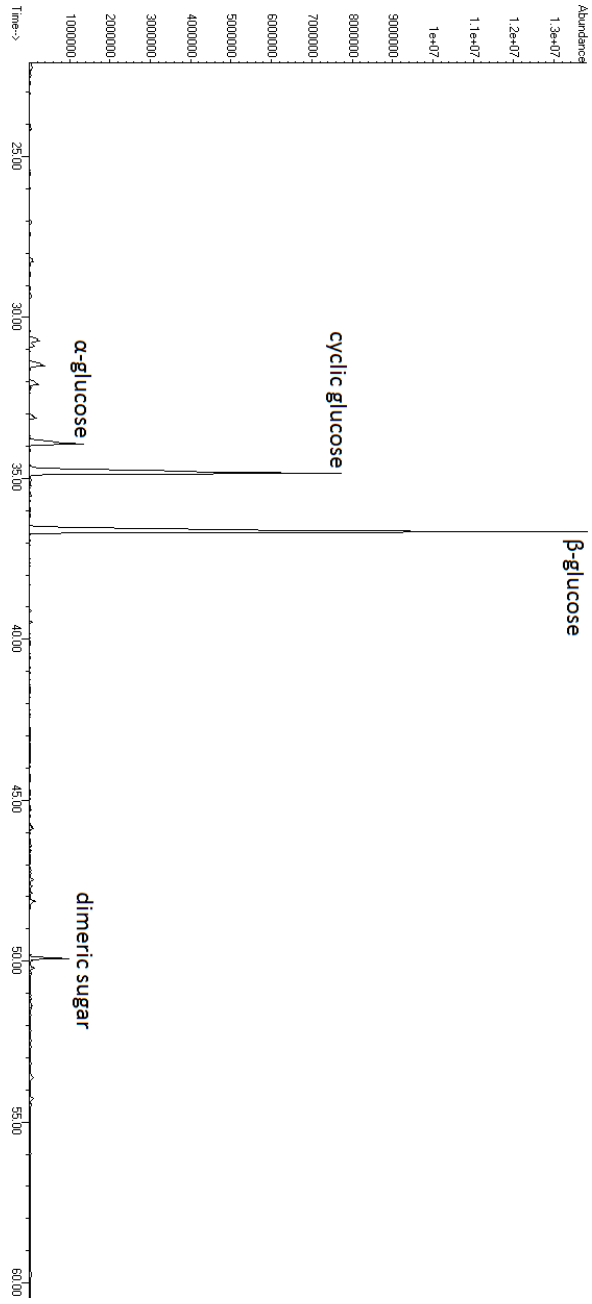
4. Chromatogram of reaction mixture after cellulose conversion into octylglycosides (Table 3.4, entry 3)



5. Chromatogram of reaction mixture after cellulose conversion into GPAc (Table 4.5, entry 4)



6. Chromatogram of reaction mixture after cellulose hydrolysis in the presence of Smopex-101 (Table 5.1, entry 2)



7. Chromatogram of reaction mixture after cellulose hydrolysis in the presence of Smopex-101 (Table 5.4, entry 2)