**Biofuels and platform chemicals using waste biomass as feedstock: making the biorefinery more economically viable**

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# Introduction

Up to date most of our fuels and chemicals come from a fossil feedstock. The facts that this fossil feedstock is becoming more difficult to access and that climate change caused by increased CO2 emissions over the past century is potentially going to have a negative impact on human civilisation ask for a renewable, carbon-neutral alternative. Biomass offers such an alternative, being biorenewable and considered carbon-neutral as the released CO2 upon combustion of bio-derived fuels is recaptured as the new plants grow.1 However, up to date biomass only accounts for around 12% of the global energy supply.2

Bioethanol is the prominent biomass derived fuel and can be obtained from any kind of plant. The ease of production however strongly depends on the type of biomass used. Ethanol is obtained by microbial fermentation directly from sucrose containing plants (e.g. sugar cane), via enzymatic or chemical hydrolysis and subsequent fermentation from starch (e.g. corn) or from lignocellulosic biomass (trees, grasses), requiring a pre-treatment step prior to hydrolysis and fermentation (figure 1).1

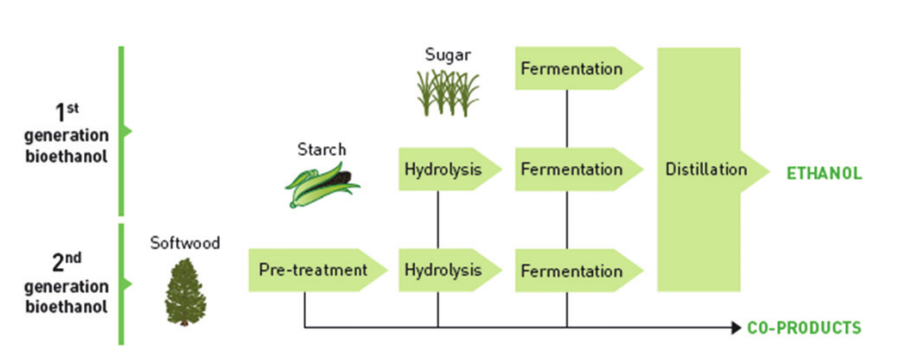


Figure 1 First and second generation bioethanol.1 1st generation bioethanol only requires fermentation and in the case of starchy plants a hydrolysis step while 2nd generation bioethanol requires a pretreatment step.

In contrary to bioethanol, biodiesel can only be isolated from plants containing oils. It can be either blended with conventional diesel or used by itself.1

Currently most biofuels are made from edible components of biomass, leading to competition between biofuel and food production and therefore an increase in food prices.1 On the other side, lignocellulosic biomass is the most abundant plant material on earth with an extensive geographical availability,3 has higher yields per land area and can be grown at a lower cost than plants that mainly contain sucrose and starch. The use of lignocellulosic biomass is thus preferential from a socio-economic as well as an environmental point of view4 but requires a pretreatment step in order to enable efficient enzymatic or chemical hydrolysis of the cellulose. This pretreatment step is currently not very cost-effective for the production of bioethanol and is therefore still under a lot of investigation.1

While feedstock costs currently constitute a third of the total costs of cellulosic ethanol,5 waste wood is a lot cheaper if not free and thus has the potential to make cellulosic ethanol competitive. Furthermore, most demolition wood is soft wood which contains a higher percentage of lignin compared to wheat straw or miscanthus (32wt% vs. ca. 20wt%), making a lignin focussed biorefinery for value added chemicals from waste wood more attractive. During the pretreatment process the metal preservatives (copper, chromium, arsenic) present in construction timber can potentially be recovered concomitantly, giving raise the a further potential source of valorisation for the integrated biorefinery.

# Ionic liquids

## General

Ionic liquids have generated huge interest over the last decade because of their unique properties. Their favourable properties for use as green solvents include their recyclability, low vapour pressure,6 their wide liquid range and the possibility to tune their properties to ones requirements which makes them popular designer solvents and catalysts. In simple terms, ionic liquids are organic salts which are liquid at or close to room temperature (i.e. melting point below 100°C). Some commonly used cations and anions are displayed in figure 2, but also task specific ionic liquids comprising e.g. amino acid derivatives or highly functionalized ionic liquids are used more often.

Ionic liquids have an extensive range of applications, from use as replacement solvents to catalysis,7,8 CO2 capture,9 electrochemistry,10 in pretreatment of biomass for biofuel production and their use as sensors.11–13 However, the high costs associated with ionic liquid synthesis and purification often undermine their application on an industrial scale. Additionally, small amounts of impurities can have a large effect on the physical and chemical properties of ionic liquids14 thus inhibiting their more general use. Ionic liquid viscosities are generally high and range from 10 mPa·s to over 1000 mPa·s. They are sensitive to impurities and often a range of values is reported in literature for one ionic liquid.15



Figure 2 Common anions and cations used for ionic liquids.

The polarity of a given solvent is defined as the sum of all interactions between a solvent and a solute, including coulombic, dipole-dipole (induced and permanent), hydrogen bonding and electron pair donor and acceptor interactions.16 It can be quantified by the solvatochromic effect of a solvent on probe molecules as the longest wavelength of absorption of a dye is influenced by its solvent and their interactions. Kamlet and Taft suggested the empirical polarity scales α, β and π\* where α is the hydrogen bond acidity, β the hydrogen bond basicity and π\* the polarizabilty of the solvent.17 Because the solute has a major influence on the interactions, the values obtained for one scale are measured for a defined set of different dyes and then get averaged. The use of these scales has been adapted to ionic liquids. π\* values, in molecular solvents normalised with cyclohexane having a value of 0 and DMSO a value of 1, are found to be close to 1 for ionic liquids, independent on the anion and cation. β values were found to depend mainly on the anion of the ionic liquid and range from values of around 0 up to 1.61 for tetrabutylphosphonium glycinate. In contrast to that, α values mainly depend on the cation of the ionic liquid and range from around 0.2 to 1.2.16

## Stability

### Thermal Stability

The higher end of the liquid range of ionic liquids is mostly governed by their thermal decomposition temperature rather than an evaporation temperature15 and this lies at a maximum of around 500°C for 1,2-dimethyl-3-ethylimidazolium hexafluorophosphate18. Furthermore it was shown that impurities can lower the melting points and decomposition temperatures of ionic liquids drastically.15 As impurities are ubiquitous when working with ionic liquids, often a range of decomposition points is reported for one ionic liquid. Typically, decomposition temperatures are measured by thermogravimetric analysis (TGA) which measures weight loss either at a fixed temperature over time (long-term stability) or over a temperature range (decomposition temperature). The temperature at which an ionic liquid is stable over a longer time is often considerably lower than the decomposition temperature and is important for the industrial application of ionic liquids.19

TGA is widely used for the determination of the decomposition temperature of ionic liquids, however it suffers from only being able to detect decomposition resulting in weight loss and is highly affected by the heating rate and the vessel material used during the TGA.20 A different way of determining the long-term stability of imidazolium based ionic liquids is the potentiometric acid-base titration to detect imidazoles, one of the major degradation products of such ionic liquids.19 The advantage of this technique is that also degradation which does not lead to weight loss can be detected. Furthermore, some degradation which happens at a much lower temperature than the decomposition temperature and is very slow might not be detectable by TGA; potentiometic titrations however allow the quantification of thermal aging of ionic liquids over longer time periods. It has been shown that [BMIM] and [EMIM][Cl] already age at temperatures at low as 140°C while having a decomposition temperature of around 200°C. Surprisingly it was found that [BMIM][PF6] degrades twice as much as [BMIM][Cl] at 140°C while [BMIM][BF4] is completely stable at this temperature. However, TGA results imply that [BMIM][PF6] is more thermally stable than [BMIM][Cl]. [EMIM] and [BMIM][EtSO3] only degrade slightly at 200°C and [BMIM][NTf2] did not show any signs of decomposition even after 10 days of 250°C.19

ESI-MS measurements have shown that the main decomposition pathways are the elimination of the side-chain, transalkylation and retroalkylation by a nucleophilic attack from the anion. As halogen anions are a lot more nucleophilic than organic anions such as [BF4] or [NTf2], halogen containing ionic liquids are significantly more prone to degradation.19 Studies with varying alkyl chain lengths only showed a minor dependence with longer alkyl chains decreasing the decomposition temperature slightly.20

## Metal Extraction Agents

The metal extraction ability from aqueous solutions of many hydrophobic ionic liquids has been studied.21 Extraction agents miscible with the ionic liquid can enable or improve liquid-liquid extraction from aqueous solutions.22,23 Alternatively, task specific ionic liquids can be used for enhanced extraction efficiencies.24,25 Different extraction mechanisms have been studied. During the ion-exchange mechanism, degradation of the ionic liquid occurs while no degradation occurs during the ion-pair extraction.26,25

## Electrodeposition

Electrodeposition from ionic liquids has been shown to be possible for many different metals and some metal alloys.27,28 It offers certain advantages over the electrodeposition from aqueous or organic solutions, such as the possibility to use them in an open atmosphere due to their low vapour pressure.20 Furthermore it is possible to use ionic liquids for the electrodeposition of reactive metals such as Ti, Al and Mg which cannot be electrodeposited from aqueous solutions.28

Copper deposition form ionic liquids has been widely studied and was shown to be possible in imidazolium, ammonium and pyrrolidinium based ionic liquids.20

Chromium deposition has been possible from the deep eutectic solvent made from choline chloride and chromium (III) chloride.20

# Biorefinery

As mentioned at the beginning, there are several incentives to replace edible plants with lignocellulosic biomass for the production of biobased fuels and chemicals. In the following chapters the use of lignocellulosic biomass will be discussed.

## Lignocellulose

Lignocellulose is made from three biopolymers, namely the aromatic polymer lignin and the polymeric carbohydrates cellulose and hemicellulose, which together account for ca. 90% for the dry weight of biomass. Figure 3 shows the structure of lignocellulose; linear cellulose fibres (yellow) are surrounded by hemicellulose (blue) and interconnected with lignin (orange.) Further, lignocellulosic biomass contains smaller amounts of pectins, inorganics, proteins and extractives such as waxes and lipids.5 Lignocellulosic biomass contains up to 70% of carbohydrates, but the composition varies depending on species, plant tissue and growth conditions. There are 3 types of lignocellulosic biomass, namely softwoods, hardwoods and grasses, which all differ not only in their carbohydrate content but also in the composition of their substructures lignin, cellulose and hemicellulose and are differently challenging for the use of bioethanol production.1

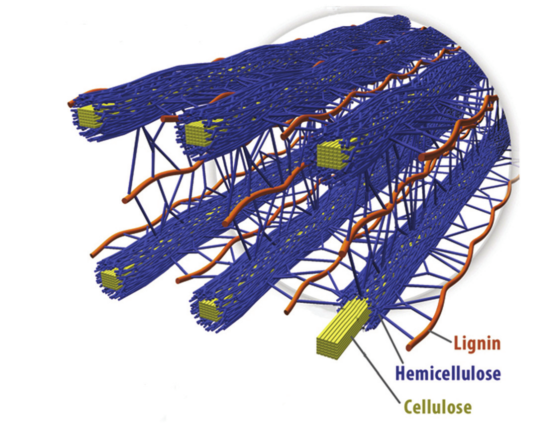


Figure 3 Structure of lignocellulosic biomass.1

For industrial purposes lignocellulose can come from agricultural residues and municipal waste but also specially grown biofuel crops can be used.1

### Cellulose

Cellulose is the largest component of lignocellulosic biomass and accounts for 35-50 wt% of the dry biomass.1 It is a linear polymer made of glucose units which are linked to each other by 1-4-β glycosidic bonds (figure 4, left). It is the β configuration that is responsible for the linearity of the polymer, opposed to the helical shape of starch due to the α configuration at the linkage (figure 4, right). Further, two intramolecular hydrogen bonds between neighbouring glucose units and one intermolecular hydrogen bond link the chains into flat sheets. These sheets mostly interact with each other through van der Waals interactions which leads to a stabilisation of the cellulose fibrils. While native cellulose (cellulose Ia and Ib) contains two intramolecular and one intermolecular hydrogen bonds, it can be converted into cellulose II which is thermodynamically more stable and contains hydrogen bonds between different sheets. The conversion can occur by swelling, dissolving and regenerating native cellulose. 1



Figure 4 1-4-β glycosidic bond found in cellulose (left) and 1-4-α glycosidic bond found in starch (right).

Cellulose has the highest degree of polymerisation of the three biopolymers, with more than 10’000 monomeric units. As a consequence of the resulting high molecular weight cellulose is water insoluble and only very few solvents are capable of dissolving cellulose. Amongst these are concentrated phosphoric acid,29 N-methylmorpholine-N-oxide (NMO) and a range of ionic liquids.1

### Hemicellulose

Hemicellulose is like cellulose a polysaccharide; however with a polymerisation degree of 100-200 it has a much lower molecular weight than cellulose.1 It makes around 25 wt% of the dry biomass and contains hexose and pentose sugars. Unlike cellulose, hemicellulose is branched and contains functionalised groups, such as acetyl and methyl groups, cinnamic, glucuronic and galacturonic acids. It is an amorphous matrix material which is suspected to bind covalently to cellulose fibrils. The substitution with hydrophobic acetyl and methyl groups enhances its affinity for lignin, creating a linkage between the lignin and cellulose. As hemicellulose is non-crystalline it is more susceptible to depolymerisation, especially under acidic conditions.1

### Lignin

Lignin is the aromatic component of biomass which is built up at a mature state of plant growth.1 It is an aromatic, water insoluble polymer with an irregular structure and serves as a structural reinforcement and adds water resistance. It is resilient to biological and physical attack and thus functions as a shield for the polysaccharides.30

Its biosynthesis goes via a radical polymerisation of three monomers: coniferyl, sinapyl and p‑coumaryl alcohol, which, once integrated in the polymeric structure, are referred to as guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) units respectively. Around half of the linkage bonds are β‑O-4 ether bonds, other C-O and C-C linkages are also present but to a lesser extent (figure 5).1



Figure 5 Linkage units in lignin.

The relative abundance of the three monomers depends on the type of biomass and impacts the reactivity of lignin and therefore the delignification process.30 For example C-C crosslinkages are found extensively between the C-5 positions of guaiacyl units, which are formed during the lignification and delignification of mainly softwoods. Such C-C crosslinks are not readily hydrolysed with acid or base and as a consequence the delignification process becomes more challenging. In contrast syringyl units, present in a significant number in hardwoods, are substituted in the C-5 position, making such crosslinks impossible. Therefore hardwoods are more easily delignfied than softwoods.1 Depending on the type of biomass lignin may also contain significant amounts of ferulates (F) and *p*-coumarates (*p*CA) (figure 6) which are involved in cross-coupling with lignin monomers and the formation of lignin-carbohydrate complexes. Softwood, which is typically used as construction wood, only contains traces of F and *p*CA but more bi-phenyls and di-phenyl ethers.5



Figure 6 Lignin subunits.

Lignin is a major barrier in the conversion of lignocellulosic biomass into biofuels; while native lignin acts as a crust and inhibits access of polysaccharide hydrolases to their substrate, modified lignin sticking to cellulose pulp binds to hydrolases, reducing their activity, increasing the necessary enzyme loading and making enzyme recycling more difficult, thus increasing the costs of the process.30 Furthermore some lignin derived compounds inhibit hydrolases and fermentative organisms completely (e.g. syringyl aldehyde and vanillic acid). Therefore the removal of lignin is necessary. Chemical deconstruction methods include a modification of lignin by breaking its ether bonds, however full removal from the pulp is only achieved by fragmentation and dissolution of the modified fragment. Traditional methods for delignification in the paper industry rely on the formation of lignosulfonates which are water soluble.1

## Deconstruction of Lignocellulose

The deconstruction of lignocellulosic biomass has been known for over a century for the production of paper with improved strength. During the so called Kraft process, the biomass is heated in an aqueous mixture of NaOH and NaHS at 130-180°C for several hours, dissolving part of the hemicellulose and most of the lignin by fragmentation and formation of lignosulfonates. The liquor is burnt afterwards for energy generation and regeneration of the suflide. This and other processes for paper production are optimised for high cellulose yield and fibre strength, the biorefinery however requires an inexpensive route to sugars that are easily fermented and a by-product stream that yields value added chemicals to increase the economic viability of the process.1

The initial focus of the deconstruction process in the context of the biorefinery is providing glucose for fermentation.1 As seen earlier, the lignin-hemicellulose shield is resistant to chemical and biological degradation.30 Therefore, to release the cellulose, this lignin-hemicellulose shield must be broken up. Different methods are available to break up this shield. In the dilute acid treatment (DA), the hemicellulose, being the most fragile component, gets depolymerised and the derived sugars solubilised, leaving a cellulose- and lignin-rich solid behind which can be hydrolysed by cellulases. However, lignin and lignin fragments sticking to the cellulose deactivate the enzymes, making high enzyme loadings necessary.31 Therefore, processes enabling biomass fractionation rather than just decomposition and removal of one component are more promising. This is possible using cellulose solvents, for example the cellulose solvent and organic solvent lignocellulose fractionation (COSLIF); the biomass is dissolved in a cellulose solvent, typically phosphoric acid. Subsequently, the cellulose is regenerated as amorphous solid by adding ethanol which then can be hydrolysed by hydrolases with low enzyme loadings as most of the lignin is removed.31 However, complete dissolution of biomass is not crucial for the successful outcome of a pretreatment.1 One successful example is the organosolv process where the biomass is pretreated in hot aqueous ethanol with a low concentration of acid catalyst (around 1-2%), leaving the cellulose undissolved in the pulp while removing the lignin and hydrolysed hemicellulose sugars which can be recovered from the liquid fraction and separated by precipitation of the lignin upon addition of additional water.32

In a second step, the saccharification, the glycosidic bonds are hydrolysed which is usually catalysed by either enzymes or chemicals. A barrier for enzymatic hydrolysis is that native cellulose exhibits a high degree of crystallinity which limits the substrate accessibility. Lignocellulose pretreatments based on cellulose solvents have been shown to be more effective than traditional pretreatments in terms of overcoming this problem; the regenerated cellulose is amorphous and has a larger and more accessible surface area, increasing enzymatic hydrolysis rates.29 Although it was found that substrate accessibility and therefore the crystallinity of the cellulose is the most important factor affecting the enzymatic hydrolysis rate,33 removal of lignin and lignin derived compounds is also important to avoid deactivation of the enzymes.31 However the broader goal of the deconstruction process is to use not only the cellulose fraction but also the sugars derived from hemicellulose and to obtain higher value chemicals especially from the lignin fraction.1 In this sense a negative consequence of harsh deconstruction conditions is the decomposition of the hemicellulose34 and the occurrence of recondensation reactions within the lignin fragments; the formation of new C-C linkages leads to products which are difficult to catalyse in further conversion steps.30

### Ionic liquid Pretreatment

Ionic liquid pretreatment is a comparably new deconstruction technology offering energy efficient biomass deconstruction under milder conditions than traditional treatments33 while producing less inhibitory side products and facilitating product separation.35 Many different factors influence the success of pretreatment of biomass such as the ionic liquid used, pretreatment temperature and time and water content, as well as the cost of the ionic liquid, the recycling step, separation techniques and the downstream processing and need to be optimised in order for the process to become economically viable.3

Two different strategies during the ionic liquid pretreatment of lignocellulosic biomass are being followed: processes where full dissolution of the biomass is attempted and process which deliberately only dissolve the biomass partially are used, sometimes referred to as dissolution process and ionosolv process respectively.1

#### Dissolution Process

Full dissolution of biomass has been observed for a range of mainly dialkylimidazolium based ionic liquids36 with [EMIM][acetate] being the most commonly used.3,37–39 It was found that the hydrogen bond basicity β is governing the dissolution ability of ionic liquids. Fractions of the biomass are reprecipitated upon addition of different antisolvents including water (neutral, acidic or basic), acetone, ethanol and methanol. The first fraction is typically enriched in cellulose, however no full delignification is achieved40 and under some conditions only the hemicellulose and none of the lignin is removed.38 Further fractions are hemicellulose and lignin rich.41 The regenerated cellulose exhibits better digestibility (ca. 50 times higher enzymatic hydrolysis rate) due to less crystallinty37,35 and lower thermal stability2 but the exact outcome is dependent on the type of biomass and the ionic liquid used as well as pretreatment time and temperature, water content of the biomass and the ionic liquid and particle size and loading of the biomass29 as they have effects on the delignification and degradation reactions.3 Important for a successful dissolution of biomass in ionic liquids is the absence of water, which acts as a potent antisolvent for especially cellulose. Water originating from the biomass or absorbed by hygroscopic ionic liquids from the atmosphere can inhibit dissolution, making an energy intensive drying step necessary.42

Typically pretreatment is run at temperatures between 90 and 160°C for 3 to 16 hours.1 Delignification is more effective at higher temperatures and longer pretreatment times, increasing the cellulose content of the recovered biomass. However glucose and xylose degradation also increases under harsher conditions, decreasing the overall recovered mass. Main degradation products are furfurals from hemicellulose and hydroxymethylfurfural (HMF) from glucose.33 Furthermore, xylose is significantly more easily hydrolysed and degrades under conditions optimised for cellulose yield; pretreatment is therefore impossible to optimise for both xylose and glucose simultaneously.34

While [EMIM][acetate] is up to date the most effective known ionic liquid for biomass dissolution, it is also very expensive. To increase the effectiveness of cheaper ionic liquids such as [BMIM][Cl] to a similar level, acid catalysts such as Amberlyst 15 can be added to the pretreatment mixtures.43

Another factor influencing the yield of biomass pretreatment is the biomass loading. For an industrial process, high loadings would be desirable, however decreasing delignification with more than 15wt% biomass were observed.1

#### Ionosolv Process

During the ionosolv process, similar to the organosolv process, not full but partial dissolution of the biomass is aimed for. Almost full delignification of miscanthus was reported by Brandt *et al.*1 using [BMIM][MeSO4], [HBIM][HSO4] and [BMIM][HSO4] which they attributed to the somewhat nucleophilic character of the neutral or acidic anions which can act as catalysts or reactants during the delignification, however the undissolved cellulose is still crystalline and digestibility is thus not enhanced.42 In their ionosolv process ca. 10-40% of water is required; pretreatment with [BMIM][MeSO4] for example released a maximum of 92% of the glucose with 10% water present. However the recovered ionic liquid contained a remarkable amount of [HSO4]- ions, suggesting partial hydrolysis of the methylsulfate anion under pretreatment conditions.42 Diedericks et *al.*33 reported only incomplete lignin removal from sugar cane bagasse with [BMIM][MeSO4], however fully digestible glucose was obtained after 2 hours at 150°C without additional water. Adding H2SO4 as an acid catalyst did not increase the glucose digestibility but led to the enhanced formation of byproducts such as acetic acid, HMF and furfural. Brandt et *a.l*42 also employed the cheaper acid-base based ionic liquid, [HBIM][HSO4], and were able to fractionate lignocellulose; the more acidic nature of this ionic liquid seemed to degrade cellulose to a higher extent than [BMIM] ionic liquids if only 5wt% water were present, leading to the formation of the water-insoluble carbohydrate degradation product pseudo-lignin. The effect was more pronounced if the pretreatment was prolonged from 4 to 20 hours. A similar effect was reported for the use of a mixture of alkylbenzenesulfonate ionic liquids ([EMIM][ABS]) for the pretreatment of sugarcane bagasse.44

#### Ionic Liquid Stability and Recycling

In order to make ionic liquid pretreatment economically viable, the ionic liquids need to be recycled after the process. There are some accounts of reuse of ionic liquids after one or several pretreatment cycle without any loss in activity, delignification efficiency or saccharifiaction yield.1,44 However, many other publications indicate the opposite, with decreasing delignification and saccharification yields, accompanied by a build-up of various degradation products in the ionic liquid.1,45 Distillation is one possible recycling route; the distillation of [EMIM][acetate] has been reported, however it requires very low pressure (ca. 0.03 mbar) and temperatures of around 150°C.46 Ion-exclusion chromatography was successfully employed to separate sugars and HMF from [EMIM][Cl] where more than 95% of the ionic liquid and 94 and 88% of glucose and xylose were recovered respectively.47

The stability of the ionic liquids under pretreatment conditions is crucial. The ability of an ionic liquid to dissolve cellulose and potentially biomass has been shown to correlate inversely to the thermal stability of these ionic liquids.46 Some ionic liquids and especially [EMIM][acetate] are not long-term stable at the temperatures used during pretreatment, making the viability of their use questionable.1 Furthermore, as the basicity of the ionic liquid increases, the reactivity towards solutes increases as well. [EMIM][acetate] was shown to react with reducing end groups of cellulose46 while, as mentioned before, acidic and neutral [MeSO4] and [HSO4] ionic liquids are suspected to react with lignin,42 which makes full recycling of the ionic liquid impossible.

#### Hydrolysis

After the pretreatment step, the now vulnerable cellulose needs to be hydrolysed to fermentable sugars. This is either done by acid catalysis34 or with the aid of enyzmes.3 Enzymes are often preferred due to higher selectivity,1 however they are costly (they constitute up to one third of the production costs of ethanol from cellulose)47 and often not tolerant towards the ionic liquids used in the pretreatment step and thorough washing to remove residual ionic liquid is required, resulting in high water consumption which is not compatible with an industrial scale-up.3 Only recently developed thermostable ionic liquid tolerant enzymes have been successfully applied in a one-pot process of biomass deconstruction and hydrolysis; after a pretreatment of switchgrass with [EMIM][acetate] the pretreatment mixture was diluted with water to 10wt% ionic liquid and the enzyme cocktail added. 81.2% of the glucose and 87.4% of the xylose were released as mono- and oligomers after saccharification for 72 h at 70°C with 5.75 mg/g enzyme loading. The optimum pretreatment conditions for this one-pot process were found to differ from the optimum conditions determind for traditional ionic liquid pretreatments; around 3 h at 160°C was shown to result in the highest glucose yield while xylose yield was maximal after 3 h at 140°C. Longer pretreatment times result in lower sugar yields due to the enhanced formation of inhibitory degradation products while shorter treatment times do not break up the lignin-hemicellulose shield effectively enough.3

Alternatively acid hydrolysis can be used to produce fermentable sugars from cellulose and hemicellulose. Acidic ionic liquids can be employed, however better sugar yields are obtained when an acid is added to the ionic liquid biomass mixture, such as hydrochloric acid, sulfuric acid, nitric acid or maleic acid.48 Best sugar yields (66%) for the hydrolysis of corn stalk were obtained when using [BMIM][Cl] in combination with HCl. After biomass dissolution in [BMIM][Cl], addition of water and HCl leads to the hydrolysis of cellulose and hemicellulose.34 The produced sugars can be recovered from the ionic liquid by extraction with high concentrated NaOH solution, resulting in a phase separation between the ionic liquid phase and the aqueous phase. 54% of glucose was recovered after a pretreatment of 160°C for 1.5 h and hydrolysis with HCl at 105°C for 2.5 h and 88% of xylose after 6 h pretreatment at 105°C and subsequent hydroysis for 1.5 h at the same temperature.34 The addition of water was found to be crucial for the pretreatment and hydrolysis of corn stover in [EMIM][Cl] catalysed by HCl; the sugars were found to be dehydrated to HMF and furfural in the absence of water under acidic conditions.47

#### Effect of Cations and Anions and the Choice of the Ionic Liquid

As discussed earlier, some ionic liquids and especially di aklkyl imidazolium based ones have the ability to dissolve cellulose and lignocellulosic biomass, where cellulose dissolving ionic liquids generally also dissolve lignocellulose and the basicity β of the anion plays the most important role. For carboxylate anions it was found that longer alkyl chains on the imidazolim cation reduce the ability to dissolve cellulose. Further also hydroxyl groups on alkyl chains lower the solubility of cellulose and protic ionic liquids are reported to not exhibit the ability to effectively dissolve biomass. Ionic liquids with high β values are generally more hygroscopic and thus absorb more water from the atmosphere which can prevent cellulose solubilisation or requires thorough drying.1 Lopes et al.41 reported the macroscopic dissolution of wheat straw in the acidic ionic liquid [BMIM][HSO4] and suspect a different dissolution mechanism as for basic ionic liquids.

More neutral or acidic ionic liquids, such as dialkyl imidazolium alkylsulphates and sulphonates and hydrogen sulphates and [HBIM][HSO4], which do not generally dissolve cellulose were found to be better delignifiers than cellulose solvents. The anions act as nucleophiles and lead to a fragmentation of the lignin and hemicellulose, giving high purity cellulose fractions.41,33 But not only these neutral or acidic ionic liquids are able to react with the biomass, also carboxylate ionic liquids are known to covalently interact with cellulose.49 A consequence of the use of acidic ionic liquids is the conversion of monosaccharides to furfurals and HMF, evidenced by the absence of glucose and xylose in the ionic liquids liquors.41 Further no acidification of the ionic liquid medium is required for the precipitation of lignin when working with acidic ionic liquids which otherwise impedes the recyclability of the ionic liquid.41

The anion of the ionic liquid in use is in most cases the deciding factor for pulp composition and mass loss and therefore glucose and xylose yield. While Brandt et al.42 found best glucose yields with [BMIM] ionic liquids with [MeSO3] and [HSO4] anions and 20wt% water for the pretreatment of miscanthus, xylose yields were low compared to pretreatment with [EMIM][acetate] with 20wt% water, indicating that the sulphate and sulphonate anions promote decomposition of hemicellulose and xylose. Pretreatment with [BMIM][Cl] and [BMIM][OTf] with 20wt% water yielded very little sugars after fermentation. When [BMIM][DCA] and [BMIM][SCN] were used for the pretreatment of wheat straw, only partial dissolution was obtained.41 The regenerated material was in both cases found to be enriched in carbohydrates. Both ionic liquids were found to be unable to cleave ester bonds between lignin and hemicellulose and thus the lignin-rich fraction still contained a considerable amount of carbohydrates, however the precipitated cellulose was of high purity (87wt%). Lopes et *al.*41 reported the use of [BMIM][HSO4] for the pretreatment of wheat straw at 120°C for 6 hours which resulted in a very pure lignin fraction without any detectable carbohydrates, and a cellulose fraction with only 3.1wt% lignin content.

Despite the differences in delignification and by-product formation, the stability, recyclability and costs of ionic liquids are important for an industrial application. Generally monoalkylated imidazolium cations are cheaper to produce as they can be produced in an acid-base reaction.42 Further protic ionic liquids are more easily recycled as they are distillable.1 Alkylsulfate ionic liquids were shown to be more thermally stable than acetates or chlorides,46 which could potentially make them more suitable for an industrial process.

#### Fate of Lignin

While the cellulose is in most cases recovered as a single fraction, there are different streams from which lignin can be recovered during pretreatment. During ionic liquid pretreatment with [EMIM][acetate], the recovered biomass still contains some lignin which can be isolated after saccharification and was found to have similar molecular weight and polydispersity as lignin before pretreatment. The molecular weight as well as the overall amount of lignin present in this solid fraction decreases with higher pretreatment temperature due to enhanced delignification at higher temperatures.5 Brandt et al.42 found that when working with [BMIM][HSO4] and [BMIM][MeSO4] more of the lignin could be kept in solution when the recovered biomass was washed with methanol instead of water and thus the lignin content in the recovered biomass decreased.

During pretreatment with [EMIM][acetate], some of the lignin is solubilised into the ionic liquid and can be partially reprecipitated upon addition of water. Higher molecular weight lignin precipitates readily while lower molecular weight fragments and oligomers stay in solution. Increasing the temperature leads to a higher amount of lignin and higher molecular weight lignin being soluble in the ionic liquid. Polydispersity of this fraction thus increased with increasing temperature.5 Acidification of the ionic liquid medium was found to reduce lignin solubility and enhance lignin precipitation when working with basic ionic liquids such as acetates1,2 which is not necessary when acidic or neutral ionic liquids such as [BMIM][Cl], [BMIM][HSO4] or [HMIM][HSO4] are used for the pretreatment.42

Pretreatment of herbaceous biomass (wheat straw and miscanthus) with [EMIM][acetate] lead to a decrease in β-O-4 interunit linkages per 100 aromatic units which was shown to be more prominent at higher pretreatment temperatures. Associated to the removal of β-O-4 linkages, an increase of cinnamyl alcohol was detectable; the cleavage of β-O-4 bonds results in more free vinylic units, such as cinnamyl alcohols. Dibenzodioxocin linkages, which are associated with branching of lignin, were undetectable in the extracted lignin and strongly reduced in the regenerated biomass, indicating the removal of branches. The G/S ratio was only slightly affected, independent of the pretreatment temperature. A decrease in *p*CA and F was found, indicating the cleavage of LCC bonds and thus the removal of hemicellulose from the lignin. The effect was more pronounced for higher temperatures and was stronger for wheat straw compared to miscanthus. For a softwood (pine), only a smaller amount of the β-O-4 linkages were removed after pretreatment with [EMIM][acetate] and using a higher pretreatment temperature (120 vs 160°C) only enhanced the removal slightly. No recondensation reactions were reported for pretreatment of miscanthus, wheat straw and pine with [EMIM][acetate] at 120 and 160°C.5 While native lignin might contain small amount of carbonyl groups, a sharp increase in carbonyls was found for the lignin isolated from the pretreatment of sugarcane bagasse with [EMIM][ABS], indicating that oxidation takes place during pretreatment. Further, the use of[EMIM][ABS] lead to a partial sulfonation of the extracted lignin as evidenced by elemental analysis.44 When yellow pine wood was treated with [HMIM][Cl], the lignin fragments after pretreatment increase in molecular weight when the temperature is increased from 110 to 150°C, indicating that under these more acidic conditions recondensation reactions of lignin take place.50

Thermogravimetric analysis has shown that lignin after ionic liquid pretreatment with [EMIM][acetate] has lower thermal stability than lignin from e.g. organosolv pretreatment but higher stability than lignin from milled wood.51

While lignin is readily isolated from the recovered biomass after hydrolysis,38 it is difficult to fully extract it from the ionic liquid due to strong π-π interactions between aromatic lignin mono- and oligomers and the ionic liquid cation.52

##### Lignin Characterisation

As discussed earlier, lignin as a polymer is very heterogeneous, which makes quantitative structural analysis very challenging. There are several wet chemistry methods, including degradation techniques, available for the quantification of several functionalities within the lignin structure, such as the thioacidolysis for the determination of lignin aromatic units,31 alkaline nitrobenzene oxidation for the degree of condensation,53 aminolysis for the detection of Phe-OH and OMe and derivatisation followed by reductive cleavage (DFRC) for beta-O-4 linkage frequency.51 However, they all only allow the detection of a specific functionality and fail to create a bigger picture. Furthermore interpretation after derivatisation is more ambiguous.54

Non-destructive techniques include NMR, IR and UV spectroscopy. The advantage of NMR spectroscopy over the optical methods is the higher resolution, giving access to more detailed information.54 Several NMR techniques offer structural analysis and are to some extent quantitative. Solid state as well as solution state NMR has been applied for lignin characterisation where ionic liquids such as [EMIM][acetate] as additives can improve lignin solubility.5 Alternatively, acetylation can improve the solubility of lignin.53 31P NMR spectroscopy offers the quantitative detection of aromatic groups with free phenolic hydrodxyls such as *p*-hydroxyphenyl, catechols, guaiacyl units and condensed and uncondensed phenolics as well as carboxylic acid groups.55 The aliphatic, phenolic and carboxylic acid hydroxyl groups are phosphitylated and an internal standard is added to the mixture for quantitative integration. A database with spectral information of various model compounds is available for comparison and identification of subunits present in lignin. Similarly 19F NMR spectroscopy can be used for the detection and quantification of cabonyl groups via a trifluoromethylation.56 Again, some data of model compounds is available for comparison and identification.57 However this technique has not received much attention in the past years.

2D techniques are used due to less spectral overlap of signals. HSQC and HMQC can be used to distinguish between aliphatic and aromatic components, and changes in the structural characteristics can be determined by volume integration of the HSQC peaks with an accuracy with less than 10% error.5 Detection limits for HMQC have been estimated to be below 0.3 per 100 aromatic units.58 The aliphatic oxygenated region can be used to estimate the relative abundance of the different interunit linkages.53 The S/G ratio is estimated from the signals in the aromatic region. Furthermore it can help to interpret 13C spectra.54 Further 2D techniques used include HMBC and TOCSY,58 which are mostly used for the confirmation of findings from other techniques. HMBC can also be used for the detection of hydroxyl groups after acetylation thereof and carbonyl groups, which is not possible with HSQC. HSQC-TOCSY 3D NMR spectroscopy has been used for the more reliable assignment of cross-peaks and giving access to information on subunits and connectivities which do not have been investigated via corresponding model compounds.59 A more comprehensive picture of the lignin structure is drawn by 13C NMR spectroscopy.53 However low natural abundance of the 13C nucleus make long measuring times necessary which can be decreased by a factor of four by adding a relaxation agent54 but still remain significantly longer (around 24 hours) than for other NMR techniques.60 1H NMR spectroscopy is used in many cases but is insufficient by itself due to extensive overlap of signals.

IR spectroscopy offers the qualitative detection of various structural units, such as carbonyl groups in various systems.61 The content of S groups can be estimated as well as the amount of residual carbohydrates present. Furthermore structural changes can be monitored inexpensively and fast.53

Gel permeation chromatography (GPC) or size exclusion chromatography is used to determine the weight-average (MW) and number-average molecular weights (MN) as well as the polydispersity of the lignin polymers.44,60

## Fuels and Platform Chemicals from Biomass

As discussed earlier, ethanol is made from sucrose containing plants via microbic fermentation (fig. xx, reaction scheme).1 Starch, a biopolymer consisting of glucose units, can be easily hydrolysed to fermentable sugar, which in return is fermented in the same way. The production of fermentable sugars from lignocellulosic biomass has been extensively discussed above. The fermentation of pentose sugars to ethanol is more difficult but becoming more feasible with genetically modified strains with higher substrate tolerance.63 However, while the main focus of most biorefieneries is the production of cellulosic ethanol, many more biological, chemical and thermal conversions can give access to a wide range of fuels, chemical building blocks and commodities from biomass and its components. The valorisation of lignin but also the carbohydrates is critical to make the biorefinery economically viable.64 A report for the United States Department of Energy suggests that lignin valorisation could increase the value of lignin by a factor of four and possible products classes are displayed in figure 7.65

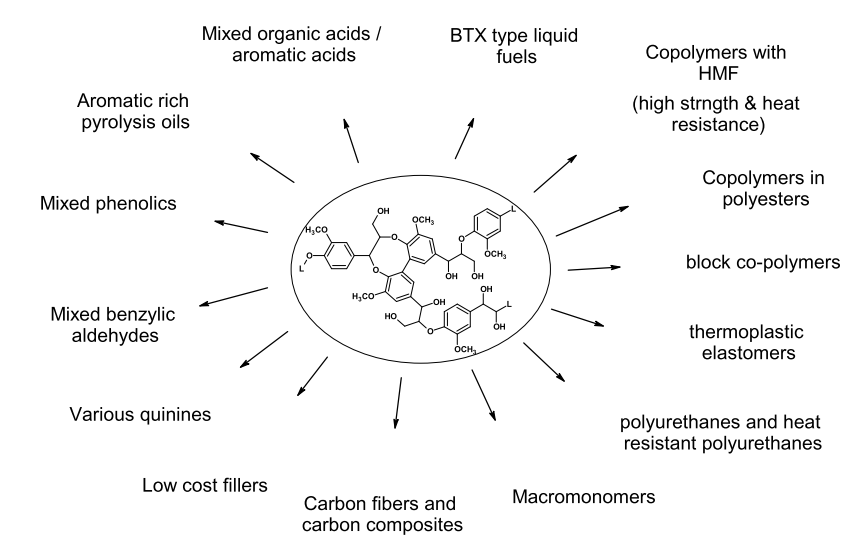


Figure 7 Product classes potentially available from Lignin.65

There are three general strategies for the conversion of lignin in something of higher value. The first strategy focuses on the gasification and pyrolysis of lignin.52 While combustion of biomass is used for heat and energy production, it suffers from low efficiencies due to Carnot-cycle limitations of low temperature combustion. The conversion of biomass into fuels with higher combustion temperatures is thus favourable. The conversion of biomass into liquid fuels, other than via fermentation, requires deoxygenation and the controlled formation of C‑C bonds to obtain hydrocarbons of a desired length, ideally by using as little hydrogen from an external source as possible.66 Gasification and pyrolysis as routes for such conversions as well as the production of syngas are discussed later on. Similar process include hydrothermal liquefaction, during which the biomass gets heated to high temperatures in the presence of water and base catalyst.67 The products obtained are a mixture of phenolic compounds. The second strategy is the defunctionalisation of the lignin monomers, yielding BTX which can be converted into a variety of products with existing technology.52 The third strategy tries to obtain highly functionalised platform chemicals via selective hydrolysis.66 These include aromatics which are difficult to synthesise conventionally from fossil feedstocks, with structures closely related to the building blocks of lignin.65 One example is the production of vanillin and vanillic acid from guaiacyl units. Challenges for a successful industrial application of the second and third strategies are that the technology for very selective C‑C and C‑O bond cleavage and, in the case of the third strategy, the markets for its products still need to be developed.

Further, more marginal applications of lignin include fermentation, which is not very developed other than some routes of academic interest, the use of polymeric lignin as surfactants, dispersants, emulsifiers, binders and sequestrants and potentially for the production of carbonfibres, adhesives, sealants65 and the use in agriculture.64

### Gasification

During gasification of biomass, partial combustion occurs, yielding syngas (H2 and CO) and some other gases such as carbon dioxide, methane and nitrogen.66 It is typically carried out at high temperatures of over 1000 K but also lower temperature process have been reported. Syngas can be used as a fuel directly or converted into high purity hydrogen and CO2 via the water-gas-shift reaction.65 Hydrogen in return can again be used for electricity production e.g. in fuel cells or as a reactant for e.g. hydrogenations. The use of syngas as a fuel offers better efficiency than the combustion of biomass as it can be burned at higher temperatures.68 Syngas is being used for the production of methanol, petrol or olefins or can be used in the Fischer-Tropsch process for the production of synthetic diesel. The addition of heterogeneous catalysts decreases the thermal stability of lignin and can improve the hydrogen yield of the gasification step.52

Gasification is a well-developed technology and extensively used with fossil feedstocks such as coal, however its economics improve with scale and it is unclear whether the biorefinery scale will be sufficient to make the gasification of lignin economically viable.65

### Pyrolysis

Pyrolysis is a method used to convert solid fuels into liquids and is carried out in the absence of oxygen, leading to a deoxygenation of around 80%66 and is as such sometimes used as a first step during gasification.69 Fast pyrolysis typically heats the solid to 400 to 600°C for seconds or a few minutes.70 During lignin pyrolysis, depending on the exact conditions, different fractions are obtained including water soluble and water insoluble pyrolysis oil, non-condensable gases and solid char. A higher condensable yield is obtained at lower residence times.66 Water insoluble pyrolysis oils typically contain phenols, alcohols and ethers, carbonyls and aldehydes and high molecular weight aromatic compounds and to a lesser extent organic acids, esters and hydrocarbons and account for up to 85wt% of the pyrolysis products of lignin pyrolysis.71 Pyrolysis of cellulose on the other hand yields mostly water soluble light oils (around 85wt%), which contain mainly water itself, as well as some methanol, levoglucosan and catechol. Pyrolysis oils from biomass are rather unstable due to their high oxygen content reflected in the presence of aldehydes and other carbonyls which lead to low heating values and polymerisation to high molecular weight molecules which make the oil too viscous for the use as fuel for many applications.55 The presence of acids such as acetic and formic acid is undesirable as they contribute to corrosion.2 Low grade pyrolysis oils are as a mixture too complex to distil.70 However, they can be upgraded to petrol like compounds such as alkanes and aliphatic alcohols by hydrogenation in the presence of heterogeneous catalysts. The water soluble fraction is more readily hydrogenated and several hydrogenation steps may be necessary to upgrade the water insoluble heavy oil.71 Alternatively, deoxygenation of the pyrolysis oil yields a mixture of benzene, tuoluene, xylenes, phenol, cresols and alkyl phenols which can be separated by distillation (figure 8)70 and for which further conversion routes to a range of chemicals are already developed.65 Pretreatment of biomass with certain ionic liquids was found to alter the product distribution in pyrolysis oils; pretreatment of bamboo with [BMIM][Cl] yielded more phenol, benzene derivatives, hydrocarbons and aliphatic alcohols and decreased the formation of aldehydes and ketones compared to the pyrolysis oil from untreated bamboo, all of which improves the quality of the pyrolysis oil.2

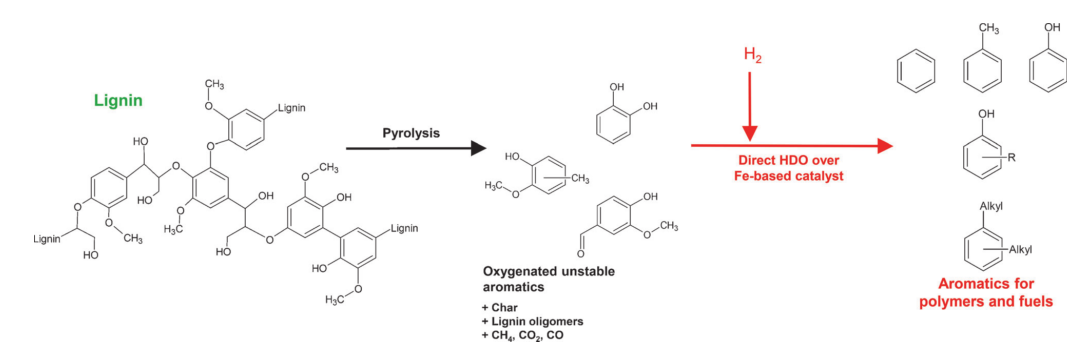


Figure 8 Schematic pyrolysis of lignin and hydrodeoxygenation of lignin pyrolysis products.70

The presence of heterogeneous catalysts can decrease the thermal stability of the biomass or its components during pyrolysis and alter the product distribution.72 The presence of nano-oxide containing natural zeolites for example was found to increase the phenolic fraction of the water insoluble pyrolysis oil to over 50wt% and decrease the amount of carbonyls.

The non-condensable gases are typically constituted of carbon monoxide, carbon dioxide and methane.73 The solid char residue can be combusted for energy generation.66

### Biological and Chemical Conversion of Sugars

Free fatty acids can be obtained by feeding ionic liquid pretreated biomass to modified E. coli bacteria without the need for hydrloysis and are used in the pharmaceutical, cosmetics and biofuel industries.43 Other fermentation products of sugars include the C-5 building blocks glutamic and itaconic acid and the C-3 building block 3-hydroxypropionic acid, which can undergo further conversion steps, giving access to a variety of products, such as acrylates, pyrrolidinones, diols and diacids.74 Lactic acid can be produced via the microbial fermentation of polymeric hexoses where saccharification and fermentation can be carried out in a single step.75 Lactic acid is being used in the food industry and can be polymerised to the biodegradable polymer polylactic acid.

Various chemical transformation routes exist for the conversion of carbohydrates into more valuable platform chemicals.74 Starch can be oxidised to 3-hydroxybutyrolactone which is an intermediate used in the pharmaceutical industry and potentially could be further reduced to furans or polymer building blocks. Cellulose and monomeric hexoses can be dehydrated to levulinic acid, which can be further reduced, oxidised or condensed, giving access to a wide range of fuel additives and chemicals with various applications. Analogously pentoses and hexoses can be dehydrated to furans, such as furfural or HMF respectively, which again are precursors for a variety of compounds and can be upgraded to linear alkenes in the diesel and jet fuel range.66 Furfural was produced from corncob in the presence of seawater.76 The reduction of fructose to HMF has been carried out in the presence of ionic liquids and metal chloride catalysts conversions of up to 97.7% in 30 min.77 Glucose is being hydrogenated with the aid of Raney nickel as catalyst on an industrial scale for the production of sorbitol.74 Similarly xylitol, which is used as a non-nutritive sweetener, can be obtained from xylose and potentially also arabinitol should be derivable from arabinose. Sorbitol, xylitol and arabinitol all have great potential as building blocks for commodity chemicals and are currently used in the food and pharmaceutical industries,78 however conversion routes such as oxidation, dehydration, hydrogenolysis and direct polymerisation still need to be developed or improved. Glucaric acid can be obtained as an oxidation product from starch, analogously the production of xylaric and arabinaric acid is potentially possible. Further dehydration yields lactones which can be used as solvents. 2,5-furan dicarobxylic acid is obtained via oxidative dehydration of sugars via the formation of HMF. Reduction and polymerisation chemistry can potentially be applied for the production of new polyesters and polyamines to replace terephthalic acid.79

While ethanol is mainly used as fuel, it can be dehydrated to produce ethene for the production of polyethylene and polyvinylchloride.79 Oxidation of ethanol yields the commodity chemcials acetic acid and ethyl acetate.

The production of hydrogen can be achieved via aqueous phase reforming of oxygenated compounds such as glucose and glycerol with the aid of noble metal catalysts. Similarly, by using different catalysts, alkanes can be obtained from polyoles.66 Alternatively, hydrogen and methane can be produced from carbohydrate hydrolysates via anearboic fermentation and can make use from effluents from bioethanol production to increase the overall fuel output from carbohydrates.80

# CCA treated wood and other waste woods

Chromated copper arsenate (CCA) has been used extensively to treat wood to extend its lifetime by up to 20-50 years for the use as construction wood.81 CCA is a mixture of CuO, CrO3 and As2O5 which forms complexes with wood components. Such treated timber can contain over 5000 mg kg-1 of arsenic and chromium.82

Although it is being or is already phased out in many countries, there are still ineligible amounts of CCA treated wood available or will become available over the next years. CCA replacement compounds include alkaline copper quaternary (ACQ), copper azole (CA) and micronized copper quaternary (MCQ) which all contain large amounts of copper (up to 3700 mg kg-1).81 Chromium and copper compounds are classified as non-volatile and thus only a small percentage escapes into the atmosphere upon combustion, gasification or pyrolysis of the contaminated biomass (less than 7%) while the remains are found in the ash and can simply be filtered off.69 However, these metal compounds leach into the environment if the wood is deposited in landfill where they continue to act as biocides.83 Arsenic on the other hand forms very volatile compounds that are partially released into the atmosphere upon combustion, pyrolysis or gasification.69 Arsenic and hexavalent chromium are known to be very toxic to human life82 and thus need to be contained.

Copper can be recovered from the treated wood by leaching with sulphuric acid which makes the copper soluble. 90-93% of the copper can be recovered with this method at a cost of ca. $180 per ton of treated wood.81 It is therefore important not only from an ecological but also economical point of view to find an inexpensive way for the extraction and recycling of copper and chromium and the appropriate disposal of arsenic.

## Extraction of CCA

Extraction of CCA usually involves one or several leaching steps using different acids such as acetic acid, oxalic acid84 or sulphuric acid,81 chelating agents such as EDTA,83 bacteria or hydrogen peroxide.82

Almost complete removal of all three elements with a oxalic acid in a first leaching step and sodium oxalate under acidic conditions in a second step was achieved accompanied by decomposition of wood.85 However, challenges remain such as the extraction and recycling of the chromium and copper from the extractant and discarding of As, as well as recycling of the acidic water.82

A problem of arsenic reduction as a recovery strategy is the formation of toxic arsine gas AsH3.86 As(III) and As(V) can be reduced to As(0) under the right conditions with negligible arsine evolution. Alternatively, arsenic can be extracted electrochemically from acidic washing solutions by concomitant reduction of the copper cation to form Cu3As and Cu5As2 deposits without the formation of arsine gas.87

## CCA Treated Wood in Pyrolysis, Gasification and Combustion

Studies with model compounds have demonstrated that As2O3 is very volatile and mass loss occurs at temperatures well below 200°C. As2O5 on the other hand is not volatile below 600°C but can be reduced in the presence of H2 at temperatures of around 425°C. Copper(II) oxide thermally decomposes at 775°C in a nitrogen atmosphere and at 1050°C if H2 is present while chromium(III) oxide does not react under pyrolysis, gasification or combustion conditions. However, arsenic(V) oxide volatelises in the presence of Cr(III) oxide or forms chromium arsenate (CrAsO5) which is very volatile too. Furthermore, the decomposition of arsenic(V) oxide is accelerated in the presence of glucose, char, wood and pyrolysis vapours which make a reducing environment.88

During pyrolysis of contaminated wood, most of the copper and chromium is found in the ashes, however the exact partitioning depends on the type of furnace and the oxygen content of the atmosphere as oxides are less volatile than e.g. chlorides.69 Arsenic however is released into the environment; 16.4% was released during pyrolysis for one hour at 275°C and 24.8% during 30 min at 350°C. The presence of CCA in wood also has an impact on partitioning of pyrolysis products. More information on it can be found elsewhere.89

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