**PROCESS DEVELOPMENT FOR BIOMASS
DELIGNIFICATION USING A DEEP EUTECTIC
SOLVENT**

Dion Sminck

PROCESS DEVELOPMENT FOR BIOMASS DELIGNIFICATION USING A DEEP EUTECTIC SOLVENT

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Samenvatting

Lignocellulose biomassa is de meest beschikbare, hernieuwbare grondstof op deze aarde. Het vervangen van fossiele grondstoffen, zoals olie, steenkool en aardgas, in de chemische industrie zal een grote reductie van de CO₂ uitstoot van de chemische industrie opleveren. Echter, de beschikbaarheid van biomassa is beperkt. Daarom is het van groot belang om deze grondstof zo efficiënt mogelijk te gebruiken. Op dit moment is het meest gebruikte proces om biomassa te verwerken het kraft proces. Hierin wordt de lignine uit biomassa verwijderd met een oplossing van natriumhydroxide en natriumsulfide. De geproduceerde cellulosepulp wordt voornamelijk gebruikt voor de productie van papier. Helaas wordt maar de helft van de grondstof gebruikt om papier van te maken. De andere helft wordt verbrand om warmte te genereren en natriumsulfide terug te winnen. Processen die meerdere producten uit hout kunnen maken, waaronder naast cellulosepulp ook lignine en/of furanen zijn noodzakelijk om de wereldwijde CO₂ uitstoot te verminderen.

Diepe eutectische oplosmiddelen (DES) zijn samengestelde oplosmiddelen die diep eutectisch gedrag vertonen bij het mengen. Deze oplosmiddelen hebben veel potentie om te worden toegepast voor delignificatie en kunnen niet alleen cellulosepulp, maar ook andere waardevolle bijproducten uit biomassa maken, zoals lignine en furanen. Daarom kunnen processen die gebruikmaken van deze DES efficiënter gebruikmaken van de biomassa grondstof dan het kraft proces. Er zijn echter een aantal kwesties die moeten worden verholpen voordat deze processen op grote schaal kunnen worden toegepast. Allereerst zijn de voordelen van de DES samenstellingen nog relatief onbekend. Ook zijn de methodes die beschikbaar zijn voor de terugwinning van lignine uit DES voornamelijk toepasbaar op laboratoriumschaal. Procedures voor in het laboratorium zijn niet altijd toepasbaar op industriële schaal en meer onderzoek is nodig om het pulpproces beter te begrijpen, net als de terugwinning van het oplosmiddel. In dit proefschrift worden deze kwesties behandeld, waarna een conceptueel proces wordt voorgesteld waarin lignine wordt verwijderd uit *Eucalyptus globulus* met een DES bestaande uit choline chloride en melkzuur.

In **hoofdstuk 2** wordt een studie naar de rol van choline chloride op de delignificatie van biomassa met DESsen die melkzuur bevatten beschreven. Hiervoor zijn pulpexperimenten uitgevoerd met *E. globulus* op 120 °C met een duur van 8 uur een DES tot biomassa ratio van 20:1. Verschillende experimenten zijn uitgevoerd waarbij de invloed van choline chloride op de lignine oplosbaarheid, afbraakreacties en massatransport is onderzocht om tot een beter begrip te komen van de gemeten pulpresultaten. Hieruit is geconcludeerd dat het chloride anion het actieve bestandsdeel is van choline chloride is waardoor de delignificatiesnelheid wordt vergroot. Het veel goedkopere NaCl, oftewel keukenzout,

werkte wat dat betreft net zo goed. Verder is choline chloride al effectief in een molratio van 1:250 ten opzicht van melkzuur. Uit studies op gemalen hout lignine is vastgesteld dat choline chloride het breken van de β -O-4 bindingen in lignine versnelt en daardoor de delignificatiesnelheid van biomassa verhoogt. Ook verlaagde choline chloride de oplosbaarheid van lignine in de DES en verlaagde het de geschatte massatransport coëfficiënt door een verhoging van de viscositeit. Een model is toegepast om de kraaksnelheid van lignine te bepalen. Deze kraaksnelheid nam 90% toe met de toevoeging van choline chloride aan melkzuur. Kort samengevat wordt de delignificatiesnelheid van eucalyptus door melkzuur verhoogd door toevoeging van halogeniden.

In **hoofdstuk 3** is een nieuwe methode ontwikkeld om lignine terug te winnen uit DES. In het laboratorium wordt de DES aan een grote hoeveelheid water toegevoegd, waardoor de lignine precipiteert. Wanneer deze methode op industriële schaal wordt toegepast moet het water vervolgens weer uit de DES worden verdampt, wat zeer veel energie kost. Daarom is er een alternatieve methode ontwikkeld die gebruikt maakt van vloeistof-vloeistof extractie (LLX). De terugwinning van lignine uit DES met deze methode was onderzocht voor verschillende melkzuur tot choline chloride ratio's. Hiervoor zijn eerst zes oplosmiddelen gescreend, waaruit 2-methyltetrahydrofuran (2-MTHF) is geselecteerd als meest geschikte oplosmiddel voor vervolgstudies. Het fase evenwicht tussen 2-MTHF en de DES is bepaald op 25, 50 en 75 °C. Er is op evenwicht ten minste 30% choline chloride in de DES nodig om twee fases te vormen. Het toevoegen van meer choline chloride verlaagd de wederzijdse oplosbaarheid van 2-MTHF en melkzuur. De evenwichtsverdeling van lignine tussen de DES en 2-MTHF veranderde nauwelijks met veranderende DES composities, maar de evenwichtsverdeling was sterk afhankelijk van de molecuulmassa van de lignine. De ligninefractie met een lage molecuulmassa had een verdelingscoëfficiënt van 1, terwijl de ligninefractie met een hoge molecuulmassa een verdelingscoëfficiënt van 0,1 had. De toevoeging van een beetje water veranderde het systeem drastisch, waardoor met name de extractie van de ligninefractie met een hoge molecuulmassa sterk verbeterde. Wanneer er 25% water in de DES aanwezig is stijgt de verdelingscoëfficiënt van elke ligninefractie tot boven de 4, wat een efficiënte extractie van lignine uit DES met 2-MTHF mogelijk maakt.

In **hoofdstuk 4** is de terugwinbaarheid van lignine uit DES middels LLX en precipitatie in koud water onderzocht dieper onderzocht, inclusief extracties in meerdere stappen en analyses op de geëxtraheerde lignine fracties. Opgeloste lignine in de DES is niet homogeen, wat betekent dat het bestaat uit verschillende fracties met verschillende molecuulmassa's en mogelijk ook verschillende dichtheden van functionele groepen. Daarom is een vergelijking tussen de terugwinbaarheid middels LLX en precipitatie erg belangrijk. Hiervoor is de terugwinning van lignine uit een DES bestaande uit 30% choline chloride en 70% melkzuur onderzocht door drie dwarsstroomextracties met 2-MTHF. Hiermee kon 95% van de lignine met een molecuulmassa rond de 2.000 g/mol en 85% van de lignine met een molecuulmassa

rond de 10.000 g/mol worden geëxtraheerd. In de resterende ligninefractie in de DES zijn geen inter-aromatische etherbindingen gevonden met heteronucleaire, enkelvoudige kwantum-coherentie spectroscopie (HSQC). Dit duidt erop dat de ligninefractie die in de DES achterblijft een sterk gecondenseerd is. Middels precipitatie in koud water kon alle lignine met een molecuulmassa van meer dan 4.000 g/mol worden geëxtraheerd door toevoeging van 3,5 kg water per kg DES. Echter, van de fractie met een molecuulmassa rond 1.000 g/mol kon met deze methode slechts de helft van de lignine worden teruggewonnen. Kort gezegd is LLX geschikter voor de terugwinning van ligninefracties met een lage molecuulmassa, terwijl precipitatie in koud water geschikter is voor de terugwinning van de ligninefracties met een hoge molecuulmassa. Voor industriële toepassingen zal een combinatie van beide technieken noodzakelijk zijn om de lignine volledig terug te winnen uit de DES.

In **hoofdstuk 5** is een conceptueel ontwerp gemaakt voor de delignificatie van *E. globulus* middels een DES bestaande uit 30% choline chloride en 70% melkzuur. In dit ontwerp worden lignine en afbraakproducten van hemicellulose teruggewonnen uit de DES middels LLX met 2-MTHF als oplosmiddel. Er zijn materiaal- en energiebalansen voor dit proces opgesteld en het proces is geoptimaliseerd op het energieverbruik middels aanvullende experimenten. De hoeveelheid DES die benodigd is voor het proces kon worden verminderd tot de hoeveelheid die nodig is om de poriën in de biomassa te vullen (5 kg DES per kg biomassa), zonder dat dit sterk ten koste ging van de celluloseopbrengst of delignificatiegraad. Het direct terugvoeren van lignine-in-DES mengsels, zonder terugwinning van lignine, kan extra energiebesparingen opleveren, maar dit weegt niet op tegen de extra verhoging de molecuulmassa van de lignine die dit tot gevolg heeft. Hierdoor zal de waarde van de lignine verminderen en het moeilijker zijn om de lignine terug te winnen middels LLX. Na de energie optimalisatie was het totale warmteverbruik van het voorgestelde proces 8,4 GJ per ton cellulosepulp, wat 24% minder is dan het kraft proces. Een bijkomend voordeel van dit proces is de mogelijkheid tot het winnen van andere bijproducten, zoals lignine en furanen die worden gevormd uit hemicellulose.

Summary

Lignocellulosic biomass is the most abundantly available sustainable raw material on earth. Replacing fossil feedstocks for the chemical industry, such as oil, coal and natural gas by biomass can reduce the CO₂ emissions of the chemical industry. However, the availability of lignocellulosic biomass is limited. Therefore, it is key to use this feedstock as efficiently as possible. The current benchmark process in biomass fractionation is the kraft process. In this process, biomass is delignified using a solution of sodium hydroxide and sodium sulfide and the produced cellulose pulp is mostly used for papermaking. However, only half of the raw material is converted into cellulose pulp, the rest of the material is combusted for the generation of heat and for the recovery of sodium sulfide. Processes that can convert biomass in multiple products, including next to cellulose, also lignin and/or furans, are required to reduce global CO₂ emissions.

Deep eutectic solvents (DES) are composite solvents that exhibit deep eutectic behavior upon mixing. These solvents have shown great potential for biomass delignification and have the potential to produce not only cellulose pulp, but also other valuable byproducts, such as lignin and furans. Therefore, DES based processes can make more efficient use of the biomass feedstock than the kraft process. However, there are a couple of issues that need to be resolved before DES delignification processes can be applied on a large scale. First, the advantages of the combination of DES constituents are poorly understood. Second, the known methods for the recovery of lignin from DES are mostly applicable for laboratory purposes. Laboratory unit operations are not always applicable on industrial scale, and research is needed to better understand the pulping process, as well as solvent recovery operations. These issues are addressed in this thesis, after which a conceptual process is designed for the delignification of *Eucalyptus globulus* using a DES comprised of lactic acid and choline chloride.

In **chapter 2**, a study on the role of choline chloride in biomass delignification by the DES containing lactic acid is described. Pulping experiments using *E. globulus* were performed at 120 °C for 8 hours with a DES to wood ratio of 20:1. Various experiments were performed to study the influence of choline chloride on lignin solubility, cleaving reactions and mass transfer in order to gain understanding of the observed pulping results. It was found that the chloride anion is the active component of choline chloride, enhancing the rate of the delignification. In fact, the inexpensive salt NaCl performed as well as choline chloride in that respect. Furthermore, choline chloride it is already effective in a 1:250 molar ratio to lactic acid. It was found by studies on milled wood lignin (MWL) that choline chloride increases the cleavage rate of β -O-4, and thereby increases the delignification rate of biomass. Furthermore, choline chloride slightly decreased the solubility of lignin in DES, and

due to an increase in viscosity the estimated mass transfer coefficient is also reduced. A model was applied to fit the lignin cleaving rate, which increased by 90% upon the addition of choline chloride to lactic acid. Overall, the delignification rate of eucalyptus by lactic acid increased by the addition of halide salts.

In **chapter 3**, a new method was developed for the regeneration of lignin from DESs. Laboratory routine has been to precipitate lignin by addition of cold water, however large amounts of water are required, resulting in energy intensive operations to remove the water from the DES afterwards. Therefore, liquid-liquid extraction (LLX) was proposed as alternative method for industrial applications. The recovery of lignin from a DES consisting of lactic acid and choline chloride was studied for various DES ratios. Six solvents were investigated for this purpose, from which 2-methyl tetrahydrofuran (2-MTHF) was selected for further studies. The phase equilibria between the DES and 2-MTHF were determined at 25, 50 and 75 °C. Addition of more choline chloride decreases the mutual solubility of 2-MTHF and lactic acid. The overall equilibrium lignin distribution between DES and solvent did not change much with varying DES compositions, but the distribution was dependent on the molar mass of lignin. The low molar weight fractions showed a distribution coefficient around 1, while for the heavy fractions the distribution coefficient was below 0.1. Addition of water changes the system greatly, and extraction of high molar mass lignin is tremendously enhanced. At 25 wt % water in the DES, the distribution coefficient was for all molar weights at least 4, allowing effective extraction of lignin from DES by 2-MTHF.

In **chapter 4**, the recoverability of lignin from DES using LLX and cold-water precipitation was studied more in-depth, including multi-stage extractions and analysis of the extracted lignin. Lignin that is dissolved in DES from biomass fractionation is inhomogeneous, meaning it has various fractions with different molar weights and possibly variations in functional group densities. Therefore, it is important to compare recoverability of every lignin fraction by LLX with cold-water precipitation. In this work, the recovery of lignin from a DES comprised of 30 wt % choline chloride and 70 wt % lactic acid was studied. Three cross-current extractions were performed using 2-MTHF. This method allowed to recover 95% of the lignin molar weight fractions around 2,000 g/mol and 85% of the lignin molar weight fractions around 10,000 g/mol. No inter-aromatic ether bonds were found in the lignin remaining in the DES raffinate by heteronuclear single quantum coherence spectroscopy (HSQC), indicating the remaining lignin in the DES is has a highly condensed nature. Cold water precipitation could fully recover the lignin fractions above 4,000 g/mol using 3.5 kg water per kg DES. However, only half of the lignin fraction of 1,000 g/mol was recovered. Briefly, LLX is more suitable for the recovery of low molar weight fractions, while cold water precipitation is more suitable for the heavy molar weight fractions. For industrial applications, a combination of both approaches appears essential for full lignin recovery.

In **chapter 5**, a conceptual process design for the delignification of *E. globulus* using a DES comprised of 30 wt % choline chloride and 70 wt % lactic acid was made. In this design, the lignin and hemicellulose by-products are recovered by LLX using 2-MTHF as solvent. Material and energy balances were made and the energy usage of the process was optimized with additional experiments. The amount of DES was reduced to the minimal amount required to fill the porous biomass (5 kg per kg wood), with minor influences on the yield and delignification. Direct recycling of lignin-in-DES mixtures without lignin removal by LLX to the delignification stage may save energy, but increased repolymerization increases the lignin's molar weight, which decreases its value and makes recovery by LLX more difficult. After optimization, the total energy usage of the proposed process is 8.4 GJ/t pulp, which is 24% lower than the kraft process. An additional benefit of DES based delignification processes is the possible valorization of byproducts, such as lignin and furans from hemicellulose.

Table of contents

1	Introduction	13
2	Understanding the role of choline chloride in deep eutectic solvents used for biomass delignification	31
3	Recovery of lignin from deep eutectic solvents by liquid-liquid extraction	59
4	Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents	79
5	Process development for biomass delignification using deep eutectic solvents. Conceptual design supported by experiments	103
6	Conclusions and outlook	141
	List of abbreviations	146
	Publications	147
	Acknowledgements	148

Chapter 1

Introduction

1. Research context

The consumption of fossil feedstocks, such as oil coal and gas, has an enormous contribution to the current standard of living. They are not only used for transport, power and heating, but also as feedstock for the production of numerous chemicals. Examples include, but are not limited to plastics, fertilizers, textiles, detergents, adhesives and paints. The fossil feedstocks used for the production of these materials are not only used as an energy source in the production process, but are also used as material feedstock. The molecules in these products are physically derived from the fossil feedstocks. In the chemical industry, roughly half of the fossil feedstocks are used as energy source, and the other half as feedstock [1]. In 2017, the fossil material demands of the chemical industry were 760 Mt (excluding demands for energy), as estimated using data from the International Energy Agency [1].

The combustion of fossil feedstocks produces CO₂, which is emitted to the atmosphere, where it accumulates. This has caused an increase in the CO₂ concentration in the atmosphere from 316 to 413 ppm from 1960 to 2020 [2]. As a result, more radiation is absorbed by the atmosphere, which has caused an increase in global temperatures. The effects of this temperature increase include rising sea levels, more extreme weather and threats to crop yields. Therefore, deep cuts in CO₂ emissions are required [3].

It is expected that alternative energy sources, such as solar, wind and geothermal energy are able to replace fossil energy sources. However, for the chemical industry, not only the energy source must be replaced, but also the material source. The number of sustainable carbon sources is limited to two: CO₂ from the air, or carbon from biomass. Direct CO₂ capture from air seems very challenging. One Olympic-sized swimming pool filled with air only contains 750 g carbon,¹ meaning enormous air flows are required for the recovery of small amounts of carbon. Therefore, it is desirable to use biomass as carbon feedstock for the chemical industry. However, extending the use of biomass also has its limitations. Grow cycles in forestry are very long, typically 15 to 50 y [4] and increasing the amount of land used for forestry will compete with land use for living, agriculture and nature. Therefore, in view of the author, it is key to use this feedstock as efficiently as possible and find technologies that can convert biomass into a spectrum of products, rather than one single product. This principle is called a biorefinery.

¹ Assuming a swimming pool of 25x50x3 m, filled with air which contains 413 ppm CO₂. Calculated using ideal gas law at atmospheric pressure and temperature.

Chapter 1

There are two main types of biomass, animal and plant based biomass. This thesis is limited to the latter type, and more specifically to lignocellulosic biomass. This type can be further divided in two categories: wood that is harvested from forestry, and agricultural residues. Agricultural residues, such as straw, corncob or sugar beet pulp, are mainly used as feed and bedding for cattle, but are also used for the production of chemicals, such as ethanol [5] or furfural [6]. The use of wood can roughly be divided in two groups: fuel wood and industrial wood. The first accounts for almost half of the total wood usage and covers 12-13% of the global energy usage. Fuel wood is almost entirely used in developing countries for heating or cooking. Despite the low energy efficiency and associated health risks, this is the sole access to energy carriers for more than 2 billion people [7].

Most of the industrial wood consists of sawlogs, which are further processes to sawnwood, railway sleepers and veneer. Not only are these the most valuable, the material losses in the production of these products is only limited to the losses during sawing. Around 30% of the industrial wood is used as pulpwood for the production of cellulose pulp, as summarized in fig. 1.1 [8].

Fig. 1.1. Global use of wood resources. A division is made between fuel and industrial wood. Industrial wood is further split out in sawlogs, pulpwood, others and residues. All values are in Mt/year and the data is used from [8].

In 2017, 456 Mt pulpwood was used to produce 184 Mt of cellulose pulp [8]. This means that 272 Mt of byproducts are produced, mainly consisting of lignin and sawdust. These high

losses are mainly due to the way pulpwood is processed to produce cellulose fibers. Most cellulose fibers are produced using the kraft process. This process removes lignin from wood by a nucleophilic substitution reaction using sulfur. As a result, the lignin produced by the kraft process contains high amounts of covalently bound sulfur, as can be seen in fig. 1.2. This makes the valorization of kraft lignin challenging since sulfur is an established catalyst poison [9]. In the kraft process, the lignin is combusted to recover the sulfur and to produce the required heat for the process.

Fig. 1.2. Reaction scheme for the cleavage of the β -O-4 bond in the kraft process [10].

Recently, deep eutectic solvents (DESs) have been proposed as solvents for biomass delignification [11-13]. DES based delignification processes can convert wood into cellulose suitable for papermaking and valuable lignin, because the mechanism of the delignification is different. This makes DES delignification processes attractive alternatives to the kraft process. Since there are many unknown aspects of DES-based delignification, and also on the recycling of these DESs, these aspects are interesting elements for scientific study. In the rest of the introduction, important aspects of DES-based delignification, including the concept of deep eutectic solvents and the structure of lignocellulosic biomass are briefly discussed. At last, a brief outline of the thesis is presented.

2. Deep eutectic solvents

Deep eutectic solvents (DESs) are a relatively new class of solvents, first named by Abbott et al. in 2004 [14]. DES are composite solvents that exhibit eutectic behavior upon mixing, attributed to the hydrogen bonding interactions between the constituents [15]. These solvents have raised wide attention in academia since 2004 and are often biocompatible, biodegradable [16] and can have a low toxicity [17]. Although it must be noted that these properties depend entirely on the constituents of a DES. Many applications have been proposed for these solvents, such as CO_2 capture [18-20], air pollutant removal [21],

Chapter 1

extractive distillation [22], metal extractions [23], desulfurization [24,25] and biomass delignification [13,26,27]. DESs are usually comprised of two compounds that are solids at room temperature. The melting point curve of a solid as function of composition can be calculated using a thermodynamic equation (1).

$$\ln(x_i \gamma_i) = \frac{\Delta_{fus}H}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \quad (1)$$

In this equation, x is the mole fraction and γ the activity coefficient of compound i , $\Delta_{fus}H$ the enthalpy of fusion, R the ideal gas constant, T_m the melting temperature of the pure compound and T the melting point of the mixture. If it is assumed that the mixture is ideal ($\gamma = 1$), the melting temperature can be calculated as a function of the composition when the melting enthalpy and temperature are known for the pure compounds. When these curves are calculated for both compounds in a DES, they will cross at certain temperature, called the eutectic temperature. An example of two of these curves is shown in fig. 1.3.

From the application point of view, it might not seem very relevant whether a mixture can be called a DES or not. However, a proliferation of mixtures entitled as DESs that are actually not DESs will decrease the value of the term DES. In order to identify DESs, some considerations should be taken into account, among which the melting point of a mixture is one aspect, but certainly not governing. For instance, the eutectic point of the cubane and tetramethylbutane is 70 °C lower than the melting point of tetramethylbutane (see fig. 1.3), as calculated assuming ideal behavior. Thus, this appears as a composite solvent that exhibits deep eutectic behavior upon mixing. However, is it unlikely that the use of this mixture will have any practical advantage over the use of *n*-octane or *i*-octane. Thus only considering the melting behavior is not really satisfying.

Fig. 1.3. Ideal solid-liquid phase diagram of tetramethylbutane (structure top right) with cubane (structure top left), as calculated according to equation (1).

A stricter definition of a DES is thus highly desirable. Some authors have proposed a stricter definition of a DES [28,15,29-31]. These are summarized in table 1.1.

The definitions proposed by Zhang [28] et al. and Paiva et al. [29] cover a very wide range of miscible systems, such as a mixture of NaCl and water. A salt in water mixture is generally not regarded as a DES, but does meet the definitions proposed by Zhang [28] et al. and Paiva et al. [29], hence, this definition does not seem very satisfactory, and an even more strict definition is required. The definition proposed by Smith [15] is clear and unambiguous, but according to this definition, any protic ionic liquid is a DES as well. Furthermore, it excludes many substances often used in DES, such as (poly)alcohols and sugars.

Chapter 1

Table 1.1. overview of proposed DES definition.

Author	Year	Definition
Zhang [28]	2012	A DES is a fluid generally composed of two or three cheap and safe components that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component.
Smith [15]	2014	DESs are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases which can contain a variety of anionic and/or cationic species
Paiva [29]	2014	Deep eutectic solvents are defined as a mixture of two or more components, which may be solid or liquid and that at a particular composition present a high melting point depression becoming liquids at room temperature.
Martins [30]	2018	In our view a ‘deep eutectic solvent’ is a mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from ideality. Additionally, the temperature depression should be such that the mixture is liquid at operating the temperature for a certain composition range.
Schuur [31]	2019	DESs are composite solvents that exhibit deep eutectic behavior, that is, upon mixing the constituents of these solvents, the mixtures’ melting points reduce considerably more (>50 °C) than would be the case for ideal mixtures.

Martins [30] and Schuur [31] proposed definitions of a DES based on the melting point reductions compared to ideal behavior. It may seem cumbersome to compare the melting point reduction to the ideal reduction, rather than the reduction compared to the starting material(s). For the comparison with ideal behavior, experimental data is a pre-requisite, whereas an estimation of the eutectic temperature can be made simply from the heats of fusion and the melting points of the pure constituents, which will ease the screening of new DES very much. Furthermore, a relation between the ideality of a DES and potential applications is not always expected. For instance, a relation between the non-ideality of DES and a reaction rate in the DES seems unlikely. However, a dissimilarity between two molecules is required to obtain non-ideal behavior. Defining a DES based on the deviation from ideality therefore excludes most combinations between similar molecules (such as the example with cubane and tetramethylbutane mentioned earlier). Since it is unlikely that

mixtures of two molecules with similar properties will have any advantages over the use of any of the pure substances, it has no benefits to define these mixtures as DESs. Therefore, defining a DES based on non-ideality is preferred, but does not come without its problems either. A mixture of water with DMSO for instance has a large negative deviation from ideality as well [32]. To the best of my knowledge, such a mixture was never proposed as DES, but this is justified according to the definitions in the paragraph.

At this moment, there is no commonly agreed definition of a DES and it has proven to be very hard to come up with a definition that can describe most of the mixtures that are currently regarded as DES, while excluding mixtures that are not generally considered as DES. Although further discussions are essential to come to a generally accepted definition of a DES, but in view of the author it should at least:

1. Have a significant decrease in melting point upon mixing the constituents.
2. This melting point depression should be significantly more than expected from ideal behavior, there must be a dissimilarity between the constituents.
3. The combination of the DES constituents should have a clear benefit over the use of (solutions of) their constituents alone.

3. Structure of lignocellulosic biomass

Lignocellulosic biomass is used as a feedstock for the production of cellulose fibers. Lignocellulosic biomass is the most abundantly available organic raw material on earth and has a fibrous structure, which mainly consists of cellulose, hemicellulose and lignin.

3.1. Cellulose

Cellulose is a polymer of D-glucose. Cellulose is always formed by a condensation reaction of the hydroxyl groups between carbon 1 and carbon 4 of two different D-glucose units, called a glycosidic bond, as shown in fig. 1.4. In this structure, each consecutive unit is twisted 180° over the 1-4 'axis'. This allows strong hydrogen bonds between adjacent glucose units in a cellulose molecule. This creates a stiff, linear polymer [4].

Fig. 1.4. Structural formula of D-glucose and one two monomers in a cellulose polymer with hydrogen bonds indicated by the dashed lines.

Multiple cellulose chains form sheets by strong hydrogen bonds between the cellulose chains, as shown in fig. 1.5. These sheets are stacked over each other and interact by van der Waals forces. Such a stack is called a fibril. Typically, the cellulose sheets are very long and narrow, making the fibrils very long and narrow. Cellulose chains may have a degree of polymerization of around 10,000, while a typical plant fibril contains around 36 cellulose chains [4].

Fig 1.5. Two monomers of two cellulose chains with intra and inter molecular hydrogen bonds indicated by the dashed lines.

3.2. Hemicellulose

As opposed to cellulose, hemicelluloses are heterogeneous and slightly branched polymers. They consist of various pentose (D-xylose and L-arabinose), hexose (D-glucose, D-mannose and D-galactose) and deoxyhexoses (L-rhamnose and L-fucose) sugars, as well as uronic acids and typically have a degree of polymerization up to 200 [4].

In lignocellulosic biomass, hemicelluloses are found between the cellulose fibrils in the cell walls. The types and amounts of hemicellulose found in lignocellulosic biomass depends greatly on the species, tissue type and growth stage and growth conditions.

3.3. Lignin

Lignin is an aromatic and amorphous polymer. Lignin is mainly found between the cell walls of lignocellulosic biomass, where they 'glue' them together. This gives stiffness to the lignocellulosic biomass. It consists of three aromatic monomers (p-Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, fig. 1.6), which form a polymer by a radical type polymerization mechanism. These monomers are linked together by different ether and carbon-carbon bonds, which are randomly distributed.

Fig. 1.6. Structures of p-Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

The aromatic carbons are indicated by numbers (1-6) and the aliphatic carbons are indicated by Greek letters (α , β and γ). Bonds are indicated by the numbers or letters of the first monomer and an O is placed in between if the two monomers are connected by an ether bond. For example, the β -O-4 bond means that the β carbon of one monomer forms an ether bond with carbon 4 from the second monomer, as indicated in fig 1.7.

Fig. 1.7. Two lignin monomers connected by a β -O-4 bond.

4. Desired process for biomass delignification using a DES

The kraft process is currently the benchmark process for biomass delignification. In this process, the lignin is cleaved by a nucleophilic substitution reaction with sulfur, as shown in fig. 1.2. As a result, the lignin produced using the kraft process contains covalently bonded sulfur, making valorization challenging (as discussed previously in section 1). Therefore, the lignin produced in the kraft process is combusted. This serves two purposes. A part of the produced heat is used for the process and the excess heat is converted into electricity and sent to the power grid. Second, the covalently bound sulfur can be recovered via a complicated recovery section.

To eliminate all CO₂ emissions, the fossil resources for the production of both energy and chemicals have to be replaced by renewable alternatives. It is much harder to replace the fossil resources for the production of chemicals, than to replace the fossil resources for the production of energy (as discussed in section 1). Lignocellulosic biomass can be a sustainable resource for the production of chemicals, which is readily available. Unfortunately, the available amounts of lignocellulosic biomass are limited. Therefore, in view of the author, it is key to use this resource as much as possible for the production of chemicals, rather than energy.

Due to the nature of the Kraft process, the produced lignin contains high amounts of sulfur, making it hard to use it as a feedstock for the production of chemicals. DES based delignification processes can delignify biomass without the need for sulfur. This means that DES delignification processes can produce lignin that does not contain any sulfur, which is more suitable as feedstock for chemicals. Therefore, DES based processes can produce more chemical products, rather than energy compared to the kraft process. Since it is harder to replace chemical resources with renewable alternatives than energy resources, DES based delignification processes are more desirable than the kraft process. Despite the advantages of the proposed process, alternative energy sources have to be implemented simultaneously to fulfil the energy demands the process and to replace the energy that the kraft process currently provides to the power grid. Examples include, but are not limited to, wind, solar, geothermal and hydropower. The input-output structure of both processes are schematically shown in fig. 1.8.

Fig. 1.8. Conceptual comparison between the input-output structures of the current industrial situation and the desired DES delignification process. Picture was adapted from the ProViDES final report [33].

5. Scope and outline of the thesis

In this thesis, one commonly used DES comprised of choline chloride and lactic acid was used for studies on biomass delignification. This DES is inexpensive, biodegradable, has a low viscosity and has a large range in which it is liquid [34]. Furthermore, it was often used in other studies on biomass delignification [12]. This DES was also used in the rest of this thesis.

Chapter 1

In **chapter 2**, the influence of choline chloride on the delignification mechanism was studied. It was clear that the delignification mechanism was based on acid-catalyzed hydrolysis [12]. Although it was clear that the addition of choline chloride to lactic acid improved the delignification rate, its exact role was unclear and further studied in this chapter.

The only known ways to regenerate lignin from DES involve precipitation of lignin by addition of cold water to DES. In an industrial process, this water has to be separated from the DES by evaporation, which is highly energy intensive. Therefore, an alternative regeneration method involving liquid-liquid extraction (LLX) was developed in **chapter 3**. Six solvents were screened and 2-methyltetrahydrofuran was selected for further studies. In **chapter 4** it was investigated whether full lignin recovery can be obtained using LLX and a comparison was made with cold-water precipitation.

In **chapter 5**, a conceptual process was designed for biomass delignification using DES. The energy consumption of this process was estimated and optimized using additional experiments.

In **chapter 6**, the conclusions of this thesis are summarized and an outlook on delignification processes using DES is given.

In chapter 2-5 the following research questions are answered:

- Chapter 2: Why does the delignification rate of biomass using lactic acid increase when choline chloride is added?
- Chapter 3: Can lignin be recovered from DES by liquid-liquid extraction using an organic solvent?
- Chapter 4: How does the recovery of lignin from DES using liquid-liquid extraction compare to recovery using precipitation in cold water?
- Chapter 5: How does a conceptual process for biomass delignification using DES compare to the kraft process?

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Chapter 1

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Chapter 2

Understanding the role of choline chloride in deep eutectic solvents used for biomass delignification

Abstract

The role of choline chloride in biomass delignification by the deep eutectic solvent (DES) containing lactic acid was investigated. In this study, the influence of choline chloride on the pulping of *Eucalyptus globulus* chips was determined. Pulping experiments were performed at 120 °C for 8 hours with a DES to wood ratio of 20:1. Various experiments were performed to study the influence of choline chloride on lignin solubility, cleaving reactions and mass transfer in order to gain understanding of the observed pulping results. It was found that the chloride anion is the active component of choline chloride. In fact, the inexpensive salt NaCl performed as well as choline chloride in that respect. Furthermore, choline chloride is already effective in a 1:250 molar ratio to lactic acid. It was found by studies on milled wood lignin (MWL) that choline chloride increases the cleavage rate of β -O-4, and thereby increases the delignification rate of biomass. Furthermore, choline chloride slightly decreased the solubility of lignin in DES and due to an increase in viscosity decreased the estimated mass transfer coefficient. Overall, the delignification rate of eucalyptus by lactic acid increased by the addition of halide salts.

1. Introduction

Lignocellulose can be converted into cellulose fibers and lignin by delignification technologies. The obtained cellulose pulp can be used for paper production, production of other materials, or can be converted to bio-ethanol or other platform chemicals [1-3]. Lignin is an aromatic biopolymer with advocated potential for the chemical industry and current research is focusing on lignin valorization [4,5].

The traditional pulp mills used in the paper making industry make use of kraft pulping, in which the extracted lignin is burnt in the solvent recovery boilers [6]. The kraft mills are highly integrated and energy effective plants [7]. Nevertheless, over the past decades continued scientific efforts have been made to develop alternative pulp mills, in which lignin could be obtained as byproduct of the cellulose fibers [8-10]. An important category is organosolv, a pulping method making use of organic solvents, such as carboxylic acids [11]. For example, Kajimoto et al. investigated delignification of Japanese sugi pine by lactic acid [12]. Lactic acid is a bio-based platform chemical that can be produced following an established fermentation route [3]. During the delignification process, chemical bonds between cellulose and lignin and hemicellulose were broken and cellulose pulp was formed. Both lignin and (hemi)cellulose breakdown products were dissolved in the solvent.

Deep Eutectic Solvents (DESs) [13] are composite solvents with a melting point considerably lower ($> 50^{\circ}\text{C}$) [14] than would be expected on the pure component melting points of their constituents. Francisco et al. proposed DESs, including mixtures of lactic acid and choline chloride, as suitable solvents for biomass delignification [15]. DES based processes offer many advantages over the traditional kraft or organosolv processes. The major disadvantage of kraft pulping is that the produced lignin contains sulfur, which makes valorization difficult, while organosolv processes requires high amounts of organic solvents, which are often volatile and flammable [16].

DESs were used by various researchers for the fractionation of various types of biomass [17-22]. Lignocellulosic biomass has a complex structure, which can change as function of species and thereby influence the delignification rate. For example, Vasco et al. [17] compared the delignification of a hard and softwood species using DES. They removed 79% of the lignin from poplar (hardwood), while the same treatment could only remove 58% of the lignin from douglas fir (softwood). Chang et al. [18] and Li et al. [22] made a direct comparison between the delignification of eucalyptus and rice straw by lactic acid and DESs consisting of lactic acid and choline chloride. Both authors found that the lignin content in the cellulose residue obtained by pulping with lactic acid – choline chloride DES was

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

significantly lower than in the cellulose residue obtained by pulping with lactic acid only. Although the presence of choline chloride appears to improve delignification, the exact role of the choline chloride is not clear. Especially since a trend was found that the lignin content in residual cellulose decreased with decreasing amounts of choline chloride from 1:2 choline chloride to lactic acid molar ratio to 1:15 [18,21,22], it is not easy to point at one single aspect of the presence of choline chloride that improves the delignification.

Various articles were published about biomass delignification using mixtures of choline chloride and lactic acid [17-22], and various hypotheses were proposed about its role in biomass delignification. Francisco et al. suggested DESs would be good solvents for biomass delignification because of the high solubility of lignin [15]. Other authors who delignified biomass using DESs also suggested that the high amounts lignin removed by the DES resulted from the high solubility of lignin in DES [17]. Liu et al. suggested that the chloride ions in the DES caused the breakdown of lignin carbohydrate complexes [23], while Li et al. presumed that chloride could help to disrupt the intermolecular hydrogen bonding network of biomass and facilitate its dissolution [22]. It can thus be concluded that there are various opinions on the role of the choline chloride, and although these not necessarily contradict each other, it is of importance to investigate these hypotheses to find the most important factors in DES pulping. A good understanding of the role of choline chloride will accelerate the search for better solvents for biomass delignification and the development of effective new pulping processes.

The aim of this paper is to improve the understanding on the role of choline chloride in biomass delignification using lactic acid-based solvents by performing pulping experiments at various lactic acid to choline chloride ratios, including pure lactic acid and aqueous choline chloride. Also pulping experiments using lactic acid with various salts other than choline chloride were studied to investigate the roles of the choline and the chloride separately. *Eucalyptus globulus* was used as biomass since it is the most cultivated species in fast-growing plantations [24]. In Europe, 13.3 Mm³/y of eucalyptus is used for papermaking, making it the most used hardwood species for papermaking after birch [25]. The effect of choline chloride on wood swelling was determined by scanning electron microscopy (SEM) and the effective mass transfer coefficients were estimated by model calculations. Next to *Eucalyptus* wood chips, also DES-pulping experiments were performed using milled wood lignin (MWL) that was obtained by ball milling the eucalyptus. These MWL experiments allowed investigation of the effect of choline chloride on the lignin cleaving reactions without mass transfer effects. Furthermore, the effect of choline chloride on the lignin solubility was studied.

2. Methodology

In the last part of the introduction, the scope of the performed study on the role of choline chloride was sketched, and in this methodology section, the various aspects of wood pulping and how to study factors of importance is discussed.

2.1. Performance of pulping media

During wood pulping, the wood matrix is delignified and the lignin dissolves in the solvent. When the lignin between the cellulose fibers is removed, the fibers are liberated from the wood matrix and cellulose pulp is formed. Pulping under too harsh conditions or too long times may also break down cellulose fibers, producing cellulose dust, which in this study is defined as fines. In previous studies, both sawdust [26] and wood chips were used [27]. Wood chips are used in the current study because wood is used industrially in this form for the production of cellulose pulp. By studying pulping including mass transfer effects in chips that can play an important role in pulping (as discussed in sub-section 2.2.3.), industrial applicability of the results is improved.

After the pulping experiments, the conversion is defined as the fraction of the chips that was converted into fibers, fines or is dissolved in the DES, and is calculated according to:

$$\text{Conversion (\%)} = 100 \cdot \left(1 - \frac{\text{Amount of chips remaining}}{\text{Initial amount of chips}}\right) \quad (1)$$

To reach the fiber liberation point, at least 80% of the lignin initially present in the wood matrix must be removed [28] and therefore, the chip conversion is a good measure for the delignification degree. Also, the yields of cellulose fibers (200 µm to 2.8mm) and fines (<200 µm) were determined. Furthermore, the lignin content in the fibers, undercooked chips and the solvent was determined by resp. the Klason method and cold water precipitation, and the lignin molar weight distribution was determined by GPC. However, ash, extractables and (hemi)cellulose degradation products in the DES were not determined. The degree of delignification was calculated according to:

$$\text{Delignification (\%)} = 100 \cdot \left(1 - \frac{\text{Amount of lignin in fibers + chips remaining}}{\text{Initial amount of lignin in chips}}\right) \quad (2)$$

2.2. Role of choline chloride

In wood pulping, many parameters play a role, like the lignin solubility in the solvent, the cleavage rate of lignin and mass transfer effects. The influence of choline chloride on these

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

roles will be investigated, so we can indicate in which fields choline chloride plays a role during DES pulping.

2.2.1. Solubility

Various authors suggested DESs as suitable solvents for biomass delignification for their high solubility of lignin [15,17]. Therefore, we studied the change in lignin solubility upon the addition of choline chloride to lactic acid by comparing the solubility of a technical lignin in lactic acid with and without the addition of choline chloride. The lignin solubility greatly depends on the used method, because the structure of lignin is highly dependent on its biomass source and method of isolation. Furthermore, lignin is an inhomogeneous polymer, meaning some lignin fractions have a higher solubility than others. In the cloud point method for example [15], the solubility of a solid in a solvent is determined by adding small amounts of solid to a fixed amount of liquid, until the mixture becomes turbid at equilibrium. This method thus determines the solubility of the least soluble lignin fraction. If more lignin is added to this mixture, some of the more soluble fractions may still dissolve and thereby increase the amount of dissolved lignin [29]. This means the lignin solubility is a function of the lignin to solvent ratio and thus, methods like the cloud point method will give a different results than methods which determine the amount of dissolved lignin at a fixed lignin to solvent ratio. This makes comparison of absolute solubility data with other authors difficult.

In this work, we study the role of choline chloride in DESs and therefore, we are merely interested in effect of choline chloride on the lignin solubility in lactic acid. For this reason, we use the most convenient method, which is to add a fixed excess amount of lignin to a fixed amount of liquid [29]. The UV-VIS adsorption of the liquids was taken as a measure of the dissolved lignin. This gives an accurate comparison of the lignin solubility in DES compared to lactic acid and an approximate measure of the absolute solubility.

2.2.2. Lignin reactions

For the study on the effect of choline chloride on lignin cleaving reactions, MWL was used as a representative lignin model [30]. Under conditions where MWL is fully soluble in both the DES and lactic acid, the reactions in lignin can be studied without any influences of mass transfer effects, which will play a role if the influence is studied directly on wood.

The cleavage of the β -O-4 bond in lignin is an important measure for the delignification of wood [31]. The change in β -O-4 bonds after treatment of MWL can be determined by HSQC

Chapter 2

spectroscopy, which is a two dimensional nuclear magnetic resonance technique which is used more often for lignin characterization [17,23,32]. With this technique the bond cleavage can be studied under varying conditions and with different DES compositions, this will show any effects of choline chloride on the cleavage of these bonds. However, multiple types of cleaving and condensation reactions are typically observed in wood delignification [33]. The sum of all these reactions results in a change of the lignin molar weight. This weight was determined by GPC and this data was used to fit an overall lignin cleaving rate constant over the treatments using the model of Marathe et al [34].

2.2.3. Mass transfer effects

During wood pulping, the DES molecules must first diffuse into the cell walls, before they can participate in delignification reactions. After the reaction, the lignin must diffuse out of the cell wall again. It was shown by Kanbayashi and Miyafuji that choline based ionic liquids can swell up cell walls to the point where the cell walls break, as they indicated clearly by SEM imaging [35]. Swelling of wood will increase its permeability and thus, lactic acid will diffuse faster into the cell walls and lignin will diffuse faster out of the cell walls, increasing the pulping rate. To investigate whether choline chloride has a similar effect, we treated a wood chip by aqueous choline chloride and checked whether similar effects as described by Kanbayashi and Miyafuji could be observed.

Apart from the diffusion of pulping chemicals into the cell walls, the diffusion of lignin out of the cell walls is another important step in pulping. Zhao made models for the diffusion rate of lignin in acetic acid pulping based on the Stokes-Einstein equation [36]. The effective diffusion constant of lignin is a function of the molar weight of the lignin and the viscosity of the pulping liquid. We measured the viscosity of the DES and lactic acid solutions after pulping and measured the molar weight of the lignins precipitated from these solutions. Using this data we calculated the effective diffusion coefficients according to the same method to investigate whether choline chloride influences the mass transfer rate of lignin in the cell walls.

3. Methods and materials

3.1. Materials

Air-dry *Eucalyptus globulus* chips were donated by The Navigator Company. The commercially sized chips (typically 25-35 x 10-25 x 2.5-6 mm, LxWxT) were used as received

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

and contained 21.6% lignin, 50.6% glucose, 14.0% xylose and 1.1% galactose, as determined by acid hydrolysis using the standard NREL method [37]. Lactic acid (>85%), choline chloride (>98%), choline hydroxide (46% in water), sodium sulfate (>99%), sodium chloride (>99.5%), TEABr (98%), TEACl-H₂O (>98%), 1,4-dioxane (99.8%), acetic acid (99.5%) and DMSO-d₆ (99.96%) were purchased from Sigma-Aldrich. n-Octane (>98%) was purchased from VWR and kraft lignin from TCI.

3.2. Wood delignification experiments

DESs were prepared by adding lactic acid and the salt of choice to a round-bottom flask equipped with a condenser, and heated to 120 °C under stirring. Choline chloride was used in a 1:10 to 1:250 molar ratio to lactic acid and all other salts were used in a 1:10 molar ratio. Eucalyptus chips (50 g, dry basis) were directly added to the hot DES (1 kg total) through a free neck in the round-bottom flask (Ø29 mm). This mixture was kept at 120 °C for 8 hours under overhead stirring. Next, the mixture was transferred to a pressure filtration setup where the liquid was filtered off under nitrogen pressure (3 bar) on a steel mesh (50 µm). The solid residue was washed with excess tap water and filtered over three consecutive steel meshes (2.8 mm, 200 µm and 50 µm) to separate the undercooked chips, the fibers and the fines. The residues were dried at 105 °C to achieve a constant weight. The errors were calculated from one experiment performed in quadruple. From these experiments the standard deviation was calculated, which was converted to the 95% confidence interval by the t-statistics method.

The Klason lignin content of the sample was determined by hydrolysis of the sample according to standardized NREL procedure [37]. The sample (0.3 g) was added to an Ace glass pressure tube. 72% sulfuric acid (3 mL) was added and kept at 30 °C for one hour while stirring every 10 min. After this, water (84 mL) was added and the tube was kept at 120 °C for another hour. The solids were filtered and dried overnight at 105 °C. The lignin content was determined by the ratio between the weights of the solid residue and the initial amount of sample added as determined by an analytical balance (+/- 0.0001 g). The acid soluble lignin was determined using a Hach Lange DR5000 UV-VIS spectrophotometer at a wavelength of 320 nm. The errors were calculated from one sample which was analyzed 8 times. From these analyses the standard deviation was calculated, which was converted to the 95% confidence interval by the t-statistics method. All other samples were analyzed in duplo.

3.3. MWL production and experiments

MWL was produced from the same eucalyptus chips as used in the pulping experiments by applying a similar method to that proposed by Björkman [38]. The chips were ground using a hammermill to pass through a steel mesh (212 μm). The wood (50 g) was extracted by acetone in a Soxhlet apparatus for 8 h to remove extractables. The extracted wood was air dried and dispersed in octane (500 mL). The suspension was then transferred to a rotary ball mill in which it was milled by 35 ceramic balls of 25 g each for seven days at a rotational speed of 32 rpm. The octane was decanted and the suspension was divided equally into eight parts, which were added separately to an agate grinding jar (250 mL), together with 40 agate grinding balls of 10 mm. Octane was added to the milling jars (100 g per jar). Each part was milled for three days in a Fritsch Pulverisette 5 planetary ball mill at 360 rpm. After milling, the suspension was rinsed off the grinding equipment with a wash bottle containing octane. The fractions were combined and the octane was decanted. The rest of the octane was evaporated by a small nitrogen flow overnight. 96% dioxane in water (500 mL) was added to the ground eucalyptus and was left seven days for extraction under continuous stirring. The dioxane was separated from the wood residue by centrifuging five min at 9000 rpm. Dioxane was removed from the lignin in a rotary evaporator at 50 °C and 20 mbar. The remaining solids were dissolved in 90% acetic acid (20 mL), and the glass was rinsed with the same solution (10 mL). The liquids were filtered over a glass-fiber filter and precipitated in purified water (300 mL) under stirring. The water was removed by centrifuging for five min at 9000 rpm. The remaining solids were washed with water (10 mL), which was then removed in the same way as previously. The solids were dried overnight under vacuum. A total lignin yield of 0.90 g was obtained from 50 g eucalyptus.

MWL (50 mg) was placed in an Ace glass pressure tube. 10 g Lactic acid or 10 g choline chloride to lactic acid DES (1:10) was added to this pressure tube. Once the lignin was fully dissolved, the pressure tube was heated to 120 °C for 1 h. After cooling to room temperature, purified water (30 mL) was added to precipitate the lignin. The solids were separated by centrifuging for three minutes at 9000 rpm and washed with purified water (10 mL), which was then removed by centrifuging for five min at 9000 rpm. The sample was dried overnight under vacuum.

3.4. Lignin solubility test

0.6 g kraft lignin was added to 3 g lactic acid or 3 g choline chloride and lactic acid DES (1:10). These mixtures were shaken overnight in a Julabo SW22 shaking bath at 200 rpm at room temperature. Excess lignin was filtered from the samples using a 0.2 μm syringe filter and

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

30 mg liquid was diluted in 50 mL ethanol in a volumetric flask. The lignin absorption of these solutions were determined by UV-VIS spectroscopy at 320 nm using a Hach Lange DR5000 spectrophotometer.

3.5. Scanning Electron Microscopy (SEM) imaging

Samples were submerged in water for 72 h, after which a small cut was made perpendicular to the longitudinal direction using a scalpel. Next, it was submerged in liquid nitrogen for a couple of minutes and split from the cut with a hammer. Next, the samples were dried under vacuum for 72 hours. A chromium layer (10 nm) was applied by a Quorum Q150T ES coater. SEM images were captured by a JEOL JSM 5600 LV at 5 kV and 6000x magnification.

3.6. NMR spectroscopy

The samples were prepared by dissolving MWL (200 mg) in DMSO-d₆ (600 µL). The samples from the MWL hydrolysis experiments were prepared by dissolving the complete precipitate in DMSO-d₆ (300 µL). All the experiments were carried out in a Bruker Avance II 600 MHz (14.1 T) spectrometer and the spectra were processed using MestReNova software. 2D HSQC spectra were acquired using the Q-CAHSQC pulse program [39] according to the method described by Constant et al. [32]. Matrices of 2048 data points for the ¹H-dimension and 256 data points for the ¹³C-dimension were collected applying a relaxation delay of 6 s and spectral widths from 14 to -1 ppm and from 200 to 0 ppm for the ¹H and ¹³C dimensions, respectively. The spectra were integrated according to the method described by Constant et al. [32].

3.7. Gel permeation chromatography

The weight distribution of the lignins were analyzed by gel permeation chromatography (GPC). For GPC, 50 mg lignin was dissolved in 5 mL tetrahydrofuran. All samples formed clear solutions in THF, indicating they were fully soluble. An Agilent 1200 series was used with a refractive index detector and a UV detector operating at 254 nm using three GPC PLgel 3 µm MIXED-E columns in series. The column oven was operated at 40 °C and tetrahydrofuran was the solvent at a flowrate of 1 ml/min. Molecular weights were determined by calibration against polystyrene solutions with molecular weights ranging from 162 to 27,810 Da.

3.8. Lignin cleavage and condensation model

The cleaving rate of MWL during treatments by lactic acid and DES was modeled by the model of Marathe et al. [34]. Although this model was originally developed for pyrolysis, pulping and pyrolysis treatments cause both cleaving and condensation reactions in lignin. Therefore, this model was deemed suitable for pulping reactions as well. In the model, the molar weight distributions before and after the treatment (as determined by GPC) were converted to a population balance of the degrees of polymerization. In this conversion it was assumed that each lignin polymer is a linear chain, consisting of identical monomers with a weight of 200 gram/mol.

Two kinds of reactions were taken into account. First, lignin polymers with a DP_i can be cracked according to:

It is assumed that only the bonds connecting the monomer units present in the DP_i segment can be cracked. Therefore, this segment can be cracked in $i-1$ different ways. It is also assumed that the possibilities of cracking have the same likelihood, thus the rate constant (k_k) is equal for all cracking reactions. Second, two lignin molecules can polymerize according to the following reaction:

It is assumed that all molecules will polymerize with each other, in all possible combinations. Like in case of cracking, all polymerization possibilities have the same likelihood, thus the reaction rate constant (k_p) is the same for all polymerization reactions. Both rate constants were fitted on the lactic acid treatment. Because the condensation and cleavage rate are highly correlated, the condensation rate of the lactic acid treatment is fixed on the DES treatment and a new cleavage rate is fitted. The ratio between the cleavage rate of the DES and lactic acid treatment is reported. A detailed description of the model can be found in the paper of Marathe et al. [34].

3.9. Lignin diffusion coefficient estimation

The effective lignin diffusion coefficients were calculated according to the method described by Zhao et al. [36]. In this method, the Stokes-Einstein equation with adaption to different temperatures by an Arrhenius expression was used to estimate the diffusion coefficient of lignin in pulping liquid. Zhao also showed a calculation for the radius of a lignin

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

molecule as function of the molar weight, and showed a factor to convert the diffusion coefficient to an effective diffusion coefficient in the cell wall. Detailed calculation can be found in the paper of Zhao et al. [36]. The molar weights of the lignins used in these calculations were determined by GPC and the viscosity of the DES liquors was measured using a Brookfield DV-E viscosity meter.

4. Results

4.1. Effect of choline chloride to lactic acid ratio on pulping

Eucalyptus chips were pulped using lactic acid, aqueous (65%) choline chloride and a 1:10 molar mixture of choline chloride and lactic acid. This high ratio was chosen because it was shown by various authors that the amount of lignin removal from biomass increases upon a decrease in the amount of choline chloride [18,21,22]. These experiments were performed at 120 °C, as this was shown to be effective by Vasco et al. [17]. The reaction time was increased to 8 h, since commercial wood chips were used instead of sawdust. The pulping trial using the aqueous choline chloride did not convert any wood chips, while the trial using only lactic acid showed a wood chip conversion of 49% to pulp or products dissolved in DES. The trial using DES showed a conversion of 95%. Analysis of the lignin obtained by precipitation after the trials showed an average molar weight of 4300 g/mol for the lignin obtained from lactic acid, while the molar weight of the lignin obtained from the DES with choline chloride was only 3200 g/mol, as can be seen in fig. 2.1. A pulping trial using only lactic acid for a prolonged time of 48 h was performed, which converted 97% of the wood chips, which is comparable to the trial with the choline chloride – lactic acid DES of 8 h. Also the fiber yield and residual lignin content in the fibers of this trial are similar to the DES trial, but the molar weight of the lignin was 4150 g/mol, which is higher than molar weight of the DES lignin.

The 8 h pulping trials using the DES at 120 °C were repeated with 5 choline chloride to lactic acid ratios between 1:10 and 1:250. It was found that the conversion did not differ significantly between the 1:10 and 1:50 choline chloride to lactic acid ratios. When this ratio was further increased to 1:250 the conversion decreased from 95 to 83%. Also, the lignin content remaining in the fibers did not show a significant difference among all experiments performed, neither did the lignin content in the fibers. The results are summarized in fig. 2.2.

Fig. 2.1. Molar weight distributions of the lignins produced by lactic acid and the 1:10 choline chloride to lactic acid DES, as determined by GPC.

4.2. Effect of other salts on lactic acid pulping

In the previous sub-section, it was shown that the addition of small amounts choline chloride to lactic acid significantly increases the biomass conversion rate, but it is yet unknown whether this effect is caused by the cation, anion, or both. Therefore, eucalyptus was treated using lactic acid and various other salts containing choline, tetraethylammonium and sodium cations and chloride, bromide, sulfate and hydroxide as anions. The same conditions were used as with the trial using choline chloride and lactic acid, the results are given in Table 1. From Table 1 it follows that for all experiments using halides as anion an equal or higher conversion than the trial using choline chloride was observed, while all trials using sulfate and hydroxide resulted in a lower conversion than the trial using only lactic acid. When the same anion is used, all tests using sodium or TEA yielded a higher conversion than all trials using choline as cation. No significant differences were found between sodium and TEA as cations. It can thus be concluded that the role of the anion is more pronounced than the role of the cation.

Understanding the role of choline chloride in deep Eutectic solvents used for biomass delignification

Table 2.1. Conversion results (as defined in eq. 1) from biomass delignification experiments using lactic acid and various added salts (column: row matrix elements representing the conversion measured for that specific anion: cation combinations). All experiments were performed using a 1:10 molar ratio of salt to lactic acid at 120 °C for 8 h.

	Cl ⁻	Br ⁻	SO ₄ ²⁻	OH ⁻
Choline ⁺	95	95	4	2
Na ⁺	99	n.d. ^a	37	n.d.
TEA ⁺	99	99	n.d.	n.d.

^an.d. is not determined (these were not part of the measured combinations, no specific reason)

4.3. Effect of choline chloride on lignin solubility

An excess amount of kraft lignin was added to the same amounts of DES and lactic acid. Kraft lignin was selected since this was also used by Franciso et al. [15]. These mixtures were equilibrated overnight in a shaking bath. After filtering off the excess lignin, the solutions were diluted in ethanol and the absorption was determined by UV-VIS. The UV-VIS absorption was multiplied by the dilution factor of DES or lactic acid in ethanol. This product was taken as a measure of lignin concentration. Lignin concentrations around 10 wt % were found and the lignin solubility in lactic acid was 4.6% (relative to the 10%) higher than in the DES. Assuming that the values obtained with kraft lignin are representative for the lignin obtained by pulping with DES, it appears that the lignin solubility is not a discerning factor for the overall rate of the delignification process. Considering that on the basis of the lignin content in eucalyptus of typically around 20 percent, and the applied DES to wood ratio of 20:1, a lignin concentration around 1 wt % is obtained when all lignin is removed from the wood. Therefore, it is not surprising that the lignin solubility under applied conditions is not a discerning factor.

Fig. 2.2. Results of biomass delignification trials of eucalyptus using lactic acid and various DES mixtures containing choline chloride at 120 °C. The symbols show results from delignification trials using the DESs after an 8 h treatment. Solid lines show the results from the trial with lactic acid for 8 h and the dashed line the results for 48 h. a: conversion, b: fiber yield, c: lignin content in the fibers and d: delignification for various molar ratios of choline chloride (1) to lactic acid (x). Terminology is defined in section 2. Error bars show the 95% t-statistic confidence intervals.

Understanding the role of choline chloride in deep Eutectic solvents used for
biomass delignification

b)

d)

Fig. 2.3. Main lignin bonds A) β -O-4, B) β -5 and C) β - β . a-c: δ ^1H and δ ^{13}C , 3.3-5.8 and 63-98 ppm, respectively, regions in the 2D HSQC NMR of a: MWL treated by lactic acid, b: MWL treated by DES, c: original MWL. d: Number of inter-aromatic bonds per 100 aromatic rings in MWL before (left) and after treatment by lactic acid (middle) and DES (right) at 120 °C for 1 h. The tinted bars show the β -O-4 (red), β -5 (purple) and β - β (green) fractions as quantified by HSQC. The grey bars represent bonds that were unidentified.

4.4. Effect of choline chloride on inter-lignin cleaving reactions

The effect of the choline chloride on the lignin cleaving reactions without mass transfer effects was investigated by applying pulping conditions to MWL that was dissolved in lactic acid and DES, respectively. Three inter-aromatic bonds in lignin were quantified by ^1H – ^{13}C 2D HSQC NMR spectroscopy and the lignin molar weight distribution was determined by GPC, both before and after treatments using lactic acid, with and without the addition of choline chloride.

Before any treatments, the MWL contained 53 β -O-4 bonds per 100 aromatic units. After treatment by lactic acid this number decreased to 18 bonds, while after treatment by the DES, this number decreased to 11, suggesting more bond-breaking activity of the DES than with lactic acid only. Also, the molar weight of the MWL decreased more after the DES treatment than after the lactic acid treatment. The HSQC spectra and the number of β -O-4, β - β and β -5 bonds before and after both treatments are shown in fig. 2.3.

The changes in the molar weight distributions after the treatments were fitted to the model of Marathe et al. [34]. In the fit, the condensation rate constant was kept constant and the cleavage rate constant was fitted to the molar weight distributions. The results of the model satisfactory fit the data and are shown in fig. 2.4. The model showed a 90% increase in the lignin cleavage rate constant upon the addition of choline chloride to lactic acid.

Fig. 2.4. Population balance of MWL before and after treatments at 120 °C for 1 hour by lactic acid and DES, as determined by GPC. Green dots show the original MWL, red diamonds MWL after treatment by lactic acid and blue squares after treatment by DES. The solid line shows the fit of the DES treatment and the dashed line the fit of the lactic acid treatment.

4.5. Effect of choline chloride on swelling and mass transfer

A SEM picture (see fig. 2.5) was taken of a eucalyptus chip treated by aqueous choline chloride for 8 hours at 120 °C. After treatment, the chip was split perpendicularly to the longitudinal direction. After cooking in aqueous choline chloride, no obvious signs of swelling, or disruption of the cell walls (as observed by Kanbayashi [35]) could be observed.

The average effective diffusion coefficient of the lignins were calculated according to the method of Zhao et al. [36]. For the calculations the mass average molar weights of the lignins were used as determined by GPC. The lignin produced by lactic acid (48 h) had an average molar weight of 4150 gram/mol and the liquor had a viscosity of 0.808 P, which resulted in an average effective diffusion coefficient of $5.0 \cdot 10^{-13} \text{ m}^2/\text{s}$. The 1:10 choline chloride to lactic acid DES had a viscosity of 0.951 P after pulping and the lignin had an average molar weight of 3200 gram/mol, which resulted in an average effective diffusion coefficient of $4.8 \cdot 10^{-13} \text{ m}^2/\text{s}$. Thus, the beneficial effect of the lower lignin molar weight in the DES was counteracted by the increase in viscosity, caused by the addition of choline chloride [40].

Fig. 2.5. SEM image of eucalyptus treated by aqueous choline chloride (65 wt %) for 8 h at 120 °C.

5. Discussion

5.1. The effect of choline chloride on pulping

The pulping experiments using lactic acid with and without addition of choline chloride show a clear increase in conversion upon the addition of choline chloride. When only lactic acid is used for a prolonged time of 48 h, a similar conversion was observed as in the experiment using DES for 8 h, meaning that although the delignification rate was increased, the addition of choline chloride is not a pre-requisite. Furthermore, this experiment did not show any significant differences in fiber yield or lignin content in the fibers, indicating the observed effects are merely kinetic.

The experiments using various salts other than choline chloride showed that only addition of salts containing halogen anions result in a similar conversion as with choline chloride or higher. However, all salts containing choline as cation show a lower conversion than salts containing TEA^+ or Na^+ and the same anion. Based on this comparison, it is concluded that the chloride anion is causing the increased delignification rate when adding choline chloride to the pulping mixture with lactic acid.

5.2. Effects on Solubility

Francisco et al. [15] investigated the solubility of kraft lignin in DESs with lactic acid to choline chloride ratios between 1.3:1 to 10:1. They found that the solubility of lignin increases with decreasing amounts of choline chloride, but the solubility in pure lactic acid was not determined. We compared the solubility of kraft lignin in lactic acid to its solubility in the 10:1 lactic acid to choline chloride DES by adding an excess amount of lignin to the solvents. Lignin solubilities around 10 wt % were found, consistent with the experiments reported by Francisco. However, the lignin solubility in lactic acid was slightly higher than in the DES. Various authors proposed DESs as suitable solvents for biomass delignification because of their high lignin solubility [15,17,41]. However, based on the effects here described, the observed increase of the delignification rate upon the addition of choline chloride to lactic acid is not caused by an increase in lignin solubility. Considering the solubility of lignin in the DES, and the expected maximum concentrations based on the lignin content and wood, and the DES to wood ratio, using DES instead of lactic acid will also not induce a limitation due to the slightly lower lignin solubility.

5.3. Effects on lignin reactions

From the MWL experiments it seems that the β -O-4 bonds in lignin are cleaved faster by the DES than by pure lactic acid. Imai et al. [42] treated a β -O-4 model compound by various acids and found that this model was cleaved faster by HCl and HBr than by H_2SO_4 . They proposed a different reaction mechanism for the cleavage of the β -O-4 bond by HCl than by H_2SO_4 . Briefly, they proposed that the mechanism using H_2SO_4 involves the liberation of formaldehyde from the γ -hydroxymethyl groups in lignin, while the mechanisms using HCl and HBr involve a benzyl cation type intermediate. Similar to the observations and conclusions of Imai et al. [42], We presume that the addition of chloride ions to lactic acid allows cleavage of the β -O-4 bond by a different (faster) reaction mechanism, such as proposed by Imai. [42]. During acidic treatments, β -5 bond may be converted to stilbene structures, while β - β structures do not seem to be cleaved by acid hydrolysis [43,44]. Thus, these bonds do not split two lignin monomers upon acidic treatments.

By fitting the lignin cleavage and condensation model of Marathe et al. [34] to the molar weight distribution curves obtained after 1 h treatment of MWL with DES and with lactic acid without choline chloride, a 90% increase in the cleaving rate of lignin was observed upon the addition of choline chloride to lactic acid. In this approach, the lignin condensation rate was kept constant in this model. Although it is recognized that any possible influence of choline chloride on lignin condensation reactions [45] cannot be excluded with the current results, it does show that chloride has an effect on the reaction rates, and the increased rate of delignification cannot be ascribed to merely mass transfer effects.

As a further support to this statement, Liu et al. postulated that chloride ions help to cleave lignin carbohydrate complexes (LCC) in biomass [23]. However, their result is not fully comparable with ours, since they found that benzyl ether bonds between lignin and carbohydrates were present in MWL, but not in the lignin after their DES treatment of biomass. In our work, we could identify benzyl ether bonds in MWL before and after treatments by both lactic acid and DES. Therefore, it seems that these bonds were not cleaved during the DES treatment. It is plausible that the LCCs from Liu's DES delignification experiments remained in the residual lignin of the cellulose residue.

5.4. Effects on mass transfer

Kanbayashi and Miyafuji [35] treated Japanese cedar wood by chloride and bromide based ionic liquids. They found by SEM analysis that the cell walls were broken and dissociated by swelling of the middle layer of the secondary cell wall, which was induced by these ionic liquids. We treated wood chips by an aqueous choline chloride solution and found the wood structure to be intact after the treatment. We did not observe swelling effects similar to those observed by Kanbayashi and Miyafuji [35]. This means the choline chloride does not act as a swelling agent for the wood chips, and increased delignification is not due to easier mass transfer due to swollen wood.

Next to swelling of the wood, also differences in lignin fractions may result in differences in mass transfer rate. As observed from the GPC results, the average molar weight of the lignin produced by DES is lighter than the lignin produced by only lactic acid. Smaller lignin fractions will diffuse faster out of the wood matrix than larger fractions and thereby increase the pulping rate. However, this benefit was counteracted by the higher viscosity of the DES compared to lactic acid.

6. Conclusions and outlook

Addition of choline chloride to lactic acid increases the pulping rate of eucalyptus chips. Choline chloride is already effective at a ratio of 1:250 to lactic acid, as opposed to the high amounts currently used by other researchers. It was found that the chloride ion is the active ingredient in choline chloride. In fact, an inexpensive salt such as NaCl performed as well as choline chloride.

The effect of choline chloride on lignin solubility, cleaving reactions and mass transfer were investigated in order to gain understanding of the observed pulping results. Addition of choline chloride to lactic acid slightly decreased the lignin solubility. Studies on MWL showed that the β -O-4 cleavage rate increased, as demonstrated by HSQC. The wood chips did not show swelling, nor break-up after treatment by aqueous choline chloride. Furthermore, the mass transfer coefficient of lignin in the cell wall slightly decreases when choline chloride is added to lactic acid.

The findings reported in this article can be used as a spur for further solvent development or optimization for biomass delignification. A suitable solvent will preferably be inexpensive, non-toxic and bio-based. The previously proposed DESs have all of these properties, but this study has shown that other options, such as mixtures of organic acids with inorganic salts, should also be considered. Alternatively, one can consider mixtures between organic solvents and HCl as a catalyst. Many of these mixtures, e.g. ethylene glycol with HCl, have been studied in earlier work [8], and those findings should be taken into account when searching for new (and deep eutectic) solvents for biomass delignification.

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Chapter 2

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Chapter 3

Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

Abstract

After biomass fractionation using deep eutectic solvents (DESs), solvent recovery is an essential step. Laboratory routine is to precipitate lignin using cold water, however large amounts of water are required, resulting in energy intensive operations. Therefore, we propose liquid-liquid extraction as alternative method for industrial applications, and have studied this to recover lignin from a DES consisting of lactic acid and choline chloride, which we applied in various ratios. In this study six solvents were investigated for this purpose, from which 2-methyl tetrahydrofuran (2-MTHF) was selected for further studies. The phase equilibria between the DES and 2-MTHF were determined at 25, 50 and 75 °C. At least 30 wt % choline chloride in the DES was required to form two phases. Addition of more choline chloride decreases the mutual solubility of 2-MTHF and lactic acid. The overall equilibrium lignin distribution between DES and solvent did not change much with varying DES compositions, but the distribution was dependent on the molar mass of lignin. The low molar weight fractions showed a distribution coefficient around 1, while for the heavy fractions the distribution coefficient was below 0.1. Addition of water changes the system greatly, and high molar mass lignin extraction is tremendously enhanced. At 25 wt % water in the DES, the minimum distribution coefficient was 4, allowing effective extraction of lignin from DES by 2-MTHF.

1. Introduction

DESs are composite solvents that exhibit deep eutectic behavior upon mixing the constituents, meaning the melting points of these mixtures is reduced considerably more ($>50\text{ }^{\circ}\text{C}$) than would be the case for ideal mixtures [1,2]. These solvents can easily be prepared in numerous ways by combining a hydrogen bond donor and acceptor [3] and are often biocompatible, biodegradable [4] and can have a low toxicity [5].

Lignocellulose can be converted into cellulose fibers and lignin by delignification technologies. The obtained cellulose pulp can be used for paper production, production of other materials, or can be converted to bio-ethanol or other platform chemicals [6-8]. Lignin is an aromatic biopolymer with advocated potential for the chemical industry and current research is focusing on lignin valorization [9]. The traditional pulp mills used in the paper making industry make use of kraft pulping, in which the extracted lignin is burnt in the solvent recovery boilers [10]. The kraft mills are highly integrated and energy effective plants [11]. Nevertheless, over the past decades continued scientific efforts have been made to develop alternative pulp mills, in which lignin could be obtained as byproduct of the cellulose fibers [12-14]. Recently, DESs have often been used for biomass delignification [15-21]. DES based processes offer many advantages over the traditional kraft or organosolv processes. The major disadvantage of kraft pulping is that the produced lignin contains sulfur, which makes valorization difficult, while organosolv processes requires high amounts of organic solvents, which are often volatile and flammable [22].

Regeneration of DESs is most often performed by precipitation of either the solute [23] or solvent [24-25] in an anti-solvent. Especially in biomass fractionation, large amounts of water are required as anti-solvent for the precipitation of lignin [16]. To recover the DES, these anti-solvents forming a homogeneous mixture with the DES must be evaporated from the DES, which is very energy intensive. Therefore, alternative separation techniques are desired, and will aid industrial applicability of DESs. Yoo et al. recovered phenolic compounds from DES using resins [26], but required large solvent volumes to elute the extractants from these resins. Tian et al. recovered flavonoids from DESs by sorption, but this required high dilutions of DES in water [27]. Liang et al. used electrodialysis membranes to recover DESs after biomass fractionation [28], but needed high dilutions of DES in water to achieve this.

Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

Liquid-liquid extraction is a separation technique that can be energy efficient [29], and has been reported for biorefineries, e.g. for lipid extraction from microalgae [30,31] and fractionation of pyrolytic bio-oils [32,33]. Stiefel et al. investigated equilibria of lignin between 2-methyl tetrahydrofuran (2-MTHF) and alkali solutions [34] and showed that lignin can be recovered by liquid-liquid extraction (LLX). Hu converted fructose to 5-HMF in DES and showed the product can be recovered later on by LLX with ethyl acetate [35]. In line with these promising results with LLX, we investigated the possibilities to recover lignin from DESs by LLX.

In this study we performed a solvent screening to find suitable solvents for extraction of lignin from a DES comprised of L-lactic acid (LA) and choline chloride (ChCl). Of primary importance for LLX is that the solvents are not miscible with the DES, or at least show limited mutual miscibility. Then, a high lignin distribution to afford a low solvent to feed ratio is beneficial for the required energy improving the sustainability. Because a low environmental footprint and low toxicity is highly desired, also the (eco)toxicity was evaluated. In the screening procedure two phase formation was investigated first, just as the sustainability and finally the lignin extractability of the suitable solvents. For the selected DES - solvent combination, the phase behavior was studied and further studies were performed on the lignin distribution between the solvent and DES.

2. Experimental Section

2.1. Materials

Lactic acid (>85%), choline chloride (>98%), 1,4-dioxane (99.8%), 2-MTHF(>99%, 250 ppm BHT), γ -valerolactone (GVL, 99%), Guaiacol (natural, >99%), cyclopentyl methyl ether (CPME, >99.9%, 50 ppm BHT) and Cyrene (99%) were purchased from Sigma-Aldrich. Crystalline L-lactic acid was kindly donated by Corbion. Eucalyptus globulus wood chips were kindly supplied by The Navigator Company.

2.2. Solvent screening

Screening of solvents for liquid-liquid extraction of lignin from DES requires a lignin-loaded DES, which was accomplished by using DES comprised of ChCl and LA in a 1:10 molar ratio that was previously used in pulping experiments [15]. In these pulping experiments, 50 g of eucalyptus chips were treated by 1 kg DES for 8 hours at 120 °C. Afterwards, the DES with dissolved lignin was filtered from the cellulose fibers over a 50 μ m steel mesh. In the LLX solvent screening experiments, 5 mL solvent was added to 2.5 mL DES obtained from pulping. The vials were shaken at room temperature over-night at 200 rpm in a Julabo

Chapter 3

SW22 shaking bath. Two phase formation was determined visually. When two phases were observed, an estimate of the lignin distribution over the phases was made using UV-vis absorption spectrometry (aromatics from lignin show much stronger UV absorbance than the solvents). To facilitate this, the settled phases were separated and diluted in ethanol. The lignin concentrations were estimated by UV-VIS absorption at 320 nm using a Hach Lange DR5000 spectrophotometer. The overall average distribution coefficients of lignin species measured at 320 nm were calculated by dividing the concentration in the solvent phase by the concentration in the DES phase. Next to the averaged distribution as determined for the solvent screening experiments, for the selected solvent also the lignin molar weight distribution was determined in both the original DES and in the organic solvents after extraction were determined by gel permeation chromatography (GPC). The lignin molar weight distribution in the DES raffinates could not be determined since they were not fully soluble in the GPC eluent resulting in solids deposition on the column.

2.3. 2-MTHF-DES phase equilibria

3 g 2-MTHF and 3 g DES composed of crystalline LA and ChCl were added to a glass vial. This vial was shaken at 200 rpm at over night at 25, 50 or 75 °C in a Julabo SW22 shaking bath. The two phases were allowed to settle and were separated. Concentrations of ChCl, LA and 2-MTHF were analyzed by high performance liquid chromatography (HPLC). An Agilent 1200 system was equipped with a Hi-Plex-H column operated at 60 °C and a refractive index detector at 55 °C. 5 mM sulfuric acid in water was used as mobile phase with a flowrate of 0.6 mL/min.

2.4. Lignin extraction experiments

Lignin extraction experiments were performed using lignin that was previously recovered from the DES by precipitation. Precipitation was done by addition of three g water per g DES. The lignin was separated by centrifugation, washed twice with water and dried in vacuum. Crystalline lactic acid, choline chloride and 2-MTHF were added to a flask to form 3 g of DES comprising of ChCl : LA ratios between 1:1.1 and 1:2.4, and 3 g solvent phase at equilibrium. 50 mg lignin that was previously obtained by cold water precipitation from another portion of DES after the same pulping procedure was added per vial. For the experiments with varying water contents a 1:1.7 ChCl : LA DES at equilibrium was used. 0.15 to 3 g water was added to the vials to create water contents varying from 5 to 50 wt % based on the DES. These vials were shaken at 200 rpm at 50 °C over night in a Julabo SW22 shaking bath. The phases were separated and analyzed by GPC.

2.5. GPC analysis

For GPC, an Agilent 1200 series was used with a refractive index detector and a UV detector operating at 254 nm using 3 GPC PLgel 3 μ m MIXED-E columns in series. The column was operated at 40 °C and a 95:5 (v:v) tetrahydrofuran and water mixture was the solvent at a flowrate of 1 mL/min. Molecular weight distributions were calibrated using polystyrene solutions having molecular weights ranging from 162 to 27,810 Da. The product of the UV absorbance and the dilution factor were used as measure for the lignin concentrations in both the DES and 2-MTHF phase. The distribution coefficients were calculated by dividing this product for the 2-MTHF phase by the product for the DES phase.

2.6. Karl-Fischer titration

The water content of the DES used in the pulping experiment was determined by Karl-Fischer titration using a Metrohm 787 KF Titrino. Hydranal composite 5 (5 mg water/mL) was titrated from a 20 mL burette in a 3:1 (v:v) mixture of methanol and dichloromethane. The sample was measured in duplo with a relative error <1%.

3. Results and discussion

3.1. Solvent screening

The first requirement for a suitable LLX solvent is the formation of two phases. Considering the high polarity of the DES phase, organic solvents that have an apolar character should be accessed. For lignin extraction from DES, in order to make a real benign process, it would be preferable if the solvent could be bio-based. Six solvents were selected for this screening that all have limited polarity. The first solvent investigated is dioxane, which is not bio-based, but serves as benchmark, since this cyclic ether is commonly used as a solvent for dissolving lignin [36,37]. Although the acute toxicity of dioxane is relatively low (5170 mg/kg is lethal for rats) and it is bio-degradable [38], because dioxane is produced from petrochemicals [39], another cyclic ether was also investigated, namely 2-MTHF [40]. This solvent is produced from pentosan [41], does not seem to be genotoxic or mutagenic [42,43], and is used in the OrganoCat process to extract lignin [34]. Also, the ether CPME was accessed, as it has been suggested that this solvent can be produced from biological sources [44,45], and its higher boiling point and greater stability and narrow explosion range make a greener and safer alternative to dioxane [46]. Guaiacol was selected as an aromatic solvent, which may be produced by hydrocracking of lignin [47], or from pyrolytic bio-oils [48]. GVL [49] and cyrene [50] were

Chapter 3

also selected as bio-based ketone solvents, which are produced from hemicellulose and cellulose.

The selected solvents were equilibrated with ChCl – LA (1:10) DES and two phase formation was determined visually. GVL, guaiacol and cyrene turned out to be miscible with the DES, and are therefore not suitable for liquid-liquid extraction using this DES. For the solvents that did form a biphasic system, the overall distribution coefficient of the lignin over the solvent phase and the DES phase (total lignin in solvent over total lignin in DES) was estimated by UV-VIS spectroscopy, see Table 3.1. The highest distribution coefficient was found for dioxane, followed by 2-MTHF and CPME showed the lowest overall average lignin distribution coefficient .

Table 3.1. Overview of solvent screening with 6 solvents for liquid-liquid extraction with lactic acid choline chloride DES. Miscibility with DES, solubility of lignin and bio-based origin are shown.

Solvent	2-phase formation	Bio-based	Distribution coefficient (-)
1,4-Dioxane	Yes	No	0.46
2-MTHF	Yes	Yes	0.31
GVL	No	Yes	-
Guaiacol	No	Possibly	-
CPME	Yes	Possibly	0.11
Cyrene	No	Yes	-

To get further insight in the lignin distribution, the molar weight distribution of the extracted lignins was compared to the molar weight distribution of the original lignin in DES. The molar weight distributions are plotted in fig. 3.1, from which it was found that both dioxane and 2-MTHF could extract lignin with a broad range of molar weight fractions from the DES, while CPME could only extract the lower molar weight fractions. Presumably, the lower polarity of CPME compared to dioxane and 2-MTHF reduces its ability to extract these lignin fractions. Although this behavior may be useful in the fractionation of lignin when low molar weight fractions are desired in further applications,

Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

it is in the current study left out of consideration since the objective of this study was to find a solvent that can recover as much lignin from the DES as possible. Considering the bio-based nature of 2-MTHF, in combination with the reasonable lignin distribution, it was decided to investigate the lignin extraction in more detail for 2-MTHF.

Fig. 3.1. Molar weight distributions of the lignin originally dissolved in the DES and the lignin extracted by the solvents. Raw variable wave detector (VWD) signals are shown. The solid green line shows the molar weight distribution of lignin in the original DES and the dashed yellow, the dotted blue, and dash-dotted red lines the molar weight distributions of lignin in 2-MTHF, Dioxane and CPME after extraction.

3.2. Phase behavior Studies for 2-MTHF with ChCl and LA

Before the extraction of lignin was studied further, the phase behavior between DES and 2-MTHF was studied further since the constituents of the DES may have a different partitioning between the DES and solvent [51]. Therefore, the partitioning of the DES constituents and the solvent were determined at three temperatures. The phase equilibrium results are shown in fig. 3.2. From this figure it follows that the temperature dependence of the equilibria is very small, because the tie lines are similar at the different temperature measurements. Furthermore, lactic acid concentrations in the 2-MTHF phase after equilibration are significant with fractions from 12 to 36 wt %. Where the lactic acid showed significant partitioning into the 2-MTHF phase, choline chloride hardly transferred, and as a result all DES phases contained more than 30 wt % choline chloride,

but no choline chloride was found in the 2-MTHF phases. A mixture comprised of 14 wt % choline chloride, 36 wt % 2-MTHF and 50 wt % lactic acid formed a homogeneous liquid. From a process point of view, the LA that leached to the 2-MTHF must be washed from the produced lignin when the 2-MTHF is evaporated. The amount of LA leached to the 2-MTHF decreased with increasing amounts of ChCl. During pulping, the ChCl concentration is an important factor in the delignification rate [15], and addition of more ChCl to a 10:1 LA to ChCl DES decreases the delignification rate. Therefore, the optimal amount of choline chloride -from a process point of view- will be a trade-off between the delignification rate and the amount of lactic acid leaching to the solvent phase.

Fig. 3.2. Phase diagram with liquid-liquid equilibrium data between choline chloride, lactic acid and 2-MTHF at 25, 50 and 75 °C. The axis show the mass fractions of the constituents.

3.3. Influence of DES composition on lignin extraction

Since the DES composition is an important factor in the process design, the distribution of lignin between the DES and solvent was investigated for 4 different DES compositions varying in ChCl to LA molar ratio from 1:1.1 to 1:2.4. The results for these trials are shown in fig. 3.3. For every DES composition, the distribution coefficient of low molecular weight fractions is higher than the high molecular weight fractions, but does not seem to be influenced much by the DES composition. It is remarkable that all distribution coefficients are lower than the distribution coefficient obtained from the initial screening. The initial screening was performed using a DES that was directly obtained from a biomass fractionation experiment, while the experiments in this series to investigate on the effect of the DES composition were performed using lignin precipitated from this biomass fractionation experiment. The lower distribution compared to the distribution obtained with the DES directly from the pulping experiment is possibly caused by a difference in nature of the UV absorbing species present in the DES, and the lignin that did precipitate. During pulping, (hemi)cellulose from the wood matrix can be hydrolyzed to form glucose and xylose, which may react further to (hydroxymethyl)furfural and humin, which are also UV responsive. Analysis by HPLC showed that (hydroxymethyl)furfural was extracted by 2-MTHF, while glucose and xylose remained in the DES. These compounds may likely not precipitate from the DES, and are thus not present in the further studies using redissolved lignin that was first precipitated. These components will thus interfere with the results of the initial screening, but not with the further studies using precipitated lignin [35]. Also, the DES used in the solvent screening experiments after fractionation contained 12.8 ± 0.1 wt % water (as determined by Karl-Fischer titration), while the DESs used in these lignin extraction experiments were ambient dry. The presence of water in the system may also have a strong influence on the lignin distribution.

Fig. 3.3. Distribution of lignin between DES and 2-MTHF at 50 °C. Choline chloride to lactic acid equilibrium molar ratios: 1:2.4 (green-solid), 1:1.7 (blue-dotted), 1:1.4 (yellow-dashed) and 1:1.1 (red-dash-dotted).

3.4. Influence of water

The lignin distribution was determined at 5 different water concentrations in the DES and the results are shown in fig. 3.4. The lignin extraction by 2-MTHF is greatly enhanced by the addition of water. Especially the extraction of the higher molar weight fractions improves more upon the addition of water than the extraction of the lower molar weight fractions. At 25 wt % water in the DES, the minimum distribution coefficient was 4, allowing effective extraction of lignin from DES by 2-MTHF using a countercurrent LLX method.

Soares et al. determined the solubility of organosolv and kraft lignin in the propionic acid – Urea DES and found the highest lignin solubility at 50% DES in water [52]. Also the lignin solubility in low hydrogen-bonding capacity solvents -such as 2-MTHF- is greatly enhanced when a little water is added to them. The presence of water thus seems to both limit the solubility of lignin in DES by interfering with the hydrogen bonds between lignin and DES, while at the same time also facilitating hydrogen bonding connections for solvents that are only hydrogen bond acceptors.

Fig. 3.4. Distribution of lignin between DES and 2-MTHF at 50 °C. Various amounts of water were added to the DES: 50% (green-solid), 25% (yellow-dashed), 10% (blue-dotted), 5% (red-dash-dotted) and dry (black-dot-dot-dashed). For the parts of the green line that are out of the graph, no lignin fractions were found in the DES phase, and thus the distribution coefficient is infinite.

3.5. Industrial applicability

In this article we describe an alternative method for the recovery of lignin from DES by LLX. However, the addition of an extra solvent inherently increases the complexity and thus the costs of the process. Therefore, the energy saving should be significant to justify the increased complexity. For this reason, we elaborate on the potential energy savings that can be achieved by replacing cold water precipitation by LLX.

The water content is an important factor in both the pulping and the recovery stage. For example, Kumar et al. [18] found that lignin removal from rice straw increased upon the addition of small amounts of water to DES. Furthermore, many authors [15,20,21] use lactic acid syrup for the preparation of DES used for biomass fractionation, which contains around 15 wt % water. Also, wood is a hygroscopic material, meaning it will naturally contain significant amounts of water. It thus seems reasonable that the DES after pulping

Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

can contain around 25 wt % water, which allows for successful extraction using 2-MTHF without adding additional water.

Soares et al. studied the solubility of two technical lignin in mixtures comprised of water and various DES [53]. They found that the lignin solubility in a DES comprised of lactic acid and choline chloride decreased by a factor 7 when the water content was shifted from 25 to 75 wt %, which seems sufficient for industrial application. In order to achieve this shift, 2 kg of water must be added to 1 kg of pulping liquid (containing 25 % water), which must subsequently be removed by evaporation. The heat of evaporation of water is 2.3 kJ/kg, meaning 4.6 kJ is required for the recovery of 1 kg pulping liquid using cold water precipitation.

In Section 3.4 we showed that the distribution coefficient of lignin is >4 for all molar weight fraction when the DES contains 25 wt % water. This means that the minimum solvent to feed ratio is $1/4 = 0.25$. However, the lignin distribution coefficient may change during multi-stage extractions. Therefore, we assume a conservative solvent to feed ratio of 0.5. This means that for the regeneration of 1 kg pulping liquid, 0.5 kg 2-MTHF must be removed from the extracted lignin, for example by evaporation. The heat of evaporation of 2-MTHF is only 0.40 kJ/kg [54], meaning the heat required to regenerate 1 kg DES used for pulping is only 0.20 kJ, and since no water evaporation is necessary in this approach, a saving of over 95% compared to cold water precipitation can be achieved. Although these calculations are still preliminary, the potential savings justify further studies on recovery of lignin from DES by more complicated LLX.

4. Conclusions

2-MTHF was found as a suitable extractant for lignin recovery from a DES comprised of choline chloride and L-lactic acid. In biphasic systems with 2-MTHF, at least 30 wt % choline chloride in the DES was found because of large amounts of lactic acid being transferred to the 2-MTHF phase. The more choline chloride in the system, the lower the leaching of lactic acid to the 2-MTHF phase. The distribution of lower molar weight fractions was higher than the high molar weight fractions, and did not seem to depend on the DES composition. Also, the influence of water on lignin extraction was studied and the lignin extraction improved upon addition of water. At 25 wt % water, the lignin distribution was larger than 4 for all lignin molar weights, showing that all lignin can be recovered by LLX with a few countercurrent stages. It can thus be concluded that LLX with 2-MTHF is an industrially applicable method for the recovery of lignin from DES. For the design of a DES based biomass fractionation process all components from biomass must be recovered from the DES. For the fractionation trial described in this paper, 55% of the initial biomass is recovered as solid material by filtration and 20% of the initial biomass consists of lignin. The rest of the biomass consists of predominantly (hemi)cellulose breakdown products, which may be separated from the DES by membranes [28] or converted in-situ [35]. More research on the identification and recovery of these components is required to design a process for biomass fractionation using DES.

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Recovery of lignin from deep eutectic solvents by liquid-liquid extraction

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Chapter 3

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Chapter 4

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

Abstract

After biomass fractionation using deep eutectic solvents (DES), solvent recovery is an essential step. Recovery of lignin from DES by liquid-liquid extraction (LLX) may provide large energy savings compared to cold water precipitation. Lignin that is dissolved in DES from biomass fractionation is inhomogeneous, meaning it has various fractions with different molar weights and possibly variations in functional group densities. Therefore, it is important to compare recoverability of every lignin fraction by LLX with cold-water precipitation. In this work, the recovery of lignin from a DES comprised of 30 wt % choline chloride and 70 wt % lactic acid was studied. Three cross-current extractions were performed using 2-MTHF. This method recovered 95% of the lignin fractions around 2,000 g/mol and 85% of the lignin fractions around 10,000 g/mol. No inter-aromatic ether bonds were found in the lignin remaining in the DES raffinate by heteronuclear single quantum coherence spectroscopy (HSQC), indicating the remaining lignin in the DES is has a highly condensed nature. Cold water precipitation could fully recover the lignin fractions above 4,000 g/mol using 3.5 kg water per kg DES. However, only half of the lignin fraction of 1,000 g/mol was recovered. Briefly, LLX is more suitable for the recovery of low molar weight fractions, while cold water precipitation is more suitable for the heavy molar weight fractions. For industrial applications, a combination of both approaches is essential for full lignin recovery.

1. Introduction

Deep eutectic solvents (DESs) are composite solvents that exhibit deep eutectic behavior upon mixing the constituents. One attempt to define DESs states that the melting points of these mixtures is reduced considerably more ($>50\text{ }^{\circ}\text{C}$) than would be the case for ideal mixtures [1,2]. Many mixtures that have been reported as being DESs do have a much lower melting point than the pure components. However, these melting points are often close to ideal melting points that can be calculated thermodynamically [3]. Furthermore, the melting points determined for these mixtures may differ significantly upon the methods used. For example, the melting point of the DES comprised of choline chloride and lactic acid in a 1:10 ratio was determined by Crespo et al. [3], and by Francisco et al. [4]. Crespo et al. [3] found the melting point to be close to the ideal melting point of $11\text{ }^{\circ}\text{C}$ using a capillary method, while Francisco et al. [4] found a melting point of $-66\text{ }^{\circ}\text{C}$ for the same mixture by differential scanning calorimetry (DSC). Possibly, the results obtained by the DSC method used by Francisco et al. [4] deviate because of supercooling in the DSC [5]. Furthermore, the hygroscopic nature of DESs may also make characterization difficult since water strongly influences phase behavior [6].

Regardless of what a formal definition of DESs should be, these composite solvents that exhibit their low transition temperatures [7] due to hydrogen bonding, raised wide attention in academia. Since these solvents can easily be prepared in numerous ways by combining a hydrogen bond donor and acceptor [8] and are often biocompatible, biodegradable [9] and can have a low toxicity [10]. DESs have been used for various applications, such as, CO_2 capture [11-13], air pollutant removal [14], extractive distillation [15], metal extractions [16], desulfurization [17,18] and biomass fractionation [19-22].

Regeneration of DESs is most often performed by precipitation of either the solute [23,24] or solvent [7,25] in an anti-solvent. Especially in biomass fractionation this approach is popular, but large amounts of water are required as anti-solvent for the precipitation of lignin [26]. In our previous study [27], we proposed LLX using hydrophobic solvents to recover lignin from DES, since LLX can be energy efficient [28]. It was found that 2-MTHF is a suitable extraction solvent to recover lignin from a DES comprising of lactic acid and choline chloride from single stage equilibrium extraction studies [27]. This solvent was selected because it could extract lignin of all molar weights and because it is bio-based [27]. In precipitation, an anti-solvent is added to the DES, which decreases the affinity of lignin with the mixture, causing the lignin to precipitate. This antisolvent must be removed from the DES before re-use of the DES. In LLX, the DES is contacted with an immiscible solvent. If

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

the lignin has a higher affinity to the solvent than to the DES, it will move from the DES to the solvent phase. The solvent can later be removed from the lignin by a simple evaporation step.

Lignin is an inhomogeneous polymer and contains various linkages and functional groups. Various authors used either LLX [29-31], fractional precipitation [32-34], or partial solubility [32,35-39] to fractionate a lignin in two or more fractions with different properties. This means that some lignin fractions may be better extracted and/or precipitated from the DES than others. Therefore, it is vital to determine to what extent different lignin fractions can be recovered from DESs. Compared to the prior study, where only single stage extractions of lignin were described, we here describe a more extensive study on multistage cross-current LLX to recover lignins from a lactic acid and choline chloride mixture. Furthermore, we compared the multistage extraction method to cold water precipitations using various amounts of cold water. The results in this paper give more in-depth insight in the extractability of the lignin fractions, and how full lignin removal can be approached.

In this study, lignin extractions from a DES comprised of lactic acid and choline chloride using 2-MTHF were studied in a cross-current sequence, and results for lignin-in-DES solutions obtained via different procedures were compared. In our studies we always used *Eucalyptus globulus* as source for the lignin, but the preparation of the lignin containing DES was varied. Lignin was extracted directly from the prepared lignin-in-DES mixture, and lignin that was previously obtained by precipitation was redissolved in the DES and then recovered again. the lignin concentrations in the extracts were determined by gel permeation chromatography (GPC). Later, the lignin fractions were isolated from all extract and raffinate streams and characterized by fourier-transform infrared spectroscopy (FT-IR) and HSQC to compare the general structure and bonds in the lignin fractions. Also, the recoverability of different lignin fractions by cold water precipitation was studied as function of the water to DES phase ratio using GPC.

2. Methods and materials

2.1. Chemicals

Lactic acid (>90%) and 2-MTHF (Emplura) were ordered from VWR. Choline chloride (>98%) and butylated hydroxytoluene (BHT) (>99%) were ordered from Sigma-Aldrich. Crystalline lactic acid was kindly provided by Corbion. DMSO-d₆ (D, 99.9%) was ordered from

Chapter 4

Cambridge Isotope Laboratories. Air-dry *Eucalyptus globulus* chips were kindly provided by The Navigator Company. The commercial size chips (typically 25–35 × 10–25 × 2.5–6 mm, L × W × T) were used as received and contained 21.6% lignin, 50.6% glucose, 14.0% xylose, and 1.1% galactose, as determined by acid hydrolysis using the standard NREL method [40].

2.2. Experimental methods

2.2.1. Preparation of lignin-in-DES mixtures

210 g Choline chloride, 490 g lactic acid (>90%) and 300 g water were added to a round bottom flask fitted with a condenser. The mixture was heated under continuous stirring to form a homogeneous liquid, which started to boil at 112 °C. Water was released from the mixture until the temperature reached 120 °C and 50 g wood chips (oven dry basis, 10.9 wt % water) were added through a free neck (ø 29 mm). The mixture was kept at 120 °C for 8 h under continuous stirring. The mixture was filtered while hot over a 53 µm steel mesh and contained 17.4 wt % water, as determined by Karl-Fischer titration (see section 2.3.4.).

2.2.2. Cross-current extraction experiments

20 g of the prepared lignin-in-DES mixture (see section 2.2.1.) and 20 g 2-MTHF were added to a 50 mL double-walled stirred cell, which was kept at 50 °C using a Julabo F25 water bath. The cell was stirred over night to reach equilibrium. After extraction, the phases were settled and the top phase was removed and renewed by a solution of 30 wt % crystalline lactic acid in 2-MTHF to avoid excess leaching of lactic acid. The lignin concentrations in the extract phases were determined by GPC. The lignin concentrations in the raffinate phases were calculated by mass balance since they were not fully soluble in the GPC eluent. The distribution coefficients were calculated as the ratios between the concentrations in the extract phases, over the concentrations in the raffinate phases, and the recoveries were calculated by mass balance.

Also three stage extractions with lignin that was obtained by cold water precipitation according to the method described in our previous paper [27] were performed. 15 g Crystalline lactic acid, 8 g choline chloride and 15 g 2-MTHF were added to the stirred cell described in the previous section. The mixture forms 18 g of extract and 18 g of DES raffinate (comprised of 30:70 w:w choline chloride to lactic acid), as determined from the equilibrium [27]. 6 g water was added to the DES to adjust the initial water content in the DES to 25 wt %. 300 mg lignin was added to the stirred cell and the mixture was stirred over-night to reach equilibrium. Three extractions were performed using the same method as described in the previous paragraph. The lignin concentrations in the extract and raffinate phases

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

were determined by GPC. The distribution coefficients were calculated as the ratios between the concentrations in the extract phases, over the concentrations in the raffinate phases, and the recoveries were calculated by mass balance according to equation (1).

$$Recovery (\%) = \frac{\sum_{i=1}^n C_{raffinate,i} * m_{raffinate,i}}{C_{DES,initial} * m_{DES,initial}} * 100 \quad (1)$$

In which C is the lignin concentration, m the mass of the phase and n the extraction stage.

2.2.3. Isolation of lignin fractions

To obtain sufficient lignin from each fraction for characterization, an additional set of extractions were performed on larger scale using a modified procedure. For the isolation of the lignin from the first raffinate and extract phase, 100 g lignin-in-DES mixture and 100 g 2-MTHF were added to a separatory funnel. The mixture was shaken vigorously for several minutes and the phases were settled and separated at room temperature. A minor amount of precipitate was found on the interface between the extract and raffinate phase. 2-MTHF was removed from the extract phase by rotavap at 50 °C and 200 mbar until no further 2-MTHF evaporated from the mixture. Both phases were added to 300 mL water under stirring to precipitate the lignin. The lignin fractions from the extract and raffinate phases and the precipitate found between the two fractions were separated by centrifuge, washed twice with 20 mL water and dried overnight under vacuum.

For the isolation of the second and third raffinate and extract phases, 330 g lignin-in-DES mixture and 330 g 2-MTHF were added to a separatory funnel. The mixture was shaken vigorously for several minutes and the phases were settled and separated at room temperature. After the extraction, 190 g DES raffinate and 450 g 2-MTHF extract were recovered and a minor amount was lost during separation. All raffinate was added to 190 g of 30 wt % crystalline lactic acid in 2-MTHF. The mixture was shaken vigorously for several minutes and the phases were settled and separated. 190 g DES raffinate and 165 g 2-MTHF extract were obtained. 100 g of this raffinate was added to another 100 g of the 30 wt % crystalline lactic acid in 2-MTHF mixture. The mixture was shaken vigorously for several minutes and the phases were settled and separated. 100 g DES raffinate and 90 g 2-MTHF extract was obtained. 2-MTHF was removed from both raffinates by rotavap at 50 °C and 200 mbar until no further 2-MTHF evaporated from the mixture. All raffinates and extracts were precipitated in excess (1:3 w:w) water. The lignin fractions from the extracts and raffinates were separated by centrifuge, washed twice with 20 mL water and dried

Chapter 4

overnight under vacuum. Insufficient lignin was recovered from the 3rd 2-MTHF extract for analysis.

2.2.4. Cold water precipitation

The lignin-in-DES mixture (see section 2.2.1.) and water were both mixed at room temperature in various ratios to form a total of 1 g in a 1.5 mL Eppendorf centrifuge tube. The mixtures were shaken thoroughly and left over night at room temperature. The solids were separated by centrifugation at 14,000 rpm for 10 minutes. The lignin content in the supernatant was determined by GPC.

2.3. Analytical methods

2.3.1. GPC

An Agilent 1200 series was used with a refractive index detector and a UV detector operating at 254 nm using 3 GPC PLgel 3 μ m MIXED-E columns in series. The column was operated at 40 °C and a 95:5 (v:v) tetrahydrofuran and water mixture was the solvent at a flowrate of 1 mL/min. Molecular weight distributions were calibrated using polystyrene solutions having molecular weights ranging from 162 to 27,810 g/mol.

2.3.2. HSQC

Lignin samples were dissolved in DMSO-d₆ and analyzed using a Bruker Ascend 400 MHz spectrometer. Data was acquired using the hsqcetgp pulse program provided by Bruker. Matrices of 512 data points for the ¹H-dimension and 256 data points for the ¹³C-dimension were collected applying a relaxation delay of 1.5 s and spectral widths from -1 ppm to 11 ppm and from 210 to 0 ppm in the ¹H and ¹³C dimensions, respectively. The 2D HSQC spectra were processed using MestReNova software.

2.3.3. FT-IR

FT-IR analyses were performed on solid lignin fractions isolated from the raffinates and extracts. The analysis was carried out at room temperature using a Bruker Tensor 27 spectrometer equipped with an attenuated total reflection system and a deuterated triglycine sulphate detector. Absorbance was measured in the range 650 to 4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹, and 16 scans were performed. No baseline corrections were applied.

2.3.4. Karl-Fischer titration

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

The water content of lignin in DES mixture was determined by Karl-Fischer titration using a Metrohm 787 KF Titrino. Hydranal composite 5 (5 mg water/mL) was titrated from a 20 mL burette in a 3:1 (v:v) mixture of methanol and dichloromethane. The sample was measured in duplo with a relative error <1%.

3. Results and discussion

3.1. Cross-current extractions using actual pulping DES

Cross-current extractions were performed to investigate the extractability of lignin from the prepared lignin-in-DES mixture. Three stage extractions were performed using 2-MTHF. The lignin concentrations in the solvent phases were determined by GPC and the concentrations in the DES phases were calculated by mass balance. From these concentrations the distribution coefficients of lignin among the 2-MTHF and DES were calculated, as well as the total recovery of lignin from the DES (see section 2.2.2.). The results are shown in fig. 4.1. From this figure, it can be seen that the total lignin recovery after 3 extraction stages was approximately 95% for the fractions around 2,000 g/mol, and decreased to around 85% for the fraction around 10,000 g/mol. The distribution coefficient in the first stage was around 2.5 for all lignin fractions, dropped below 1 in the last stage. Therefore, further extraction stages seemed ineffective. Because the lignin remaining in the DES could not be extracted by 2-MTHF, we conjecture that the remaining lignin has a different chemical nature compared to the lignin that was extracted by 2-MTHF. Therefore, lignin from each fraction was isolated using a modified procedure for FT-IR and HSQC analysis to elaborate on their structures (see section 3.3.).

Fig. 4.1. Results of the cross-current extractions of lignin from the lignin-in-DES solution by 2-MTHF in 3 stages (Stage 1 is dashed, 2 dotted and 3 solid lines). A 1:1 DES to solvent ratio was used and extractions were performed at 50 °C. The initial DES contained 17.6% water. The top figure shows the distribution coefficients and the bottom figure shows the total lignin recovery, as calculated by mass balance.

3.2. Cross-current extraction using precipitated lignin

In the previous section, lignin was extracted directly from the prepared lignin in DES mixture. However, this mixture does not only contain lignin, but also (hemi)cellulose

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

breakdown products, such as glucose, xylose, furfural, HMF or humins. These substances may influence the lignin distribution, and therefore, the extraction experiments from section 3.1. were repeated using lignin that was previously obtained by cold water precipitation, to see whether extraction of a model lignin produced by the same pulping procedure is representable for the actual system. However, some lignin fractions may remain soluble during cold water precipitation (see section 3.4.), and are therefore not present in the precipitated lignin used in the previous section. This means that the distribution of these fractions cannot be measured in this experiment. The results from this experiment are shown in fig. 4.2. From this figure it can be seen that the distribution coefficient in the 1st stage is between 4 and 10, which is in accordance with the earlier determined equilibrium [27]. In the 3rd stage, the distribution coefficient dropped to a value lower than 1 for all lignin fractions. This was also seen in the direct extractions from the lignin-in-DES mixture. The lignin recovery after 3 stages of the fractions between 1,000 and 10,000 g/mol was around 95%, while the recovered dropped to 85% for the lignin fractions around 20,000 g/mol.

The main difference between the total recovery of lignin extracted directly from the lignin-in-DES mixture and the lignin that was previously obtained by precipitation can be found in the region between 3,000 and 10,000 g/mol. For the first lignin, the recovery drops from 95% to 85% between these molar weights, while for the second lignin (previously precipitated) the recovery remains constant around 95% and only drops to 85% at a molar weight around 20,000 g/mol. However, for both lignins the full recovery for the lowest molar weight fraction is around 95% and the recovery of the highest molar weight fraction around 85%, indicating that the lignin model is reasonably representative for the actual lignin-in-DES mixture.

3.3. Analysis of DES fractions

In the previous sections it was shown that the lignin extractability from DES decreased one order of magnitude in the 3rd extraction stage, compared to the 1st stage. We conjectured that this was caused by a difference in chemical nature between the lignin extracted by 2-MTHF and the lignin remaining in the DES. Therefore, we performed larger scale extractions using a modified procedure to be able to isolate enough lignin from each raffinate and extract fraction, in order to study the chemical natures by FT-IR and HSQC. In this procedure, lignin was extracted from the lignin-in-DES mixture using multiple extractions with 2-MTHF using a separatory funnel at room temperature. The lignins were isolated from each fraction using cold water precipitation.

Fig. 4.2. Results from the cross-current extractions of lignin by 2-MTHF from a DES comprised of lactic acid and choline chloride in 3 stages (Stage 1 is dashed, 2 dotted and 3 solid lines). Extractions were performed at 50 °C using a 1:1 DES to solvent ratio. The initial DES contained 25% water. The left figure shows the distribution coefficients and the right figure shows the total lignin recovery, as calculated by mass balance.

In theory, FT-IR provides information on all chemical bonds present in a lignin structure [35] and HSQC gives information on the general structure and ether bonds present in lignin [35,41]. These factors may influence lignin solubility and by performing these analysis on both lignin fractions, it may become clear why some lignin fractions are better extracted than others. The FT-IR spectra (see fig. 4.3) of the lignins in the DES raffinate and 2-MTHF extracts show only minor differences. There are only minor differences between the spectra of the lignin from the 1st and 2nd DES raffinate, while the spectrum of the lignin in the 3rd

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

raffinate is similar to the 2nd raffinate. Also the spectrum of the lignin in the 1st 2-MTHF extract is similar to the three spectra of the lignins in the three DES raffinates. Some extra peaks appear in the 2nd 2-MTHF extract at 859, 888, 1157, 1133, 1310 and 1358 cm⁻¹. However, all of these peaks can be attributed to the presence of a contamination of BHT in the lignin. The FT-IR spectrum of BHT is shown in the supplementary data. BHT is an additive that is present as stabilizer in 2-MTHF, which was left in the lignin sample after the removal of 2-MTHF. Since the lignin concentration in the 1st extract is much higher than in the 2nd extract, and the BHT concentration in 2-MTHF is constant, the BHT contamination in lignin from the 2nd extract is much higher than from the 1st extract. Not enough lignin could be isolated from the 3rd extract phase for analysis.

Fig. 4.3. FT-IR spectra of the lignins isolated from the DES raffinates (dotted) and 2-MTHF extracts (solid).

Fig. 4.4. ^1H - ^{13}C HSQC spectra of the lignin isolated from the DES raffinates and 2-MTHF extracts in the aliphatic oxygenated side chain region ($\delta_{\text{C}}/\delta_{\text{H}} = 47\text{-}93/2.7\text{-}5.8$ ppm). On top of the figures, the structures of the three main inter-aromatic ether bonds are shown: β -O-4 (left, red), β -5 (middle, purple) and β - β (right, green). The peaks identified to these bonds in the spectra are labeled by color (β -5 bonds were not found in the spectra). Top left: lignin from the 1st 2-MTHF extract, Top right: lignin from the 2nd 2-MTHF extract, Bottom left: lignin from the 1st DES raffinate, Bottom right: lignin from the 2nd DES raffinate.

Comparing multistage liquid-liquid extraction with cold water precipitation
for improvement of lignin recovery from deep eutectic solvents

**Comparing multistage liquid-liquid extraction with cold water precipitation
for improvement of lignin recovery from deep eutectic solvents**

Fig. 4.5. ^1H - ^{13}C HSQC spectra of the lignin isolated from the DES raffinates and 2-MTHF extracts in the aromatic region ($\delta_{\text{C}}/\delta_{\text{H}} = 98\text{-}132/5.8\text{-}8.2$ ppm). On top of the figures, the structures of the two main aromatic units are shown: syringyl (left, orange) and guaiacyl (right, blue). The peaks identified to these units in the spectra are labeled by color. Top left: lignin from the 1st 2-MTHF extract, Top right: lignin from the 2nd 2-MTHF extract, Bottom left: lignin from the 1st DES raffinate, Bottom right: lignin from the 2nd DES raffinate.

Chapter 4

The HSQC spectra of the lignins in the DES raffinates and 2-MTHF extracts are shown in fig. 4.4. and fig. 4.5. The spectra of the oxygenated side chain region show the presence of ether bonds between the aromatic units. The β -O-4 bonds ($\delta_C/\delta_H = 72.1/4.9$) and β - β bonds ($\delta_C/\delta_H = 85.8/4.7$) can be clearly identified in the spectra of the two 2-MTHF extracts and the first DES raffinate. However, they do not show in the 2nd and 3rd DES raffinate. The β -5 bonds could not be identified in any lignin fraction. Furthermore, the spectra show the methoxy groups in the lignin ($\delta_C/\delta_H = 56.3/3.7$) and impurities of lactic acid ($\delta_C/\delta_H = 69.0/5.0$ and $66.6/4.2$) and choline chloride ($\delta_C/\delta_H = 53.6/3.2$). The spectra of the aromatic region show the presence of guaiacyl ($\delta_C/\delta_H = 115.7/6.8$) and synapyl ($\delta_C/\delta_H = 103.9/6.7$) units in all lignin fractions. Furthermore, the spectra of the two 2-MTHF extracts clearly show the contamination of BHT ($\delta_C/\delta_H = 125.5/6.9$). Reference spectra of all impurities are shown in the ESI.

There are two main differences between the lignin that was extracted by 2-MTHF, compared to the lignin that remained in the DES raffinate. First of all, the lignin that remained in the raffinate has a higher molar weight than the lignin that was extracted by 2-MTHF. Second, the lignins that were extracted by 2-MTHF contained inter-aromatic ether bonds, such as β -O-4 and β - β bonds, whereas these bonds were not found in the lignin that remained in the DES raffinate. These observations suggest that the lignin that remains in the DES raffinate has a highly condensed nature, compared to the lignin that was extracted by 2-MTHF.

3.4. Recovery by cold water precipitation

The current laboratory benchmark to recover lignin from DES is precipitation of lignin by addition of the DES to water or aqueous mixtures [26]. We also studied the recovery of lignin by cold water precipitation to make a direct comparison between both techniques. Water and the lignin-in-DES mixture were mixed in various ratios. The precipitated lignin was separated by centrifuge and the concentration of lignin remaining in the supernatant was determined by GPC. The recovery was calculated from the lignin concentration in the supernatant and the lignin concentration in the original DES. The results of these experiments are shown in fig. 4.6.

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

Fig. 4.6. Recovery of lignin by cold water precipitation using various DES to water mass ratios, 1:3.5 (solid), 1:1.7 (dot), 1:0.85 (dash), 1:0.42 (dash-dot), 1:0.22 (dash-dot-dot).

From Figure 7 it becomes apparent that only minor amounts of water are required to precipitate a fraction of the lignin, 0.22 g water per g DES was enough to precipitate roughly half of the lignin fraction around 20,000 g/mol. However, the lower molar weight fraction remained partly soluble in the water-DES mixture. Even when 3.5 g water per g DES, about half the lignin fraction around 1,000 g/mol was recovered from the DES. We reckon that higher water to DES ratios are not viable for industrial application since the added water must be removed from the DES by evaporation, which is highly energy intensive. Therefore, these ratios were not studied in this work.

3.5. Comparison between LLX and cold water precipitation

The recovery of lignin from a DES comprised of lactic acid and choline chloride was studied for two methods, LLX using 2-MTHF and precipitation using cold water. Large differences were found between the two methods. For LLX around 95% of the lignin fraction around 2,000 g/mol could be removed, while for lignin fractions exceeding 10,000 g/mol, only 85% could be removed. Cold water precipitation could fully remove all lignin fractions above 4,000 g/mol, while only 50% of the lignin around 1,000 g/mol could be removed. In summary, recovery of the low molar weight lignin fractions is preferred by LLX, while recovery of the high molar weight fraction is preferred by cold water precipitation. Industrially, LLX is preferred over cold water precipitation since further removal of water from DES is highly energy intensive. However, a high (>95%) lignin recovery is required for industrial applicability. In this study, the application of LLX was limited to DES with a water content equal or smaller than 25 wt %. In a previous study, we showed that the lignin

distribution is highly dependent on the water concentration [27], and especially the distribution of the high molar weight fractions is affected by the water content. Therefore, we suggest LLX as the preferred method, with the addition of water to a total amount of 25 to 50 wt % based on the DES. In principle, the high molar weight lignin fractions can be precipitated by water addition prior or after LLX, but since the addition of water aids LLX, it is preferred to add water before LLX. Water can also be added during LLX to aid the extraction of the high molar weight fractions [27]. The advantage of this method is that the number of unit operations is reduced, but precipitation before LLX produces a light and a heavy molar weight lignin fraction, which may bring more value to the produced lignins.

4. Conclusion

Cross-current extractions of lignin from a DES comprised of choline chloride and lactic acid were performed. It was found that 95% of the molar weight fraction around 2,000 g/mol and 85% of the fractions above 10,000 g/mol could be recovered in 3 stages. Additional extraction stages were not performed, since the distribution coefficients dropped one order of magnitude from stage 1 to 3. Similar results were obtained when the lignin was directly extracted from the pulping DES, compared to the extraction of precipitated lignin that was re-dissolved in the DES. The lignin in DES was fractionated using a one stage extraction by 2-MTHF. Both fractions were analyzed by FT-IR and HSQC. It was found that the lignin that remained in the DES raffinate after two extractions did not contain any β - β or β -O-4 bonds. Together with the high molar weight of the lignin remaining in the DES, this suggests that the lignin remaining in the DES is highly condensed. Recovery of lignin by cold water precipitation could fully recovery the lignin fractions heavier than 4,000 g/mol, but only half of the lignin fraction around 1,000 g/mol could be removed by the addition of 3.5 g water per g DES. For industrial applications, a combination of both approaches will be desirable due to their complementary nature of lignin recovery.

Comparing multistage liquid-liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents

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Chapter 5

Process development for biomass delignification using deep eutectic solvents. Conceptual design supported by experiments

Abstract

Deep eutectic solvents (DES) have been proposed as solvents for biomass delignification. This paper describes a conceptual process design for the delignification of *Eucalyptus globulus* using a DES comprised of 30 wt % choline chloride and 70 wt % lactic acid. In this design, the lignin and hemicellulose by-products are recovered by liquid-liquid extraction (LLX) using 2-MTHF as solvent. Material and energy balances were made and the energy usage of the process was optimized with additional experiments. The amount of DES was reduced to the minimal amount required to fill the porous biomass (5 kg per kg wood), with minor influences on the yield and delignification. Direct recycling of lignin-in-DES mixtures without lignin removal by LLX to the delignification stage may save energy, but increased repolymerization increases the lignin's molar weight, which decreases its value and makes recovery by LLX more difficult. After optimization, the total energy usage of the proposed process is 8.4 GJ/t pulp, which is 24% lower than the kraft process. The main benefit of DES based delignification processes is the possible valorization of byproducts, such as lignin and furans from hemicellulose.

1. Introduction

Deep eutectic solvents (DESs) are composite solvents that exhibit deep eutectic behavior upon mixing the constituents. Various authors proposed a definition for a DES [1-5], but no final definition or consensus has been achieved yet. Regardless of what a formal definition of DESs should be, these composite solvents that exhibit their low transition temperatures [6] due to hydrogen bonding, attracted wide attention in academia. Since these solvents can easily be prepared in numerous ways by combining a hydrogen bond donor and acceptor [7] and are often biocompatible, biodegradable [8] and can have a low toxicity [9], DESs have been used for various applications. Examples include CO₂ capture [10-12], air pollutant removal [13], extractive distillation [14], metal extractions [15], desulfurization [16,17] and biomass fractionation [18-21].

Lignocellulosic biomass is a renewable raw material source and can be converted into cellulose fibers and, among other byproducts, lignin by delignification technologies. The obtained cellulose pulp can be used for paper production, production of other materials, or can be converted to bio-ethanol or other platform chemicals [22-24]. Lignin is an aromatic biopolymer with advocated potential for the chemical industry and current research is focusing on lignin valorization [25,26]. Other byproducts, such as hemicellulose and extractables can be converted into furans and turpentine respectively [27,28].

Most conventional cellulose fiber producing installations make use of the kraft process, in which lignocellulose is delignified using sodium hydroxide and sodium sulfide to form cellulose fibers suitable for papermaking. The lignin is depolymerized by a nucleophilic substitution reaction with the sulfide, meaning the lignin that is finally obtained is highly sulfurized. As a consequence, to be able to recycle the sodium sulfide, the lignin has to be combusted. Kraft mills may also produce lignin as byproduct, but the scale and applications are limited. Kraft lignin is mainly used for low-value applications, such as heat recovery [29].

Although kraft plants are highly integrated and energy effective plants [30], they still have an average heat usage around 11 GJ/t [31]. This heat is provided from the combustion of the extracted lignin and other parts of the tree that are unsuitable of papermaking, such as the bark. Most modern kraft mills have an energy surplus, which is most often used to provide power to the grid.

DESs have been reported for the delignification of various types of lignocellulose, including softwoods (spruce [32,33], pine [34-36]), hardwoods (beech [21,37], poplar [34,38-40], eucalyptus [18,41-43] and willow [44,45]), grasses (miscanthus [46]) and agricultural

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

byproducts (wheat straw [21,32,47,48], rice straw [27,49-52], corncob [53-55], corn stover [44,56]). Lignin that is produced using DESs often shows very little signs of condensation [34] and typically has a low molar weight [34,57]. Many studies have been performed on biomass delignification using DES and many DES, biomass types and processing conditions have been studied. However, to the best of our knowledge, no conceptual design has been made for biomass delignification using DES yet.

Especially DESs comprised of lactic acid and choline chloride were very often used for biomass delignification [18,34-40,42,43,45,48,50,52,54,57]. Although the optimal lactic acid to choline chloride ratios for delignification are between 10:1 and 50:1, [18] a DES comprised of 30 wt % choline chloride and 70 wt % lactic acid was used in this study since it is possible to regenerate lignin from this DES by LLX, which has potential for significant energy savings [58].

In this work, a conceptual design was made according to the method described by Douglas [59], which is easy to use and relevant for industrial applications [60]. Using this approach, a complex process design is divided into multiple, much simpler problems. Following the Douglas method, the input-output structure of the process was defined first, after which the separations were defined. Later, the mass and energy balances were made using rigorous calculations. Therefore, it is relatively easy to screen alternatives and thereby optimize the design. In this work, the process was optimized for energy usage.

2. Methods and materials

2.1. Materials

Air-dry *E. globulus* chips were donated by The Navigator Company. The commercially sized chips (typically 25–35 × 10–25 × 2.5–6 mm, L × W × T) were milled to produce wood meal using a hammer mill and sieved (mesh -25/+70) and contained 5.6 wt % moisture. The wood contained 21.6% lignin, 50.6% glucose, 14.0% xylose, and 1.1% galactose (oven dry basis), as determined by acid hydrolysis using the standard NREL method [61]. Lactic acid (>85%), choline chloride (>98%) and sulfuric acid (95-98%) were purchased from Sigma-Aldrich. 2-MTHF (emplura) was purchased from VWR.

2.2. Experimental procedures

2.2.1. Biomass delignification experiments

1 to 2 g wood meal (oven dry basis) was added together with 10 g DES to a Teflon-lined autoclave. This autoclave was inserted into a direct contact heater, which heated the autoclave to 130 °C in a couple of minutes. After 1 h, the autoclave was taken out of the heater and gently cooled down to room temperature. The contents were washed using ethanol and filtered over a Whatman glass fiber filter before drying of the residue to a constant weight at 105 °C in a convection oven. All experiments were performed in duplo. The yield was calculated according to equation 1.

$$yield (\%) = \frac{Solid\ residue\ (g)}{biomass\ (g) * \left(1 - Water\ content\ in\ wood\left(\frac{g}{g}\right)\right)} * 100 \quad (1)$$

The acid insoluble lignin in the solid residue was determined by acid hydrolysis according to the NREL method [61]. The degree of delignification was calculated according to equation 2

$$Delignification (\%) = 100 - Yield (\%) * \frac{Lignin\ in\ residue (\%)}{Lignin\ in\ wood (\%)} \quad (2)$$

2.2.2. Lignin extraction experiments

3 mL lignin in DES mixture, 3 mL 2-MTHF and 0.5 to 3 mL water were added to a glass vial with a screw cap. The vials were placed in a Julabo SW22 shaking bath at 50 °C and shaken overnight at 200 rpm. The phases were settled under gentle shaking at 20 rpm until they were fully separated. The lignin contents in both phases analyzed by GPC.

2.2.3. Preparation of lignin in DES mixture

700 g lactic acid and 300 g choline chloride were added to a round bottomed flask (2L) with a condenser. The mixture was heated to 130 °C and 200 g (oven dry basis) commercially sized chips were added to the flask. The mixture was stirred gently for 3 or 8 h and the mixtures were filtered while hot over a 53 µm steel mesh. The lignin content in the mixtures was determined by acid hydrolysis, for which 20 mL of the lignin-in-DES mixture was added to a Teflon-lined autoclave, together with 60 mL water. 3 mL 72% Sulfuric acid was added to the mixture using a pipette and the autoclave was inserted into a direct contact heater at 120 °C and kept there for one hour. The mixture was cooled down to room temperature and filtered over a Whatman glass fiber filter. The residue was dried in a convection oven at 105 °C and the acid insoluble lignin content was determined gravimetrically.

2.3. Analysis

2.3.1. Acid hydrolysis

The acid insoluble lignin content of the sample was determined by hydrolysis of the sample according to standardized NREL procedure [61]. 0.3 g Sample was added to a Teflon-lined autoclave, together with 3 mL sulfuric acid (72%) and the mixture was kept at 30 °C for 1 h while stirring every 10 min. After this, 84 mL water was added and the tube was kept at 120 °C for another hour. The solids were filtered and dried overnight at 105 °C. The acid insoluble lignin content was calculated according to equation 3.

$$\text{Acid insoluble lignin (\%)} = \frac{\text{Residue (g)}}{\text{sample (g)} \cdot \left(1 - \text{Water content} \left(\frac{\text{g}}{\text{g}}\right)\right)} * 100 \quad (3)$$

2.3.2. GPC

An Agilent 1200 series was used for the gel permeation chromatography (GPC) with a refractive index detector and a UV detector operating at 254 nm using 3 GPC PLgel 3 µm MIXED-E columns in series. The column was operated at 40 °C and a 95:5 (v:v) tetrahydrofuran and water mixture was the solvent at a flowrate of 1 mL/min. Molecular weight distributions were calibrated using polystyrene solutions having molecular weights ranging from 162 to 27,810 g/mol.

2.3.3. HPLC

The lactic acid content in the hydrolysis liquids was determined by high performance liquid chromatography (HPLC). An Agilent 1200 system was equipped with a Hi-Plex-H column operated at 60 °C and a refractive index detector at 55 °C. 5 mM sulfuric acid in water was used as mobile phase with a flowrate of 0.6 mL/min.

2.3.4. Karl-Fischer titration

The water content of lignin in DES mixture was determined by Karl-Fischer titration using a Metrohm 787 KF Titrino. Hydranal composite 5 (5 mg water/mL) was titrated from a 20 mL burette in a 3:1 (v:v) mixture of methanol and dichloromethane. The sample was measured in duplo with a relative error <2%.

2.3.5. Determination of ash content

The ash content in the eucalyptus was determined according to the standard NREL procedure [62]. 1.5 to 2 g biomass was pre-dried in a convection oven at 105 °C and added to a porcelain crucible which was pre-dried at 575 °C. This crucible was inserted into an oven at 575 °C to oxidize all organic material. The analysis was performed in duplo. The ash content was determined gravimetrically by equation 4.

$$\text{Ash content (\%)} = \frac{\text{Residue after oxidation (g)}}{\text{Dry biomass (g)}} * 100 \quad (4)$$

3. Results and discussion

3.1. Conceptual process design and initial energy requirement estimation

3.1.1. Input-output structure

First, the type of lignocellulosic biomass must be selected. In principle, every type of lignocellulosic biomass (hardwood, softwood, grasses, agricultural wastes) can be selected for the process. We selected *E. globulus* for further studies because this species is the most cultivated species in fastgrowing plantations [63] and because eucalyptus was also used in our previous studies [18,58]. However, the methodology applies to majority of the lignocellulosic biomass sources.

Next, the morphology of the feed must be selected. Obviously, the DES impregnation rate increases if the particles are smaller and therefore, the cooking will be faster and more homogeneous. Cutting wood chips inherently cuts cellulose fibers and therefore decreases the average fiber length, which compromises the fiber quality. Therefore, chip size is a tradeoff between these two variables and chips are generally 20 to 30 mm long. For other applications, such as cellulose fermentation to bio-ethanol, the fiber quality is irrelevant. In these cases, chip size will be a tradeoff between ease of impregnation and the energy costs involved in chipping. The chip size is very important for the design of the digester, but not for further processing of the pulp and DES recovery. Therefore, this is no factor in the rigorous calculations.

Feed impurities are important for any (chemical) process. In the case of lignocellulosic biomass, three major impurities are present: water, extractables and ash. Presence of water in the feed is not expected to pose any problems in the process. Addition of some water to

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

DES will decrease the viscosity and is beneficial in the recovery process. However, little is known yet on the influence of water on the pulping process. Also, high water contents may result in significant evaporation at the pulping temperature, which may require the use of pressurized equipment or venting during pulping. Extractables are low molar weight compounds, such as fatty acids, sterols, terpenoids and waxes that can be extracted from biomass using neutral solvents. Considering the hydrophobic nature of these compounds, they will end up in the 2-MTHF during the lignin extraction. Extractables may be removed by steaming biomass prior to further processing. Ash present in the feed dissolves in the DES and will accumulate in the DES recycle loop. Since purging a fraction of the DES is very costly, it will be highly desirable to remove ash prior to DES processing, for instance by acid leaching [64]. Salts that do end up in the DES recycle will have to be removed by complicated separation techniques, such as electrodialysis. The ash content in the eucalyptus used for this study was only 0.38 wt %, but can be much higher for other biomass sources. For example, straw can have an ash content of 6 to 8% [65]. For the rigorous calculations only the presence of water in the feed was included.

The outlet streams of this process must at least consist of a stream for the produced cellulose and lignin. Besides these products, some of the hemicelluloses will also break down during DES processing. During treatment with acid DESs, hemicellulose breaks down to sugar fractions, which further react to furans. Li et al. [28] and Hou et al. [27] studied the fractionation of rice straw using acid based DESs. Both authors [27,28] could only recover less than half of the hemicellulose removed as either sugar or furanic compound, with the remainder referred to as 'Loss'. We expect these losses to be furanics and sugars that reacted further to form polymeric byproducts called 'humin'. Separation of sugars from DES is complicated. Both compounds are completely non-volatile, excluding separation by distillation. Furthermore, both compounds are highly polar, making affinity based separation very challenging. The only options appear to be a delicate membrane-based process based on the small difference in size of the molecules and ions in the system, another option is to let the sugars react further to furans. These furans may be separated by LLX using organic solvents, such as 2-MTHF [22,66,67]. Small sugars produced in the cooking will for a major part already be converted into furans, and in the proposed process it seems likely that produced furans will also be extracted by 2-MTHF and thus leave the process together with the lignin. Little is known about the humins, but with its furanic structure, it seems possible that these by-products are also extracted by 2-MTHF and thus leave the process together with the lignin. Alternatively, humins may precipitate during the process on the reaction equipment, as in the commercial production of furfural from

hemicellulose rich agricultural wastes [68]. In the used lignin-in-DES mixtures, only 3% of the initial amount of xylose present in the biomass was found back by HPLC. For the rigorous calculations, we assumed that all hemicellulose that is removed from the biomass structure leaves to process as ‘hemicellulose byproduct’ (HBP) together with the lignin. This means that the input-output structure looks as described in Fig. 5.1.

Fig. 5.1. The input-output structure of the conceptual process.

3.1.2. Batch versus continuous

In kraft pulping, continuous digesters have become standard. Although some batch digesters are still in operation, batch pulping has become out of date. In a typical continuous digester, wood chips are fed at the top of the reactor vessel and slowly sink through cooking liquor with various compositions. Compared to the current aqueous pulping liquors, DESs have a much higher density and viscosity [69]. The increased density of the DES increases the buoyant forces exerted on a wood chip and the increased viscosity increases the drag force on a wood chip. This will decrease the flow rate of chips through a continuous digester filled with DES and thus greatly complicates the design of such a digester. As a consequence, much data must be gathered to make a detailed design. More than half of all European pulp mills had a capacity exceeding 200 kt per year in 2018 [70]. Although some older mills still operate semi-batch wise, this is highly unusual at this scale. Therefore, pulping must be executed continuously, just as other operations, such as solvent recovery and pulp washing.

3.1.3. The separation system

After the pulping reactor, a mixture of cellulose pulp, DES, lignin and hemicellulose by-products must be separated. In this mixture, the lignin and hemicellulose by-products are dissolved in the DES. It is convenient to separate the solid pulp from the liquid DES first, for instance by pressing. During pressing, part of the liquid remains as stagnant liquid in the fibers in the porous pulp beds. Therefore, the liquid in the pulp must be displaced by

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

another liquid. Washing with water is very convenient since water is inexpensive, non-toxic and non-flammable. However, if water is used to displace the DES in the cellulose fibers, the water will mix with the DES, causing lignin to precipitate on the fibers, which is very undesirable. Therefore, the DES in the cellulose fibers must first be displaced by clean DES, before it can be displaced by water.

After the separation between the DES and pulp, the liquid mixture containing DES, water, lignin and hemicellulose by-products must be separated. In our previous paper we made a brief comparison between the regeneration of lignin from DES using cold water precipitation [71] and concluded that the low molar weight lignin fractions could not be recovered by cold water precipitation. Furthermore, LLX using 2-MTHF has the potential to save 95% energy compared to cold water precipitation [71]. Therefore, lignin is recovered from the DES using LLX. Water is removed later from the mixture, since it aids LLX of lignin from the DES. We assume that the hemicellulose-byproducts are also extracted by 2-MTHF (see section 3.1.1.). The 2-MTHF can be recovered by evaporation and the lignin and hemicellulose by-products remain in the evaporation residue, together with any DES that may have leached to the 2-MTHF during extraction. This DES can be washed from the products using water and the washing water is recycled back to the extraction stage.

At last, the DES must be separated from the water and any 2-MTHF that leached to the DES phase during extraction. Water and 2-MTHF may be separated from the DES by evaporation. After condensation, the water and 2-MTHF can be separated in a settler vessel because of the immiscibility between water and 2-MTHF. Altogether, the flowsheet as shown in Fig. 5.2 is obtained.

Fig. 5.2. Structure of the conceptual process. In the left figure, the process is shown by function and in the right figure, the process is shown by operations. After pulping, the pulp in used DES suspension (3) is pressed and washed to form a clean pulp suspension (6). All Used DES and water from the washing and pressing stages are combined in stream (7), which is mixed with water from the lignin wash (13) and the lignin and HBP present in this mix (8) are extracted using 2-MTHF (9 and 10). The clean DES recycle (16) is dried and the clean DES (18) is used again for pulping (2) and washing (4).

3.2. Mass balance

In the conceptual process, biomass is fractionated into pulp, lignin and hemi-cellulose by-products. Any other byproducts or losses are not taken into account in this process design. Therefore, the amount of biomass entering the process (stream 1, fig. 5.2) ($M_{B,in}$) is equal to the amounts of pulp (stream 6, fig. 5.2) ($M_{P,out}$), lignin ($M_{L,out}$) and hemicellulose byproducts ($M_{HBP,out}$) produced (stream 15, fig. 5.2), as shown in equation 5.

$$M_{B,in} = M_{P,out} + M_{L,out} + M_{HBP,out} \quad (5)$$

The amount of pulp produced is the sum of the amount of biomass entering the process, multiplied by the pulp yield (y_P), as shown in equation (6). This yield was determined experimentally at 57%.

$$M_{P,out} = M_{B,in} * y_P \quad (6)$$

The amount of lignin produced is equal to the amount of lignin removed from the biomass. This is the amount of biomass entering the process, multiplied by the lignin fraction in the biomass ($x_{L,B}$) and the degree of delignification (y_L), as shown in equation 7. These fractions were determined experimentally at respectively 21.6% and 94.1%.

$$M_{L,out} = M_{B,in} * x_{L,B} * y_L \quad (7)$$

For convenience, the pulp production is set to 1000 kg/h and therewith, the system of 3 equations can be used to solve the 3 unknowns ($M_{B,in}$, $M_{L,out}$ and $M_{HBP,out}$).

The amount of DES used for pulping in the digester (stream 2, fig. 5.2) ($M_{DES,pulping}$) is equal to the amount of biomass, multiplied by the DES to biomass ratio (DB), as shown in equation (8). Prior to optimizing the flow sheet, this ratio is set to 10 since this is a common ratio in literature [34].

$$M_{DES,pulping} = M_{B,in} * DB \quad (8)$$

After pulping, the pulp is first washed using DES to remove lignin from the pulp. To the best of our knowledge, no data is available on pulp washing using DES yet. Therefore, data used on water washing is used to give an estimate on the amount of DES required for washing. It is common to use around 3 kg water per kg pulp in industry [72]. This washing factor (WF) is multiplied by the amount of pulp produced to calculate the amount of DES required for washing ($M_{DES,wash}$), as shown in equation (9).

$$M_{DES,wash} = M_{P,out} * WF_P \quad (9)$$

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

Water is required to aid LLX of lignin from the DES. Therefore, the water fraction in the DES recycle stream (stream 16, fig. 5.2) ($x_{W,DESrecycle}$) is defined as the amount of water in the recycle (stream 16, fig. 5.2) ($M_{W,DESrecycle}$) over the sum of the amounts of water and DES (from pulping and washing), as shown in equation (10). A water mass fraction of 0.5 is assumed, since this is sufficient for full lignin recovery using LLX [71].

$$x_{W,DESrecycle} = \frac{M_{W,DESrecycle}}{M_{DES,pulping} + M_{DES,washing} + M_{W,DESrecycle}} \quad (10)$$

The amount of solvent required for the extraction stage (stream 9 + 10, fig. 5.2) ($M_{MTHF,extraction}$) is equal to the total mass of the DES and water in the recycle (stream 16, fig. 5.2), multiplied by the solvent to feed ratio (SF), as shown in equation (11). A ratio of 0.5 was used, since this is sufficient for full lignin recovery [71].

$$M_{MTHF,extraction} = (M_{DES,pulping} + M_{DES,washing} + M_{W,DESrecycle}) * SF \quad (11)$$

Since the extraction solvent and DES are partially miscible, some of the extraction solvent leaches to the DES recycle (from stream 9 to stream 16, fig. 5.2). This amount ($M_{MTHF,leached}$) is determined by the solubility factor ($x_{MTHF,leached}$) of 2-MTHF in DES, as shown in equation (12). This factor was estimated at 0.1 from equilibrium data [58].

$$M_{MTHF,leached} = x_{MTHF,leached} * (M_{DES,pulping} + M_{DES,washing} + M_{W,DESrecycle}) \quad (12)$$

Besides leaching of solvent to the DES recycle, some DES will also leach to the solvent (from stream 8 to stream 11). It must be noted that DESs are not pseudo-pure compounds, and especially during LLX, their composition changes since every DES constituent has a different leaching characteristics. In this case, lactic acid has a much higher solubility in 2-MTHF than choline chloride [58] and thus, relatively more lactic acid than choline chloride will leach to the 2-MTHF phase (from stream 8 to stream 11, fig. 5.2). However, after extraction any leached DES will end up in stream 12 of the process, where it is washed of the lignin and HBP and furthermore recycled directly back to the extraction stage via streams 13 and 8 (see fig. 5.2). Therefore, it is not expected that the composition of the leached DES will have any influence on the energy usage of the process and is therefore not taken into consideration. This amount ($M_{DES,MTHFleach}$) is determined from the solubility factor of DES in 2-MTHF ($x_{DES,MTHF}$), as shown in equation (13). This factor was estimated at 0.3 from equilibrium data [58].

$$M_{DES,MTHFleach} = M_{MTHF,extraction} * x_{DES,MTHF} \quad (13)$$

Chapter 5

At last, the water balance is made. Some water is naturally present in this wood. Since it was decided not to pre-dry the wood, this amount has to be taken into account as well. The fraction of water naturally present in biomass ($x_{W,B}$) is 0.5 [73]. This is defined as the amount of water in the biomass ($M_{W,B}$), divided by the amounts of water and biomass entering the process, as shown in equation (14).

$$x_{W,B} = \frac{M_{W,B}}{M_{B,in} + M_{W,B}} \quad (14)$$

Since pulp is a porous material, some water will always remain in the pulp after washing (stream 6, fig. 5.2). If the process is integrated with for instance a papermaking plant, this amount does not need to be removed since cellulose pulp must be fed to a papermaking machine in an aqueous suspension. Alternatively, the water can be removed if the pulp is sold on the market. The water fraction in the pulp ($x_{W,P}$) is defined by the amount of water in the pulp ($M_{W,P}$), divided by the amount of pulp and water in the pulp, as shown in equation (15). The water fraction in pulp was set at 0.67, since this amount can typically be achieved by pressing of the pulp [74].

$$x_{W,P} = \frac{M_{W,P}}{M_{P,out} + M_{W,P}} \quad (15)$$

After evaporation of 2-MTHF from the lignin and HBP, any DES that remains with the lignin and HBP (stream 12, fig. 5.2) must be removed from the lignin by washing with water. The amount of water required for lignin and HBP washing (stream 14, fig. 5.2) ($M_{W,Lwash}$) is determined by the amount of DES that must be washed from the lignin and HBP, multiplied by a washin factor (WF_L), as shown in equation (16). The washing factor is estimated at 2, it is assumed that 2 kg water is required to wash 1 kg DES from the lignin and HBP.

$$M_{W,Lwash} = M_{DES,MTHF} * WF_L \quad (16)$$

In addition, the amount of water required for the washing of pulp must be determined. Industrially, 3 kg water is used to wash 1 kg pulp. After the pulp washing step, DES is sent to a LLX operation to remove lignin. In this step also water is needed. It is expected that for LLX additional water is needed. This additional amount can be added during LLX, but it is better to add it during pulp washing, because using more water for washing will ease the washing operation. This amount of water goes to the extraction stage together with the DES mixture (from stream 5 via streams 7 and 8, fig. 5.2). Therefore, the amount of water required for pulp washing ($M_{W,Pwash}$, stream 5) is calculated from a mass balance between the water required in the DES recycle (stream 16), the water entering the recycle from the biomass (stream 1), lignin wash (stream 14) and the water that leaves the process in the pulp (stream 6). This is shown in equation (17).

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

$$M_{W,Pwash} = M_{W,DESrecycle} - M_{W,B} - M_{W,Lwash} + M_{W,P} \quad (17)$$

The amount of water used from pulp washing must always be higher or equal to the minimum amount of water required for pulp washing. This amount is 3 kg water per kg pulp and called the wash factor (WF_P), shown in equation (18). In case the amount of water calculated by equation 17 is lower than the lower boundary stated in equation (18), the amount of water required for washing will be determined according to equation (18) and the water fraction in the DES recycle (calculated from equation 10) will increase.

$$M_{W,Pwash} \geq M_{P,out} * WF_P \quad (18)$$

Table 5.1. Assumptions made for the mass balance of the conceptual process with their justifications.

Symbol	Description	Value	Unit	Justification
DB	DES to biomass ratio	10	kg/kg	Common ratio used in literature [34]
I_B	Lignin fraction in biomass	0.216	kg lignin/kg biomass	Measured by acid hydrolysis, see [18]
$M_{P,out}$	Total cellulose production	1000	kg/h	For convenience ^a
SF	Solvent to feed ratio	0.5	kg/kg	Estimated from [58]
WF_L	Washing factor lignin	2	kg/kg DES	
WF_P	Washing factor pulp	3	kg/kg	Estimated from water washing data ^b
$X_{DES,MTHF}$	Solubility of DES in 2-MTHF	0.3	kg/kg	Estimated from [58]
$X_{MTHF,DESrecycle}$	Solubility of 2-MTHF in DES	0.1	kg/kg	Estimated from [58]
$X_{W,B}$	Water fraction in biomass	0.5	kg/kg	[73]
$X_{W,DESrecycle}$	Water fraction in DES after LLX	0.5	kg/kg	Estimated from [71]
$X_{W,P}$	Water fraction in pulp	0.67	kg/kg	Typically achievable by pressing [74]
Y_L	Lignin removal from biomass	0.94	kg lignin in biomass/kg lignin removed	Measured in this work
Y_P	Solid yield after delignification	0.57	kg/kg biomass	Measured in this work

a Normalized to 1 t/h for convenience. All numbers can be scaled linearly to any desired production capacity.

b Only data about water washings are available, which state that 2.5 m³ water [74] per t of pulp is required. Based on the density of DES, being higher than water, 3 kg DES per kg pulp was assumed to be the minimum for DES washing of pulp.

3.3. Energy balance

During pulping, the mixture of DES and wood is kept at 130 °C. After pulping, the pulp is first washed using clean DES from the evaporation plant. The clean DES is not heated, nor cooled before the washing stage. After the clean DES wash, the pulp is washed using fresh water. The use of hot water is beneficial because it increases diffusion rates and decreases the viscosity of the liquid mixtures. It is assumed that this water enters the washing plant at 80 °C because at this temperature, no pressurized equipment is required and this temperature can easily be achieved using waste heat of the process. Either water from the evaporation plant may be used directly in the washing stage, or the heat in this stream may be used to pre-heat water for the washing stage. It is assumed that the suspension of cellulose fibers in water exits the washing plant at the inlet temperature of the washing water (80 °C) and that the rest of the liquids from the washing plant are mixed. Before LLX, this stream (stream 7, fig. 5.2) is cooled down to 75 °C. This is slightly lower than the boiling point of 2-MTHF (which is 80 °C), so that no pressurized equipment is required for LLX.

After LLX, water is removed from the DES recycle (stream 16, fig. 5.2.) by multi-effect flash evaporation. It is assumed that these multi-effect flash evaporators have the same characteristics as the multi-effect flash evaporators currently used in the kraft process. Typically, these evaporators use a 7 effect evaporation train and have a steam efficiency of 5.95 [75] (1 ton of steam is used to evaporate 5.95 ton of water). If it is assumed that the heat content of steam is 2.2 GJ/t [75], the heat duty of the water evaporation step can be calculated using equation 19.

$$Q_{water\ evaporation} = 2.2 * \frac{M_{W,DESrecycle}}{steam\ efficiency} \quad (19)$$

In multi effect flash evaporation, the first stage or stages are heated using direct steam. The steam that evaporates from this liquid is used to heat the next stage, and so forth. The DES enters at the last effect and is thus heated further with each consecutive stage. It is assumed that the total heat increase is equal to the heat increase in a kraft evaporator, which is typically 40 °C [76]. This means that the dry DES exits the evaporation train at 75 + 40 = 115 °C.

Table 5.2. Mass balance of the conceptual process.

Materials in process streams (kg/h)	Process stream									
	1	2	3	4	5	6	7	8	9	10
Wood	1754									
DES		17,544	17,544	3000			20,544	25,979		
Water	1754		1754		5065	2000	8819	19,689		
2-MTHF									18,116	3623
Pulp			1000			1000				
Lignin			356				356	356		
HBP			398				398	398		

Process development for biomass delignification using deep eutectic solvents.
 Conceptual design supported by experiments

Materials in process streams (kg/h)	Process stream									
	11	12	13	14	15	16	17	18	19	20
Wood										
DES	5435	5435	5435			20,544		20,544		
Water			10,870	10,870		15,689	15,689		194	20,350
2-MTHF	18,116					3623	3623		3038	1071
Pulp										
Lignin	356	356			356					
HBP	398	398			398					

Chapter 5

After LLX, the 2-MTHF is also recovered using multi-effect flash evaporation. It is assumed that the setup of the multi stage flash evaporation is similar to the setup of the water evaporation. However, the heat of evaporation of 2-MTHF is only 0.40 MJ/kg, which is much lower than the heat of evaporation of water, which is 2.2 MJ/kg. This means that in the first stage, 1 kg steam is required to evaporate $2.2/0.4 = 5.5$ kg 2-MTHF and thus the heat duty is reduced by this factor. The 2-MTHF vapor from the first stage is then used to heat the next stage, and so forth. It is assumed that the same evaporation efficiency is achieved as for the evaporation of water from DES, thus the heat duty is reduced by the same efficiency factor of 5.95. The total heat to evaporate the 2-MTHF after LLX can be calculated according to equation (20).

$$Q_{MTHF\ evaporation} = 2.2 * \frac{0.40}{2.2} * \frac{M_{MTHF,extraction}}{Evaporation\ efficiency} \quad (20)$$

After the evaporation train, the DES is clean and ready to be used again in the pulping step. The DES and wood chips are added to a digester. For the energy calculations we assume that the wood chips enter the digester at room temperature. Both the DES and the chips (with water in them) must be heated to 130 °C in the digester. This heat can be calculated using the heat capacities of wood, water and DES, according to equation (21).

$$Q_{Digester} = (C_{P,wood} * M_{B,in} + C_{P,water} * M_{W,B}) * (T_{digester} - T_{room}) \\ + C_{P,DES} * M_{DES,pulping} * (T_{digester} - T_{evaporation,end}) \quad (21)$$

Little is known about the heats of reaction in DES delignification. To the best of our knowledge, only one study was performed on the heats of kraft delignification [75]. However, these results cannot be used to make an estimation for DES delignification since the delignification chemistry is completely different. Courchene et al. [75] found that the heat released during kraft pulping indicating an exothermic process, is due to the neutralization of acidic carbohydrate breakdown products with NaOH, a reaction that does not occur in DES delignification. The question whether biomass conversion processes are endothermic or exothermic also plays in other fields, such as pyrolysis. In the pyrolysis process, many endothermic and exothermic reaction zones were observed. Overall, it is believed that pyrolysis of wood is slightly endothermic with a heat of reaction around 0.6 MJ/kg [76], although it must also be noted that lignin breakdown reactions are more exothermic than cellulose breakdown reaction [77] (which remain mostly inert during pulping). Furthermore, the fraction of the polymers that reacts in the pulping is much smaller than in pyrolysis. Taken together, it appears justified to neglect the heat that is

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

produced or required during DES pulping, but further research is necessary to find out whether this assumption is realistic.

At last, the pulp may be dried. For many cellulose applications, such as papermaking or enzymatic hydrolysis for the production of other chemicals, the cellulose is used in an aqueous slurry. When this plant is integrated with the pulping plant, drying of the pulp is unnecessary. In this study the heat of drying is taken into account, since we study a non-integrated pulp mill. It is assumed that the heat required for pulp drying is the same as in a commercial pulp mill, which is 3 GJ/t [31]. In short, heat is required for the digester and to evaporate water and 2-MTHF and cooling of the DES is required before LLX. Furthermore, the produced pulp may be dried. Unfortunately, the heats for multi-effect flash evaporation and pulping must be provided at high temperatures (>120 °C) and thus, there are little opportunities for heat integration.

Table 5.3. Energy usage in the conceptual process before and after optimization.

Operation	Heat before optimization (GJ/t)	Heat after optimization (GJ/t)
Digester	1.7	1.3
Water evaporation	7.6	3.2
2-MTHF evaporation	1.4	0.7
Pulp drying	3.0	3.0
Total	13.7	8.2

3.4. Process improvement

The amount of heat required for a non-integrated DES based pulping process was estimated at 13.7 GJ/t using rigorous calculations. To put this number into perspective; a typical kraft process uses 11.0 GJ/t in heat. In order to make a DES based pulping process competitive to the kraft, the energy usage should be lower than in the kraft process. Considering that many decades of optimization have taken place in the development of the kraft process, also optimization of the DES-based process should be done, and starting from the values

taken from laboratory observations, a first set of improvements is considered based on a combination of experiments and calculations.

3.4.1. DES to biomass ratio

The most obvious parameter to change in the process is the DB ratio. Using less DES will reduce the duty in the digester and require less water and 2-MTHF for extraction. However, a decreased DB ratio will increase the lignin concentration in the DES, which may decrease the delignification rate. Furthermore, there is a minimum DB ratio because biomass itself is a porous structure and biomass in a digester has a packing density. This typically results in a packing density around 230 kg/m^3 for hardwoods [74]. Assuming the density of wood is $1,500 \text{ kg/m}^3$ [74] and the density of the DES applied in this study is 1140 kg/m^3 [69], at least 4.2 kg DES is required to fill the empty spaces in the wood packing. For convenience, the DB ratio was reduced from 10:1 to 5:1 kg/kg. It was found that delignification degree decreased from 94.1% to 87.0% and the yield increased from 57% to 59%. Although the delignification degree decreased, it is still well above the fiber liberation point, which is at 80% delignification [78]. This is schematically shown in fig. 5.3 [78]. The total energy use in the process decreased to 9.3 GJ/t pulp.

Fig. 5.3. Delignification of eucalyptus as function of the DB ratio. The three experimental delignifications of eucalyptus were obtained by treating the wood 1h at 130 °C. The region in which the DB ratio is too low to fill the porous biomass bed with DES is indicated in red blocks and the region below the fiber liberation point is indicated with orange stripes.

3.4.2. Water addition

Reducing the amount of water used in the LLX of lignin from the DES will decrease the energy requirement in the water evaporator. The water content in the DES must be between 25 and 50 wt% for full lignin recovery [58]. The lignin recoveries in one extraction stage were determined for 6 water contents in the raffinate between 20 and 55 wt%. It was found that the single stage recovery did not improve much when the water content in the raffinate increased more than 40 %.

Water has two functions in the process, it is required for full extraction of the lignin from the DES, and it is required for the washing of the cellulose fibers and lignin. The water that is required for washing the cellulose and lignin is recycled to the extraction stage. When the minimum amounts of washing water are mixed with the DES, the water contents in the raffinate are between 38% and 43% for a BD of 1:10 and 1:5 respectively. These values are shown in Fig. 5.4 as the dashed and dash-dot lines. It can be seen from the figure that the single stage recovery does not increase much further when more water is added than the water that is already present from the recycling of the water washings. Therefore, the amount of water required for the process is limited by the amount required for the washing stages, rather than the lignin recovery. At a DB ratio of 5:1 and 43% water in the raffinate, the total energy usage of the process drops to 8.2 GJ/t cellulose pulp.

Fig. 5.4. Single stage lignin recovery from DES using 2-MTHF for various amounts of water in the DES raffinate at equilibrium. The water contents in the raffinate that are obtained in the proposed process by mixing the minimum amounts of water (see equation 18) are indicated by dashed lines for two DB ratios. These are the minimum amounts of water that can be reached from a process point of view.

3.4.3. Recycling of washing DES

The DES that is currently used for washing is sent directly to the LLX stage, where lignin and HBP are removed from it. The lignin contents in the eluent streams are however lower than the lignin contents in the DES that exits the digester. Thus, the lignin that exits the washing stream may be considered as not fully saturated. Therefore, it may be considered to send the eluent from DES washing with a low lignin content back directly to the pulping stage. If this DES is recycled back directly to the digester, the total energy usage can be further reduced from 8.2 to 7.1 GJ/t. However, when more lignin is present in the digester, this may cause lignin and hemicellulose polymerization reactions, which may inhibit the delignification rate and increase the lignin molar weight. To investigate on the severeness of the repolymerization, delignification experiments were carried out with previously prepared lignin-in-DES mixtures.

From fig. 5.5 it can be seen that the delignification decreases with the initial lignin content. However, the delignification stays above 80%, even when the initial lignin content exceeded 2.5 wt%. The lignin molar weight distribution in these liquids was also investigated by GPC. First, the lignin molar weight distributions in the previously prepared lignin-in-DES mixture,

Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

and in the DES that was obtained after the delignification experiment using clean DES were determined. When the lignin-in-DES mixture is used for a consecutive delignification experiment, the lignin that is added to the DES during the delignification experiment is added to the lignin that was already present in the mixture. If we assume that the lignin that was initially present in the lignin-in-DES mixture is inert during the delignification experiment, it would be expected that the lignin obtained by the delignification experiment using the lignin-in-DES mixture is the sum of the lignin in the initial lignin-in-DES mixture and the lignin obtained using the clean DES. We can then expect the molar weight of the lignin obtained from the delignification experiment using the lignin-in-DES mixture to be the weighted average of the lignin in the lignin-in-DES mixture and the lignin obtained by delignification using a clean DES. This expected molar weight distribution was compared to the distribution that was actually obtained in the delignification experiment using a lignin-in-DES mixture, as shown in fig. 5.6. In this figure, it can clearly be seen that the obtained molar weight is much higher than the expected molar weight and thus, additional condensation reactions must have taken place with the lignin that was initially present in the mixture. This will not only make it harder to valorize the obtained lignin, but it will also make lignin recovery by LLX much harder. Therefore, recycling of washing DES without lignin recovery is not considered for the conceptual design.

Fig. 5.5. Delignification of eucalyptus as function of the initial lignin content of the DES. Eucalyptus was treated 1 h at 130 °C.

Fig. 5.6. Obtained and expected molar weight distributions for a delignification experiment using a lignin-in-DES mixture. The obtained graph is the GPC spectrum from the trial with 2.6 wt % initial lignin. The expected molar weight graph is the weighted average of the GPC spectrum of the lignin-in-DES mixture and the GPC spectrum obtained from the delignification experiment using clean DES.

3.5. Solvent losses

Lactic acid can form esters with hydroxyl groups in other molecules, just like any other carboxylic acid. This means that lactic acid may also form esters with hydroxy groups in lignin and cellulose. For example, Kajimoto et al [79]. produced cellulose fibers from Sugi pine using lactic acid and found that the produced fibers contained 6 to 9 % lactic acid, which was polymerized to the cellulose fibers. The lactic acid fraction in the lignin and cellulose produced by DES was determined by acid hydrolysis. It was found that the cellulose contained 3.6 wt % lactic acid, while the lignin contained 6.4 wt % lactic acid. By mass balance this means a loss of 36 kg lactic acid in the pulp and 20 kg in the lignin per t cellulose produced, adding up to a total loss of 56 kg lactic acid per t cellulose pulp. Possibly, lactic acid can be removed from cellulose fibers by ozone bleaching [80].

More research is required to determine the losses by solvent degradation during DES processes. Rodriguez et al. [81] researched degradation by esterification between the lactic acid and choline chloride. However, these esterification reactions are equilibrium reactions. This means that the formed degradation product (the ester between lactic acid and choline chloride) reacts back to the initial DES, and especially by operating the pulping stage wet, the presence of water dramatically reduces the esterification of lactic acid.

4. Outlook

The energy use in this process is mainly due to the evaporation of water used for washing the cellulose fibers. This means that there is relatively little room for an improvement in energy use by the optimization of pulping and regeneration conditions. Nevertheless, the heat duty of the proposed DES process is around 25% lower than the kraft process. Washing with other solvents, such as ethanol instead of water may further decrease the energy usage of the process since the heat of evaporation of ethanol is much lower than water. Another possible reduction of the heat duty can be obtained by reducing the evaporation of water, by (at least partially) dewater the DES using a membrane. Further research on this subject is necessary to accurately estimate the technical feasibility of such process and to estimate the possible savings in energy use.

Deep eutectic solvents offer many advantages over other delignification processes. The proposed DES is non-toxic, non-flammable and non-volatile, which means that operations with DES are inherently safe. However, this is not the case for 2-MTHF, which is used in the recovery. Although 2-MTHF a bio-based solvent and its use is justified by the significant energy savings, it is very volatile and flammable. It is desirable to find non-flammable alternatives to 2-MTHF.

It seems that all operations can be performed using readily available technology. Furthermore, no pressurized equipment is required since the proposed DES is non-volatile. This means that the process may have a very low capital expenditure. The biggest opportunity for DES based products is the valorization of by-products. Next to the produced cellulose, lignins may be produced as well. Furthermore, the process may be adjusted to produce valuable furanic products from the hemi-cellulose, such as (hydroxymethyl)furfural [82,83]. These chemicals may be used as feedstock for chemical industry as a replacement of fossil resources, as schematically shown in fig. 5.7.

In the proposed process, DES losses are significant due to polymerization of lactic acid to lignin and cellulose. This means that the process either has high solvent losses, or expensive post-treatments to recover DES. Furthermore, some 2-MTHF leaches to the DES during LLX. This is evaporated from the DES together with the water and can be separated using a simple settler since 2-MTHF is immiscible with water. However, 2-MTHF and water do have a mutual solubility [85]. A solubility calculation using the data from Glass et al. [85] results in a loss of 456 kg 2-MTHF per t cellulose. This amount must also be recovered from the water, for instance by extraction using either a high boiling solvent, such as dodecane, or

Chapter 5

solvent impregnated resins. In this case, the 2-MTHF can be recovered from the extractant by flash evaporation, meaning heat of evaporation of 2-MTHF must be added to the total heat duty. This amount is $0.456 * 0.4 = 0.18$ GJ/t cellulose. Alternatively, membrane separations may be considered for this separation, but more work is required to find out whether a membrane separation is technically feasible. Membrane separations do not require additional heat, but will require some additional electric power [86]. The kraft process is currently favored over other biomass fractionation processes since the cellulose fibers produced by this process have good properties for papermaking. More research is required to see whether DESs can produce a similar fiber quality.

5. Conclusions

A conceptual process design was made for the delignification of lignocellulosic biomass using a deep eutectic solvent comprised of lactic acid and choline chloride. Mass and energy balances were made using rigorous calculations. Optimizing the amounts of water and DES used in the process reduced the estimated heat duty from 13.7 to 8.4 GJ/t cellulose, which is 24% lower than the kraft process. The amount of DES in the process could be reduced to the amount that is physically required to fill the porous biomass bed. The amount of water required for sufficient lignin recovery by LLX is already achieved when the water used for washing of the cellulose and lignin are recycled to the LLX stage. Recycling of lignin-in-DES mixtures directly back to the delignification stage may save a minor amount of energy, but will increase the molar weight of the lignin, which decreases its potential for valorization and makes recovery by LLX more difficult. Valorization of by-products, such as lignin and furanics from hemi-cellulose is key in DES based delignification processes.

Fig. 5.7. Conceptual comparison of the feedstocks and products in the current industrial situation and the desired DES process. Picture was adapted from the ProViDES final report [84].

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Process development for biomass delignification using deep eutectic solvents.

Conceptual design supported by experiments

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Conceptual design supported by experiments

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Chapter 6

Conclusions and outlook

This thesis describes research and design for a conceptual process for the delignification of biomass using a deep eutectic solvent (DES) comprised of choline chloride and lactic acid. In **chapter 2**, the delignification mechanism of the DES was studied. Although it was clear that the lignin is cleaved by an acid hydrolysis mechanism, the influence of choline chloride on delignification was unclear. The influence of choline chloride on the lignin solubility, cleaving reactions and mass transfer were investigated and it was found that the choline anion increased the lignin cleavage reaction rate and thereby the delignification rate. These findings are a spur for further solvent development or optimization for biomass delignification. Since the chloride anion is the active part of choline chloride, other salts such as sodium chloride may be used for delignification processes just as well, but choline chloride offers great advantages in the DES recovery. This was studied in **chapter 3**, where an alternative lignin recovery method to cold water precipitation was proposed, involving liquid-liquid extraction using an organic solvent. Six solvents were screened for this purpose and 2-methyltetrahydrofuran (2-MTHF) was selected as the most suitable one. It was found that choline chloride is required for two phase formation. At equilibrium, at least 30% choline chloride must be present in the DES to form two phases and addition of more choline chloride reduces the mutual solubility of 2-MTHF and lactic acid. It is expected that this method saves significant amounts of heat compared to the current benchmark. In **chapter 4**, the recovery of lignin from DES using LLX was further studied and compared with cold water precipitation. It was found that LLX was more suitable for the removal of lignin fractions with a low molar weight, while cold water precipitation was more suitable for the recovery of lignin fractions with a high molar weight. For industrial applications, a combination of both approaches is desired. Also, the lignin composition was investigated of the various fractions that were extracted by 2-MTHF and fractions that remained in the DES and it was found that the fractions remaining in the DES had a highly condensed nature. In **chapter 5**, all previous findings were combined to design an conceptual process for the delignification of eucalyptus globulus using a DES comprised of choline chloride and lactic acid. Mass and energy balances were made and the heat consumption of the process was optimized using additional experiments. It was found that the DES to biomass ratio could be reduced to 5, the minimum required to fill the porous structure of the wood. After the optimization, the predicted final process used 8.4 GJ heat per ton pulp produced, which is a 24% reduction compared to the Kraft process. A further reduction to 7.1 GJ/t is possible if lignin-in-DES mixtures from the washing plant are recycled back to the delignification stage without any purification. This is not considered, since it increases the molar weight of the produced lignin, which makes recovery more difficult and decreases the value of the produced lignin. Furthermore, the DES based process offers great opportunities for the valorization of byproducts, such as lignin or furans from hemicellulose.

Chapter 6

This thesis provided initial studies on a conceptual design for the delignification of eucalyptus using a mixture of choline chloride and lactic acid. The results from these studies were highly encouraging and show great potential for industrial application. However, a couple of issues need to be addressed before industrial implementation of this process. The quality of the produced cellulose fibers was not addressed in this thesis. It is key to produce cellulose that is suitable for papermaking, since the value of cellulose for papermaking is much higher than cellulose for other purposes, such as fermentation to bio-ethanol. Furthermore, lactic acid formed esters with the hydroxyl groups present in the cellulose and lignin, which will cause significant solvent losses. Also, the studied DES seems corrosive to metals, as some corrosion was observed on the metal laboratory equipment. However, since the entire process is operated at atmospheric pressure and at relatively mild temperature, it seems viable to investigate alternative construction materials, such as high performance plastics.

In this thesis, only one DES was studied, which used acetic hydrolysis reactions, catalyzed by a halide salt, to cleave the lignin. However, there are more types of DES and therewith more mechanisms in which biomass can be delignified, such as hydrolysis using alkaline DESs. Also, DESs can be used as solvents for various catalysts, such as metallic catalysts, which may also improve delignification. More research is also required on the role of the halide ion, which was used in these studies. Although it is clear that it increases the delignification rate, the effects on carbohydrate degradation are not known yet. Since both lignin cleavage and carbohydrate breakdown are important for the quality of the cellulose pulp, further studies must be conducted to see whether the addition of chloride increases the selectivity of delignification over carbohydrate breakdown.

Although only one DES was studied in this thesis, one great advantage of a DES is its tunable character. The constituents of a DES can be altered, just as the ratio between the constituents. For instance, a 1:250 molar ratio of choline chloride to lactic acid was already effective for biomass delignification, while at least 30% is required at equilibrium to form a two phase system with 2-MTHF, allowing efficient lignin recovery. This character contributed to the huge popularity of DES, but has one drawback. A proliferation of mixtures that are entitled as DES, will hollow the value of the term DES.

The proposed DES process has a great potential to produce byproducts from cellulose production, which may be used as feedstocks for the chemical industry as replacements for fossil feedstocks. However, it must be pointed out that the pulp industry only produces 272 Mt of byproducts per year, whereas the total fossil material feedstock for the chemical industry is 760 Mt/y. This means that a

Conclusions and outlook

significant part of the material demands can be replaced by byproducts from the pulp and paper industry, but other sustainable resources are required as well to fully replace fossil resources.

List of abbreviations

Abbreviation	Description
2-MTHF	2-methyl tetrahydrofuran
BHT	Butylated hydroxytoluene
ChCl	Choline Chloride
CPME	Cyclopentyl methyl ether
DB	DES to biomass ratio
DES	Deep Eutectic Solvent
DSC	Differential Scanning Calorimetry
FT-IR	Fourier-transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
GVL	γ -valerolactone
HBP	Hemicellulose byproduct
HPLC	High Pressure Liquid Chromatography
HSQC	Heteronuclear single quantum coherence spectroscopy
LA	Lactic Acid
I _b	Lignin fraction in biomass
LCC	Lignin Carbohydrate Complexes
LLX	Liquid-liquid extraction
M _{P,out}	Total cellulose production
MWL	Milled Wood Lignin
SEM	Scanning electron microscopy
SF	Solvent to feed ratio
VWD	Variable Wave Detector
W _{F,L}	Washing factor lignin
W _{F,P}	Washing factor pulp
X _{DES,MTHF}	Solubility of DES in 2-MTHF
X _{MTHF,DESrecycle}	Solubility of 2-MTHF in DES
X _{W,B}	Water fraction in biomass
X _{W,DESrecycle}	Water fraction in DES after LLX
X _{W,P}	Water fraction in pulp
Y _L	Lignin removal from biomass
Y _p	Solid yield after delignification

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