University of Potsdam

Max Planck Institute of Colloids and Interfaces

Master Thesis

Synthesis and Application of Sustainable Ionic Liquids

Biomass derived Ionic Liquids and Biomass Treatment

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Abstract

Herein we present the synthesis of *N*-substituted 3-hydroxypyridinium zwitterions from furfural and amino acids and their decarboxylation to form ionic liquids. The zwitterions and the ionic liquids derived from them are formed from renewable resources obtainable from biomass. By virtue of the reaction, the amino acid is incorporated into the ring to form *N*-substituted pyridinium cations that already resemble the structure of modern pyridinium based ionic liquids. This makes the use of quaternization reactions to achieve *N*-substitution unnecessary, further contributing to the sustainability of this reaction. By use of this reaction three ionic liquids were synthesized, all of which are room temperature ionic liquids with glass transition temperatures below 0 °C. The decarboxylation of the amino acid moieties proceeded under hydrothermal conditions at rather low temperatures indicating a favorable catalytic effect of the pyridinium ring during decarboxylation. Also the use of a pyridinium based, hydrophobic ionic liquid as a solvent for Sonogashira-Hagihara coupling of iodobenzene and phenylacetylene was tested.

In addition we used 1,3-*N,N*-diethylimidazolium acetate, another ionic liquid obtainable from renewable resources in a sustainable synthetic scheme, and a dissolution of this ionic liquid in dimethyl sulfoxide to treat beech wood and coconut shell material. With both solvent systems, partial dissolution of the biomass was achieved. Several fractions were in turn recovered from the mixtures by stepwise precipitation and analyzed by elemental analysis and infrared spectroscopy. At least one of the fractions obtained seems to contain lignin.

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Eigenständigkeitserklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt habe. Alle Stellen, die in wörtlicher oder übertragener Form aus anderen Werken entnommen sind, sind als solche gekennzeichnet.

Ort, Datum   Steffen Tröger-Müller

Abbreviations

ACS   –   American Chemical Society

ATR-IR   –   Attenuated Total Reflection - Infrared

DMSO   –   Dimethyl sulfoxide

DSC   –   Differential Scanning Calorimetry

EA   –   Elemental Analysis

EEIMOAc   –   1,3-*N,N*-Diethylimidazolium Acetate

GC   –   Gas Chromatography

IL   –   Ionic Liquid

KL   –   Kraft Lignin

LS   –   Calcium Lignosulfonate

MS   –   Mass Spectrometry

nmr   –   Nuclear Magnetic Resonance

OECD   –   Organisation for Economic Co-operation and Development

OSL   –   Organosolv Lignin

PS   –   Solution used for Precipitation (Ethanol:Acetone, 1:1, v/v)

SAL   –   Soda-Anthraquinone Lignin

TGA   –   Thermogravimetric Analysis

wt.%   –   Percentage by Mass

1 Introduction

1.1 Sustainable and Green Chemistry

Within the last century the western world experienced the advent of oil as the most important source of energy. The availability of cheap energy led to decades of growth and development with the emergence of plastics, antibiotics and the first computers.[1] In this time of rapid change economists, engineers and politicians seemed to believe that every possible obstacle could be overcome by human creativity and invention. Even though the finiteness of fossil resources was already known and acknowledged, it was expected that the advent of nuclear energy would overcome the limits of oil as a source of energy. In short, every finiteness would be overcome by the advent of a new technology.[1] But it also became apparent that prosperity and growth did not encompass all the world and adverse environmental effects, such as the pollution of Cuyahoga river that actually caught on fire in the 1970ies[2], manifested in increasing numbers. This caused scientists and the public alike to question the ideals of growth as a sustainable way of life[1].

Chemistry and the chemical industry have enabled our way of life today and contribute to our modern society in many ways. In order to enable a sustainable society, chemists have to play their part. In the last years, the paradigm of green and sustainable chemistry has emerged in the scientific community. The OECD (Organisation for Economic Co-operation and Development) defines sustainable chemistry as "a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services"[3]. The American Chemical Society (ACS) gives a broader perspective, calling upon a classical definition of sustainability as employing policies that meet today's "needs without compromising the ability of future generations to meet their own needs."[4] Closely related is the concept of *green chemistry*, which encompasses the "utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products."[2] In order to give some guidelines, the *12 Principles of Green Chemistry*, which are also supported by the ACS, have been developed. One key idea of green chemistry is to consider possible consequences not after but at any stage of the design of a molecule or process.[2]

In order to achieve this mindful approach, solvents play an important role. The assessment of the *greenness* of a solvent requires comprehensive considerations, taking into account risks, production, disposal and all related issues. The use of ionic liquids, a novel class of solvents that have interesting characteristics, which will be discussed later, is one approach to improve the sustainability of processes[5]. The aim of this work will be the synthesis of ionic liquids derived from renewable resources as well as the exemplar application of these liquids.

1.2 Ionic Liquids

Ionic liquids (ILs) have first been documented in a publication by P. Walden in 1914, although he did not name them ILs[6]. Figure 1 shows some examples of ionic liquids.
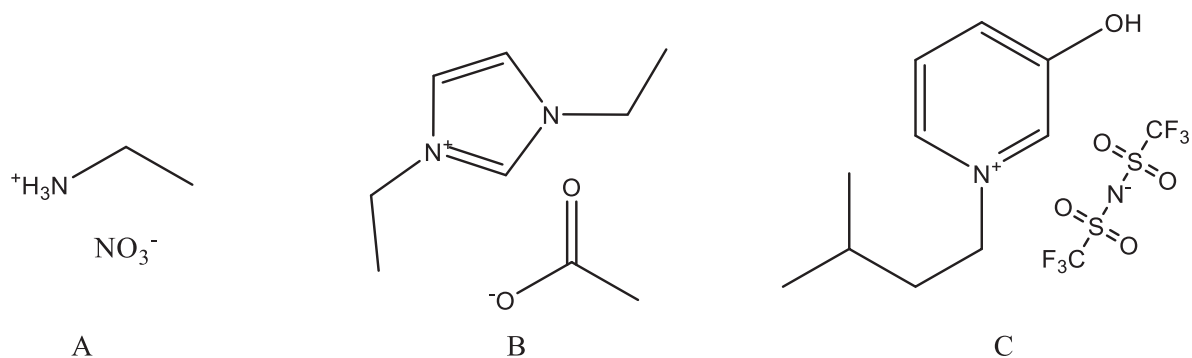

Figure 1 Examples of ionic liquids. A) The IL discovered by P. Walden, synthesized by neutralization of ethylamine with conc. nitric acid[6,7]. B) 1,3-*N,N,*-diethylimidazolium acetate, used in this work. C) 3-hydroxy-1-isopentylpyridin-1-ium bis((trifluoromethyl)sulfonyl)imide, also used in this work.

They are defined as liquid below 100 °C and composed of ions[8,9]. Initially, this class of compounds did not receive a great deal of attention until recently the number of publications concerning ILs is rapidly increasing. Also it was not until the end of the 20th century that air and water stable ILs were reported that could be synthesized on the bench[7]. ILs comprise a very variable group of substances. In addition, most physical as well as chemical characteristics of ILs may be adjusted by combination of different ions[8]. Due to that variability, it was stated that ILs may make it possible "to design a solvent to optimize a reaction (with control over both yield and selectivity)"[10], instead of choosing the most appropriate solvent out of the usual repertoire[10]. This notion might be further emphasized considering, that compared to roughly over 1000 organic solvents (with about 600 that are commercialized) there are theoretically more than one million possible ILs from combination of different

Ions[7]. As a rule of thumb, physical characteristics of an IL may be attributed to the cation and chemical behavior may be related to the anion[7].

But this must be regarded carefully as for example imidazolium based ionic liquids are known to form *N*-heterocyclic carbenes from their cations. Those carbenes have attracted much interest in catalysis and as ligands for metal complexes[11–13]. It must be noted here, that the exact *a priori* determination of IL characteristics to define chemistry and physics is still relatively challenging. The possibility to tune the characteristics of ILs to their application indicates great potential to comply with green chemistry's call for efficiency in use of resources and selectivity in reactions. Ionic liquids have been regarded as green and non-toxic solvents due to their negligible vapor pressure. This cancels most pathways for atmospheric contamination.[7] Nevertheless a lot of other factors influence the *greenness* of any chemical, such as the individual synthetic route used, so general statements should be avoided. Toxicity is a special issue, since it is possibly to produce even edible ILs, but it is also possible to synthesize outstandingly toxic ILs[7].

Apart from the negligible vapor pressure, ILs may exhibit other interesting characteristics, such as low surface tensions, wide thermal range of liquidity, large window for electrochemical reactions and good thermal stability. They also usually show the formation of extensive hydrogen bond networks forming highly structured solvents. As such ILs have been termed "supramolecular solvents"[9]. Due to their innate polarity it is also possible to conduct reactions under very polar conditions with exclusion of water in ILs.[9] It has to be kept in mind though, that one of the reasons why ILs receive so much attention is the fact, that their abilities may be tuned and that no individual ionic liquid will exhibit all of the characteristics from the vast spectrum of possibilities.

The solvent abilities of ILs have made them quite successful in a variety of applications including paint additives, batteries and they reached even commercial application with the DIFASOL or BASIL processes[7]. More recently their solvent capabilities have been evoked in the context of biomass processing

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1.2.1 Ionic Liquids with Imidazolium or Pyridinium based Cations

Pyridinium and imidazolium were among the first cations used in ionic liquids, with the pyridinium based IL 1-ethylpyridinium bromide being reported in a patent as early as 1948[7]. Ionic liquids based on substituted imidazolium rings became popular sometime later and are among the most commonly applied ILs today, outrivaling the pyridinium based ones. Traditionally the synthesis of imidazolium cations is often carried out by using quaternization reactions between imidazolium and alkyl halides[14,15]. However, the great interest in imidazolium based ILs has prompted research for simple and more sustainable routes towards those cations. As an interesting approach towards imidazolium moieties our group applied a modified Debus-Radziszewski reaction to synthesize 1,3-*N,N*-alkyl-imidazolium zwitterions from renewable resources such as amino acids[16,17] which can subsequently be decarboxylated under hydrothermal conditions in presence of an acid to yield renewable imidazolium based ionic liquids [16,18]. This synthetic route is much more sustainable than the normally applied quaternisation routes for the synthesis of *N*-substituted imidazoliums as it uses chemicals available from renewable resources. As such it presents a nice example of a possible green chemical approach to the synthesis of fine chemicals. The reaction scheme of the modified Debus-Radziszewski reaction is displayed in Figure 2.
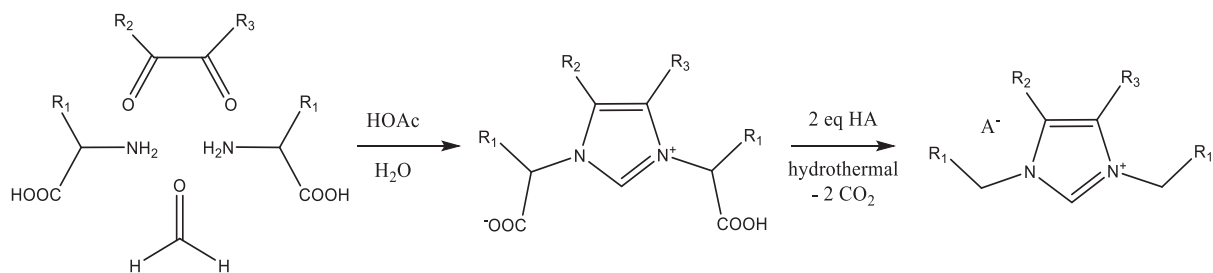
Figure 2 Scheme of the synthesis of imidazolium based ILs by use of the modified Debus-Radziszewski reaction and subsequent decarboxylation under hydrothermal conditions. R_1 = side chain of the amino acid. R_2, R_3 = H, CH_3. Figure adapted from ref. [18].

Using a similar strategy, our group has recently published the synthesis of ILs based on 3-hydroxypyridinium cations from renewable resources[19]. In order to obtain the IL, it is first necessary to synthesize 3-hydroxypyridinium zwitterions from furfural and an amino acid. The zwitterion can then be decarboxylated under hydrothermal conditions[19]. Furfural has been listed among the top 30 biomass derived platform chemicals in a study supported by the US Department of Energy. It is derived from xylose via dehydration and can be produced on a 300,000 - 700,000 ton scale at a

cost of about 1000 dollar per ton from biomass, such as crop residues[20]. Amino acids on the other hand are produced enantiomerically pure by nature and are potentially available from a variety of waste streams of the food industry. The utilization of those waste streams, such as those that arise from poultry and shrimp flesh production in the form of feathers and husks, open a sustainable source of amino acids, for example by use of the ammonia fiber expansion treatment[21]. However, since most waste streams have a value[21], concurrency with other uses of those waste streams, such as the production of methane or protein rich animal food from feather based waste streams[22,23] may still present economic challenges.

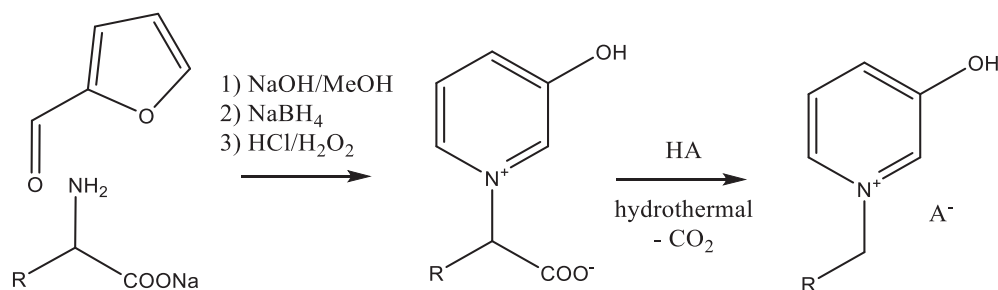The 3-hydroxypyridinium zwitterions synthesized from furfural and amino acids are shown in Figure 3.

Figure 3 General structure of the 3-hydroxypyridinium based zwitterions that have been synthesized from amino acids and furfural as well as their subsequent decarboxylation to ionic liquids. R denotes the side chain of the amino acid.

It has to be noted that, in principle, the use of amino acids makes it possible to introduce chiral centers and thus opens up a possible and easy approach towards chiral ILs.

1.2.2 Ionic Liquids to facilitate Palladium catalyzed Reactions

One of the *12 principles of green chemistry* states that "Catalytic reagents (as selective as possible) are superior to stoichiometric reagents."[2] In that regard palladium catalyzed cross couplings, such as Mizoroki-Heck, Suzuki-Miyaura and Sonogashira-Hagihara couplings are among the most powerful C-C bond formation tools within the toolbox of the organic chemist. They are as such among the most investigated transition metal catalyzed cross coupling reactions in organic chemistry[24]. Ionic liquids have received significant interest as reaction media for such transformations because they are suitable for multiphase systems, can immobilize and stabilize the catalyst and offer convenient options for the separation of products. The applicability and in many cases the enhancement of such reactions

in ILs, especially in the case of imidazolium ILs that can form *N*-heterocyclyc carbenes[13], is attributed to the formation and stabilization of palladium nanoparticles, that act as reservoirs for the catalytically active palladium species[24]. This phenomenon has also been reported for other transitional metals such as iridium[25]. The use of ionic liquids for the production of nanomaterials, nanoparticles and related applications is also a growing field of research, where ILs are valued especially for their ability to form superstructures[26]. Reactions in ILs have been described as "reactions in a pure "universal" ligand."[9] In line with this knowledge Kirchhecker et. al. have successfully used a hydrophobic pyridinium based IL derived from renewable resources for Heck reactions with high yield[19].

1.3   Lignocellulosic Biomass as a Replacement for Fossil Feedstocks

As pointed out by P. T. Anastas and J. C. Warner already in 1998 the "most obvious concern for the extensive utilization of limited or depleting resources is the fact that, by definition, they can run out […]"[2]. As society may struggle to meet its energy demands while breaking the dependency on fossil feedstocks, it is easy to miss that the chemical industry is almost completely dependent on fossil resources as well. In order to find a replacement for oil, gas and their derivatives, biomass has been proposed as a valuable alternative, as it is the only really renewable resource on our planet. The use of biomass for energy supply has distinct advantages in comparison to solar or wind energy. For example, biomass benefits from a rather stable availability as well as good storability and may be converted to liquid fuels compatible with existing industrial pathways with only little adaptation necessary[27]. Apart from renewable energy supply biomass is especially interesting due to the possibility to derive chemicals from it. Two main possibilities exist to obtain biomas, if the use of animal based biomass is to be left aside[1]. The first possibility is agricultural production and the second is forestry. The use of agricultural crop land for the production of biomass that is fed into biorefinery schemes instead of food production is, however, viewed with skepticism as it has rather complex implications and subverts the whole idea of a sustainable world (*Food vs. Fuel* debate).[27] The use of agricultural wastes, such as rise husks and sugar cane bagasse, on the other hand is

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[1] Animal based biomass is generally not considered as a source due to efficiency issues. Chemicals that need to be derived from animal biomass should be derived from waste streams of the food industry or the like due to the higher need of water and other resources in comparison to plant based biomass. For treatment of waste streams see for example ref. [21].

a rather attractive scheme since both waste streams are unavoidable during food production[21]. This also applies to other unavoidable waste streams that accompany established production routes for commodities. The second possible source of large quantities of plant biomass is forestry. It may be noted here, that the use of a sustainable approach with the notion of giving the forest time to recover from lumbering is documented for forestry in a written form since 1661 in Germany[28] and regulations for the use of wood can be dated back to lease agreements before 1400[28], making timber one of the oldest sustainable raw feedstocks known. The use of lignocellulosic biomass derived from the cultivation of woody plants in forestry has received much attention recently due to the exclusion of food concurrency[27].

1.3.1 Constitution of lignocellulosic Biomass

Lignocellulose is the most abundant plant material found on our planet, as it makes up the cell walls of all woody plants including grasses and shrubs[29]. The yearly production is estimated at about 200 billion metric tons worldwide[30]. It is composed mainly of cellulose, hemicellulose and lignin. Figure 4 shows the structure of lignocellulosic biomass and the monomers it is built up from.
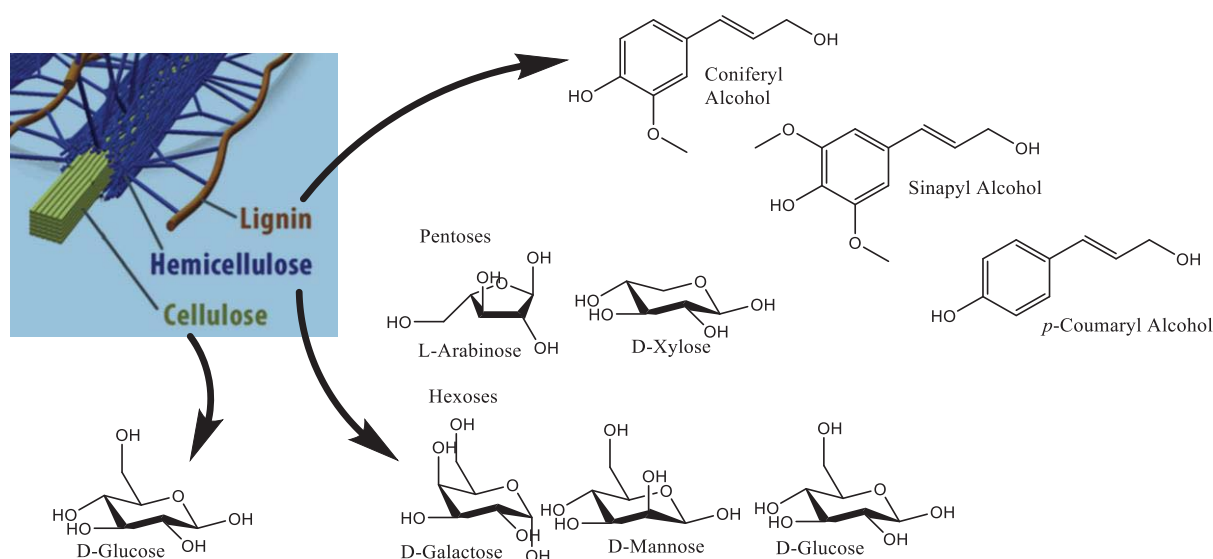
Figure 4 Structure of lignocellulosic biomass and monomers of its constituents. Cellulose, hemicellulose and lignin form the three major parts of lignocellulosic biomass. Cellulose is built up from glucose monomers, hemicellulose is formed from a variety of hexoses and pentoses and lignin is synthesized from the three aromatic monolignols. Figure adapted from ref. [29].

Cellulose is a linear polymer of glucose interconnected via 1-4-β glycosidic bonds. Due to the β conformation, linear chains are formed which may exceed 10 000 glucose units per molecule. The conformation of the 1-4 glycosidic bond greatly

influences the characteristics of the polymer formed. The cellulose chains form sheets, held together by hydrogen bonds. Starch on the other hand, differing from cellulose by the presence of 1-4-α glycosidic bonds instead of 1-4-β glycosidic bonds, forms helical structures. The cellulose sheets are packed into strands held together mostly by van-der-waals forces[29]. Hemicellulose on the other hand denotes polysaccharides with about 100-200 monomer units per molecule. Hemicellulose is synthesized from a variety of hexoses (glucose, galactose, mannose) and pentoses (xylose, arabinose)[29]. In the cell walls of most plants xylose is the dominant monomer in the backbone of hemicellulose[31]. In contrast to the linear cellulose chains, hemicellulose can form branched molecules. Hemicellulose may also carry different functional groups and its constitution is dependent on the plant species, type of tissue, as well as the location and conditions of growth. Hemicellulose holds the crystalline cellulose strands in place by binding non-covalently to their surface. As such it forms an amorphous matrix around the cellulose component.[29] The cellulose-hemicellulose composite is embedded into a lignin layer.

Lignin is an aromatic hetero-polymer composed of varying ratios of coniferyl, sinapyl and *p*-coumaryl alcohols (see also Figure 4). These three compounds are usually referred to in terms of their aromatic structure within the polymer as guaiacyl, syringyl, and *p*-hydroxyphenyl units, respectively, as displayed in Figure 5.[29]

Guaiacyl   Syringyl   *p*-Hydroxyphenyl
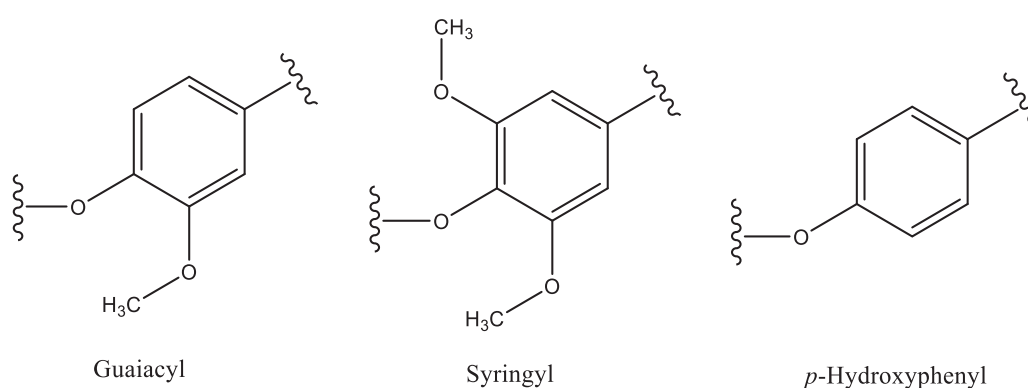
Figure 5 The names of the three monomeric units included in the lignin polymer. Wavy lines indicate the transition to the backbone of the polymer. The guaiacyl unit is derived from coniferyl alcohol, the syringyl unit from sinapyl alcohol and the *p*-hydroxyphenyl unit from *p*-coumaryl alcohol. Figure adapted from ref. [29].

Lignin has a supporting role in lignocellulosic biomass, introducing structural reinforcement, water insolubility and protection from physical and biological degradation. It is a highly complex and recalcitrant aromatic polymer with a variety of

linkages[2], including both C-O and C-C bonds. About 50% of the linkages are β-O-4 ether bonds that contribute to the length of the polymer chain, but the structure of lignin also includes crosslinks and branches.[29] The exact composition of lignin is dependent on the type of wood and the conditions of growth[29], as well as the type of tissue of the plant it is obtained from[33]. Rather linear lignin has been reported in seed coats, which is interesting because linear lignin is less resistant to deconstruction[33]. Lignification of lignocellulosic biomass is thought to take place after plant growth stopped[29]. The exact nature of the lignin biosynthesis is still subject to debate. Literature lists several theories that range from random radical polymerization[29] to more ordered reactions similar to the synthesis of most biomolecules with the use of enzymes or dirigent proteins[34,35]. Eleven enzymes are acknowledged to take part in the synthesis of the lignin monomers[35]. Interestingly one approach to biomass valorization and lignin recovery is the genetic manipulation of those enzymes and the associated metabolism in order influence lignin content and lignification of woody plants.[33] Most deconstruction attempts of lignin focus on the cleavage of the ether-bonds. Delignification and deconstruction is complicated by the heterogeneity of the polymer and the dependency on wood type, with softwood usually posing the greatest challenge. Another significant issue of delignification is the formation of new C-C-bonds crosslinking the molecules during deconstruction attempts. Additionally lignin is incorporated into lignocellulosic biomass by covalent and non-covalent bonds to hemicellulose forming lignin-carbohydrate complexes which further complicates deconstruction.[29] The deconstruction of lignocellulosic biomass is one of the great challenges for proficient biorefinery schemes.

1.3.2 Ionic Liquids and the Treatment of lignocellulosic Biomass

The most well established processes for the treatment of lignocellulosic biomass have been developed by the paper industry. The goal of those treatments is the separation of cellulose from lignin (and in part hemicellulose). In those cases, lignin is usually subsequently burned for heat supply[29].

In a proficient biorefinery scheme all streams, including those that are currently waste or low value streams, must be converted to valuable products. Most waste streams

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[2] The exact nature of the linkages are beyond the scope of this work. The reader may resort to other sources for detailed information and further reading, such as reviews (for example ref. [29]) or textbooks (for example ref. [32]).

are already used to some extent, such as the lignin fraction in paper industry. As such they have a value that needs to be compensated in order to design a functioning biorefinery scheme.[21] Lignin presents an interesting fraction of lignocellulosic biomass because it is composed of aromatics. As such it has great potential for production of bulk chemicals and fine chemicals as well as fuels[34]. Due to the structure of lignocellulosic biomass and the characteristics of its components, the separation of different fractions and the subsequent conversion still presents a considerable challenge. This paragraph shall give brief information on the use of ionic liquids for the treatment of lignocellulosic biomass.

Dissolution of cellulose has been reported for various ionic liquids by now and is desired for cellulose fibers and fuel production from cellulose[29]. It might be the ability to dissolve cellulose that sprung the initial interest in lignocellulose processing with ILs. Since then the influence of the different factors on the ability of ILs to dissolve biomass has been subject of intense research. This paragraph will focus mostly on pyridinium and imidazolium based ILs in order to outline several factors influencing the ability of ionic liquids to dissolve lignocellulosic biomass or parts of it. During cellulose dissolution anions are thought to participate in hydrogen bonding, disrupting the inter- and intramolecular hydrogen bonds between cellulose chains[36]. The solvent characteristics of ionic liquids are often described via the Kamlet-Taft parameters α, β, and π* which describe hydrogen-bond donor ability (acidity), hydrogen-bond acceptor ability (basicity) and dipolarity/polarisability respectively. Such parameters are determined via UV/Vis-spectroscopy using special solvatochromic dyes.[29,36,37] In the context of cellulose dissolution it has been pointed out that a large β value (≥ 0.82) is necessary to disrupt the hydrogen bonding of cellulose and thus facilitate dissolution of lignocellulosic biomass[36]. In general, *N*-heterocyclic cations show better biomass solubilisation capabilities than other ILs, probably due to favorable interactions with the aromatic lignin[36]. Small cations also seem to be favorable. Substituents on the cation also influence the dissolution ability. Electron withdrawing substituents and small substituents seem to further enhance the dissolution ability. Hydroxy-groups on the cation on the other hand decrease the solubility of biomass. This is probably due to concurrency with the hydroxy-groups of cellulose in terms of hydrogen bonding. The viscosity of an IL is mainly controlled through the anion and the side chains of the cation. Generally a lower viscosity is favorable for dissolution.[36] Higher temperature is usually also viewed to enhance

dissolution but at the expense of possible degradation of the IL. Last but not least the type of biomass and particle size must be considered for any treatment. Large particle sizes are generally disadvantageous due to a more intact superstructure of the material. The type of biomass on the other hand determines its chemical constitution and is as such also a key factor to keep in mind in the design of biomass treatment processes.[36]

The two main approaches for the treatment of lignocellulosic biomass with ILs have been classified as: a) dissolution process, which implies the solubilization of the entire biomass (complete dissolution); b) ionosolv process that targets the selective solubilization of lignin and hemicellulose (partial dissolution). The aim of the ionosolv approach is the disruption of the lignocellulose material without complete solubilization. It is worth noting that the dissolution process can include the use of acids to hydrolize carbohydrate polymers, somewhat blurring the distinctions between ionosolv and dissolution process.[29]

Keeping in mind that ILs can be viewed as designer solvents[10], the possibility is given to tailor-make ILs specially for lignocellulosic biorefinery. It has also been speculated, that applications may utilize systems composed of three ILs. In such a case the ILs are used to tune chemical (1st IL) and physical (2nd IL) properties inside an inert (and cheap) medium (3rd IL)[7]. The combination of ionic liquids with traditional organic solvents (organic electrolyte solutions – OES) for dissolution of cellulose is also documented[29,38]. This approach has great potential to aid the solution of viscosity and cost-based issues for the application of ILs in biorefinery. In order to form a promising electrolyte solution the used organic solvent should be rather polar, possessing a high π^* value (>0.8) low hydrogen bond acidity (α <0.5) and moderate hydrogen bond basicity compared to the IL ($\beta \geq 0.4$)[29].

1.4 Objectives

As a very versatile class of substances, ionic liquids are promising candidates for applications in a variety of fields. Their low volatility reduces the risk for atmospheric contamination in most cases and makes it possible to operate processes at atmospheric pressure that would otherwise be carried out in pressurized apparatuses with the entailed security risks and costs. Also ILs are appreciated for the possibility to tune them to the application they are intended for. As such ILs are good candidates for use in a green chemistry as they comply with various principles of green chemistry. In this work an approach towards the synthesis of pyridinium zwitterions from renewable resources is presented. The variability of the zwitterions will be discussed. The conversion of such zwitterions into ionic liquids using hydrothermal decarboxylation will be presented. In order to evaluate the applicability of ILs in cross coupling reactions, the Sonogashira-Hagihara coupling of iodobenzene and phenylacetylene was tested. The second aspect of this work is the use of 1,3-*N,N*-diethylimidazolium acetate, which may also be obtained from renewable resources[16,18] for the treatment of biomass. Since the chemical industry is dependent on fossil feedstocks, the use of biomass for production of fine chemicals is one of the main challenges of chemistry on its way to become greener and more sustainable. The use of biomass derived chemicals for the treatment of biomass is an especially interesting approach as it symbolizes a detachment of chemical industry from fossil feedstocks and the reorientation to renewable resources. The main aim of the conducted biomass treatment is the separation of different fractions of biomass, with the hope of separating lignin as a source of aromatics.

2   Methods

2.1   Introduction

The aim of the following section is to convey a brief foundation of the underlying theoretical principles as well as basic operational modes of the techniques employed during this project to gather experimental data.

2.2   Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (nmr) spectroscopy is one of the most common analytical techniques in organic chemistry. The measurement is based on the behavior of nuclei with an angular momentum in an external magnetic field[3]. As such, only the nuclei of isotopes with an angular momentum show nmr activity. The most common nuclei in organic chemistry are the ^{1}H and ^{13}C, of which the ^{13}C can be problematic due to the low natural abundance of this isotope. More specialized applications also include ^{15}N, ^{19}F and a variety of other nuclei. Nmr spectroscopy reveals information about the local electric environment of the nuclei and their interaction with each other. The *chemical shift*, that means the location of the signals within the spectrum, gives information about the functional group of the nucleus causing the signal. The respective values can be found in tables and textbooks. The multiplicity of the signal, that is the number of peaks in each signal, gives information on the number of coupling nuclei. Coupling occurs only between nuclei that are connected by chemical bonds. Coupling becomes weaker over distance and is usually only visible over a maximum of three bonds. As such it reveals information about the connectivity. The coupling constant, that is the (frequency) difference in between two peaks of one signal, reveals further information about the connectivity. In ^{1}H nmr spectroscopy it is also possible to identify the number of nuclei that cause a signal by integration of the respective peaks. More advanced nmr techniques include the measurement of correlated spectra (COSY, HSQC, etc.) as well as identification of spatial vicinity of nuclei for large molecules (not via bonds, nuclear overhauser effect).[39] Nmr spectroscopy is usually carried out in solution. In order to enable the interpretation of spectra special solvents are used. Those solvents are synthesized to carry no protons but deuterium nuclei that do not show nmr activity.

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[3] For detailed information on the principles of nmr spectroscopy see specialized literature and text books (for example ref. [39]).

Solid state nmr techniques also exist, but in this work all measurements were carried out in deuterated solvents.

2.3 Infrared Spectroscopy

Infrared (IR) spectroscopy is another very common and useful technique of analysis. IR spectroscopy is an absorption based technique and as such the Y-axis of a spectrum usually gives either transmittance or extinction. The X-axis usually gives either wavelength, frequency or, most often, wavenumber. The IR spectrum ranges from 400 to 4000 cm^{-1} and is usually displayed from 4000 to 400 cm^{-1} (left to right). It can be divided into two important regions: a) characteristic absorption (4000 - 1500 cm^{-1}); b) fingerprint region (below 1500 cm^{-1}). In the region of characteristic absorption, information about individual functionalities of the molecule subjected to analysis can be obtained. Data of those characteristic absorptions are listed in special databases. Signals in the fingerprint region on the other hand originate from the lattice of the molecule and usually not from individual functional groups. The can be seen as characteristic for a particular molecule.[39] In traditional IR spectroscopy, the sample inside a cuvette or inside a specially prepared pellet is irradiated with infrared light. The light is then absorbed by the molecule and excites vibrational levels. The energy that is absorbed is dependent on the strength of the bond and the mass of the nuclei that are forming the bond that is excited. As such the energy is characteristic and qualitative information about the molecule can be obtained. Another IR technique is based on attenuated total reflection. In this mode, a beam of IR light is directed at a surface in an angle that causes total reflection of the beam. An evanescent field originates at the point of total reflection. The sample is placed behind the surface and interaction of the sample with the evanescent field gives the IR spectrum. The spectra obtained from different modes of measurement are not identical but reveal similar information. It is worth noting, that only vibrations that incur a change of dipole moment are visible in IR spectroscopy[39].

2.4 Mass Spectrometry

In mass spectrometry (MS) information is obtained as the mass/charge ratio of ions formed from the molecule. Figure 6 shows the general structure of a mass spectrometer.
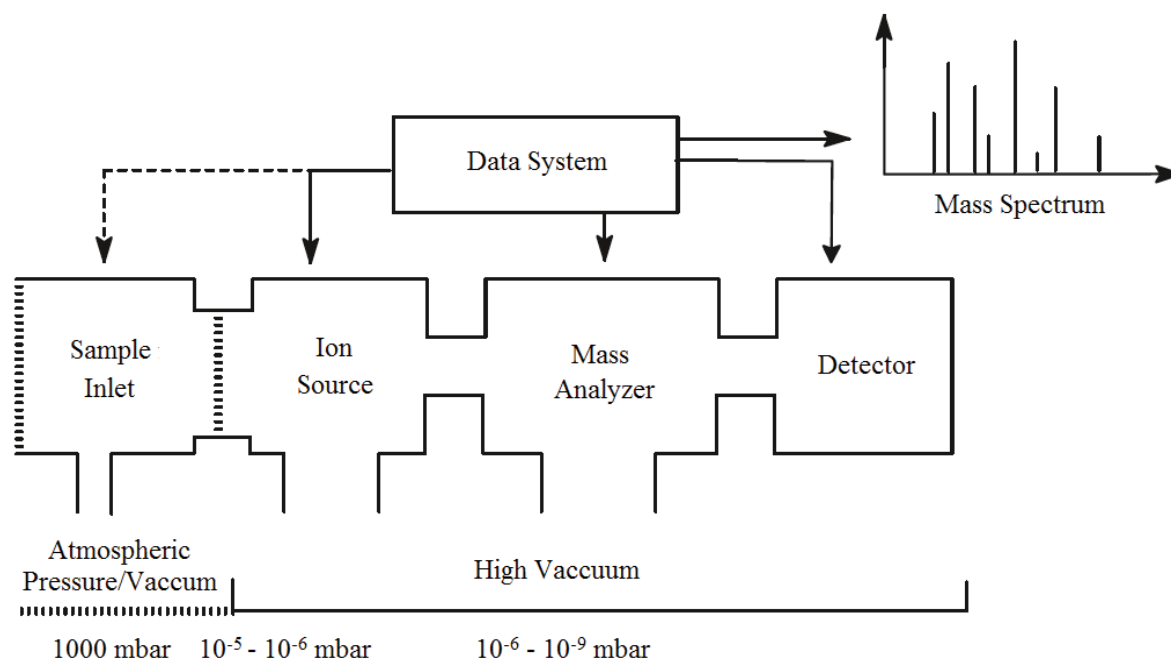

Figure 6 General structure of a mass spectrometer. The modular setup is implied by the different boxes. Figure reproduced and translated from ref. [40].

The basic steps of mass spectrometry are *introduction of the sample, ionization, separation* and *detection*.[40] MS is carried out under reduced pressure to avoid unwanted collision of the ions with gas molecules. To achieve this, mass spectrometers are constructed as given in the general scheme of Figure 6. The steps can be realized in different ways and as such MS instruments are oftentimes modular to adopt them according to the aim of the analysis. One key step is the ionization of the sample. This can be achieved from the condensed phase, in the gas phase or during evaporation. The many different modes of ionization can also incur fragmentation of the molecule or leave it mostly intact. If the molecule is fragmented, it is possible to derive structural information from the pattern of fragmentation. This application is, however, mostly replaced by the more potent but far less sensitive nmr spectroscopy. In this work, MS is used exclusively with a rather soft mode of ionization that produces mostly molecular ions. In this case it is possible to obtain the molecular weight of the sample from MS. Modern MS instruments are extremely

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sensitive and can possess excellent mass resolutions, making trace analysis and determination of the exact elemental composition possible via MS.[39]

2.5 Gas Chromatography

Gas chromatography (GC) is not only a technique of analysis but also one of separation. Like all chromatographic methods it relies on the use of a mobile and a stationary phase. The mobile phase is an inert gas that will carry the sample through a line that is packed with the stationary phase. In order to be separated by GC, samples must be vaporizable without decomposition. The temperature of the line influences the equilibria that cause the chromatographic separation. Both adsorption and distribution equilibria may be utilized for the separation of different fractions of the sample.[41] GC and other chromatographic methods are usually used with some sort of detector in order to identify the different fractions of the sample that have been separated on the column. Detectors commonly applied in GC are for example the thermal conductivity and flame ionization detectors[41].

2.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) or thermogravimetry, as it is also called, "is a technique in which the *mass* of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed."[42] By monitoring the weight of the sample, changes in mass can be determined. Relation of the changes in mass to the temperature where they occur makes it possible to identify components that are released during the thermal treatment by evaporation, e.g. water contained in a sample, or by sublimation and decomposition. TGA may also be coupled with MS (or other analytics) in order to obtain further information about the processes and reactions that result in a change of mass at a given temperature. In this work, TGA was primarily used in order to determine the temperature window for differential scanning calorimetry and to determine the water content of samples.

2.7 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique where "the *difference in heat flow* (power) to a sample (pan) and to a reference (pan) is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is […]"[42] changed. Figure 7 gives the general structure of a DSC instrument.
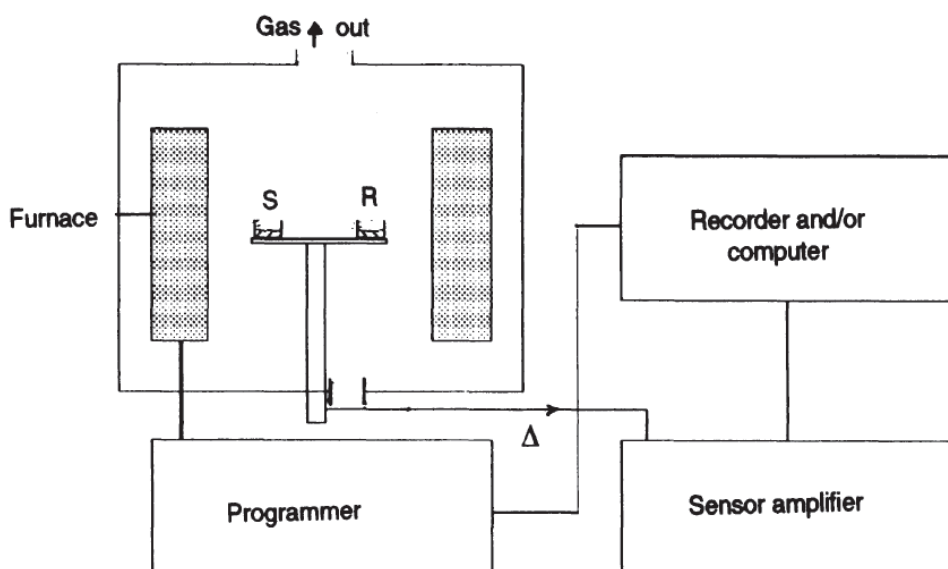

Figure 7 Schematic structure of a DSC instrument. One furnace contains the sample, the other is used as a reference. Δ indicates the differential signal. Figure taken from ref. [42].

There are two different operation modes for DSC that are called power compensated (PC) DSC and heat flux (HF) DSC. In PC DSC sample and reference are kept at the same temperature by heating with two different heat-sources. Since sample and reference are different, the necessary electrical power for heating will differ. This difference in electrical power is measured and displayed in the DSC curve. In HF DSC sample and reference are heated by one heater and as such the resulting temperature will differ. The difference in temperature is then converted into a difference in power for analysis.[42] In DSC, changes within the sample that influence heat capacity or require/release energy will be obvious. As such, melting points, partial crystallization, glass transitions and the like will be visible in the resulting DSC curve. This information is not visible in TGA since such physical changes do not involve a change of mass. DSC is usually conducted in a temperature window by heating to a maximum and cooling to a minimum, with holding times at the end points. As the thermal treatment, including heating rate, may alter the properties of

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the sample in analysis, several cycles are usually measured in order to exclude artifacts.

3 Results and Discussion

3.1 Synthesis of sustainable Ionic Liquids from Pyridinium Zwitterions

3.1.1 Synthesis of 3-Hydroxypyridinium Zwitterions

The formation of 3-hydroxypyridin from furfurylamine under oxidative conditions is a known reaction[43]. Furthermore the formation of N-(1-carboxyethyl)-6-(hydroxymethyl)pyridinium-3-ol, an adduct of 5-(hydroxymethyl)-furfural and alanine, has been identified as a taste enhancing molecule formed during Maillard reaction from glucose and the amino acid[44]. Interest in the taste enhancing ability has resulted in the synthesis of this molecule[44] and the expansion of the synthetic route to include other amino acids[45]. With dependency of chemistry on fossil feedstocks in mind, our group pursued this interesting reaction to produce renewable pyridinium zwitterions. The aim of the synthesis was the application of hydrothermal decarboxylation to produce renewable ionic liquids. We chose to synthesize 3-hydroxypyridinium zwitterions from furfural, which is significantly cheaper than 5-(hydroxymethyl)furfural or furfurylamine and is produced from lignocellulosic biomass in large scale[20]. The synthesis was carried out according to the scheme given in Figure 3 from furfural and amino acids. In this work valine and leucine have been used for synthesis of the respective zwitterions 1A and 1B, as shown in Figure 8.
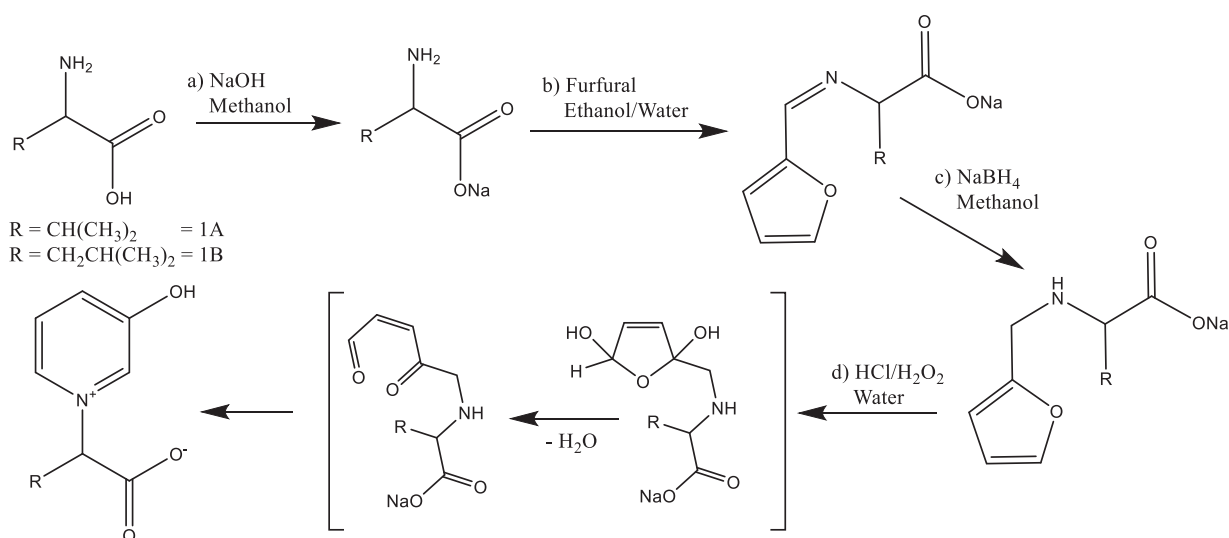

Figure 8 Route applied for the synthesis of the valine and leucine based zwitterions 1A and 1B, respectively.

The amino acid is first converted into the respective sodium salt with sodium hydroxide (a in Figure 8). Then furfural is added to form the corresponding imine (b), which is subsequently reduced by addition of sodium borohydride (c). The so formed

amine is then oxidized via addition of hydrogen peroxide to form the zwitterion (d). The reaction can be carried out in one pot, with removal of the respective solvents by rotary evaporation or freeze drying. We have recently shown, that the synthesis shown in Figure 8 is viable for the production of a library of 3-hydroxy pyridinium based zwitterions that vary by the side chain introduced via the amino acid[19]. The use of starting material from renewable resources is the first step to make a synthesis green. Yet there are a few steps that need be addressed to further improve the sustainability of this reaction. The use of methanol and ethanol as solvents for the reaction is a good approach as both can be obtained from lignocellulosic biomass[46,47]. The use of large quantities of solvents, even if green, is still to be avoided. To contain the use of solvent their possible recycling via distillation was tested and successfully applied in this work without adverse effects. While optimization of the reaction was not the aim of this work, the use of catalysts, especially for the reduction, would further improve the economic footprint of the reaction. Our group recently reported the successful use of a FeNi catalyst for the reduction of imines formed from sodium salts of amino acids and furfural on flow[48], which could complement the synthesis. Since the zwitterions were synthesized in order to test decarboxylation in order to form ionic liquids (see 3.1.2) impurities must also be addressed.

The purification of ionic liquids is challenging since standard means of purification such as distillation are usually not applicable. Although it may be noted that distillation of ILs has been reported at reduced pressure.[49] The least extensive approach for IL purification is usually to keep their application in mind and synthesize them directly in the necessary degree of purity. Apart from borates that may be avoided by catalytic reduction, there is mainly the contamination with sodium and chloride ions as well as water. Water is not problematic since the decarboxylation is carried out in aqueous solution anyway. With the aim of biomass treatment in mind, the presence of chloride is probably not problematic as well. It has been pointed out that ILs containing chloride are suited for the treatment of biomass due to favorable hydrogen bonding ability and size of the chloride anion[29,36]. As such the presence of chloride may even be beneficial for this application. Sodium is unavoidable in the given synthetic approach. Table 1 lists the yields of the synthesized zwitterions.

Code	Sidechain	Amino Acid	Yield [%]
1A	$CH(CH_3)_2$	valine	41.3 %
1B	$CH_2CH(CH_3)_2$	leucine	38.9 %

Table 1 Yields of the synthesized zwitterionic compounds, sidechain and amino acid used.

3.1.2 Conversion of Zwitterions to Ionic Liquids

In order to synthesize renewable pyridinium based ionic liquids from the zwitterions presented in the previous section their negative charge must be removed. There are several approaches possible to convert the zwitterions into cations. This work focusses on the decarboxylation of the zwitterions.

The decarboxylation of amino acids has received a lot of attention in the past. Several important chemicals, such as 1,4-diaminobutane (one of the monomers for Nylon-4,6) can be derived from biomass streams with the aid of this reaction[21]. In order to achieve decarboxylation of amino acid moieties, the use of enzymes or catalysts, such as (aromatic) aldehydes, is usually necessary[21,50]. Recently, our group published the successful decarboxylation of imidazolium zwitterions synthesized from amino acids without the use of catalysts or enzymes. In this case the imidazolium ring is formed via a modified Debus-Radziszewski reaction using the nitrogen atoms of the amino acids and the resulting imidazolium ring is 1,3-*N,N*-disubstituted with amino acid sidechains. The decarboxylation of those moieties was consecutively carried out under hydrothermal conditions in the presence of an acid with good yields using a flow reactor[18]. A simplified mechanism illustrating the necessity for an acid during the reaction is illustrated in Figure 9.
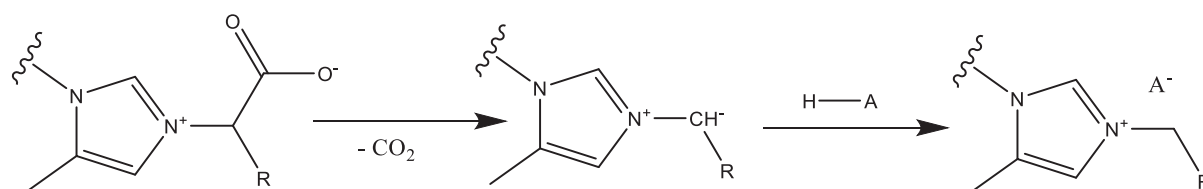

Figure 9 Decarboxylation of imidazolium zwitterions. The reaction is carried out under hydrothermal conditions. The acid (H-A) compensates the negative charge that forms during decarboxylation and provides the anion for the ionic liquid produced. Picture reproduced from ref. [19].

Amino acids could not be decarboxylated under the same conditions[18]. This indicates that the imidazolium ring plays a crucial role during decarboxylation. The catalytic mechanism of aromatic aldehydes in the decarboxylation of α-amino acids

includes the formation of an imine. The dissociation of the C-C bond between carbonyl carbon and the α-carbon during decarboxylation leaves a negative charge on the α-carbon. In the case of aromatic aldehydes as catalysts, it has been pointed out that this charge can be stabilized over the α-carbon, the C=N bond and the aromatic ring of the aldehyde.[50] The imidazolium ring may promote the decarboxylation in a similar way.[18,19]

In this work, the procedure originally developed for imidazolium zwitterions was successfully applied to pyridinium zwitterions. The synthesis of ionic liquids from pyridinium zwitterions in this fashion is appealing, because the zwitterions already resemble the structure of the cation of pyridinium based ionic liquids. This makes the use of quaternization reactions to convert an aromatic pyridine into the corresponding *N*-substituted pyridinium cation superfluous, but on the other hand the betaine nature of the zwitterion is problematic. Using a flow reactor, the decarboxylation of the pyridinium zwitterions was carried out using a dissolution of the zwitterion and an acid under hydrothermal conditions. The use of different acids in this reaction is possible which allows for a wide variety of anions within the final IL structure and accesses the designer solvent character of ionic liquids. The reaction is optimal at a temperature of 250 °C and a pressure of 120 bar. As such the temperature necessary for optimal decarboxylation results was about 50°C lower than in the case of imidazolium zwitterions[18]. This may be explained by the presence of only one carboxylic acid group in the case of pyridinium zwitterions in comparison to the two groups in the case of imidazolium zwitterions. It is also possible that the pyridinium ring better stabilizes the negative charge, or that both effects contribute. To yield ionic liquids, zwitterion 1B was chosen for the decarboxylation with different acids. Figure 10 shows the decarboxylation of the pyridinium zwitterions under hydrothermal conditions.
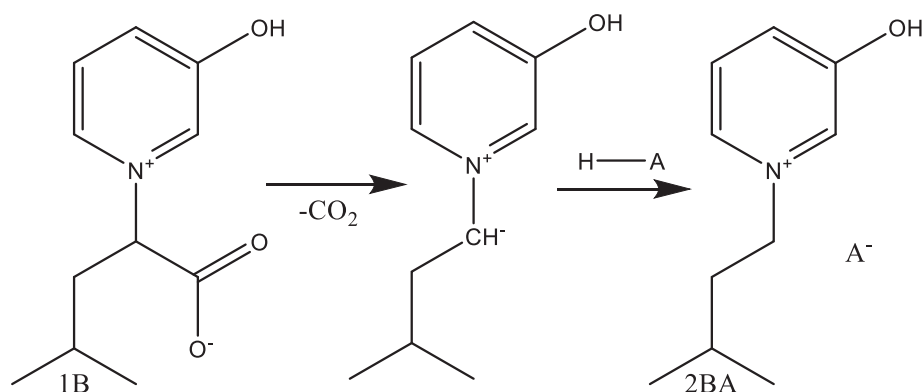
Figure 10 Scheme of the decarboxylation carried out under hydrothermal conditions (120 bar, 250 °C) in a flow reactor. Different acids (H-A) were used.

Using this approach, three different ionic liquids were synthesized in good yields. Table 2 lists the yields and glass transition temperatures for the respective decarboxylation reactions.

Code	Acid	Yield [%]	T_G [°C]
2BAc	acetic acid (2 eq.)	80.7	-32.0
2BLac	lactic acid (1 eq.)	84.0	-6.0
2BSuc	succinic acid (1 eq.)	82.4	-11.7

Table 2 Decarboxylation of pyridinium zwitterions: Acids used to compensate the negative charge and produce the counter ion, yields of the reactions and glass transition temperatures (T_G) of the respective ionic liquids.

All of the substances formed in this reaction are room temperature ionic liquids. Hydrothermal decarboxylation therefore seems to be a very useful and efficient way to form ionic liquids from the zwitterionic compounds. The fact that it can be done on flow even underlines this, as rather large quantities can be synthesized efficiently with the use of continuous flow reactors. Also the use of different acids opens a simple pathway to a variety of ionic liquids. Naturally the decarboxylation removes the stereocenter on the amino acid sidechain. It is interesting to see that the glass transition temperature of the three ILs varies over more than 25°C. This nicely illustrates the possibility to tune individual characteristics of ILs by simple changes in their composition. In this case glass transition temperature can be tuned by variation of the counter ion.

3.2 Application of biomass derived Ionic Liquids

3.2.1 Treatment of lignocellulosic Biomass

The first patent concerning dissolution of cellulose with ionic liquids was issued only about 20 years after their discovery[51], but it was not until the beginning of the 21st century that this area of research gained renewed attention[52]. The possibility to tune ionic liquids in their characteristics and the enormous number of available ion combinations makes them excellent candidates for the dissolution of biomass. Also the diversity of biomass and treatment methods reveals a lot of possible approaches. As such, this research topic has received a considerable amount of attention, but there is still a lot to do. As discussed in the introduction, a variety of factors influence the interactions between lignocellulosic biomass and ionic liquids and as such the ability of an IL to dissolve or deconstruct biomass. The aim of this chapter was to evaluate the ability of 1,3-*N,N*-diethylimidazolium acetate[4] (EEIMOAc), pure and in combination with other solvents (organic electrolyte solutions), as possible solvent systems for the dissolution or fractionation of lignocellulosic biomass obtained from beech wood and coconut shell.

Since particle size severely influences the surface area and thus the process of dissolution, the samples were ball milled before treatment. The samples used consisted of beech wood obtained from GOLDSPAN® smoke, while coconut shell material was obtained from coconuts bought in a local supermarket. Both samples were ball milled prior to use. Water content was accessed via thermogravimetric analysis and determined to be 2.5 wt.% and 2.1 wt.% for beech and coconut material after drying, respectively. The ionic liquid, in turn, was characterized by a water content of about 14.1 wt% (determined by TGA). Coconut shell was chosen since seed coats may contain more linear types of lignin, as recently reported by Ragauskas et. al., which would be easier to deconstruct or dissolve[33]. The experimental procedure chosen was inspired by the assessment of disintegration kinetics of wood chips done by Viell and Marquardt[53] but adapted to the needs and conditions of this work.

In order to choose the right approach and make necessary adaptations, a series of preliminary experiments was carried out. During those experiments, several solvents

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[4] Obtained from IoLiTec Ionic Liquids Technologies GmbH

and conditions were tested for their applicability for biomass treatment. Among the solvents tested were ethanol, 1- and 2-propanol and dimethyl sulfoxide (DMSO). Among all of them DMSO yielded the best results, which is why it was chosen for the later experiments. Apart from the screening of different solvents and temperatures, the use of a simple espresso machine for biomass extraction was tested. Since the preparation of espresso is basically the treatment of biomass with water at elevated temperature and pressure in order to extract ingredients from it, a coffee machine is basically a device for hydrothermal extraction. Unfortunately extraction could not be achieved in a satisfying manner using this approach. The use of such a simple device for the purpose of biomass extraction is still alluring, but several problems require technical modifications on the machine in order to improve the results, which was beyond the scope of this work. Modifications should include prolongation of the contact time of the solvents with the biomass and a better sealing of the device to avoid the loss of pressure while working with solvents other than water.

After carrying out the preliminary screening, four extraction experiments were performed. IL-B and IL-C refer to the extraction of beech wood and coconut shell with EEIMOAc, respectively. IL/D-B and IL/D-C refer to the extraction of beech wood and coconut shell with the organic electrolyte solution formed by the dissolution of EEIMOAc in DMSO, respectively. In order to achieve biomass dissolution, 4.9 wt.% biomass were dispersed in the solvent and stirred for 24 hours at 120 °C. Table 3 and Table 4 list the constitution of the four samples prepared for extraction as well as the codes assigned to them.

Run	Biomass	Mass [g]	Solvent	Mass [g]	Loading [wt.%]
IL-B	Beech	0.2511	EEIMOAc	5.1533	4.9
IL-C	coconut shell	0.2436	EEIMOAc	4.9645	4.9

Table 3 Types of biomass used for the treatment of biomass with 1,3-diethylimidazolium acetate as well as masses used. *Loading* denotes the mass of biomass used in relation to the mass of solvent used.

Run	Biomass	Mass [g]	Solvent 1	Mass [g]	Solvent 2	Mass [g]	Loading [wt. %]
IL/D-B	Beech	0.2513	EEIMOAc	2.1918	DMSO	2.9477	4.9
IL/D-C	Coconut	0.264	EEIMOAc	2.1142	DMSO	3.2901	4.9

Table 4 Types of biomass and solvent used for treatment of biomass with the chosen organic electrolyte system as well as masses used. *Loading* denotes the mass of biomass used in relation to the mass of solvents used.

Figure 11 gives an overview of the procedure that was chosen for the separation of three solid fractions from the mixture (labelled *M* in Figure 11, see 5.4 for the exact procedure). The intended complete dissolution of the biomass was not achieved. M showed a dispersed fraction that could not be separated due to the high viscosity of the gel. This fraction was observed in all four experiments carried out. In order to facilitate separation, a solution of ethanol and acetone (1:1, v/v, called *PS* for brevity) was added to M. The resulting solution was filtered, resulting in the separation of the first solid fraction F1. The filtrate was concentrated by rotary evaporation to yield the first filtrate L1, to which PS was added to induce further precipitation. Consecutive filtering yielded the second solid fraction F2. The filtrate was concentrated by rotary evaporation to yield L2. Addition of water precipitated the third solid fraction F3 that was recovered by centrifugation. F1 and F2 were washed with the PS and F3 was washed with water. All solid fractions were dried at 38 °C under reduced pressure. In order to compare the solid fractions obtained to other biomass samples, ATR-IR spectra of the fractions F1 through F3 were recorded.
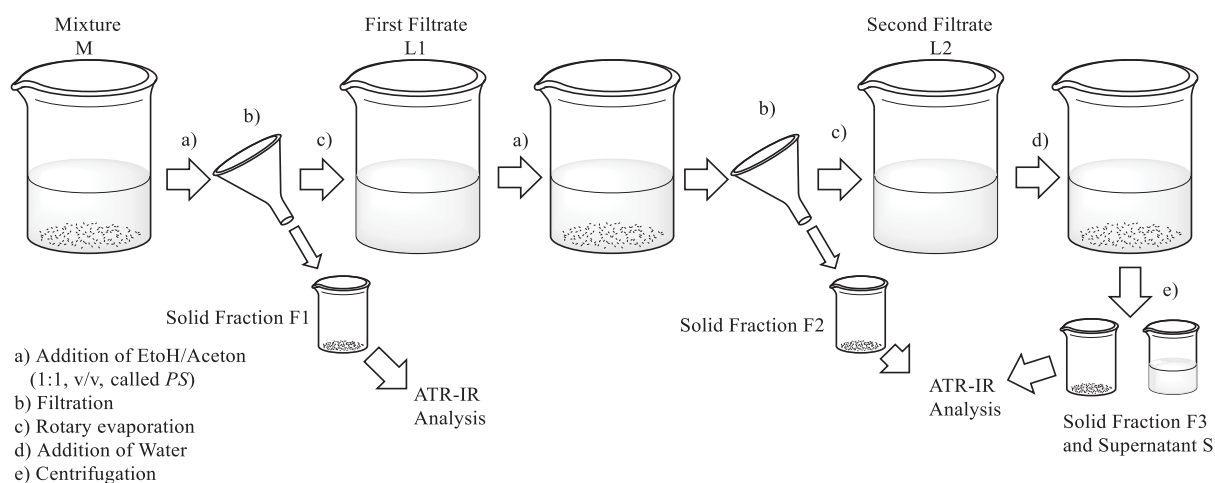

Figure 11 Flowchart of the biomass treatment carried out in this work. The mixture M was obtained after stirring and heating the mixture of biomass and ionic liquid/organic electrolyte solution. After addition of ethanol/acetone (1:1. v/v) a solid fraction F1 was separated by filtration. The filtrate was concentrated by rotary evaporation to yield L1. Addition of ethanol/acetone induced precipitation of a solid fraction F2 that was recovered by filtration. Rotary evaporation of the filtrate yielded F2. Addition of water induced the precipitation of a third solid fraction F3 that was recovered by centrifugation.

Table 5 lists the masses of the fractions F1 through F3 for the four experiments, respectively.

	IL-B	IL-C	IL/D-B	IL/D-C
F1	0.3715	0.2100	0.2673	0.2571
F2	0.0336	0.0185	0.0161	0.0591
F3	0.0098	0.0178	0.0052	0.0324

Table 5 Masses of the three fractions obtained by treatment of beech wood and coconut shell material.

The fractions F1 obtained for all runs must contain residual IL due to their high weight. In order to evaluate the ATF-IR spectra of fractions F1 through F3 for all four experiments, ATF-IR spectra of the ball milled but otherwise untreated biomass samples were acquired as references. Also spectra of EEIMOAc, DMSO and the ethanol/acetone solution were acquired as references. Characteristic peaks for all substances were identified and labelled in order to compare the reference spectra to the spectra of fractions F1 through F3 for each run[5].

For each of the four experiments, the spectra of F1, F2 and F3 were then compared to the reference spectra in order to identify deviations from the spectrum of the untreated biomass. For brevity, only the results will be summarized. Firstly, it has to be noted that the spectra of the untreated biomass samples exhibit only little difference compared to each other. There is only one noteworthy peak at around 1270 cm^{-1} which is only visible in the case of coconut shell material (see Figure 14). Secondly, the spectra obtained from fractions F1, F2 and F3 of the beech wood treatment with pure ionic liquid (IL-B, see Figure 16) show now deviation from the spectra obtained from fractions F1 to F3 of the beech wood treatment with the organic electrolyte solution (IL/D-B Figure 17). The same applies to the experiments conducted on coconut shell material (IL-C, see Figure 18 and IL/D-C, see Figure 19). This indicates that the transition from pure IL to organic electrolyte solution does not significantly influence the quality of the fractions obtained. However, the change of the solvent system does influence the quantity of each fraction obtained. Interestingly, the mass of fractions F2 and F3 is higher in the case of coconut shell material and lower in the case of beech wood when the treatment is carried out with organic electrolyte solution instead of pure IL.

Comparison of the individual fractions of all runs to the reference spectra revealed that fraction F1 does contain residual ionic liquid. This indicates that the washing

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[5] Table 9 in section 5.6 lists the relevant peaks. The spectra with labelled peaks can also be found in 5.6.

procedure chosen for that step requires optimization. The spectra of fractions F2 of all runs also deviate from the spectra of untreated biomass. Even though the spectra of F2 seem reminiscent of the spectra of EEIMOAc at first glance, comparison of the respective peaks' wavenumbers reveals, that the spectrum of F2 is more similar to the spectra of the original biomass than to that of ionic liquid (see also Table 9 in section 5.6). This indicates that F2 does not contain residual solvents from treatment but has undergone some changes by treatment.

The most interesting result is visible in F3. The spectra of fraction F3 obtained from beech wood and coconut shell differ slightly from each other, with the already mentioned peak at around 1270 cm^{-1} being much stronger in coconut shell material. This peak might result from C-O stretch vibrations as caused from ethers and alcohols. Comparison of the spectra of F3 to the references reveals no striking similarities to the solvents used. Also the spectra of F3 are significantly different from the original biomass samples. The spectra of all fractions F3 show bands in regions that are characteristic for aromatics and C-O vibrations. Some peaks are especially noteworthy. The three peaks visible in the region between 1400 and 1500 cm^{-1} may be interpreted as in-ring stretch vibrations of aromatic rings, which is supported by the rather strong band at about 1590 cm^{-1} visible in all F3 spectra. The spectra also show bands in between 1000 and 1320 cm^{-1}, a region that is characteristic for the C-O stretch vibrations of alcohols, esters, ethers and carboxylic acids. Other vibrations that may be visible in those regions include halides and amines, which cannot be contained in the analyzed samples by virtue of their treatment and that can as such be excluded from the discussion. The presence of aromatic vibrations and C-O stretch vibrations hints at the presence of lignin in the fractions F3 of all four experiments. In order to further investigate this, the spectra were compared to samples produced by alkaline extraction methods within our group[6].

Figure 12 shows the spectra of fractions F3 of run IL-B and IL-C in comparison to lignin extracted with alkaline extraction methods and cellulose.
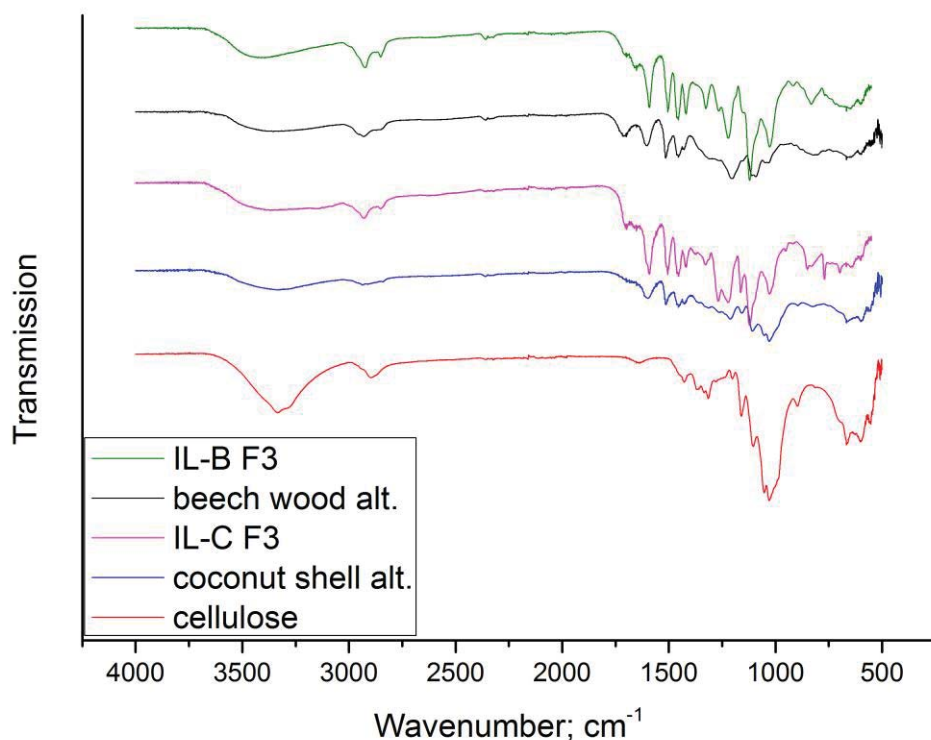
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[6] Preparation see 5.1

Figure 12 Spectra of the fractions F3 obtained from treatment of beech wood and coconut shell with EEIMOAc and lignin extracted from the same biomass sources by alkaline extraction (beech wood alt. and coconut shell alt.). For further comparison, a spectrum of cellulose is also added.

It is obvious, that the samples IL-B F3 and IL-C F3, as well as the references from alkaline extraction are different from the cellulose sample. The peaks of the samples obtained by the extraction of biomass with ionic liquids are much sharper than those in the spectra of lignin prepared by alkaline extraction. It has to be noted that the coconut shell based lignin from alkaline extraction does not show the large peaks around 1270 and 1220 cm^{-1}. Apart from that, the spectra are very similar to each other, showing peaks in the same regions. This further indicates that the obtained fractions F3 may be lignin.

In order to gather further evidence for the presence of lignin in fractions F3, elemental constitution was analysed and compared to elemental analysis of technical lignins published in literature. The value of oxygen was calculated by subtraction of the sum of S, N, H and C from 100 %. The values are averages calculated from two runs of repeat determination.

The composition of technical lignins varies greatly by way of their preparation, as seen in Table 6 in the case of calcium lignosulfonate in comparison to the other technical lignins. Interestingly, the four fractions obtained in this work do not vary greatly from each other, with the coconut shell based fraction containing slightly larger amounts of carbon and nitrogen. In comparison to the references, the fractions obtained seem to be most similar to organosolv lignin, possessing similar carbon, hydrogen and oxygen content. This may also be seen as further evidencing the presence of lignin in the fractions F3.

Fraction	C	H	N	S	O
IL-B F3	60.23	6.607	1.285	0.6925	31.19
IL/D-B F3	60.45	7.344	1.255	0	30.96
IL-C F3	61.25	5.642	2.410	0	30.70
IL/D-C F3	62.58	7.195	2.870	0.0750	27.28
KL	65.00	5.410	0.050	1.2500	28.24
SAL	65.00	6.120	0.170	0	28.64
LS	44.84	5.150	0.020	5.8500	44.14
OSL	63.51	5.550	0.020	0	30.92

Table 6 Elemental composition of different technical lignins[54] and the fractions F3 obtained from biomass treatment in this work. KL: Kraft Lignin (softwood), SAL: Soda-Anthraquinone Lignin (long fiber plants), LS: Calcium Lignosulfonate (no source given), OSL: Organosolv Lignin (*Miscanthus Sinensis).*

Concluding the analysis and comparisons carried out it can be stated, that the recovered fractions F3 contain lignin. Table 7 gives the weight of fractions F3 in relation to the biomass initially used.

	IL-B F3	IL/D-B F3	IL-C F3	IL/D-C F3
initial weight of biomass	0.2511	0.2513	0.2436	0.2640
mass of fraction	0.0098	0.0052	0.0178	0.0324
wt.% recovery	3.9	2.1	7.3	12.3

Table 7 Overview of the isolated weight of fractions F3 for all runs. The table also shows the recovered weight as percentage of the initially used biomass (wt.% recovery).

From Table 7 it is visible, that the use of coconut shell material seems to be favorable for the separation of lignin. Also the use of DMSO in conjunction with EEIMOAc seems to have beneficial effects on the recovery of lignin from coconut shell material, as the recovery of lignin is largest in this case, with as much as 12.3 wt.%. This is especially beneficial since the use of organic electrolyte solutions can aid to

significantly reduce the cost of treatment by reducing the cost of the chemicals used in comparison to pure IL. In addition the organic electrolyte solution exhibits a lower viscosity than the pure IL, which is favorable for the dissolution processes and handling.

3.2.2 Sonogashira-Hagihara Coupling of Iodobenzene and Phenylacetylene

The application of ionic liquids for carbon-carbon cross coupling reactions is documented in literature with Heck-reaction and others being rather common by now. Sonogashira-Hagihara coupling on the other hand has been reported with the use of catalyst immobilized on a certain substrate[55] or as part of a metalorganic framework or within a poly (ionic liquid)[56]. The use of an IL as the replacement of the traditional solvent is usually not reported. Just recently the use of an IL with integrated basic group was reported for successful Sonogashira-Hagihara coupling without the use of copper or an external base, which highlights the great potential of ILs as designer solvents for specific purposes[57]. We recently reported the use of a hydrophobic ionic liquid synthesized from 2BAc by anion metathesis with lithium bis((trifluoromethane)sulfonimide for heck reaction[19]. In order to test the applicability of this hydrophobic ionic liquid for Sonogashira-Hagihara coupling, the same ionic liquid was synthesized. As a model system, the reaction of iodobenzene and phenylacetylene was chosen. Palladium acetate was chosen as the catalyst and tested (see Figure 13).
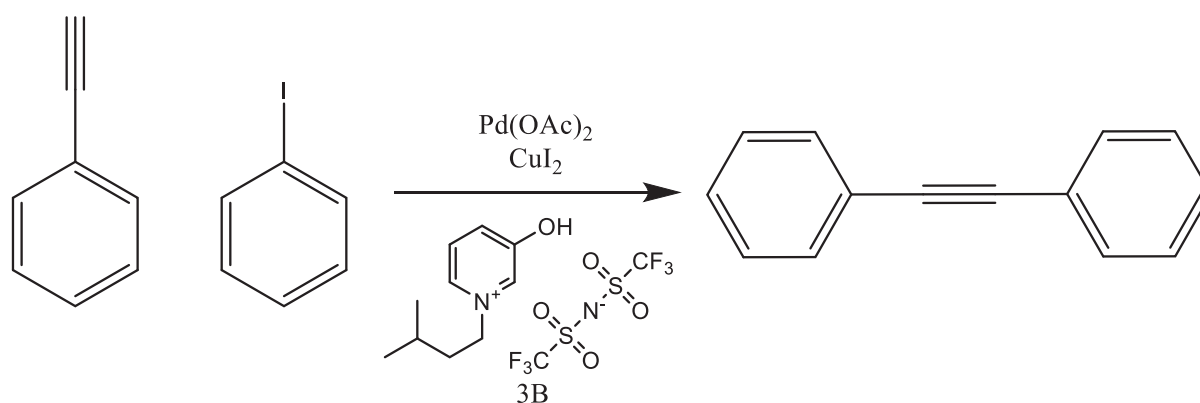

Figure 13 Reaction scheme for the Sonogashira-Hagihara coupling of phenylacetylene and iodobenzene using palladium(II)acetate and copper(II)iodide in the ionic liquid 3B.

Since copper iodide free Sonogashira reactions are reported [58], the reaction was first tested without copper(II)iodide but no conversion was observed. The reaction mixture was worked up and after addition of copper(II)iodide to the already used reaction mixture and addition of new starting material, good conversion was observed. The system was then recycled two more times but the conversion decreased gradually from about 90 % to about 60 %. This may be caused by accumulation of iodide in the ionic liquid. Another possible explanation could be leaching of the catalyst. Concluding this experiment, it has to be said, that the use of the hydrophobic ionic liquid synthesized from 2BAc is suitable for Sonogashira-Hagihara coupling using simple palladium(II)acetate, but the recyclability of the system requires further improvement to allow more cycles and a higher yield. The use of imidazolium based ionic liquids which are known for their ability to form *N*-heterocyclic carbenes that can stabilize palladium species[13] seems more promising for palladium catalyzed cross coupling reactions.

4 Conclusion and Outlook

The convenient synthesis of 3-hydroxypyridinium zwitterions from furfural and amino acids was presented. The so obtained zwitterions can be converted to ionic liquids via decarboxylation under hydrothermal conditions. The synthesis of pyridinium moieties in this fashion is very appealing because the zwitterions already resemble the pyridinium cations from modern ionic liquids. As such there is no need for quaternization reactions, which could be especially interesting to make halide free ILs. The ion pairs obtained by hydrothermal decarboxylation were ionic liquids in all cases, with glass transition temperatures below 0°C. Decarboxylation of the zwitterions could be carried out under rather mild conditions in a flow reactor, whereas amino acids could not be decarboxylated with the same setup, indicating a catalytic effect of the pyridinium system. The synthesis of zwitterions seems to be expandable to other amino acids, and maybe amines suggesting the possibility to synthesize a library of biomass derived fine chemicals and ionic liquids. Also the use of furfural analogue chemicals may prove to be interesting in terms of zwitterion design. While beyond the idea of using biomass derived starting material for the production of fine chemicals, it has to be noted that the synthesis may also be expanded to non-biomass derived molecules as well. One ionic liquid synthesized was successfully tested for Sonogashira-Hagihara cross-coupling.

The use of ionic liquids for biomass treatment is a hot topic in research. In this work, the use of 1,3-*N,N*-diethylimidazolium acetate, which is also available from renewable resources, for the extraction of beech wood and coconut shell material was tested and monitored by IR spectroscopy. The separation of several solid fractions was achieved of which two were significantly changed in terms of IR spectra. Comparison to lignin extracted via alkaline extraction, elemental analysis and interpretation of spectral data suggest, that at least one fraction is lignin. Furthermore the results indicate that seed coats are an interesting material to test for biomass extraction and other materials such as walnut or cocoa shells just wait to be tested. The use of dimethyl sulfoxide in conjunction with the ionic liquid even enhanced the results of extraction in the case of coconut shells, which implies that the use of ion pairs that may not be ionic liquids for the formation of organic electrolyte solutions and biomass extraction may be promising, making use of the best characteristics of organic solvents and ionic liquids.

5 Additional Information

5.1 Chemicals, Materials and Reference Samples

All chemicals were used as supplied with the exception of furfural, which was distilled under reduced pressure prior to use and 1,3-*N,N*-diethylimidazolium acetate, which was stirred at 70 °C for up to 2 days with water and activated carbon, filtered and freeze dried to yield a pale yellow, clear liquid. Water used for preparation and treatment was purified using an Integra UV Plus Reinstwasseranlage. 1,3-*N,N*-diethylimidazolium acetate was supplied by IoLiTec Ionic Liquids Technologies GmbH, Salzstrasse 184, D-74076 Heilbronn, Deutschland.

Beech wood was supplied by GOLDSPAN® smoke, Brandenburg, Germany, coconut shell was obtained from coconuts bought in a local supermarket, both were ball milled using a RETSCH@ MM400 ball mill at a frequency of 20 Hz.

The IR reference sample for beech wood lignin was prepared by our group by hydrothermal treatment at 220°C for 15h in a stainless steel autoclave. 5.8 g of $Ba(OH)_2$ and 20 ml of distilled water were added to 2.2 g of beech wood. The autoclave was sealed and put in an oven. After cooling down the autoclave, the dark liquor was filtered over paper and the pulp was washed with 1M HCl and water. When the pH of the water was neutral, the pulp was dried overnight at 38°C, under reduced pressure. The dried solid was dissolved in THF, the insoluble part was filtered away on paper and the THF soluble lignin is dried overnight at 38°C in a vacuum oven.

The IR reference sample for coconut shell lignin was prepared by our group by heating of 80 g coconut shell material to 175°C for 12h in a stainless steel autoclave in the presence of 500 ml of water and 30g of NaOH. After cooling down the autoclave, the dark liquor was filtrated on paper and 4M HCl was added to the liquor to a pH of 7-6. The mixture was aged overnight at room temperature and the precipitate was recovered, washed with water and dried overnight at 80°C.

5.2 Analytics

Nmr spectroscopy was carried out either on an BRUKER AVANCE DPX 400 using a BBO head and an ULTRASHIELD 400 magnet and on an BRUKER AVANCE 3i using a Prodigy semi cryo head and an ASCEND 400 magnet. ATR FT-IR spectra were measured on a Thermo Scientific FT-IR spectrometer (Nicolet™ iS5 Spectrometer equipped with an iD5 ATR accessory). Thermogravimetry was carried out on a Netzsch TG 209 F1 Libra at a heating rate of 10 K/min under nitrogen atmosphere at 20 ml/min. Elemental analysis was performed using a Vario Micro device. DSC of the ionic liquids was carried out on a Mettler-Toledo DSC1 System.

5.3 Synthesis and Characterization of Zwitterions and Ionic Liquids

5.3.1 General Procedure for the Synthesis of Pyridinium Zwitterions

A suspension of amino acid (40 mmol) in methanol was prepared. To this suspension a solution of sodium hydroxide (1.6 g, 40 mmol) in 40 ml methanol was added under stirring. The solvent was removed by rotary evaporation. The resulting amino acid sodium salt was dissolved in 100 ml ethanol/water (96:4, v/v). Furfural (40 mmol) was added under stirring and the mixture was stirred at 55 °C for 1 hour. The solvent was removed by rotary evaporation and the residue was freeze dried to remove water. The residue containing the imine was dissolved in 100 ml methanol and cooled to 0 °C using an ice bath. Sodium borohydride (1.51 g, 1.05 eq.) was slowly added under stirring. The mixture was left to warm to room temperature and stirred for another hour. The solvent was removed by rotary evaporation. The residue was dissolved in 50 ml 3M HCl and aqueous hydrogen peroxide solution (30 %, 8 ml) was added. The mixture was refluxed for 30 minutes, cooled to room temperature and neutralized using conc. ammonium hydroxide solution. Water was removed by rotary evaporation and the crude product was heated in ethanol. The solid residue was filtered and the product recovered from the ethanol phase by rotary evaporation. The solvents used in this reaction have been reused after removal by rotary evaporation.

5.3.1.1 2-(3-hydroxypyridin-1-ium-1-yl)-3-methylbutanoate (1A)
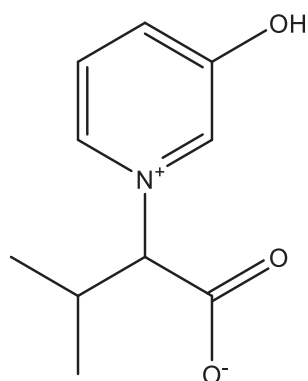
Yield 38.9 %

1H NMR (400 MHz, Deuterium Oxide) δ 8.26 – 8.13 (m, 2H), 7.84 – 7.62 (m, 2H), 4.50 (d, J = 9.7 Hz, 1H), 2.45 (dp, J = 9.7, 6.7 Hz, 1H), 0.98 (d, J = 6.6 Hz, 3H), 0.71 (d, J = 6.6 Hz, 3H). 13C NMR (101 MHz, Deuterium Oxide) δ 172.52 , 158.81 , 133.77 , 132.78 , 132.44 , 127.87 , 82.25 , 31.32 , 18.63 , 17.43. ESI-MS (m/z): [M+H]+ calcd. for C10H13NO3: 196.09, found, 196.22

5.3.1.2 2-(3-hydroxypyridin-1-ium-1-yl)-4-methylpentanoate (1B)
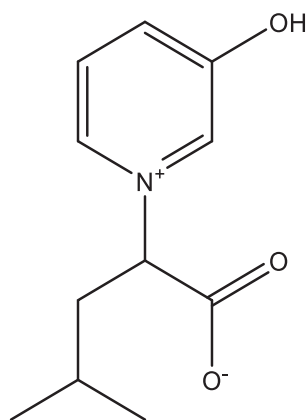
Yield: 41.3 %

1H NMR (400 MHz, D2O) δ 8.32 – 8.27 (m, 2H), 7.77 – 7.70 (m, 2H), 5.02 (dd, J = 10.4, 5.2 Hz, 1H), 2.21 – 2.06 (m, 2H), 1.31 – 1.22 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H); 13C NMR (101 MHz, D2O) δ 173.38, 157.86, 134.63, 132.58, 132.51, 128.17, 74.10, 40.66, 24.32, 22.19, 20.39; ESI-MS (m/z): [M+H]+ calcd. for C11H15NO3: 210.11, found, 210.10

5.3.2 General Procedure for the Synthesis of ILs by Decarboxylation

5 ml of an aqueous solution containing compound 1B (0.1 M) and the respective acid was prepared and injected into the flow reactor. The mixture was reacted at 250 °C and 120 bar for 4 min, collected and diluted with water. The product was obtained after extraction with diethyl ether and freeze drying.

#### 5.3.2.1 *3-hydroxy-1-isopentylpyridin-1-ium Acetate 2BAc*
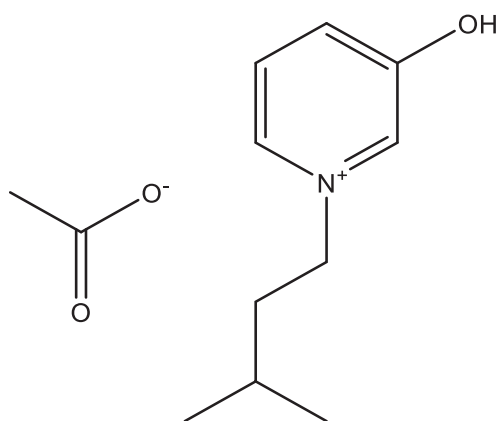
Yield: 80.7 %

The 0.1 molar solution of compound 1B was prepared to contain two equivalents of acetic acid.

1H NMR (400 MHz, D2O) δ 8.14 – 7.92 (m, 2H), 7.76 – 7.56 (m, 2H), 4.43 (t, J = 7.7 Hz, 2H), 1.95 (s, 3H), 1.86 (q, J = 7.4 Hz, 2H), 1.61 (dt, J = 13.4, 6.7 Hz, 1H), 0.95 (d, J = 6.6 Hz, 6H); 13C NMR (101 MHz, D2O) δ 179.48, 160.78, 133.09, 132.55, 132.38, 128.01, 60.04, 39.35, 24.85, 22.04, 21.29; ESI-MS *(m/z):* [M]+ calcd. for C12H12NO+: 166.12, found, 166.21; Tg (DSC) = -32.04 °C

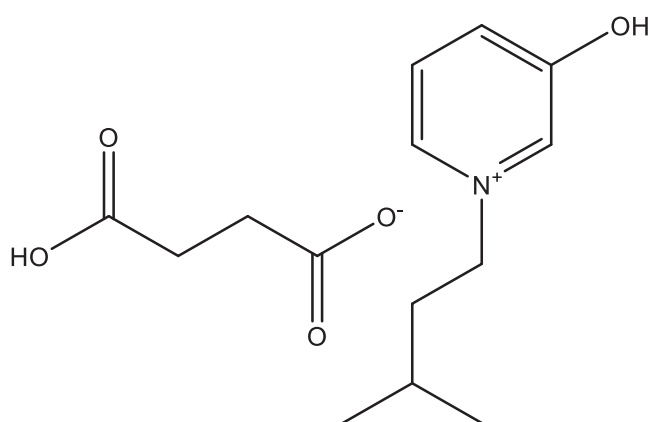#### 5.3.2.2 *3-hydroxy-1-isopentylpyridin-1-ium Lactate 2BLac*
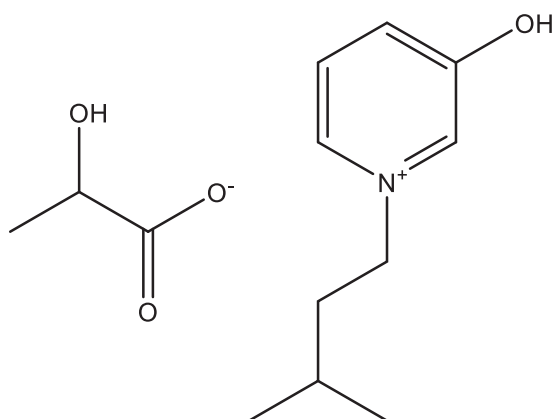
Yield: 84.0 %

The 0.1 molar solution of compound 1B was prepared to contain one equivalent of lactic acid.

1H NMR (400 MHz, D2O) δ 8.28 – 8.22 (m, 2H), 7.84 – 7.73 (m, 2H), 4.48 (t, *J* = 7.7 Hz, 2H), 4.15 (q, *J* = 6.9 Hz, 1H), 1.85 (q, *J* = 7.4 Hz, 2H), 1.59 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H); 13C NMR (101 MHz, D2O) δ 180.29, 157.02, 135.34, 132.52, 131.61, 128.38, 67.29, 60.39, 39.33, 24.86, 21.28, 21.26, 19.57; ESI-MS *(m/z):* [M]+ calcd. for C12H12NO+: 166.12, found, 166.17; Tg (DSC) = -6.0 °C

### 5.3.2.3 3-hydroxy-1-isopentylpyridin-1-ium Succinate 2BSuc

Yield: 82.4 %

The 0.1 molar solution of compound 1B was prepared to contain one equivalent of succinig acid.

1H NMR (400 MHz, D2O) δ 8.43 – 8.03 (m, 2H), 7.95 – 7.62 (m, 2H), 4.46 (t, *J* = 7.7 Hz, 2H), 2.53 (s, 4H), 1.84 (q, *J* = 7.1 Hz, 2H), 1.58 (dt, *J* = 13.0, 6.5 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 6H); 13C NMR (101 MHz, D2O) δ 179.08, 158.79, 134.04, 132.79, 131.98, 128.21, 60.23, 39.35, 30.72, 24.87, 21.29; ESI-MS *(m/z):* [M]+ calcd. for C12H12NO+: 166.12, found, 166.23 Tg (DSC) = -11.7 °C

5.3.3 Synthesis of 3-hydroxy-1-isopentyl-pyridin-1-ium bis ((trifluoro-methyl)sulfonyl) amide 3B

Ionic liquid 2BAc (0. 0572 mol) was dissolved in 50 ml of deionized water and lithium bis(trifluoromethane)sulfonimide (0,085725 mol, dissolved in 50 ml deionized water) was added. The mixture was stirred overnight. The crude product 3B formed as a dark brown liquid insoluble in water. The ionic liquid was separated and washed with water 5 times to yield 3B (9.044g 0.0203 mol).
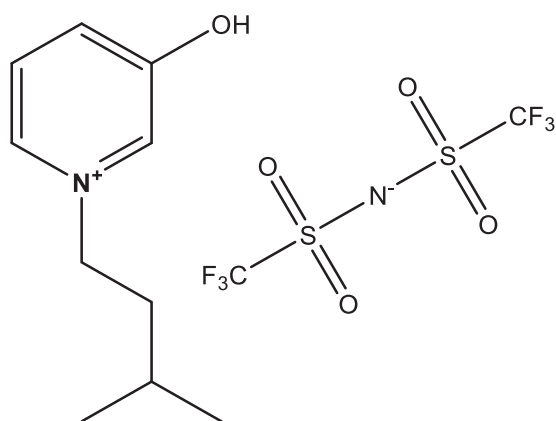
Yield: 35.5 %

1H NMR (400 MHz, DMSO-d6) δ 8.46 – 8.21 (m, 2H), 7.73 (ddd, J = 34.7, 8.8, 4.2 Hz, 2H), 4.57 – 4.37 (m, 2H), 1.78 (q, J = 7.1 Hz, 2H), 1.55 (dp, J = 13.4, 6.7 Hz, 1H), 0.93 (dd, J = 6.7, 2.1 Hz, 6H). 13C NMR (101 MHz, DMSO-d6) δ 160.98 , 133.60 , 132.47 , 131.92 , 128.59 , 121.54 , 118.34 , 59.46 , 25.57 , 22.52. ESI-MS (m/z): [M]+ calcd. for C10H16NO+: 166.12, found, 166,26; [M]- calcd. for C2F6NO4S2-: 279,92, found 280,00

5.4 Procedure for Biomass Extraction

The biomass samples were ball milled for 2.5 min at 20 Hz in a ball mill and dried at reduced pressure at 38°C overnight. The next day both samples were ball milled for another 10 minutes at a frequency of 20 Hz to yield a fine powder that was subjected to treatment. In order to test biomass dissolution, 4.9 wt.% (relative to the mass of solvent) of ball milled material was dispersed in 1,3-*N,N*-diethylimidazolium acetate or a mixture of dimethyl sulfoxide and 1,3-*N,N*-diethylimidazolium acetate, as given in Table 3 and Table 4. The mixture was stirred at 120 °C at 500 rpm for 24 hours. After that the mixture was left to cool to room temperature and 5 ml of a solution of ethanol and acetone (1:1, v/v labelled *PS* for brevity) was added to reduce viscosity. The addition of PS resulted in precipitation of a solid fraction which was filtered off to yield solid fraction F1. The filter cake was washed with PS and the filtrate was concentrated *en vacuo* to yield the first filtrate L1. Table 8 lists the volumes of liquids added to induce precipitation of all solid fractions obtained as well as the volumes of liquids used for washing.

Run	Fraction	Precipitation via	Volume	Washed with	Mass
IL-B	F1	addition of PS	5 ml	15 x 1 ml PS	0.3715
	F2	addition of PS	15 ml	7 x 1 ml PS	0.0336
	F3	addition of water	15 ml	3 x 5 ml water	0.0098
IL-C	F1	addition of PS	5 ml	15 x 1 ml PS	0.21
	F2	addition of PS	15 ml	7 x 1 ml PS	0.0185
	F3	addition of water	20 ml	3 x 5 ml water	0.0178
IL/D-B	F1	addition of PS	5 ml	18 x 1 ml PS	0.2673
	F2	addition of PS	20 ml	10 x 1 ml PS	0.0161
	F3	addition of water	20 ml	3 x 5 ml water	0.0052
IL/D-C	F1	addition of PS	5 ml	15 x 1 ml PS	0.2571
	F2	addition of PS	20 ml	10 x 1 ml PS	0.0591
	F3	addition of water	15 ml	3 x 5 ml water	0.0324

Table 8 Masses of fractions F1 through F3 obtained for all four biomass treatment experiments as well as the liquids added to achieve precipitation. PS denotes a solution of ethanol and acetone (1:1, v/v). Water refers to deionized water.

Fraction F2 precipitated from the first filtrate L1 after addition of PS. F2 was recovered by filtration and washed with PS as given in Table 8. The filtrate was concentrated *en vacuo* to yield the second filtrate L2. Fraction F3 was precipitated from L2 by addition of water. The solution was left to age for 30 minutes and F3 and recovered by centrifugation at 6000 rpm for 15 minutes. The supernatant was collected and freeze dried as a viscous, clear liquid of brown color.

5.5 Sonogashira-Hagihara Coupling

Four cycles of the reaction were performed. The first cycle was tested without the use of copper(II)iodide. 0.2058 g (1 mmol) iodobenzene, 0.1031 (1 mmol) phenylacetylene, 0.277 ml (2 mmol) triethylamine and 1.5 mg (0.6 mol%) palladium(II) acetate were added to 1.5 ml of the ionic liquid 3B and the reaction was stirred at 115 °C for 1 hour. Reaction was stopped by immersion of the flask into ice water. The mixture was extracted three times with 5 ml n-hexane. The organic fraction was evaporated and 10 ml n-hexane were added. An aliquot of 250 µl was taken and 250 µl of a 1 mmolar 1-decanol solution was added as the internal standard for GC-MS analysis. The first cycle did not show any conversion. In order to test the reactivity using copper(II)iodide, the same reaction mixture was used again. In order to remove residual hexane, the reaction mixture was concentrated by rotary evaporation and subsequently washed with three times with water (5 ml). After freeze

drying, 0.2045 g (1 mmol) iodobenzene, 0.1068 (1 mmol) phenylacetylene, 2.8 mg (1.4 mol%) copper iodide and 0.277 ml (2 mmol) triethylamine were added. The system was stirred at 115 °C for one hour. After one hour the reaction was stopped by immersion of the flask into ice water and the mixture was extracted three times with 5 ml n-hexane. A sample was prepared for GC in the same way given above. The conversion was calculated by division of the peak area of the product peak through the sum of the areas of residual starting material and product. The second cycle showed a conversion of roughly 90 %. The reaction mixture was worked as described and used for two more cycles by addition of new starting material. The conversion dropped with each cycle and was already at about 60 % on the fourth cycle.

5.6 Additional Data

Range	EEIMOAc	PS	DMSO	Coconut	Beech	IL-B F1	IL-B F2	IL-B F3	IL/D-B F1	IL/D-B F2	IL/D-B F3	IL-C F1	IL-C F2	IL-C F3	IL/D-C F1	IL/D-C F2	IL/D-C F3
>3000	3141,5; 3099,3					3139,3; 3094,9			3142; 3099,3			3145,3; 3107,5			3147,7; 3107,7		
>2000	2983,6; 2883,8	2973; 2912	2994,9; 2912	2929,3; 2883,8	2922,3; 2883,8; 2873,7	2978,5; 2915,6; 2883,8	2912,9; 2883,1; 2850,1	2923,3; 2850,3	2913; 2882,6	2915,6; 2882,6; 2849,6	2918,3; 2849,6	2900,4; 2873,9	2981,7; 2938,3; 2850,3	2928,6; 2850,3	2913,2; 2847,9; 2883,1	2981,4; 2915,8	2920,2; 2850,3
>1500	1557,7	1435,7	1716,8; 1593,4; 1505,2	1733,2; 1652; 1592,9; 1504,9		1563,5	1593,2	1652; 1591,5; 1505,2	1568,8; 1506,1; 1505,9	1652,5; 1593,4; 1591,5	1652,9; 1591,5; 1505,9	1558,7; 1506,1; 1505,2	1652; 1563,3; 1591	1699,5; 1591; 1505,2	1558,2; 1506,4; 1505,9	1652,7; 1563,7; 1652,5	1699,5; 1652,5; 1591; 1505,7
<1500	1393,3; 1166,2; 913,9; 748; 644,6	1221,7; 1087,7; 1046,4; 879,9	1309,2; 1042,6; 696,4			1455,5; 1418,4; 1372,8; 1327,8; 1270,9; 1233,3; 1162,9; 1033,2; 895,8; 849,2; 770,4	1455,6; 1409,2; 1248,7; 1162,6; 1036,6; 982,3; 896,3; 603,1	1455,8; 1418,4; 1326,1; 1265,6; 1221; 1121,2; 1026,9; 832,4; 600	1456,2; 1398,4; 1328,5; 1232,5; 1161; 1104,8; 1031,8; 897,5; 648,9; 595,7; 896,3	1456,2; 1418,4; 1373,6; 1324,9; 1248,4; 1161,9; 1075,1; 1038,2; 987,4; 896,3; 603,1	1457; 1419,1; 1326,3; 1265,8; 1221,9; 1121,6; 1026,9; 917,2; 832,4; 596,1	1456,5; 1418,9; 1373,8; 1330,2; 1266,3; 1161,9; 1032,9; 896,3; 852,7; 804,4; 770,9; 648,4; 604,1	1450,4; 1401,5; 1335,7; 1268,4; 1163,3; 1113,2; 1077,3; 1041,6; 982,1; 896,3; 742,5; 685,8; 647,2; 602,4	1455,8; 1418,4; 1327,8; 1268; 1221,9; 1162,9; 1121,4; 1028,1; 850,9; 770,4; 698,6	1456; 1393,8; 1330,2; 1265,8; 1161,2; 1104,3; 1049,8; 1032,7; 897,7; 853,8; 771,6; 645,3; 596,1	1456; 1403,7; 1339,1; 1266; 1247,7; 1215,4; 1163,8; 1109,1; 1074,9; 1037,8; 980,4; 896,5; 737,9; 687; 648,7; 602,7	1418,4; 1328; 1266,8; 1222,9; 1162,1; 1121,6; 1025,9; 951,5; 851,2; 830,4; 803,9; 770,9; 743,2; 698,8; 647; 602,9

Table 9 List of all relevant peaks as obtained from the measurement of ATF-IR spectra of the respective fractions, solvents and biomass used in the extraction experiments.
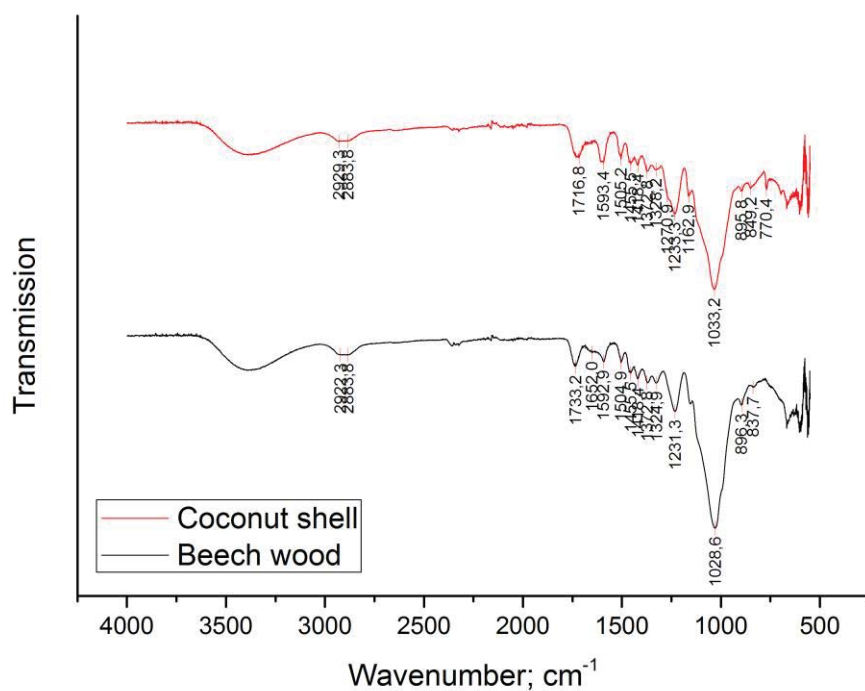
Figure 14 ATR-IR spectra of coconut shell and beech wood. Both samples were ball milled but otherwise untreated. The spectra are very similar and differ only slightly in the region between 1200 and 1700 cm^{-1}.
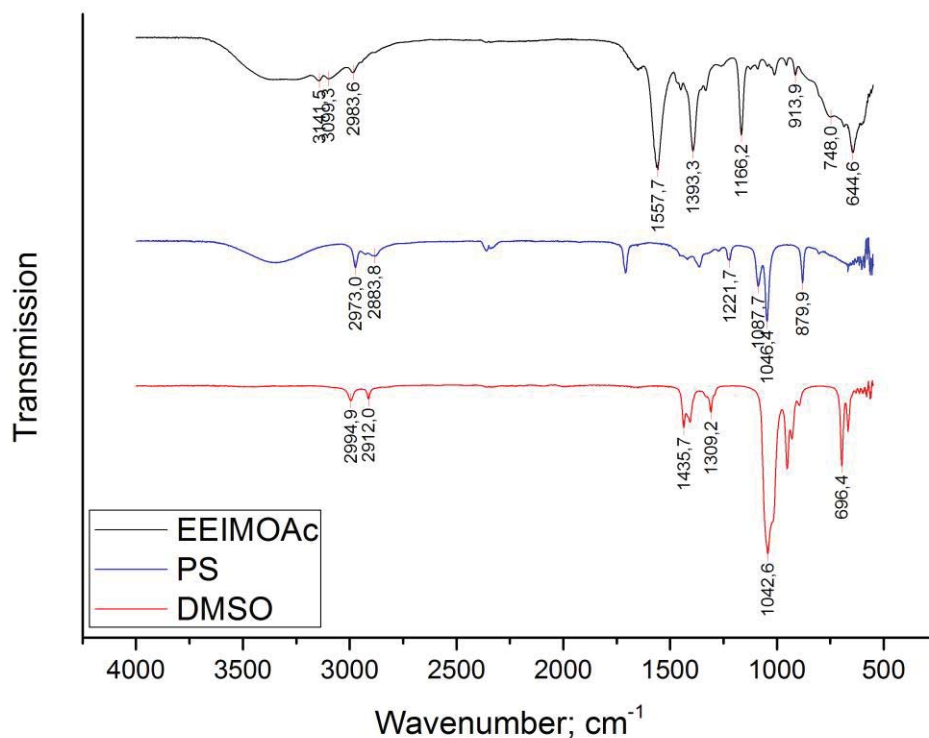

Figure 15 ATR-IR spectra of the three solvents used for the treatment experiments. Peaks relevant for analysis are labelled. EEIMOAc denotes the ionic liquid 1,3-*N,N*-diethylimidazolium acetate, PS denotes the solution of ethanol and acetone (1:1, v/v) and DMSO denotes dimethyl sulfoxide.
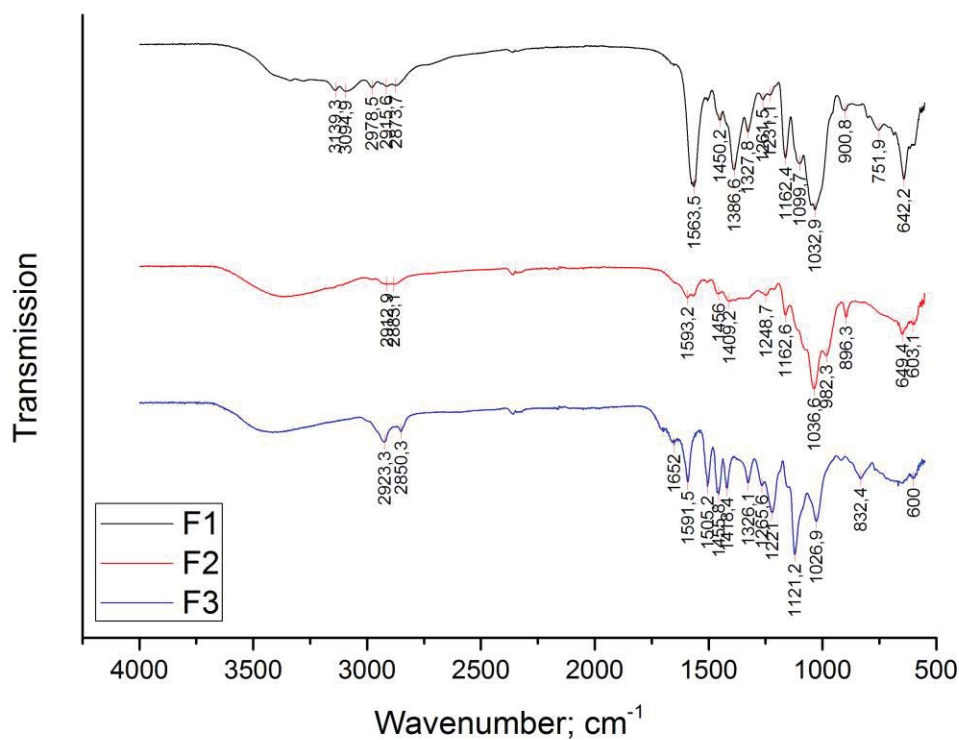
Figure 16 ATR-IR spectra of the fractions F1 to F3 of the treatment of beech wood with pure ionic liquid (experiment IL-B).
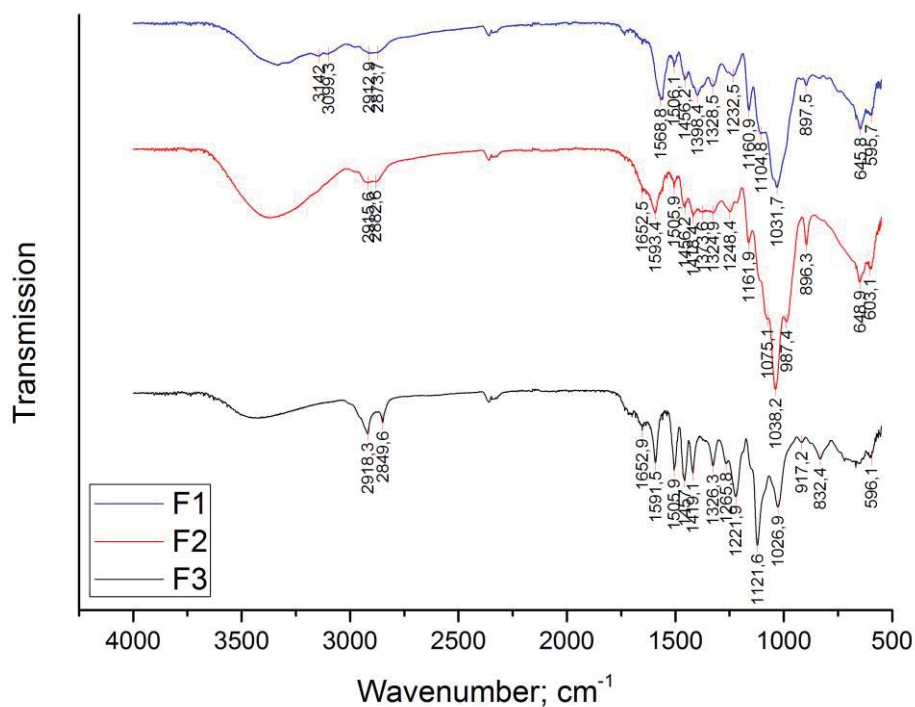

Figure 17 ATR-IR spectra of the fractions F1 to F3 of the treatment of beech wood with the organic electrolyte solution (IL/D-B).
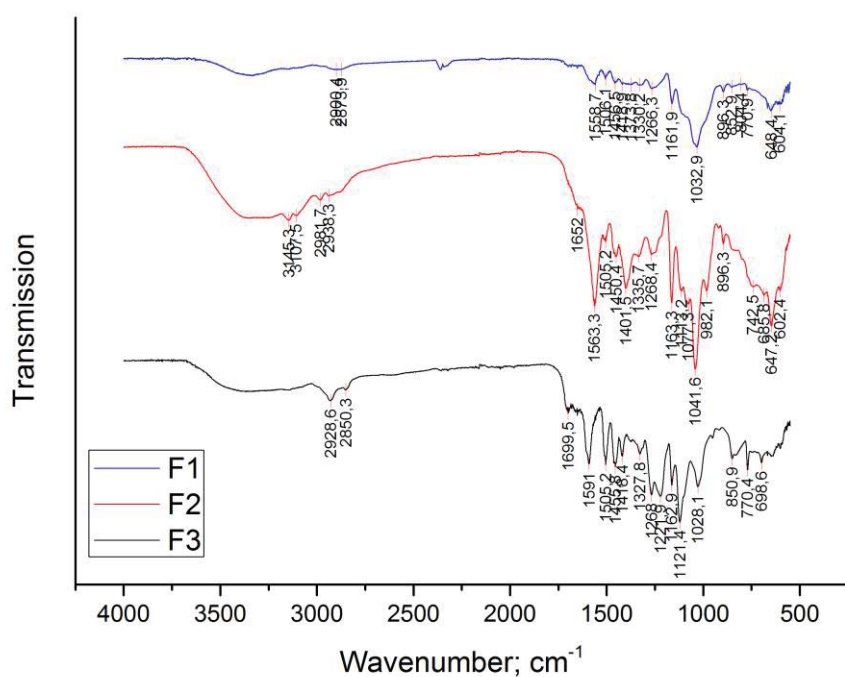
Figure 18 ATR-IR spectra of the fractions F1 to F3 of the treatment of coconut shell material with pure ionic liquid (IL-C).
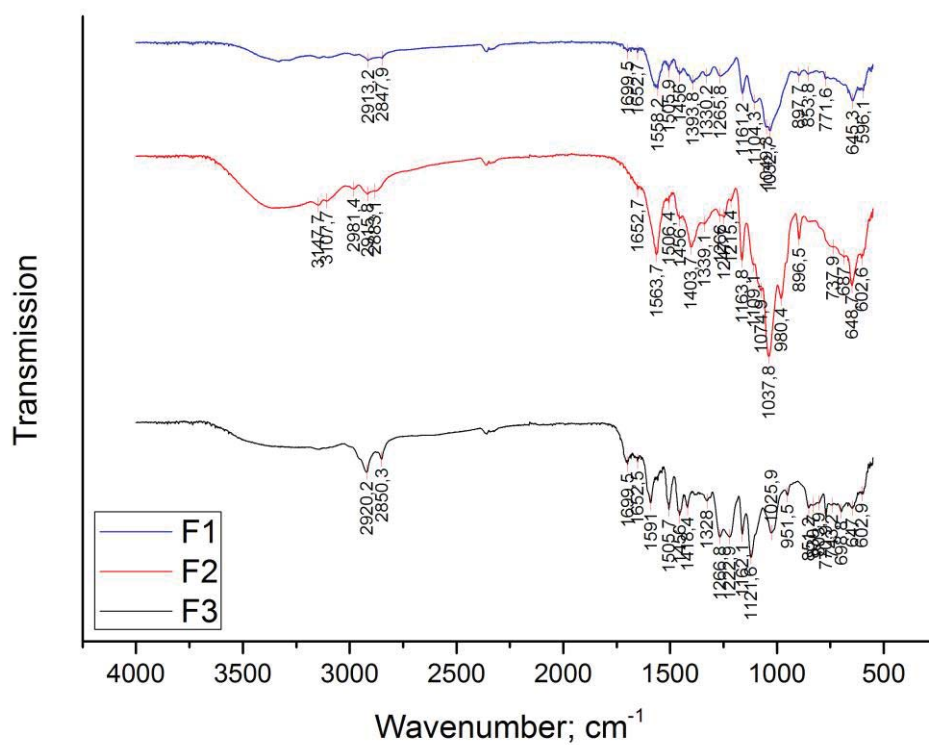

Figure 19 ATR-IR spectra of the fractions F1 to F3 of the treatment of coconut shell material with organic electrolyte solution (IL/D-C).

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