Ionic liquid as a tool for cost-effective fractionation of biomass to obtain lignin with high β-O-4-content

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University of Groningen, Bachelor research project chemical engineering degree, June 18, 2020

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This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

Abstract

The fractionation of lignocellulosic biomass allows for obtaining lignin, the world most abundant aromatic polymer in the world. The extraction of lignin could replace chemicals and materials derived from petrol. Ionic liquids (ILs) have been seen as suitable solvents for extraction of lignin, due to its excellent solubility for natural polymers. The wide variety of ILs makes it an adjustable solvent to fractionate biomass. Moreover, the process of each ionic liquid can be tuned to effectively optimize the fractionation process. Several process variables are being discussed in this review, like the adjustment of the temperature, dissolution time and the addition of an acid. With a goal to separate the lignin in high quality from the biomass cost effectively. The quality of lignin is being determined by the amount of β-O-4-linkages in lignin after pretreatment. One of the cheap ILs [TEA][HSO_4] was proposed as a good candidate for this process, due to its low cost of 1.24 $/kg. However, the recycling rate of the ILs seems to be the hindrance of cost effective biomass fractionation, emphasis on effective reuse of the ILs is necessary to make the process industrial-relevant.

Introduction

The wide spread usage of petroleum based fuels and chemicals the last century have provided low-cost energy and products, but this also led to a fast increase in global temperature. As a consequence, more focus has been laid in the use of renewable energy and chemicals. Lignocellulosic biomass is a promising feedstock for renewable energy and materials, since it does not compete with food or animal feed. Lignocellulosic materials contain a mixture of carbohydrate polymers, such as cellulose and hemicellulose, lignin and in a minor fraction proteins and extractives.

Lignin is large complex molecule that is found in all types of biomass, but the quantity and composition of lignin depends on the species of biomass [1]. Lignin contributes roughly 15-25 wt% of the lignocellulosic biomass, other components are cellulose 38-50 wt% and hemicellulose 23-32 wt%. The average proportion of lignin is being found higher in softwood, slightly lower amounts in hardwood and the lowest in switchgrass [1]. Lignin is characterized as an amorphous polymer which acts as glue, binding cellulose and hemicellulose via ester linkages and hydrogen bonding [2], see figure 1. Moreover, lignin plays a supporting role in the plant, providing antimicrobial resistance and limits the loss of water in the plant [3]. In contrary to cellulose, lignin consists of aromatic rings, made from three compounds, p-coumaryl alcohol / p-hydroxyphenyl (H), coniferyl alcohol / guaiacyl (G) and sinapyl alcohol / syringyl (S).

Fractionation of biomass is necessary to separate the three major components in biomass. The problem of efficient fractionation is the complex chemical and physical structures inside the lignocellulosic biomass. Several methods have been developed of separation of biomass like steam, ammonia, dilute acid, the organosolv process and in the last two decades more focus has been on ionic liquids [4]. This group of liquids only began a more interesting since 1998, when the magazine *Chemical & Engineering News***,** reported that over 1 million different combinations between cations and anions [5].

Ionic liquids are a salt with a melting point lower than 100 °C, which consists only of cations and anions. Due to the bulkiness of the ions, the solid lattice structure is harder to form [6]. One of the first reported ionic liquid was reported in 1914, when Walden discovered a molten salt $[EtNH_3][NO_3]$. Ionic liquids have already been applied in a broad spectrum such as; advanced batteries, dye-sensitized solar cells, doublelayer capacitors, actuators, fuel cells, thermo-cells, and water splitting, essentially related to highly efficient carbon capture and storage technologies [7].

Ionic liquids are able to fractionate biomass into cellulose, hemicellulose and lignin. Two distinct strategies of pretreatment of lignocellusic biomass are in development: one strategy is the disruption of the structure of the biomass, which dissolves the cellulose, hemicellulose and lignin and affect the crystallinity of cellulose. The other more recent strategy uses ionic liquids to fractionate the lignocellulose through dissolving lignin and hemicellulose but leaving the cellulose behind as a filterable solid (ionoSolv pretreatment) [4]. For fractionating wood, a small portion of water is added to the IL. This in order to dissolve the lignin in the IL, see figure 1. During the dissolution the structure of lignin is affected. The ether bonds in lignin like β-O-4, β-β and β-5 are rearranged to a more stable C-C-bond, which changes the original structure of the lignin. In order to get high quality lignin, the structure has to look similar to original lignin, thus containing a relative high amount of ether bonds. The quality of lignin is often displayed as a ratio between the amount of β-O-4-linkages per 100 aromatic rings. Since aromatic rings are generally stable, it makes them a good reference point. Lignin is obtained by precipitation of an antisolvent and the IL is subsequently reused.

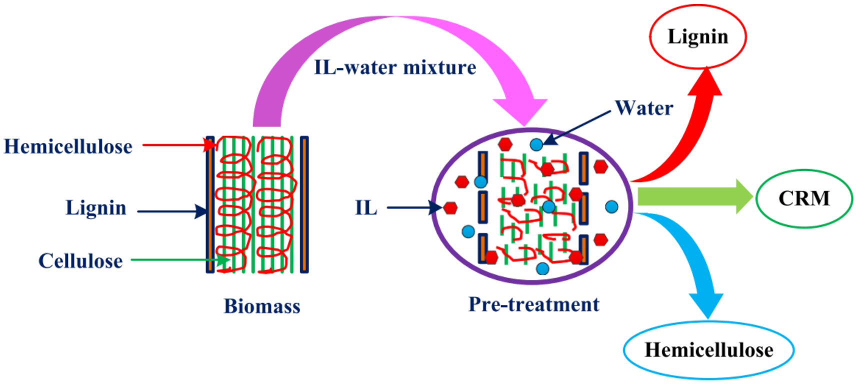

Figure 1: Schematic illustration of pre-treatment of complex lignocellulosic biomass structure, based on the work of [8].

Unfortunately, more studies have been focusing on extracting/fractionation cellulose from biomass with ILs. While lignin has a width range of applications, with high value products like: plasticizers, binders, emulsifiers and sequestrants. Lignin can even act as a high-value molecule like polyphenols and tannins [2]. High molecular weight lignin is suitable in carbon fibers, due to its relative high thermostability and T_g. While low molecular weight lignin could be used in polymeric and adhesive applications [9] or lignin-based composites [10]. Moreover, the shift of ILs from fossil based imidazolium cations towards renewable amine-based cations, reducing the price significantly. The main question is: are ionic liquids economic feasible to extract lignin from biomass with a high β-O-4 value?

In this research, different types of ILs are being discussed and how they perform in the biomass dissolution. Moreover, the analysis of the quality of lignin is explained in detail. Herein, a variety of factors are being discussed that affect the overall quality of lignin. Subsequently, the process of fractionating biomass is explained in detail. Finally, the economical aspect is being discussed.

Ionic liquids

The large amount of combinations in ionic liquids are divided into groups and are mainly based on their cation. The five common types of cations are pyridinium, imidazolium, pyrrolidinium, quaternary ammonium and tetra alkylphosphonium [11]. Imidazolium cations have been studied extensively the two last decades, due to their good performance properties. Imidazolium cations like [bmim], [emim] and [amim] exhibit good acid/base properties, therefore resulting in better dissolving properties [12]. Moreover due to its aromatic character, n-π and π-π interacts with the aromatic rings of the lignin, resulting in higher solubility [2]. Imidazolium based cations could be synthesized via nucleophilic substitutions or via a reaction with an anhydride, see figure 2.

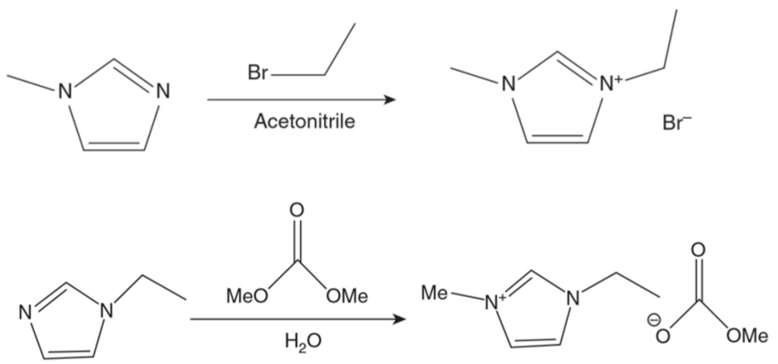

Figure 2: synthesis of an imidazolium based IL [13].

Amine-based cations are a class of IL containing a protonated nitrogen atom as a cation, like triethylammonium [TEA] or triethyl-(2-(2-methoxyethoxy)ethoxy)ethylammonium, [DMEA]. [TEA] could be prepared by the alkylation of ammonia with ethanol, shown in figure 3 [14]. Amine-based ILs can be easily synthesized by adding a tertiary amine with a strong acid [13] or with a weak acid like carboxylic acid and propionic acid [15]. This reaction is called a quaternization reaction or a nucleophilic substitution reaction, where neutral tertiary nitrogen reacts from a 3- to a 4- coordinated nitrogen with a positive charge. Because amine-based cations can be easily synthesized, the price is much lower than an imidazolium based cation, as can be seen in table 1. Moreover, amine-based cations are more biodegradable, than imidazolium based [16]. In green chemistry this is beneficial in case losses of the solvent in the process occur.

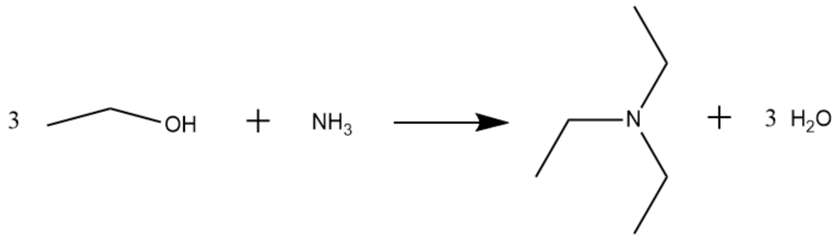

Figure 3: synthesis of triethylammonium [TEA] [14].

The solubility of biomass in ILs is majorly depending on the anion [17], other properties influenced by the anions are its thermal stability, melting point and viscosity [12]. Anions often mentioned in literature are [Cl], [HSO$_4$], [MeSO$_4$], [OAc]. The acetate anion has compared to the other anions the highest dissolution power. According to [18] this has to do with the proton acceptability of the anion. Kalmet-Taft parameter shows the proton donating (α) and proton accepting (β) capabilities of anions. [OAc] has compared to [Cl] or [MeSO$_4$] higher β-values (1.20, 0.84, 0,67 respectively), thereby increasing the rate swelling of biomass and subsequently the rate of dissolution. The proton accepting ability is also triggered by the amount of water present in the ionic liquid. The Kalmet-Taft parameters are not constant and often depend of the amount of water present in the solution. An increase of the amount of water will decrease the β-value, but increase the proton donating abilities. An improvement in the α-

value increases the ability of the dissolution of biomass, especially for lignin [19]. Akiba et al. concluded when IL mixed with water, the polarity of the mixture changed from lignin-insoluble region towards soluble. However an excess of water changed the polarity that the lignin became insoluble. This observation is visualized in figure 4. Akiba et al. concluded this correlation with [C_2mim] cation and 13 different anions.

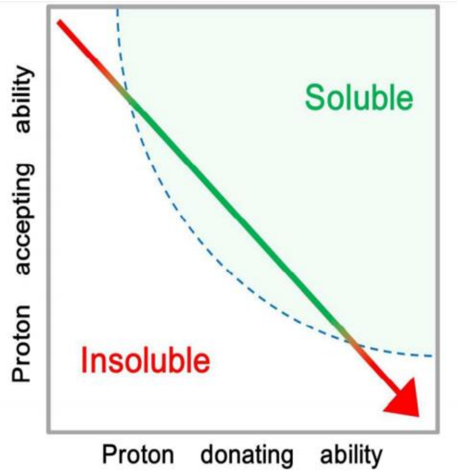

Figure 4: effect on proton donating and accepting ability of ILs by addition of water [19].

The difference in price between imidazolium based-cation and amine-based cation is significant. In the optimum scenario imidazolium IL is 4 times more expensive than amine-based IL, see table 1 . The price based on the optimal scenario for imidazolium IL is an average between the manufacture price of the ions; [C_2mim][OAc] (4.1, 0.84 $/kg). Under the assumption that 30-60% of the costs are made from raw materials, an average price of average price between 4.5-9 $/kg was determined [20]. However several sources estimated higher prices of imidazolium based ILs, in the range around 10-20 $/kg [21], but without references. [22] claimed a price of 20$/kg for [bmim][OAc] and [23] a price of $10/kg for [emim][Cl]. The price minimum price of [TEA][HSO_4] (1.24 $/kg) and 1-methylimidazolium [HSO_4] (2.96–5.88 $/kg), was estimated using ASPEN simulation by [16]. Current market prices in bulk production are not reliable or available by companies. Due to the synthesis and the often the bio-based origin, [TEA][HSO_4] is more preferred in the green chemistry, than imidazolium based.

Ionic Liquid	Year source	Price / kg	Company	Reference
[TEA][HSO_4]	2014	$1.24, $1.45	-	[16], [21]
1-methylimidazolium [HSO_4]	2014	$2.96–5.88	-	[16]
[C_2mim][OAc]	-	$20	BASF	[21]
[C_2mim][OAc]	-	$850	Sigma-Aldrich	[21]
[$(C_8)_3C_1N$][Br]	-	$30	Solvent InnovaVons	[21]
1-methylimadizole [OAc]	2011	$4.5-9	ICIS	[20]

Table 1: price of several commonly used ionic liquids.

Ionic liquids in biomass

Due to the great solubility capacity of ionic liquids, they are able to dissolve many compounds. If the non-ionoSolv-route is chosen, the crystallinity of cellulose will be reduced significantly. The cellulose becomes more amorphous, which facilitates the hydrolysis catalyzed by the several enzymes still present in the mixture [24]. Figure 5 shows the mechanism of the hydrolysis of cellulose. (i) showing the swelling of the biomass, (ii) the dissolution of the biomass followed by, (iii) the hydrolysis to oligosachharides and (iv) conversion of enzymes to glucose. This rate of hydrolysis increases when lignin is removed from the solution [25].

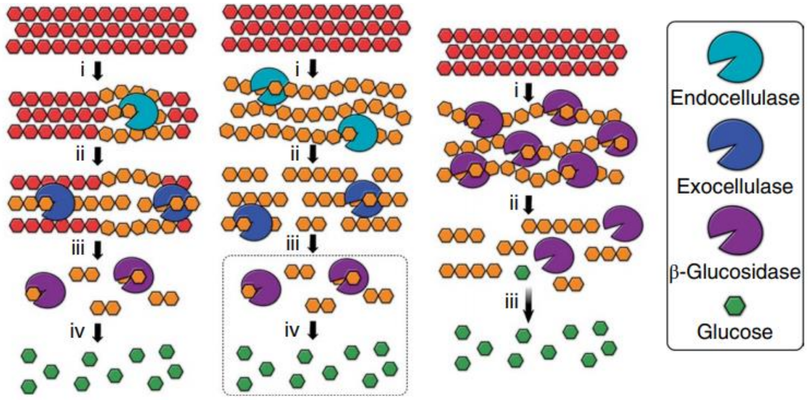

Figure 5: mechanism of the hydrolysis of cellulose [24].

Lignin is also affected by ILs, because many linkages are being de- or repolymerized. The decomposition is especially facilitated by addition of an acid. During this process, the linkages in lignin are being broken and often repolymerized in a more stable C-C bond, see figure 6. β-O-4 linkages contribute the majority of all the linkages in lignin, 49-51% in softwood and 65% in hardwood [1]. Since this linkage is the most common and also often broken, it is a good measurement about the quality of the lignin. Normally, lignin is being decomposed into smaller particles, however if the dissolution time of biomass in the lignin occurs for a long period, the molecular weight and the molecular number increases. Repolymerization reactions create large, complex lignin structures and in smaller amounts a mixture of molecules with a low molecular weight [26]. This trend can be seen in figure 7, where the average molecular weight increases with a lower amount of β-O-4-content.

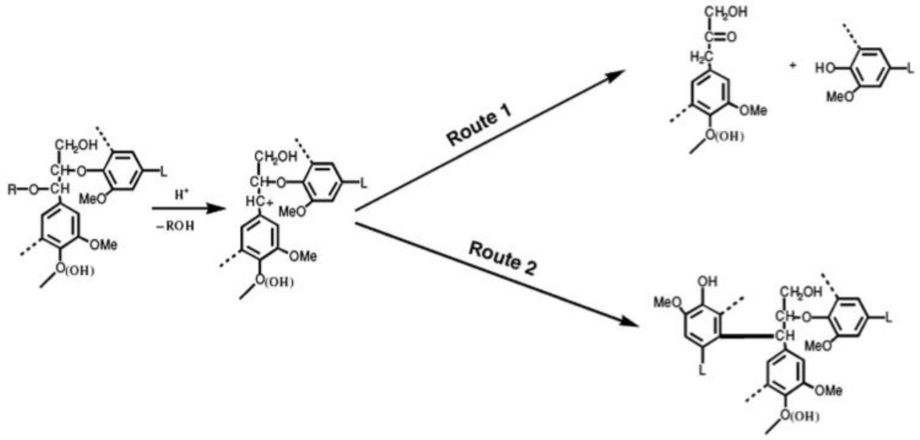

Figure 6: Scheme of depolymerization of β-O-4 structure (Route 1) and repolymerization with a reactive aromatic carbon (Route 2) Pandey et al.

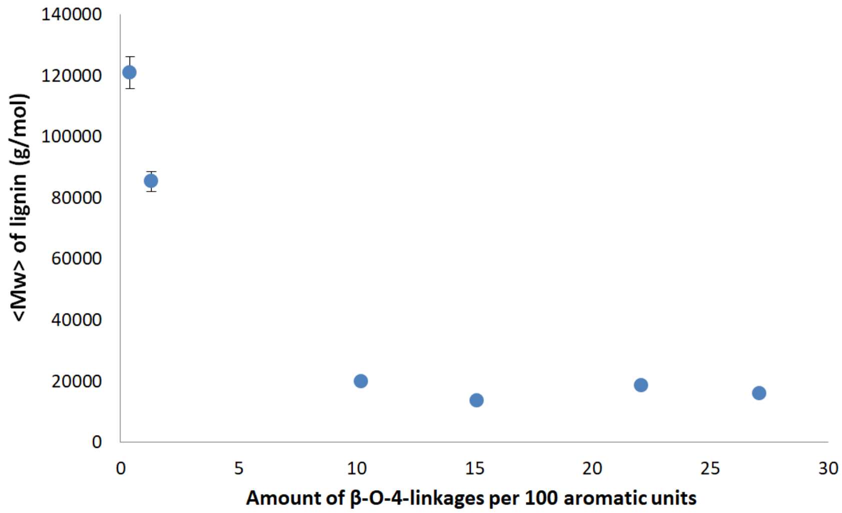

Figure 7: correlation between amount of β-O-4-linkages and the average molecular weight based on the work of Ovejero-Pérez et al.

Lignin analysis

The dissolution of biomass contains many complex structures, making analysis challenging. Heteronuclear Single Quantum Coherence NMR (2D-HSQC NMR) makes use of two dimensional ^{1}H- ^{13}C-NMR and is used most frequently to assess the ether content because it avoids the issue of overlapping peaks [27]. To determine the β-O-4-content in dissolution, this linkage has to be compared with a stable region in the biomass dissolution. Most commonly used technique is the amount of β-O-4-linkages per 100 aromatic units, but the amount β-O-4-linkages per 100 G_2 + G_{cond} volume integral is also often mentioned. The G_2-signal is detected from the carbon and hydrogen atom at the second position of guaiacyl (G). So only the guaiacyl-monomer is detected via this technique, while the other technique makes use of all the aromatic structures. As a result, the ratio of the amount of β-O-4-linkages per 100 aromatic units is lower than the 100 $G_2 + G_{cond.}$ As illustrated in figure 8 and 9, the aliphatic oxygenated side chain region could be found in the region (δ_C/δ_H 50–90/2.5–5.8) and the aromatic/unsaturated between (δ_C/δ_H 90–150/5–8.5) [27], see figure 8 and 9 as illustration. Note that in this example the author used three different techniques of extracting the lignin; (a) Indulin Kraft, (b) soda P1000, (c) Alcell.

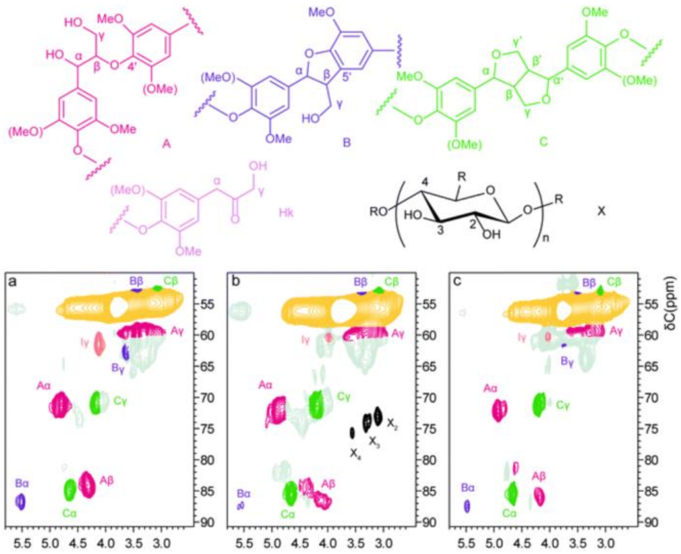

Figure 8: the main lignin side chain structures identified (A) β-O-4, (B) β-5, (C) β–β, yellow peaks correspond to OMe groups [27].

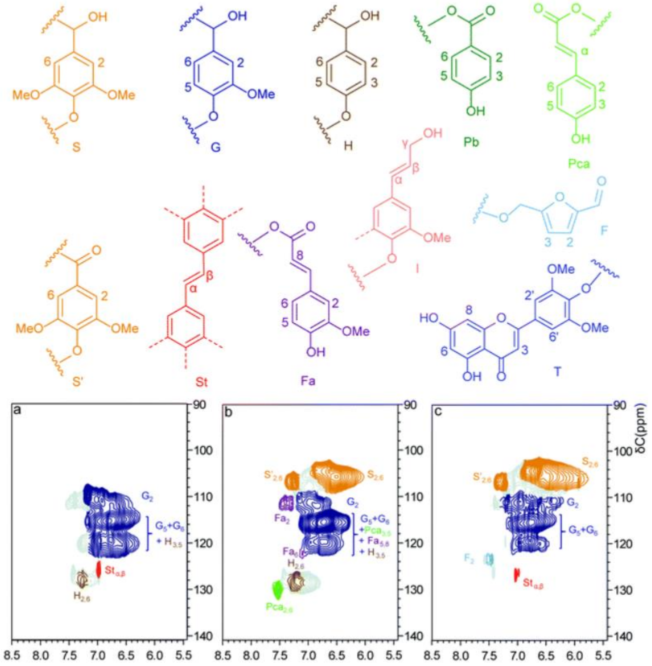

Figure 9: the main lignin aromatic structures identified; bottom: aromatic/unsaturated regions in the 2D HSQC NMR spectra [27].

The structure of lignin is affected during the dissolution. Factor depending on the yield and quality of the extracted lignin are discussed in this section. These factors are; dissolution time, an excess of acid and temperature.

Brandt-Talbot et al. investigated the dissolution of Miscanthus x giganteus biomass in [TEA][HSO_4] as IL, with 20 wt% water as an additive, at 1:10 solid loading and a temperature of 120 °C. Their first setup contained an acid:base ratio of 1, while the second setup had an excess of 9 wt% sulfuric acid. As it can be seen in figure 10, the duration of dissolution significantly decreases. On contrary the relative amount of β-O-4-linkages decreases, due to ether-bond cleavage.

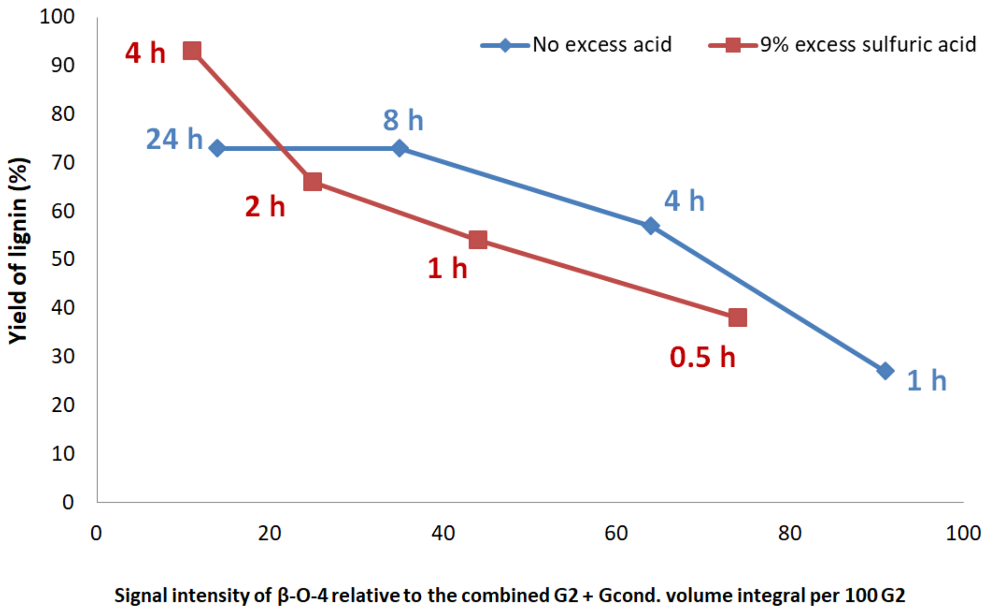

Figure 10: relative amount of β-O-4-linkages compared to the yield of the lignin, with [TEA][HSO_4] as ionic liquid with 20 wt% water, based on the work of Brandt-Talbot et al.

Ovejero-Perez et al. demonstrated temperature and time as factor that are influential for the quality and quantity of lignin. Eucalyptus globulus was used as biomass source, with 1-methylimidazolium chloride as ionic liquid. In figure 11 both solutions contain a load of 10%, the temperature in the red line remained at 135 ^{0}C, the blue line operated at a duration of 6 hours. The ratio of β-O-4-linkages versus aromatic rings at t_0 was 75.9%. Although figure 11 contains only 5 data points, it can be concluded that an optimum condition exists. A too long dissolution time resulted in attached condensed- and pseudo-lignin to the pulp, resulting in a lower yield of the lignin [4]. As temperature increases the rate of swelling and dissolution of biomass also increases [2]. This correlation is justified by [28], using eucalyptus as biomass source (10% solid loading), treated with [TEA][HSO_4] with 20 wt% water. As the temperature increase from 120 °C to 150°C, the amount of β-O-4-linkages is reduced with factor 6. However the increase in temperature facilitated the dissolution time significantly, see figure 12.

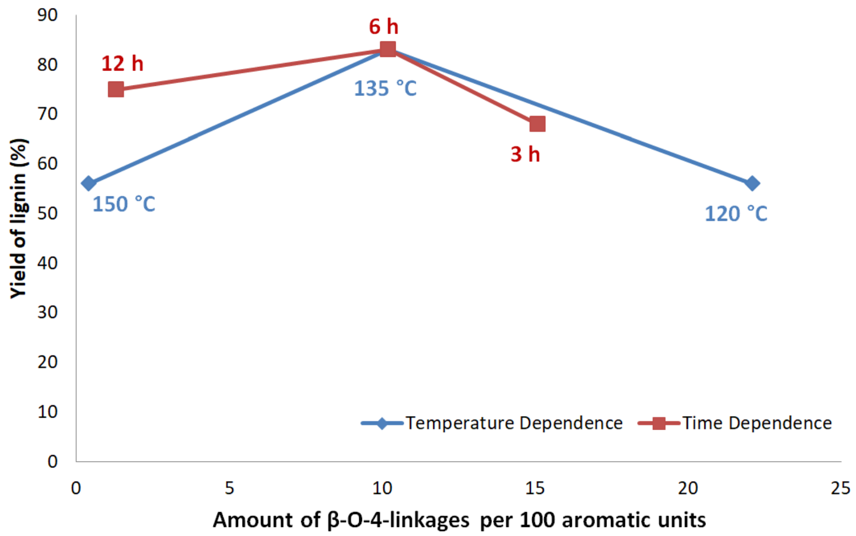

Figure 11: relative amount of β-O-4-linkages compared to the yield of the lignin with 1-methylimidazolium chloride as ionic liquid based on the work of Ovejero-Perez et al.

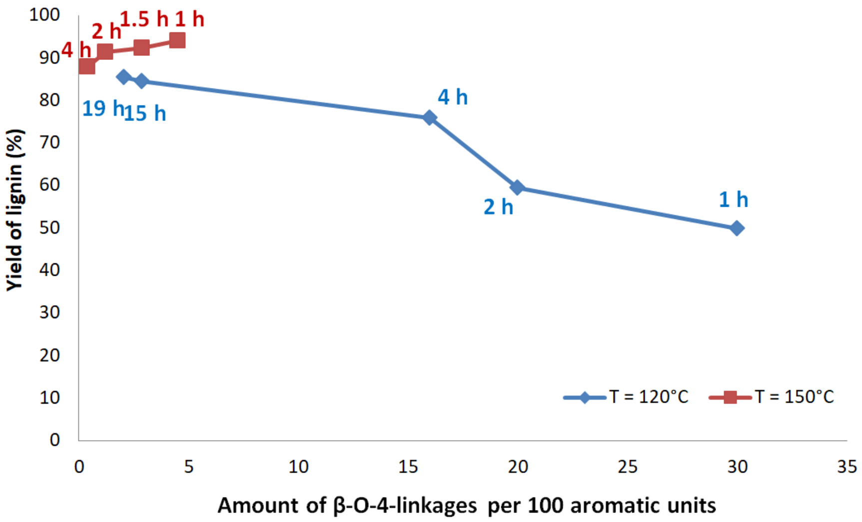

Figure 12: relative amount of β-O-4-linkages compared to the yield of the lignin with [TEA][HSO_4] as ionic liquid with 20 wt% water based on the work of Malaret et al.

According to Wang et al. it is also possible to extract lignin around a temperature of 80 °C in high yield and β-O-4 content. Their research focused on an excess of at 75 % p-Toluenesulfonic acid [p–TsOH] and 25 % [Ch][Cl]. In the work of Wang et al. a value was claimed of 76.6 % of miscanthus lignin and 88.9 % of wheat straw lignin with β-O-4 content of 30.9 and 33.6 % per 100 aromatic units, respectively. The experiment was performed in a short period of time (20 min).

Process

An overview of the extraction of lignin can be found in figure 13. At first the biomass is milled to create smaller particles. The surface area of the biomass increases, which is beneficial of increasing the rate of swelling and finally the rate of dissolution. Moreover, smaller particles increase the mechanical pumping. On contrary a smaller particle size of the biomass increases the energy demand of milling [2]. Although the exact size of the particle is dependent on the biomass type used, common ranges are between 2-5 mm [29]. Water is added to facilitate the dissolution of lignin in the system, besides that it reduces the costs. The temperature is increase in order to increase the dissolution of the biomass and lower the viscosity. After the dissolution step, cellulose and hemicellulose are obtained by precipitation of an antisolvent and collected via filtration. For lignin extraction, several techniques are mentioned. The most common methods are evaporation of the antisolvent and water or the lignin could be obtained by adding more antisolvent in the solution. The ionic liquid is being filtered, washed and dried and subsequently be regenerated. More detail of this process is discussed in this section.

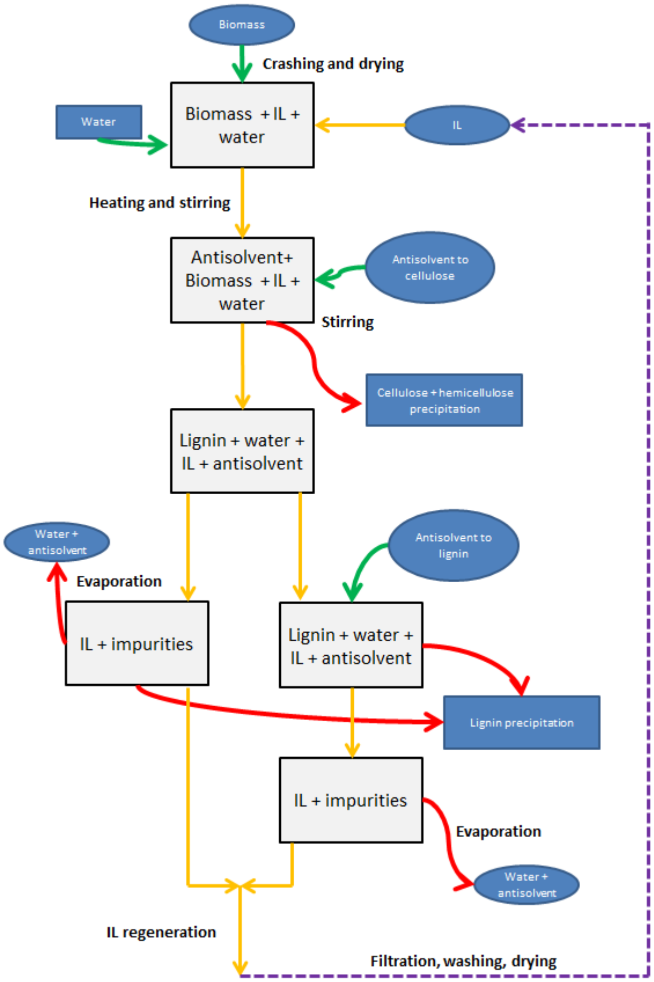

Figure 13: schematic overview of biomass separation process.

Solid-liquid ratio

As earlier mentioned, ILs are excellent solvent to dissolve biomass. The amount biomass dissolved in ionic liquid is often mentioned to be around 10% (w/w). A change in yield of biomass fragments with the same conditions was barely observed until 10% (w/w), but after 15% (w/w) biomass in the solution the yield of lignin appeared to be reduced to a large extent [26]. The temperature of the dissolution step is raised between 100-150 °C to increase the rate of dissolution and lowering the viscosity of the system, facilitating mixing and pumping.

Antisolvent

After the biomass dissolution, the antisolvent is added into the mixture to precipitate cellulose and hemicellulose. A common ratio between antisolvent:mixture is between 2-2.5 : 1(w/w) [30], [25]. A wide range of antisolvents could be used; alcohols with various alkyl chain length [30], but also acetone, acetonitrile, water or an acetone/water mixture. However methanol, ethanol, acetonitrile, acetone and water are favored to be used as antisolvent. They are able to precipitate the dissolved material efficiently and due to their volatility they are easy to remove from the IL [2]. The precipitated consist of enriched fractions of cellulose, hemicellulose and ash [25]. This solid is being separated via filtration, while the filtrate (lignin, IL and antisolvent) is further processed.

According to [9], there are four major approaches to obtain the lignin, (1) selective precipitation by acid addition, (2)(anti)solvent extraction via distillation, (3) fractional precipitation by addition of antisolvent and (4) membrane-assisted ultrafiltration. Acid precipitation is the most common method, due to the easiness and low-cost. However the acidic condition affects the quality of the lignin, by increasing their molecular weight. Due to this reason Chambon et al. suggested precipitation of lignin via an antisolvent.

The lignin precipitate contains all ranges of molecular-weights and relative β-O-4-linkages. [9] reported that sequential precipitation of lignin controlled the molecular weight precipitation. When a minimum amount of water was added, high molecular weight lignin was obtained. When more volumes of water were mixed with the IL, the precipitated contained lower average molecular weight. The deviation in M_w also affects the properties of the lignin. Higher molecular weight lignin (40 kDa) shown to be more thermal stable and a higher $T_{g.}$ The major benefit of sequential precipitation is that the quality of the lignin can be tuned. However, it should be noted that to in order to get this fractionation, they used harsh condition. Temperature was set to be 160 ^{0}C which is considerably high. Therefore they got a broad range of molecular-weight distribution.

Recycling

The efficiency of recycling of the IL is a key variable in the process economics [4], [20], [28]. Therefore much focus is laid on a high yield of recycling. In the last decade several technologies have been investigated for the recovery and purification of IL i.e. distillation, extraction, adsorption, membrane separation, aqueous two-phase extraction and crystallization. This was either performed in lab or in pilot scale [31].

The dissolution ability of ILs heavily complicates possible recycling. ILs often contaminated with by different chemicals like, salt, water or hydrocarbon solvent, *etc.* [31]. Eventually, this results in an energy consuming method (distillation), loss of IL and product (extraction) or high cost (two-phase extraction)

[32]. According to Mai et al. distillation and extraction still is the most common usage of recycling of the IL.

Nevertheless, literature claimed to have a high recovery of IL during distillation. The work of Brandt-Talbot et al. claimed an IL recovery of 99%. Their process was to extract the volatile liquids from the IL at 2 mbar, overnight. Tan et al. claimed even a higher recovery of the IL, 99.4%, with similar conditions as Brandt-Talbot et al. (vacuum, >12h). While Dibble at al. recovered 89% of the [emim][OAc] ionic liquid with distillation in vacuum, overnight. They claimed this lower value without the addition of acid or other catalysts for the recovery of lignin and other solutes from the used IL. The relative lower amount of recovery might come to the extensive washing of the IL with acetone before distillation, whereas previous mentioned literature had not been washed the IL. The long duration and low pressures of the purification method is very energy consuming. Higher yield of recycling is also almost not possible. Many studies have shown ionic liquids degrade due to high temperatures in the dissolution, causing side reactions with the components in the biomass [12].

Washing of the IL after lignin precipitation is important. Without washing the IL during recycling, all types of contaminants will build up in the system. For example lignin accumulates during the cycles of reuse, and the delignification efficiency decreased slightly [33]. Therefore, the most promising methods for separating ILs from contaminated recycling streams will likely require 2 steps involving an initial removal of biomass residues followed by removal of water [34]. As mentioned before, the washing procedure will result in a lower recovery of the IL.

Economics

Unfortunately, little research has been preformed of the economics in large scale applications of the extraction of lignin from biomass with IL. As aforementioned, the efficiency of recycling of the IL is the key variable of economics. [20] observed a high uncertainty in the recovery of ILs, but suggested that the efficiency of IL might slightly increase on industrial scale compared to lab/pilot scale. Sen et al. performed an economic analyze of fractionation cellulose from 80 000 tons/yr (10 tons/hr) dry biomass. Although, lignin extraction and separation was not mentioned, a comparison of the major operational cost could be made. Sen et al. assumed a 98% recovery of the IL with a price of \$10/kg. The operational cost further consisted of (biomass) feedstock, labor, maintenance and repair, insurance, plant overhead and waste disposal. It was concluded that the operational cost was mainly dependent on the fresh feedstock of the IL by a factor of 7.3 compared to the other operational costs. No clear argumentation of the benefits was given. With the assumed bulk price of [TEA][HSO_4] being \$1.24/kg, the costs of fresh inflow of IL will be reduced 8 times and will almost have the same value of total other operational costs.

Figure 14 is divided in three different recycling efficiency of the IL, the costs in the figure is only the costs for fresh feed of the IL into the system. The data is obtained from Brant-Talbot et al., their lignin content in the pulp was determined to be 31 wt%, using 8 times more IL compared to biomass and an addition of 20 wt% water. A price of \$1.24/kg of the IL [TEA][HSO_4] was taken in this calculation. As the quality of the lignin increases, the yield of the extraction decreases. This eventually leads to a higher price, since less lignin is recovered.

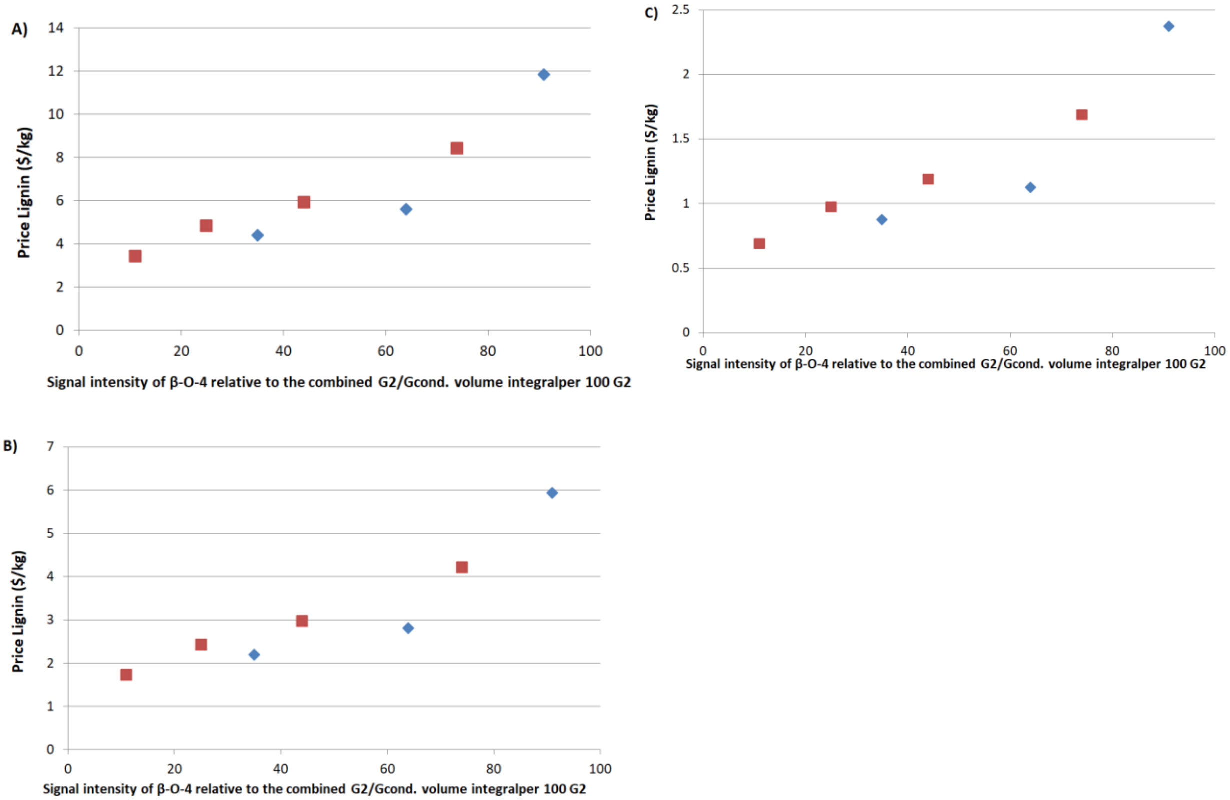

Figure 14: quality of the lignin versus costs of fresh feed of [TEA][HSO_4] against various recycling rates of IL, A) 90%, B) 95%, C) 98%. The red points refer to an excess of 9% of acid, while blue points have no excess of acid.

Conclusion

Ionic liquids are able to separate lignin from lignocellulosic biomass in a high yield. Several examples from scientific literatures conducted their experiments under variety of conditions. The dissolution time of lignin extraction could be decreased by an increase of temperature or an excess of acid. On contrary, these harsher conditions led to a significantly change in the originally lignin structure, causing cleavage on the ether bonds. The relative amount of β-O-4-linkages could be increased by a shorter dissolution time, which resulted in a lower yield of the extracted lignin. Moreover, the quality of lignin could be tuned by sequential precipitation by adding smaller portions of antisolvent. Less expensive ILs are increasingly investigating the last years, making this process more economic feasible. However, effective recycling of the IL is still the key variable of the cost in this process. Even at reuse of 98% the cost of fresh inflow IL of [TEA][HSO_4] is in the range between 0.8-2 \$/kg, while a higher β-O-4-value results in an increase of costs.

In order to be more cost effective, more research should be performed in large scale operation of ILs in biomass fractionation, especially in the reuse of ILs. The large number of adjustable parameters suggests that larger yields of recycling IL could be achieved, with high content of β-O-4-linkages. This process optimization could also be improved by better IL or a mixture of ILs with higher dissolution power or a higher addition of water in the solution. Furthermore, biomass with high content of lignin should preferably by used in order to reduce the relative costs.

It should be noted that the price of the IL [TEA][HSO_4] was 1.24 \$/kg based in 2014 and the prices of ILs could be further decrease in the future. This relative young field of science might also offer many new ideas and techniques to optimize the process. As in the future, the industry has to shift to a more renewable source of chemicals. Therefore, fractionation of biomass is almost unavoidable.

List of abbreviations

IL, ionic liquid; wt%, weight percentage; C-C-bond, carbon-carbon bond; T_g, glass transition temperature; yr, year; hr, hour; OMe, methoxy; [bmim], 1-butyl-3-methylimidazolium; [emim] or [C_2mim], 1-ethyl-3methylimidazolium; [amim], 1-allyl-3-methylimidazolium; [TEA], triethylammonium; [DMEA], triethyl-(2-(2-methoxyethoxy)ethoxy)ethylammonium; [p-TSOH], p-Toluenesulfonic acid; [Ch], cholinium; [OAc], acetate; [$MeSO_4$], methylsulphate.

Acknowledgements

My sincere thanks go to my supervisor Zhenlei Zhang and my professor Peter J. Deuss. In the COVID-19 epidemic, physical meetings were not possible. This resulted in a self-study at home and I would like to address my gratefulness for helping to plan different stages of my project and great feedback given during this period.

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